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TABLE I

Glycine	Sucrose	VPH[1]	MSG[2]	5¹-Ribo.[3]	Fat
5	102	305	203	1	20
5	203	305	203	1	20
5	203	305	509	2	20
7	203	407	509	2	40
7	203	509	509	2	50
7	203	611	509	2	50
10	407	611	1527	2	50
10	407	611	1527	5	100
51	407	1018	1527	5	1527
51	407	1527	1018	10	102
5	0	611	0	2	0
5	203	611	509	2	00
5	203	611	509	0	50
5	203	0	509	2	50
5	0	611	509	2	50
10	203	814	0	5	10
5	203	611	509	1	40

[1] Vegetable protein hydrolysate.
[2] Monosodium glutamate.
[3] 5¹-Ribonucleotides, a 50:50 by weight mixture of disodium inosinate and disodium guanylate.

EXAMPLE VIII

To a 2-liter, 3-necked flask fitted with a mechanical stirrer, thermometer and reflux condenser, are added 60 ml. water, 6.0 grams L-cysteine hydrochloride and 7.0 grams L-cystine hydrochloride, 6.7 grams glycine hydrochloride, 10.8 grams dextrose and 8.0 grams arabinose and the mixture is stirred after the addition of each ingredient. The solution is adjusted to pH 7.5 by the addition of about 10 ml. of 50% aqueous sodium hydroxide. The solution is then heated at 100°C. for about 10 minutes. After cooling to 20—25°C., 100 ml. water is added and the acidity is adjusted to pH 7.5 with 1N aqueous sodium hydroxide. The resulting composition has a chicken taste and aroma.

Similarly, when the ingredients of the chicken flavored product are neutralized to a pH of 6.5 rather than 7.5 and the solution is heated at 70°C. for 4 hours, a chicken flavored product is obtained.

WHAT WE CLAIM IS:—

1. A method for making a chicken-flavored composition which comprises mixing in an aqueous medium a hexose or pentose monosaccharide or mixtures thereof, cystine or cysteine or mixtures thereof, and glycine in an amount to provide a range of from 0.05 to 0.5 part per part by weight of the total mixture; neutralizing to a pH in the range of 6.5 to 7.5 and thereafter heating at a range of from 70°C. to 100°C. for a range of from 10 minutes to 4 hours.

2. The method according to claim 1, wherein said hexose is dextrose and said pentose is arabinose.

3. The method according to claim 1 or 2, wherein the chicken-flavored product is cooled and there is then added from 0.2 to 16 parts by weight of edible fat.

4. A method according to claim 1 or 2 wherein, after said heating, there is added to the product

(a) from 2 to 15 parts by weight of monosodium glutamate,

(b) from 3 to 15 parts by weight of vegetable protein hydrolysate,

(c) from 1 to 4 parts by weight of sucrose, and thereafter heating the resulting mixture to 70 to 75°C. for 1 to 4 hours.

5. The method according to claim 4, wherein the chicken-flavored composition is cooled and blended with from 0.2 to 15 parts of edible fat and from 0.01 to 0.1 part by weight of a 50:50 by weight mixture of disodium inosinate and disodium guanylate, based on the weight of chicken-flavored product and then heating to a range of from 50—55°C. for a range of from 10 to 30 minutes.

6. The method according to claim 4, wherein coconut oil is added before or after said heating to 70 to 75°C.

7. A method for preparing a chicken-flavored composition substantially as described.

8. A chicken-flavored composition whenever prepared by the method substantially as described.

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Agents for the Applicants.

Reference has been directed in pursuance of Section 9, sub-section (1) of the Patents Act, 1949, to Patent No. 836,694.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1970.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.

PATENT SPECIFICATION

NO DRAWINGS

1,198,398



1,198,398

Date of Application and filing Complete Specification: 20 Aug., 1968.
No. 39823/68.
Application made in Japan (No. 54204) on 25 Aug., 1967.
Complete Specification Published: 15 July, 1970.

Index at acceptance: —**A2** B6A

International Classification: —**A 23 I 1/26**

COMPLETE SPECIFICATION

A Process for Preparing Meat Extract-Like Seasoning

We, KYOWA HAKKO KOGYO CO., LTD., a corporation organised under the laws of Japan, of 4, Ohtemachi-1-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for preparing seasonings having a meat extract-like flavor by decomposing to a suitable extent a vegetable protein or cell of yeast, bacterium or fungus with an enzyme or acid to form an amino acid-containing peptide mixture composed mainly of peptide, adding to the mixture effective amounts of saccharides, organic acids, inorganic salts, 5'-nucleotides, nucleosides, gelatine, and sodium alignate and then reacting the mixture at an elevated temperature.

Meat extracts characteristically contain large quantities of anserine, carnosive and like peptides. The peptides play important roles in the development of the complex tastes of the resulting seasonings. It is well known fact that a meat-like flavor is generated by the amino-carbonyl reaction of a saccharide, an amino acid and a peptide. A brown product produced in the above case contains various carbonyl compounds, mainly aldehydes, and develops a characteristic flavor. Furthermore, in the case of meat extracts, organic acids, 5'-nucleotides and nucleosides also play important roles in the generation of flavor.

One of the objects of the present invention is to provide an improved process for the preparation of meat extract-like seasonings.

Another object of the present invention is to produce a meat extract-like seasoning which is substantially undistinguishable from meat extracts and is an excellent seasoning substitute for meat extracts.

A further object of the present invention is to provide an improved process for producing meat extract-like seasonings which are excellent in quality.

According to the present invention we provide a process for preparing a meat extract-like seasoning which comprises subjecting a vegetable protein or a cell of yeast, bacterium or fungus to decomposition to form an amino acid-peptide mixture having an average peptide length of 4 to 5 units, adding to said mixture an additive comprising at least saccharide, organic acid, inorganic salt, 5'-nucleotide, nucleoside together with gelatine and/or sodium alginate and reacting the resultant mixture at an elevated temperature.

In the process of the present invention, the following aspects of the present process are significant:—

1. The composition of the protein decomposate;

2. The particular additives, that is saccharides organic acids 5'-nucleotides nucleosides and gelatine and/or sodium alginate, added in the process; and

3. The proportions of the individual components used and the reaction conditions adopted.

In the case of seasonings of this kind, the harmony and balance of taste are important. Thus, the particular components and the amounts thereof should be well harmonised. In order to form these components into a mild, natural and harmonised seasoning, the mixture thereof is heated and reacted to generate a meat extract-like flavour.

The process of the present invention, as illustrated below, can be divided into three steps.

The first step is that of forming a peptide mixture decomposing a starting protein by

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the action of an enzyme and/or acid. This step is carried out in the following manner. To the starting protein 0.1 to 0.5% of protease is added to effect enzyme decomposition, and the reaction is stopped when a desired peptide mixture is formed. In the case of a crude starting material containing cell walls and the like, 0.5 to 1N hydrochloric acid is added in an amount of 3 to 6 times the amount (V/W) of the starting material, and the mixture is treated at a temperature of 100 to 130°C. for 1 to 5 hours to decompose the cell walls, to liberate the saccharides constituting the cell walls and to extract the cell protein. Subsequently, the decomposate is neutralized and the extracted protein is decomposed by the aforesaid protease to form a sugar and amino acid-containing peptide mixture composed mainly of peptides. Alternately, peptides obtained from various different starting materials may be mixed together to form a mixture having a desired composition. The average peptide length (hereinafter referred to as "A. P. L.") of the thus formed peptide mixture should be adjusted to a length of 4 to 5 units. The A. P. L. value can be calculated according to the formula $T\text{-}N/NH_2\text{—}N$. Furthermore, in the composition, the ratio of free amino acid to peptides should be 1 to 4 to 5. The above requirements are conditions necessary for the development of the tasty flavor of the product as a meat extract-like seasoning.

The second step of the process of the present invention is that of adding various components to the peptide mixture formed in the first step so that the amount of peptide mixture becomes 60 to 70% of the total components of the final product (calculated for dry product). Examples of saccharides which can be added in the process of the present invention include one or more of hexose, pentose, disaccharide, hexose monophosphate, pentose monophosphate, and sugar alcohol. Advantageously, the saccharides are present in an amount of 2 to 5% by weight, based on the total components present. In the case glycoprotein is used as the starting material in the first step, free saccharide is formed and therefore only a small amount, which normally would be an insufficient portion, need be supplemented. As organic acids there are added 3 to 10% based on the weight of the total components of, for example, one or more members selected from the group consisting of malic acid, succinic acid, glycolic acid, citric acid, lactic acid, fumaric acid and salts thereof. As 5'-nucleotides, there are added 0.2 to 2.5%, based on the weight of the total components, of at least one member of the group consisting of 5'-inosinic acid, 5'-guanylic acid and 5'-xanthylic acid, and salts thereof. The nucleosides which are added during the process of the present invention include guanosine, inosine, adenosine and xanthosine. Advantageously, the nucleosides are present in an amount of 0.1 to 1% by weight based on the weight of the total components. Furthermore, 0.1 to 1% by weight, based on the weight of the total components, of gelatine and/or sodium alginate is added in the process of the present invention. By the incorporation of the above components, a harmonized meat extract-like seasoning having a complex taste can be effectively prepared.

In the third step of the process of the present invention, the water content of the mixture obtained in the second step is controlled to 15 to 85%, and the pH thereof is adjusted to 5 to 7 by the addition of a basic material, for example sodium carbonate or caustic soda or by the addition of a mineral acid such as for example hydrochloric acid. The mixture is then heated and reacted at a temperature of 50 to 80°C. for 0.5 to 5 hours with stirring in the open at atmospheric pressure. In this step, an amino-carbonyl reaction takes place to produce various flavors derived primarily from the carbonyl compounds. Furthermore, a browning reaction progresses to form Elson-organ reaction-positive substances, whereby a meat extract-like flavor is produced. In this step, the individual components are aged and harmonized, whereby the mixture develops a mild taste. After completion of the above reaction, the reaction mixture is adjusted to a pH of 5.5 to 6.5 to prepare a paste or powdery seasoning.

The following examples are given merely as illustrative of the present invention and are not to be considered as limiting. Unless otherwise noted, the percentages therein are by weight.

Example 1

To 100 kg. of a dry cell of *Corynebacterium glutamicum* syn. (*Micrococcus glutamicus*) ATCC 13761 which has been isolated and dried after completion of a glutamic acid fermentation, is added water to make the substrate concentration 10%. Subsequently, the suspension is adjusted to a pH 7.2 and is charged with 300 g. of "Prozyme" (trade name for a protease produced by Kyowa Hakko Kogyo Co. Ltd.), and enzyme decomposition is effected at a temperature of 45—47°C. for 14 hours. In this step, the protein is decomposed to form peptide, amino acid. The decomposate suspension is adjusted to a pH of 5.5 by adding 4N HCl and is then subjected to centrifuge to separate and remove the undecomposed materials. Thereafter, the supernatant is charged with 5 kg. of active carbon is treated at 60°C. for 1 hour, and is then filtered to remove the active carbon. This active carbon treatment is effected in order to harmonize the taste of the resulting product. The filtrate

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has an A. P. L. of 4.5, contained 50 kg. of peptide, 11 kg. of amino acid, 4 kg. of arabinose, mannose and glucose, and other inorganic salts, and has a total solid content of 80 kg. To this filtrate are added 1 kg. of sodium malate, 0.5 kg. of sodium succinate, 1 kg. of sodium glycolate and 1.5 kg. of sodium lactate as organic acids: 1.2 kg. of sodium 5'-inosinate as 5'-nucleotide; and 0.2 kg. of inosine as nucleoside. After dissolving the additives in the filtrate, the solution is adjusted to a pH of 6.5 by the addition of sodium carbonate, and is concentrated under reduced pressure at 35°—45°C. to a total solid content of 80%. The concentrate is heated at 60°C. for 4 hours with stirring in the open at atmospheric pressure. In this step, a meat flavor is generated and, at the same time, aging and harmonization achieved. Furthermore, water is vaporized, and 100 kg. of a meat extract-like seasoning having a total solid content of 85% and containing 12% of sodium chloride and the above-mentioned various components are produced. This seasoning is formed into soup B having the composition shown in Table 1, and the soup is subjected to sensory test according to paired preference test, using a panel composed of 31 experts, to distinguish said soup from soup A, to which has been added an equal amount of a meat extract. The results are shown in Table 2.

TABLE 1

Composition of Soup A

Meat extract*	0.2%	Sodium succinate	0.01%
Sodium chloride	0.8%	Carrot powder	0.01%
Sugar	0.5%	Onion salt	0.03%
Sodium glutamate	0.3%	Garlic salt	0.01%
H. P. P.**	0.3%	Curry powder	0.01%
Sodium inosinate	0.01%	Beef tallow	0.1%

* In soup B, 0.2% of the meat extract-like seasoning of this example is used in place of the meat extract.

** An amino acid mixture resulting from hydrolyzed plant protein.

TABLE 2

Results of Organoleptic Tests

Those who preferred soup A	16 members
Those who preferred soup B	15 members
Significance	None

From the above results, it is confirmed that the seasoning in accordance with the present invention is entirely undistinguishable from meat extracts and is an excellent seasoning substitutable for meat extracts.

EXAMPLE 2

90 kg. of wheat protein is ground and is suspended in water to a substrate concentration of 10%, and the suspension is adjusted to a pH of 7.2. The suspension is charged with 0.2 kg. of the protease "Prozyme", is subjected to enzyme treatment at 45°—47°C. for 1 hour and is then filtrate free from disagreeable taste, bitter taste and the like. This filtrate contains 55 kg of peptide mix-

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ture having an A. P. L. of 5.5. On the other hand, 15 kg. of wheat protein is hydrolyzed with 45 l. of 3N hydrochloric acid at 120° C. for 3 hours. Water is added to the hydrolysate, to make the substrate concentration 10%. Thereafter, vaporization and concentration are repeated to remove one-half of the hydrochloric acid. Subsequently, the liquor is adjusted to a pH of 4.5 by means of caustic soda and is charged with 0.7 kg. of the aforesaid active carbon. The mixture is treated at 60°C. for 1 hour and is then filtered to obtain a filtrate. This filtrate contains 12 kg. of an amino acid mixture having an A. P. L. of 1.1. The filtrate is mixed with the aforesaid wheat protein enzyme decomposate to obtain a peptide mixture having an A. P. L. of 4.6 and containing 55 kg. of peptide and 12 kg. of free amino acid. To this mixed liquor are added 3 kg. of glucose and 0.5 kg. of sorbitol as saccharides; 2 kg. of sodium malate, 0.6 kg. of sodium succinate and 1 kg. of sodium citrate as organic acids; 0.5 kg. of sodium 5'-guanylate; 0.2 kg. of inosine; and 0.2 kg. of gelatine. After dissolving the additives in said mixed liquor, the solution is neutralized to a pH of 6.5 by means of sodium carbonate, and is concentrated under reduced pressure to a total solid content of 55%. The concentrate is heated at 65°C. for 3 hours with stirring in the open at atmospheric pressure and is powderized by the use of a spray-dryer to obtain 98 kg. of a powdery seasoning. This seasoning contains 14% sodium chloride, 6% sodium glutamate, 0.5% sodium 5'-guanylate, and like organic acids, and brown products, and is an excellent seasoning having a meat extract-like flavor.

To 100 kg. of "Soymilk" (trade name for a purified soybean protein produced by Honen Seiyu Kogyo Co. Ltd.), 200 l. of 0.5N hydrochloric acid is added, and the mixture is hydrolyzed at 130°C. for 3 hours. In this step, a part of the protein in the starting material is decomposed and, at the same time, the saccharide portion is decomposed to free saccharides. After cooling, the hydrolyzate is neutralized to a pH of 7.2 by means of caustic soda or sodium carbonate, and water is added to make 1000 l. Subsequently, the suspension is charged with 0.15 kg. of "Prozyme B" (trade name for a protease produced by Kyowa Hakko Kogyo Co. Ltd.) and enzyme decomposition is effected at 45—47°C. for 16 hours. By thus effecting the acid decomposition in combination with the enzyme decomposition, a peptide mixture having an A. P. L. of 4.0 is obtained. After completion of the enzyme decomposition, the suspension is adjusted to a pH of 6.5 by means of hydrochloric acid and is then centrifuged to obtain 800 l. of a transparent decomposate liquor. To this liquor is added 4 kg. of the active carbon used in Example 1. and the mixture is treated at 60°C. for 2 hours and is then filtered to obtain 780 l. of a filtrate free from bitter taste. This filtrate has a total solid content of 74 kg. and contains 11 kg. of amino acid, 46 kg. of peptide, 4 kg. of such saccharides as mannose, arabinose, glucose, and the like, and 10.5 kg. of sodium chloride.

To this decomposate are added 3 kg. of sodium malate, 4 kg. of sodium lactate, 0.5 kg. of sodium succinate, 1.2 kg. of sodium 5'-inosinate, 0.15 kg. of ionsine, 0.15 kg. of gelatine and 0.15 kg. of sodium alginate. After confirming that the pH is 6.5, the mixture is concentrated under reduced pressure at 40°—45°C to obtain a concentrate having a total solid content of 80%. Subsequently, the concentrate is heated at 60°C. for 2.5 hours with stirring in the open at atmospheric pressure. In this step, a meat flavor is generated. In the above manner, 103 kg. of a meat extract-like seasoning having a total solid content of 83% is obtained. This seasoning contains 2.8% of sodium glutamate, 1.16% of sodium inosinate, 10% of sodium chloride and like organic acids, saccharides, and peptides, and is an excellent seasoning having a meat extract-like flavor.

WHAT WE CLAIM IS:—

1. A process for preparing a meat extract-like seasoning which comprises subjecting a vegetable protein or a cell of a yeast, bacterium or fungus to decomposition to form an amino acid-peptide mixture having an average peptide length of 4 to 5 units, adding to said mixture an additive comprising at least saccharide, organic acid, inorganic salt, 5'-nucleotide, nucleoside, together with gelatine and/or sodium alginate and reacting the resultant mixture at an elevated temperature.

2. The process of claim 1, wherein decomposition is effected by the addition of an enzyme and/or an acid.

3. The process of claim 2, wherein 0.1 to 0.5% of enzymes is added to effect enzyme decomposition.

4. The process of claim 2, wherein 3 to 6 times the amount (V/W) of the starting material, of 0.5 to 1N hydrochloric acid is added at a temperature of 100—130°C to effect acid decomposition.

5. The process of claim 1 wherein the ratio of free amino acid to peptide in the composition is 1 to about 4 to 5.

6. The process of any of the preceding claims, wherein the saccharide is hexose, hexose monophosphate, pentose, pentose monophosphate, disaccharide or sugar alcohol or a mixture of any thereof.

7. The process of any of the preceding claims, wherein the organic acid is malic acid, succinic acid, glycolic acid, citric acid, lactic acid, fumaric acid, a salt of any thereof or a mixture of any of said acids and/or salts.

8. The process of any of the preceding

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claims, wherein the 5′-nucleotide is 5′-inosinic acid, 5′-guanylic acid, 5′-xanthylic acid, a salt thereof or a mixture of any of said 5′-nucleotides and/or salts.

9. The process of any of the preceding claims, wherein the nucleoside is guanosine, inosine, adenosine or xanthosine or a mixture of any thereof.

10. The process of any of the preceding claims, wherein the resultant mixture is reacted at a temperature of 50 to 80°C.

11. The process of any of the preceding claims, wherein the enzyme is protease and the protein is glycoprotein.

12. The process of any of the preceding claims, wherein the additive comprises, based on the total components, 2 to 5% saccharide, 3 to 10% organic acid, 0.2 to 2.5% 5′-nucleotide, 0.1 to 1% nucleoside, 0.1 to 1% gelatine or sodium alginate or mixtures thereof and it is added to the amino acid-peptide mixture until the mixture reaches 60 to 70% of the total components of the final product.

13. The process of claim 12, wherein before the reaction, the water content of the mixture is controlled to 15 to 85% and the pH thereof is adjusted to 5 to 7 by the addition of an acidic or basic metal.

14. The process of any of the preceding claims, wherein after completion of the reaction, the reaction mixture is adjusted to a pH of 5.5 to 6.5 to prepare a paste or powdery seasoning.

15. The process of any of the preceding claims, wherein the bacterium cell is a strain belonging to the genus *Micrococcus glutamicus* ATCC 13761.

16. A process of preparing a seasoning substantially as described in any of the foregoing Examples.

17. Seasonings prepared by the process of any preceding claim.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1970.
Published by The Patent Office, 25 Southampton Buildings London WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 206 265

1 206 265

NO DRAWINGS

(21) Application No. 14814/69 (22) Filed 20 March 1969
(31) Convention Application No. 20545 (32) Filed 29 March 1968 in
(33) Japan (JA)
(45) Complete Specification published 23 Sept. 1970
(51) International Classification A 23 l 1/26
(52) Index at acceptance A2B 6A
(72) Inventors NAGAYOSHI KITADA, HIDEO SHIMAZAKI and YASUSHI KOMATA

(54) IMPROVEMENTS IN OR RELATING TO A PROCESS FOR PRODUCING A MAILLARD REACTION PRODUCT HAVING A MEAT-LIKE FLAVOUR

(71) We, AJINOMOTO CO., INC. a corporation organized under the laws of Japan, of No. 7, 1-chome, Tabara-cho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing a Maillard reaction product having a meat-like flavour.

The Maillard reaction is the reaction of the amino group of an amino acid, peptide or protein with the "glycosidic" hydroxyl group of a sugar, followed by other, more complex, changes which result eventually in the formation of brownish pigments, see the Merck Index 1968, 8th Edition.

It is known that those Maillard reaction products obtained by heating a mixture of a sulphur containing amino acid and a reducing sugar, have a characteristic flavour similar to meat to some extent, and the flavour may be improved when this Maillard reaction product is combined with another Maillard reaction produce of the type obtained by employing another kind of amino acid or with vegetable protein hydrolyzate. Recently, it has been found that these Maillard reaction products can be employed as a flavouring material for foodstuffs.

However, generally speaking, the solubility of cystine or cysteine (which are examples of sulphur-containing amino acids) in water of neutral pH is very small, and the velocity of the Maillard reaction between sulphur containing amino acids and reducing sugar is very slow.

It is an object of the present invention to increase the velocity of Maillard reaction between cystine or cysteine and a reduced sugar.

According to the present invention, there is provided a process for producing a Maillard reaction product having a meat-like flavour, which comprises heating a solution containing (a) cystine and/or cysteine and (b) a reducing sugar at a temperature of from 50°C. to 120°C. at a pressure of from 70 to 200 Kg./cm^2 so as to produce the desired flavoured Maillard reaction product.

Generally, the meat-like flavour of the Maillard reaction product prepared by the process of the present invention is produced in a better yield and with a better flavour.

Generally, in the process of the invention, the pH value of the aqueous solution of cystine and/or cysteine and of the reducing sugar is adjusted to from 8 to 10, and the process effected in an autoclave. The Maillard reaction is usually carried out with agitation.

Examples of the reducing sugars which may be employed in the present invention include the pentoses hexoses, and they may be aldoses or ketoses. The ratio (by weight) between cystine and/or cysteine and the reducing sugar is preferably from 0.1 to 5.0 : 1.

The pressure during the reaction is from 70 to 200 Kg./cm.^{2}, and the optimal value depends to some extent on the reaction temperature and time. If the reaction is carried out at the same temperature for the same time, but under atmospheric pressure, the flavour of the resulting Maillard reaction product is very weak and far from meat-like flavour. If on the other hand, the reaction is carried out under a pressure of more than 200 Kg/cm.^{2}, decomposition of the reducing sugar in the mixture occurs to a great extent and, accordingly, it produces an undesirable irritating smell. The reaction temperature is, as mentioned above, from 50°C. to 120°C, preferably from 80°C. to 100°C. When the reaction is carried out at a temperature of more than 120°C, unpleasant smells, for example a burning smell and an undesirable irritating smell

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become apparent. The duration of the reaction is usually from 1 to 10 hours, preferably from 3 to 5 hours.

The colour of the solution prepared by the Maillard reaction under elevated pressure is yellowish brown and it has a strong stimulating smell. However, a powder having a very favourable flavour like meat may be obtained by, for example, usual drying and powdering methods such as spray drying and drying under reduced pressure.

The strength of the meat-like flavour of the resulting powder is increased significantly and its quality is improved in comparison to those of the corresponding Maillard reaction products prepared under atmospheric pressure. This is apparent from the results of the following experiments and Examples.

The powder of the Maillard reaction products obtained by heating a mixture of cystine and/or cysteine and a reducing sugar, can improve the flavour of foodstuffs and drinks when added in a concentration of from 0.01 to 0.5% based on the weight of the foodstuff or drink.

The powder may be also used in foodstuffs or drinks in the form of a mixture in concentration of from 0.05 to 2% by weight of the powder and another Maillard reaction product prepared by the reaction of another amino acid, for example glutamic acid, aspartic acid, tryptophan, histidine, threonine, valine, leucine, isoleucine, glycine, alanine, lysine and arginine, with a reducing sugar.

It is also preferable to use hydrolyzed vegetable protein or yeast extract with the powder produced by the process of the present invention in order to improve the meat-like flavour of the foodstuff or drink.

EXPERIMENT 1

An aqueous solution of a mixture of cystine and xylose in a 1:1 weight ratio was adjusted to pH 9.5, heated at 100°C. at a pressure of 130 Kg./cm.^{2} for 6 hours and then dried to a powder by spray-drying. This powder was designated (A). As a control, a powder, designated (B), was prepared in the same manner as mentioned above but under a pressure of 1 Kg.-cm.^{2} instead of 130 Kg./cm.^{2}. The spray-drying was performed by employing a nozzle type spray-dryer in which the temperature at the entrance was in the range from 200 to 220°C, and that at the outlet was in the range from 110 to 120°C.

Each of the powders (A) and (B) was dissolved in water in a concentration of 10 mg%, 50 mg% and 100mg%.

The aqueous solutions of powders (A) and (B) at the different concentrations were offered to a panel of 50 members for an organoleptic test. The test was performed by "pair test" method wherein the member selected the sample having the stronger meat-like flavour. The results are shown in the following table 1.

TABLE 1

Concentration (mg %)	Persons who selected sample (A)	Persons who selected sample (B)	
10	38	12	***
50	44	6	***
100	34	16	**

(Note) **: significantly different at 1% level

***: significantly different at 0.1% level

EXPERIMENT 2

10 Grams of cystine and 10g. of xylose were added to 60 ml. of water and the pH of the resulting solution ion was adjusted to 9.5. The solution was poured into an autoclave and kept air-tight; then the Maillard reaction was carried out at 100°C. for 3 hours, having first adjusted the pressure to one of the values shown in the following Table 2 by the introduction of nitrogen gas.

(1) The amount of residual unreacted xylose was measure and the results are as follows:

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TABLE 2

Beginning pressure (Kg/cm²)	Residual xylose (%)
40	2.06
50	1.92
70	1.54
100	1.30
Atmospheric pressure (control)	1.94

As is apparent from the results shown in Table 2, the amount of residual xylose was small, i.e. the reaction velocity was increased, when the Maillard reaction was carried out under a pressure of more than 70 Kg/cm².

(2) The Maillard reaction product prepared under a pressure of 100 Kg./cm.², as mentioned above and that prepared under atmospheric pressure were subjected to a thin layer chromatography test.

The Rf values of a coloured product (A) of the Maillard reaction and of the coloured product (B) of a ninhydrin reaction were measured. The developer was a mixture of methanol, butanol and water (1 : 1 : 1), and the results are shown in the following Table 3.

TABLE 3

	RF value	
	(A)	(B)
Atmospheric pressure	0.68	0.57
100	0.60	0.57

When methanol-$CHCl_3$ (1 : 1) solvent was employed as the developer, the Rf values of (A) and (B) were as shown in the following Table 4.

TABLE 4

	Rf value	
	A	B
Atmospheric pressure	0.54	0.48
100 Kg./cm.²	0.50	0.48

As is apparent from the results of Table 3 and Table 4, the character of the Maillard reaction product prepared under elevated pressure is different from that of the product prepared under atmospheric pressure and, accordingly, the character of the flavour is also different.

(3) The absorbancy at λmox 330mu was measured for each solution containing 0.1% of each of the Maillard reaction products prepared by reacting cystine and xylose for the the time shown in the following Table 5 under a pressure of 100 Kg./cm.² and those prepared at atmospheric pressure. The results were as follows:

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TABLE 5

Reaction Time (min.)	Absorbancy (—log T)	
	100 Kg./cm.²	Atmospheric pressure
30	538	493
60	580	530
90	600	530
120	630	570
210	620	560

As is apparent from the results shown in Table 5, the absorbancy of the Maillard reaction product prepared under elevated pressure was larger than that of the product prepared under atmospheric pressure, when compared for the same reaction time. Thus, it is clear that the velocity of the Maillard reaction of the present invention is promoted by reaction at elevated pressure.

The invention will now be illustrated by the following Examples.

EXAMPLE 1

20 Grams of cystine and 1.5 g. of xylose were dissolved in 50 ml. of water and the pH of the resulting solution was adjusted to 9.5 by the addition of caustic soda. The resulting solution was poured into an autoclave and the reaction was carried out with agitation at 100°C. at a pressure of 140 Kg./cm², for 3.5 hours. By spray-drying the reacted solution, there was obtained a powder which had a very favourable flavour, at a yield of 90%.

The colour of the powder was orange-yellow and it was readily soluble in water.

An aqueous solution containing 0.5% by weight of the powder was offered to a panel of 20 members for an organoleptic test. When the panel was asked "What kind of smell has the solution?" 18 members of the panel indicated that it smelt like an animal foodstuff and 15 members also indicated that it had a meat-like smell.

EXAMPLE 2

10 Grams of cystine and 10g. of xylose were dissolved in 60 ml. of water and the pH of the resulting solution was adjusted to 10.0 by adding caustic soda. The solution was heated at 85°C. for 20 minutes under aeration and its pH adjusted to 8.0. The solution was then poured into an autoclave, the pressure in the autoclave was kept at 100 Kg./cm.² with nitrogen gas and the solution heated at 100°C. for 3.5 hours with agitation. The resulting solution of the Maillard reaction product was spray-dried to a powder.

A solution containing 0.1% of this powder was offered to a panel of 20 members for an organoleptic test and, as a result, 17 members of the panel indicated that the solution had a favourable flavour like that of meat.

EXAMPLE 3

20 Parts by weight of sodium glutamate, 1 part by weight of xylose and 0.05 part by weight of a mixture containing an equivalent amount of cystine and ribose were added to 5 parts by weight of water, and the pH of the resulting solution was adjusted to 9.0. The solution was then reacted at 90°C. at a pressure of 100 Kg./cm². for an hour, and the reacted solution was dried to a powder in a spray-dryer of the nozzle type.

0.05% by weight of this powder was added to a buckwheat noodle soup and the soup was offered to a panel of 20 members for an organoleptic test. As a result of a "pair test" 19 members of the panel indicated that the flavour of the soup containing the powder was preferable to a soup not containing the powder. It was also pointed out by 12 members of the panel that the soup containing the powder had a meat-like flavour.

WHAT WE CLAIM IS:—

1. Process for producing a Maillard reaction product having a meat-like flavour, which comprises heating a solution containing (a) cystine and/or cysteine and (b) a reducing sugar at a temperature of from 50°C. to 120°C. at a pressure in the range of from 70 to 200 Kg./cm². so as to produce the desired flavoured Maillard reaction product.

2. Process according to Claim 1, wherein the reaction is effected for from 1 to 10 hours.

3. Process according to Claim 2, wherein the reaction is effected for from 3 to 5 hours.

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4. Process according to any preceding claim, wherein the process is effected at a temperature of from 80 to 100°C.

5. Process according to any preceding claim, wherein the pH of the solution is from 8 to 10.

6. Process according to any preceding claim, wherein the solution contains from 01 to 5.0 parts of cystine and/or cysteine per part of the reducing sugar.

7. Process according to any preceding claim, wherein the reducing sugar is a hexose or pentose.

8. Process according to Claim 7, wherein the reducing sugar is xylose.

9. Process according to Claim 1, substantially as described in any one of the foregoing Experiments or Examples.

10. Process according to Claim 1, and further comprising drying the Maillard reaction product and converting it into a powder.

11. A Maillard reaction product whenever produced by the process claimed in any one of Claims 1 to 9.

12. A Maillard reaction product in powder form, whenever produced by the process of Claim 10.

13. Process for improving the flavour and/or aroma of a foodstuff or drink, which comprises mixing from 0.01 to 0.5% by weight of the Maillard reaction product claimed in Claim 12 with a foodstuff or drink.

14. Process for improving the flavour and/or aroma of a foodstuff or drink, which comprises mixing from 0.05 to 2% by weight of a mixture of the Maillard reaction product claimed in Claim 12 and another Maillard reaction product obtained by reacting a different amino acid with a reducing sugar, with a foodstuff or drink.

15. A foodstuff or drink whenever prepared by the process claimed in Claim 13 or 14.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 205 882

1 205 882

NO DRAWINGS

(21) Application No. 2789/68 (22) Filed 18 Jan. 1968
(31) Convention Application No. 6700991
(32) Filed 20 Jan. 1967 in
(33) Netherlands (NL)
(45) Complete Specification published 23 Sept. 1970
(51) International Classification A 23 1 1/26
(52) Index at acceptance
A2B 6A

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(54) FLAVOUR COMPOSITION

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to new and valuable artificial flavouring mixtures, including concentrated as well as ready-for-use foodstuffs, and to processes for the preparation of such mixtures.

The taste of meat of many commercially available foodstuffs, such as soups, gravy, is obtained by incorporating, during their preparation, a produce commercially known as meat extract, indicated below as commercial meat extract. This commercial meat extract is generally obtained by extraction with water of the meat of slaughtered cattle, especially horned cattle, followed by evaporation of the greater part of the water. The commercial meat extract thus obtained is a brown product generally containing 15-25% of moisture. This commercial meat extract is expensive, its preparation is time-consuming and requires much energy, and the yield is only a few percent by weight of the expensive starting material (meat).

This commercial meat extract is not only expensive and of variable quality but after dilution with water, it has a taste different from that of a broth or gravy prepared direct from meat. This difference is probably caused by certain reactions between various substances taking place during the prolonged heating when preparing the commercial meat extract, such as between amino acids and sugars, which during the preparation of the fresh extract proceed less far or not at all. Thus undesirable "shades of" taste and the dark colour may develop in the commercial meat extract and the foodstuffs prepared with it.

An object of the invention is to provide new, improved, artificially prepared flavouring mixtures that do not possess certain undesired shades of taste and that are of a light colour, and provides concentrated as well as ready-for-use foodstuffs and a process for the preparation thereof.

Using the product of this invention commercial meat extract may be partly or entirely replaced by a meatless composition, so that, beside giving an improved taste and a lighter colour, a considerable cost saving can be realized. A partial replacement of commercial meat extract by an artificial flavouring mixture according to the invention may already lead to a shifting into the background of an undesirable shade of taste of the commercial meat extract in the final foodstuff. An additional advantage is that —in contrast with the commercial meat extract—the compositions obtained according to the invention may have a constant quality and a constant price.

Various publications have been issued on the composition of commercial meat extract, e.g. by *T. Wood and A. E. Bender in "The Biochemical Journal" 67, 366-373 (1957)*, entitled "Analysis of tissue constituents (commercial ox-muscle extract"). In a later publicaton of *A. E. Bender, T. Wood and J. A. Palgrave in "Journal of the Science of Food and Agriculture" 9th December, 1958, pp 812-817, entitled* "Analysis of tissue constituents. Extract of fresh ox-muscle", the compositon of commercial meat extract was compared with an extract of fresh beef obtained by treating beef with ice-water.

Various groups of compounds were qualitatively indicated and quantitatively determined, among which:

Amino acids and peptides
Organic phosphates (inter alia phosphate containing amino acids) and inorganic phosphate

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Guanidines (especially creatine—creatinine)
Purines (free and combined in nucleotides)
Organic acids (lactic acid, glycolic acid, succinic acid, β-hydroxybutyric acid)
as well as reducing sugars and products such as carnitine, urea, ammonia and inorganic material not further specified.

In a later publication of *T. Wood in "Journal of Science Food and Agriculture", 12th January, 1961, pp 61-69,* entitled "The browning of ox-muscle extracts", especially on page 65, artificial extracts are described, which were composed based on the results mentioned in the above publications.

Of these artificial extracts, in which a peptide and the phosphorus containing amino acids were lacking, but to which a small amount of the nucleotide inosinic acid (inosine-5'-monophosphate) had been added, the authors state that this product had only a faint taste of meat due to the presence of this nucleotide.

In Dutch patent specification 6604570 in the name of Ajinomoto Co., Inc. Tokyo, artificial flavouring mixtures are described which serve as a substitute for meat extract.

These mixtures include amino acids, phosphates, 5'-nucleotides and organic acids (especially lactic acid and succinic acid). As to the amounts of succinic acid and lactic acid this specification states that the total amount of organic acid is less than 3 parts by weight, preferably between 0.1 and 2 parts by weight calculated on the amino acids excluding the glutamic acid, and that the amount of succinic acid should not be too high (although no upper limit is given) because if the amount of succinic acid is too high a taste of crustacea (shell-fish) is obtained. In this connection the publications of Wood and Bender mention for commercial meat extract 1.42% succinic acid and 16.40% lactic acid, i.e. a mutual weight ratio of 1:11.7 and for a product obtained by extraction of meat with ice-water 0.88% succinic acid and 23.04% lactic acid, i.e. a mutual weight ratio of 1:26. The artificial product obtained by these research workers on the basis of the latter composition tasted faintly like meat and therefor provide no good substitute for commercial meat extract or meat broth.

The above-mentioned Dutch specification shows in the examples (i.e. II to VIII) weight ratios of succinic acid to lactic acid of about 1:6 so that upon comparison with the products with a meaty taste described by T. Wood the former products show a considerably higher quantity of succinic acid.

Surprisingly it has now been found that a "fuller" taste of meat may be obtained if the weight ratio of succinic acid to lactic acid is considerably lower than that which is described in the above Dutch Specification. This better taste is obtained if the weight ratio succinic acid:lactic acid is between 1:30 and 1:150 and preferably between 1:40 and 1:80. This is unexpected if one bears in mind that the patent application of Ajinomotor points in the direction of applying more succinic acid relative to lactic acid, whereas it now appeared that by the very application of considerably lower amounts of succinic acid with regard to lactic acid better results may be obtained.

Accordingly the present invention provides an artificial flavouring mixture comprising amino acids, including glutamic acid, a nucleotide, succinic acid and a hydroxycarboxylic acid, which has 2 to 5 carbon atoms in the molecule and consists of at least 50 mol %, based on the hydroxy carboxylic acid, of lactic acid, in which the weight ratio of succinic acid to hydroxycarboxylic acid, calculated as the equimolar amount of lactic acid, is between 1:30 and 1:150.

It has also been found that phosphates (other than the nucleotides) such as inorganic and organic phosphates—in contrast with what has been stated in the above-mentioned Dutch Specification—do not constitute essential ingredients of flavouring mixtures with a meaty taste. The presence of these other phosphates is therefore according to the present invention superfluous. However since the use of phosphates in the foodstuffs industry is wide spread, the invention also includes the use of the new flavouring mixtures in the presence of phosphate.

As the present invention is concerned with flavouring mixtures, including concentrated and ready-for-use foodstuffs, it is impossible to indicate absolute concentration areas. For a ready-for-use broth or soup it is in general desirable to work in such concentrations, observing the above ratio, that the quantity of succinic acid amounts to between 5 and 100 milligrams per litre.

For the present invention improved artificial flavouring mixtures are obtained with mixtures in which are present:

Amino acids, including glutamic acid (or its salts)
Nucleotides
Succinic acid
Lactic acid and any other lower hydroxycarboxylic acid in a weight ratio succinic acid:hydroxycarboxylic acid of between 1:30 and 1.150; preferably this weight ratio lies between 1:40 and 1:80.

In order to determine this weight ratio lactate, succinate and any other salts are calculated in the form of the free acid. Any hydroxycarboxylic acid present other than

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lactic acid is calculated in the form of the equimolar amounts of lactic acid. The weight ratio in question is critical for obtaining a good taste and therefore important.

Since products from natural starting materials such as commercial meat extract often vary in composition in view of their changeable starting material, and since it is possible that some naturally occurring products fulfill the qualitative and quantitative limits of this invention, it is to be understood that the invention therefore does not include natural products such as extracts of meat, nor the incorporation thereof in foodstuffs, but is related to artificially composed flavouring mixtures.

Amino acids can be defined here as the building units of proteins. As to the selection of the amino acids and their mutual ratios, it is preferable to simulate the amino acid composition of beef broth.

The amino acids required for carrying out the invention may be obtained by hydrolysis, autolysis or fermentation, or combinations of these processes applied to vegetable or animal proteins, such as soybean protein, gluten, casein and yeast, or extracts of these. Although they differ from the composition according to the invention, the mixtures thus obtained form an excellent starting material for such compositions. By the addition of at least some of the components: nucleotides, succinic acid and lactic acid and any other lower hydroxycarboxylic acid, the artificial flavouring substance according to the invention can be obtained. To obtain the best results it is desirable that the amino acid mixture has a good taste and is purified, if necessary. In addition the inclusion of an extra quantity of certain amino acids, such as glutamic acid, methionine, alanine, tryptophane, cysteine, may be desirable. It is necessary that glutamic acid and its salts are present in sufficient amounts to give the desired contribution to the taste in the final ready-for-use foodstuff, for example in a broth or soup in a concentration of 0.05-7 grams per litre. As to the amount of amino acids, especially the amount of hydrolysate it is necessary that this is present in the ready-for-use foodstuff in an amount sufficient to give the desired contribution to the taste, for example, in a broth or soup in a concentration of 0.1-7 grams per litre.

It is usual for manufacturers of foodstuffs to add to their products various materials including compositions with a taste of meat, amino acids such as hydrolysates, autolysates, and glutamate in variable amounts. It is therefore not possible to define exactly the relative amounts of these components in the artificial flavouring mixtures according to the invention since some components may be present in the foodstuff. Thus the amount by weight of amino acid, including glutamic acid to lactic acid (calculated on hydroxycarboxylic acid) is preferably between 1:0.05 and 1:20.

The nucleotides employed according to the invention are flavour boosters, particularly the 5′-ribonucleotides. As such are known for example adenosine-5′-monophosphate (5′-AMP), guanosine-5′-monophosphate (5′GMP), inosine-5′-monophosphate (5′-IMP), xanthosine-5′-monophosphate (5′XMP), uridine-5′-monophosphate (5′-UMP), cytidine-5′-monophosphate (5′-CMP), their amides, desoxy derivatives and salts.

According to the present invention one special nucleotide may be applied, but it may be advantageous to use a combination of nucleotides. Owing to their differing flavouring properties the amount of nucleotide that is employed depends, among other things, on the nature of the nucleotide used; when 5′-GMP is used, the amount is 0.05-5 parts by weight per part of succinic acid and for 5′-IMP 0.1-20 parts by weight per part of succinic acid. With commercially available mixtures containing 5′-GMP and 5′-IMP in about equal parts, addition of 0.1-10 parts by weight per part of succinic acid is sufficient.

According to the invention succinic acid and lactic acid are employed together, lactic acid being preferred to other lower hydroxycarboxylic acids. However, the acid may partly, i.e. to 50 mol % be replaced by other lower hydroxycarboxylic acids containing 2-5 carbon atoms, such as glycolic acid, α-hydroxybutryic acid and malic acid.

A satisfying meaty taste was obtained with a mixture of amino acids including glutamic acid, nucleotides, as well as succinic acid and lactic acid in a weight ratio between 1:30 and 1:150, preferably between 1:40 and 1:80. In a soup such a mixture was appreciated as "good" by a tasting panel. The appreciation was clearly less if one of the components was left out or did not fulfil the indicated weight ratio of succinic acid to lactic acid. Too high a dosage of the succinic acid appeared to cause a less good appreciation of the product.

The two carboxylic acid components will not exclusively occur in the free acid form in the composition according to the invention, but partially in the form of their salts, since the acidity of the ready-for-use product is adjusted such that the pH is from 4 to 8, preferably from 4.8 to 6.8. These salts of succinic acid and lactic acid as well as those of any other lower hydroxy acids are reduced to the corresponding equimolar amounts of succinic acid and lactic acid for the purpose of calculating quantities.

In order to obtain a composition with a fuller meaty taste, other substances may be

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utilized. Thus the amino acids, nucleotides, succinic acid and lactic acid in the proportions according to the invention may be employed together with at least one compound of at least one of the following classes of substances:

1. Amino acids such as homocysteic acid, ornithine, oxypropline, 3-hydroxy glutamic acid.
2. Peptides such as alanyl-alanine, alanyl-phenylalanine, alanyl-asparagine, carnosine, anserine.
3. Sweetening substances, both artificial sweetening substances, such as saccharine or cyclamates, and sugars, particularly mono- and disaccharides.
4. Substances with the flavour of meat or broth, particularly sulphur containing compounds, such as reaction products of amino acids like cysteine/cystine with reducing sugars or ascorbic acid, reaction products of hydrogen sulphide with lower aliphatic aldehydes and ketones (e.g. propion aldehyde, croton aldehyde, methional, mercaptoacetaldehyde).
5. Other volatile sulphur compounds, such as H_2S, mercaptans, disulphides and sulphides, such as dimethyl sulphide and diallyl sulphide.
6. Guanidines, such as creatine and creatinine.
7. Salts, such as NaCl and phosphates and particularly in connection with pH control, acid phosphates like Na_2HPO_4, NaH_2PO_4 or other alkali or ammonium phosphates and organic phosphates, such as phosphorus containing amino acids. However, it is by no means essential to incorporate phosphates.
8. Nitrogen compounds, such as ammonia, amines, urea, indole and skatole.
9. Unsaturated or saturated carboxylic acids with e.g. 2-12 carbon atoms.
10. Unsaturated or saturated higher hydroxycarboxylic acids and γ and δ-lactones derived therefrom, such as deca- and dodeca-5-olides 2.3 dimethyl-2.4-alkadiene-4-olides.
11. Lower saturated and unsaturated aldehydes, such as acetaldehyde, propion aldehyde, iso-butyraldehyde and hepten-4-al.
12. Lower saturated and unsaturated ketones, such as acetone, butanone and diacetyl.
13. Tricholominic acid and ibotenic acid or their salts.
14. Aromatic or nonaromatic carbocyclic and/or heterocyclic compounds, such as ortho amino-acetophenone, N-acetonyl pyrrole, maltol, isomaltol, ethyl maltol, lenthionine, hypoxanthine, guanine, inosine and guanosine.
15. Lower saturated and unsaturated alcohols, such as ethanol, glycerol, octanol.
16. Colouring substances, such as e.g. curcuma, caramel.
17. Thickening agents such as gelatin and starch.

The dosage of these optional ingredients is dependent on the kind of flavour one wishes to imitate, on the nature of the foodstuff to which it is added and or the other ingredients added, such as herbs and spices.

By flavouring mixtures according to the invention are to be understood products such as: substitutes for commercial meat extract, as one employed in the foodstuffs industry, "powdered flavour" such as that which may be sprinkled over foodstuffs shortly before consumption, gravy cubes, dried and concentrated soup and in general all ready-for-use foodstuffs and concentrated foodstuffs which usually possess a meat or broth flavour or in which such a shade of flavour is appreciated. Thus a more pronounced meat flavour can be imparted especially to soup, concentrated soup (e.g. tinned or dry soup), preserved meals, gravy, rissoles, preserved meat, e.g. tinned ham, with the flavouring mixture according to the invention.

The flavouring mixture according to this invention may also be used to impart a meaty flavour to potato chip and puff type products and to mayonnaise based products.

The flavouring mixture according to the invention may be prepared simply in the form of a paste. Likewise it is possible to prepare a granulated or powder product by using for example fillers such as kitchen salt, starch and gelatin.

Further it is possible to coat the powdery or granulated product with a substance such as a fat or saccharide.

The following examples are given to illustrate the invention.

Example 1

A flavouring mixture was prepared by dissolving the following ingredients in water:

1.0 g. casein hydrolysate
1.0 g. monosodium glutamate
0.6 g. inosine-5'-monophosphate
0.15 g. succinic acid
10.0 g. lactic acid

The pH of this solution was adjusted at 6.0 and subsequently the solution was diluted to 1 litre. This solution is referred to as solution A.

A soup base was prepared by mixing the following ingredients and diluting them with water to 1 litre:

6.0 g. kitchen salt
1.0 g. monosodium glutamate
0.5 g. yeast extract supplied by Kon. Ned. Gist- en Spiritusfabriek N.V., Delft, Holland.
2.0 g. lard
0.5 g. onion powder

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0.02 g. curcuma
0.05 g. parsley
2.0 g. casein hydrolysate
0.07 g. mixed herbs for soup.

To 1 litre of this soup base 100 ml of solution A was added. Another sample was prepared by adding to 1 litre of soup base 2 g of meat extract dissolved in 100 ml of water. After cooking for 10 minutes the two samples were tasted by a panel of 25 persons in a triangle-test. In this test 19 persons recognised the deviating sample, whereas 15 persons out of these 19 preferred the sample containing flavouring mixture A. This indicates a significant preference for the product prepared with the artificial flavouring mixture.

Example 2

A flavouring mixture was prepared by dissolving the following ingredients in water:
1.0 g. protein hydrolysate (casein)
1.0 g. monosodium glutamate
0.6 g. inosine-5'-monophosphate
0.15 g. succinic acid
3.0 g. lactic acid

The pH of this solution was adjusted at 6.0 and subsequently diluted to 1 litre. This solution is referred to as solution B.

To 1 litre of the soup base described in Example 1 100 ml of solution A was added. Another sample was prepared by adding to 1 litre of this base 100 ml of solution B. After cooking for 10 minutes, the two samples were judged by a panel of 36 persons. 26 persons preferred the soup with the higher content of lactic acid.

This shows that a flavouring mixture in which the weight ratio succinic acid: lactic acid is 1:66 is preferred to a flavouring mixture in which this ratio is 1:20.

Example 3

Two flavouring mixtures were prepared by dissolving the following ingredients in water:

	Solution C	*Solution D*
Casein hydrolysate	2.00 g.	2.00 g.
Monosodium glutamate	2.00 g.	2.00 g.
Inosine-5'-monophosphate	0.05 g.	0.05 g.
Succinic acid	0.10 g.	0.10 g.
Lactic acid	0.60 g.	3.50 g

The pH of these solutions was adjusted at 5.2 and subsequently the two solutions were diluted to 1 litre. Then two samples were prepared by diluting 100 ml of the two solutions described above to 1 litre and cooking for 10 minutes. In an organoleptic examination by a panel of 29 persons, 23 persons preferred the solution in which the weight ratio succinic acid: lactic acid is 1.35.

Example 4

Two flavouring mixtures were prepared by dissolving the following ingredients in water:

	Solution D	*Solution E*
Casein hydrolysate	2.00 g.	2.00 g.
Monosodium glutamate	2.00 g.	2.00 g.
Inosine-5'-monophosphate	0.05 g.	0.05 g.
Succinic acid	0.10 g.	0.10 g.
Lactic acid	3.50 g.	6.00 g.

The pH of these solutions was adjusted at 5.5 and subsequently the two solutions were diluted to 1 litre. Then two samples were prepared by diluting 100 ml of the two solutions described above to 1 litre and cooking for 10 minutes. The two samples were tasted in a triangle-test by a panel of 47 persons. 25 persons indicated the deviating sample correctly and of these 25 persons 18 persons preferred the solution with the higher content of lactic acid. The mixture in which the weight ratio succinic acid: lactic acid=1:60 was preferred to the mixture in which this weight ratio is 1:35.

Example 5

A flavouring mixture was prepared by dissolving the following ingredients in water:
1.0 g. casein hydrolysate
1.0 g. monosodium glutamate
0.6 g. inosine-5'-monophosphate
0.15 g. succinic acid
10.0 g. lactic acid
2.5 g. phosphoric acid

The pH of the solution was adjusted at 6.0 and subsequently the solution was diluted to 1 litre. This solution is referred to as Solution F.

To 1 litre soup base from Example 1 100 ml of solution A was added. Another sample was prepared by adding to 1 litre of this base 100 ml of solution F.

After 10 minutes cooking, the two samples were judged in a triangle-test by a group of 36 persons. 13 persons recognized the deviating sample. So it appears that the panel did not taste a difference between soups to which phosphate had or had not been added.

Example 6

A flavouring mixture was prepared by dissolving the following ingredients in water:
10.0 g. casein hydrolysate
5.0 g. monosodium glutamate
0.6 g. inosine-5'-monophosphate
0.6 g. guanosine-5'-monophosphate
0.2 g. succinic acid
14.0 g. lactic acid
0.1 g. malic acid
0.5 g. fumaric acid
1.0 g. taurine
2.0 g. carnosine
0.1 g. guanosine
1.0 g. fructose
10 g. kitchen salt

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The pH of this solution was adjusted at 5.2 and subsequently the solution was diluted to 1 litre. This solution is referred to as Solution G.

A gravy base was prepared by mixing the following ingredients and diluting them with water to 1 litre:

3.0 g. gelatin
5.0 g. potato starch
2.5 g. onion powder
3.0 g. monosodium glutamate
5.0 g. lard
0.8 g. caramel
0.02 g. pepper
0.02 g. laurel
0.02 g. cloves
3 g. kitchen salt

To 1 litre of the above-mentioned gravy mixture were added 100 ml of solution G. Another sample was prepared by adding to the gravy base 2.5 g. of meat extract in 100 ml of water. Both samples were cooked for 10 minutes and subsequently judged by a panel of 23 persons. 19 persons of the panel preferred the sample containing solution G.

Example 7

30 g. of butter were melted and then mixed with 30 g. of flour. To this were added while stirring and heating 200 g. of broth made from 80 g. of meat; the sauce obtained was finished with 0.01 g. of pepper, 2 g. of kitchen salt and 0.5 g. of monosodium glutamate. 100 g. of finely divided veal, well-done in an ample amount of water, were mixed therewith. After shaping and dusting the rissoles so produced were fried in frying fat.

In the same way rissoles were made in which, instead of 200 ml of broth, 200 ml of a 10 times diluted solution G (see Example 6) were added.

A panel of 25 persons did not detect a significant difference between the two formulations.

Example 8

Spun soybean protein fibres were thoroughly washed and subsequently roughly cut. The pieces thus obtained were ground with an excess of water in a household-mixer and then sieved out. The mixture was then cooked in water for 15 minutes, and after cooling separated using a sieve from the superfluous water. Further water was removed by pressing the sieved out product in a cloth. To 100 g. of this product was subsequently added 1 g kitchen salt, 20 g of pasteurised egg-white and some caramel. After mixing thoroughly the mixture was pressed into an artificial sausage casing and coagulated in a boiling water bath for 30 minutes.

In exactly the same way imitation meat was made to which besides 1 g. of kitchen salt, 20 g. white of a chicken egg and caramel, a dry mixture was added of:

0.040 g. casein hydrolysate
0.010 g. inosine-5'-monophosphate
0.005 g. succinic acid
0.300 g. sodium lactate

All tasters were unanimously of the opinion that the latter product had a good taste of cooked meat, whereas the former product only had a salty taste.

Example 9

Two flavouring mixtures were prepared by dissolving the following ingredients in water:

	Solution H	*Solution J*
Casein hydrolysate, non-saline	1.10	1.0
Monosodium glutamate	0.19	—
Inosine-5'-monophosphate	0.10	0.45
Succinic acid	0.18	0.18
Lactic acid	1.20	12.5
Kitchen salt	0.30	1.0
Phosphoric acid	0.20	—
Sodium tartrate	0.10	—
Ammonium chloride	0.16	—
Glucose	0.50	—
Lactose	0.16	—
Maize starch	0.05	—
Creatine	0.31	0.30

The pH of these two solutions was adjusted at 5.5 and subsequently the two solutions were diluted to 1 litre.

2 litres of soup base were prepared by mixing the following ingredients and diluting them with water to 2 litres:

3.92 g. lard
0.28 g. garlic powder
0.34 g. carrot powder
0.22 g. caramel dye
4.92 g. sugar
14.6 g. salt
0.112 g. onion powder
3.92 g. monosodium glutamate
11.2 g. casein hydrolysate
1.34 g. meat extract

To this soup base were added per litre 100 ml solution H and 100 ml solution J, respectively. After cooking for 10 minutes the two soups were judged organoleptically by a taste panel of 29 persons. 26 persons preferred the soup prepared with solution J.

Example 10

A dried pulverized flavouring mixture was prepared in the following way: 825 g. sodium lactate solution (60% by weight pH=6.0) were mixed with 1200 g. potato starch. After setting a loose mass resulted, which was dried and subsequently ground. To 1100 g. of the powder obtained in this way the following ground ingredients were added:

6.0 g. succinic acid
15.0 g. inosine-5'-monophosphate
3.0 g. guanosine-5'-monophosphate
100 g. casein hydrolysate
100 g. kitchen salt
10.0 g. taurine

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10.0 g. glucose
2.0 g. malic acid

By thoroughly mixing these components a pulverized flavouring mixture was obtained. Subsequently two samples were prepared, one by dissolving 5 g. of commercial meat extract in 1 litre of water and another by dissolving 7 g. of the flavouring mixture described above in 1 litre of water. After cooking for 10 minutes the two samples were judged organoleptically.

The taste of the solution containing the artificial flavouring mixture was almost unanimously preferred.

Example 11

A dry soup was prepared by mixing the following ingredients:

70.0 g. pulverized artificial flavouring mixture (see Example 10)
10.0 g. monosodium glutamate
20.0 g. casein hydrolysate
30 g. dried onions
40 g. dried meat
10 g. milk powder
50 g. fat
4 g. paprika
2 g. dried green leek
0.2 g. pepper
0.2 g. thyme
0.1 g. laurel
0.1 g. mace
60.0 g. salt.

A ready-for-use soup was prepared by adding 65 g. of this dry powder to 2 litres of hot water. After cooking for 10 minutes this soup was organoleptically judged and qualified as a very good beef soup.

Example 12

A soup base of a volume of 2 litres was prepared from the following ingredients:

200 g. leeks
120 g. noodles
100 g. carrots
70 g. onions
32 g. kitchen salt
25 g. fat
10 g. celery leaves
10 g. parsley
5 g. monosodium glutamate
2 g. hydrolysed soy protein
0.2 g. pepper

A flavouring mixture was prepared by dissolving the following ingredients in water:

16.0 g. lactic acid
10.0 g. kitchen salt
0.3 g. succinic acid
0.7 g. inosine-5′-monophosphate
0.1 g. 5′-guanosine-5′-monophosphate
2.0 g. creatine
0.2 g. malic acid

The pH of this solution was adjusted to 5.8 and the volume of the solution was made up to 1 litre.

A concentrated soup was prepared by mixing 400 ml of the soup base with 100 ml of the flavouring composition. The resulting product was sterilized in 0.5 litre cans for 1 hour at 120°C. A reference sample was prepared by mixing 400 ml of the soup base with 100 ml of water containing 1.5 g. of meat extract of first quality. This reference sample was sterilized in the same way as the sample with the flavouring composition.

A product ready for consumption was prepared by mixing the contents of four cans with 2 litres of water and by heating the resulting mixture to the boil.

Both samples were tasted by a panel consisting of 35 persons. 27 members of the panel preferred the sample containing the artificial flavouring composition.

WHAT WE CLAIM IS:

1. An artificial flavouring mixture comprising amino acids, including glutamic acid, a nucleotide, succinic acid and a hydroxycarboxylic acid, which has 2 to 5 carbon atoms in the molecule and consists of at least 50 mol %, based on the hydroxycarboxylic acid, of lactic acid, in which the weight ratio of succinic acid to hydroxycarboxylic acid, calculated as the equimolar amount of lactic acid, is between 1:30 and 1:150.

2. An artificial flavouring mixture according to Claim 1, in which the weight ratio of succinic acid to hydroxycarboxylic acid as defined in Claim 1 is between 1:40 and 1:80.

3. An artificial flavouring mixture according to Claim 1 or 2, in which all the hydroxycarboxylic acid is lactic acid.

4. An artificial flavouring mixture according to any of the preceding claims, in which the nucleotide comprises a 5′-ribonucleotide.

5. An artificial flavouring mixture according to any of the preceding claims, in which the nucleotide comprises guanosine-5′-monophosphate.

6. An artificial flavouring mixture according to any of the preceding claims, in which the nucleotide comprises inosine-5′-monophosphate.

7. An artificial flavouring mixture according to any of the preceding claims, in which the weight ratio of succinic acid to nucleotide is between 1:0.05 and 1:20.

8. An artificial flavouring mixture according to any of the preceding claims, in which the weight ratio of amino acid, including glutamic acid, to hydroxycarboxylic acid is between 1:0.05 and 1:20.

9. An artificial flavouring mixture according to any of the preceding claims, in which the amino acids are obtained by hydrolysis, autolysis, or fermentation of vegetable or animal proteins or extracts thereof and in which at least one additional amino acid selected from methionine, alanine, trypto-

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phane, cysteine has been added.

10. An artificial flavouring mixture according to any of the preceding claims, which is free of phosphates, either inorganic or organic other than nucleotides.

11. An artificial flavouring mixture as claimed in Claim 1 and substantially as described herein with reference to any one of the examples of the invention.

12. A process for the preparation of an artificial flavouring mixture by mixing amino acids including glutamic acid, nucleotides, succinic acid and hydroxycarboxylic acid having 2-5 carbon atoms and including at least 50 mol % lactic acid, in which the weight ratio of succinic acid to hydroxycarboxylic acid containing 2-5 carbon atoms in the molecule and consisting of at least 50 mol % of lactic acid, reduced to the equimolar amount of lactic acid, is between 1:30 and 1:150.

13. A foodstuff comprising an artificial flavouring mixture as claimed in any one of the Claims 1 to 11 or produced by a process as claimed in Claim 12.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1970
Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY from which copies may be obtained.

PATENT SPECIFICATION (11) 1221482

1221482

NO DRAWINGS

(21) Application No. 24669/68 (22) Filed 23 May 1968
(31) Convention Application No. 6707232 (32) Filed 25 May 1967 in
(33) Netherlands (NL)
(45) Complete Specification published 3 Feb. 1971
(51) International Classification A 23 l 1/26
(52) Index at acceptance
A2B 6A 6G

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(54) FLAVOURING COMPOSITIONS

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process of preparing artificial flavouring compositions having a meaty taste, and to artificial flavouring compositions.

The meaty taste of many commercially available foodstuffs, such as soups, gravies and preserved meats, is often obtained by incorporating during their preparation a product which is known in trade as a meat extract, herein referred to as "commercial meat extract". This product, however, which is normally obtained by water extraction of meat, particularly beef, followed by evaporation of the greater part of the water, has various drawbacks. In the first place, owing to the costly and time-consuming method of preparation it is not only relatively expensive, but its quality is not very constant, and after dilution with water its taste is different from that of the broth as gravy directly prepared from meat.

In the preparation of foodstuffs having a meaty taste attempts have been made to replace this commercial meat extract partly or completely by artificial flavouring compositions. The components of such flavouring compositions include compounds which either as such or in combination have a taste approximating that of meat extracts or of meat-containing foodstuffs.

Such artificial flavouring compositions are used both in the preparation of concentrates (such as "powdered flavour", gravy cubes, gravy powder and concentrated soup) which by dilution with other foodgrade ingredients can be processed into ready-for-use foodstuffs having a meaty taste, and in the industrial preparation of foodstuffs which are ready for use (such as soup and preserved meals).

[*Price 5s. 0d. (25p)*]

Although such artificial flavouring compositions are in the first place used for obtaining and/or improving tastes corresponding with those of meat originating from warm-blooded animals, they can also be used for obtaining and/or improving tastes corresponding with those of meat originating from other animals, such as fish (e.g. tunny), crustaceans (e.g. lobster), shell-fish (e.g. mussels).

In the following specification, therefore, by artificial flavouring composition having a meaty taste are understood, besides concentrates, also ready-for-use foodstuffs having a meaty taste, including those already containing meat and meat extracts, the term "meat" including meat originating from warm-blooded animals as well as that from other animals mentioned above. Examples of flavouring compositions according to the invention are artificial meat extract, "powdered flavour", gravy cubes or gravy powder, concentrated soup (in tins or in dry form), soup, lobster soup, preserved meals, preserved meat, such as tinned ham, preserved fish, such as tinned tunny, risoles, "nasi goreng", potato chips, and the like.

Known components of such artificial flavouring compositions include: protein hydrolysates, single amino acids, particularly L-glutamino acid and/or a salt thereof, more particularly the monosodium salt (usually abbreviated to MSG) and nucleotides, particularly 5'-ribonucleotides, such as guanosine-5'-monophosphate (5'-GMP), inosine-5'-monophosphate (5'-IMP) and adenosine-5'-monophosphate (5'-AMP). It has further been proposed to incorporate in such flavouring compositions succinic acid or a salt thereof. Although the flavouring compositions thus obtained possess a characteristic taste indeed, yet they do not always fulfil the purpose aimed at, as this taste or sometimes their aftertaste is often experienced as "sharp".

Thus, the taste of flavouring compositions containing glutamic acid and/or 5'-ribonucleotides but in particular of compositions containing succinic acid can be rounded and

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made milder by combining these acids or their corresponding salts with pyrrolidone carboxylic acid.

Accordingly the present invention provides an artificial flavouring composition comprising pyrrolidone carboxylic acid and succinic acid in which the weight ratio of the acids, calculated as free acids, is pyrrolidone carboxylic acid 1 part to succinic acid 0.01 up to 5 parts.

A preferred ratio to 1 part of pyrrolidone carboxylic acid to 0.02 up to 1 parts of succinic acid.

These flavouring compositions of this invention can also usefully contain glutamic acid in which case the weight ratio of pyrrolidone carboxylic acid to glutamic acid, calculated as the free acid, is 1 part pyyrolidone carboxylic acid to 0.02 up to 50 parts of glutamic acid, preferably 1 to 0.25 up to 25 parts.

Flavouring compositions according to the invention can also contain 5'-ribonucleotides together with the pyrrolidone carboxylic acid and succinic acid and, optionally glutamic acid, the weight ratio, calculated as free acid, is 1 part of pyrrolidone carboxylic acid to 0.01 up to 10 parts of 5'-ribonucleotide, preferably 1 part to 0.03 up to 5 parts.

Since the present invention relates to flavouring compositions for use in both concentrated and ready-for-use foodstuffs, it is not possible to indicate absolute concentration ranges applying to all flavouring compositions. For a ready-for-use foodstuff, such as soup, broth, ragout and nasi goreng, it is generally desirable to employ such concentrations that the amount of pyrrolidone carboxylic acid (calculated as free acid) is 0.01—10, preferably 0.1—3 g/kg. For concentrated flavouring compositions, such as liquid or solid "sprinkling flavour", gravy cubes or gravy powder and concentrated soup (in tins or in dry form), which by dilution with other food-grade components can be converted into a ready-for-use foodstuff, it is generally, desirable to choose such a concentration of pyrrolidone carboxylic acid that after addition of the flavouring composition or processing it to ready foodstuffs the concentration obtained therein corresponds with the aforesaid concentration of 0.01—10, preferably 0.1—3 g/kg.

Pyrrolidone carboxylic acid contains an asymmetric carbon atom hence 2 optical isomers exist. The L-pyrrolidone carboxylic acid has particularly favourable taste-modifying characteristics, so that in the preparation of artificial flavouring compositions according to the invention, it is preferred to use this compound or precursors thereof.

Although it is preferred to incorporate in these flavour compositions pyrrolidone carboxylic acid as such, it may also be partly or completely replaced by a compound acting as precursor, i.e. a compound which under the conditions applied during preparation of the ready-for-use foodstuffs with or from the flavouring composition is converted to a considerable degree, preferably for more than 20%, into pyrrolidone carboxylic acid, which eventually also leads to the above result. An example of such a precursor is glutamine.

When the pyrrolidene carboxylic acid is partly or completely replaced by a precursor, such as glutamine, such an amount thereof is taken, that the weight ratio of the pyrrolidone carboxylic acid present in the ready-for-use products will fall within the above given limits, both in relation to the other aforementioned flavouring compounds (succinic acid, glutamic acid and 5'-ribonucleotides) and in relation to the ready-for-use product.

The pyrrolidone carboxylic acid is a well-known compound, which in an aqueous medium is in equilibrium with glutamic acid. The factors which are of importance with respect to this equilibrium have been the subject of extensive investigations, in which it was found, inter alia, that ring closure is complete at pH 7. The rate of reaction of this ring closure reaction is, however, very slow at this pH. Thus, on heating glutamic acid in an aqueous medium at pH 7 at 100°C for 2—3 hrs. only about 1% of this product is converted into pyrrolidone carboxylic acid. Further, pyrrolidone carboxylic acid can be formed by ring closure of glutamine with splitting off of ammonia, which ring closure proceeds far more rapidly.

Although in the literature many investigations have been described with regard to the substances occurring in meat and meat extracts which might contribute to the taste of these products, which investingations were usually based on sensitive methods of separation and identification, there is not a single case in which mention is made of pyrrolidone carboxylic acid as component of meat extracts.

Neither does the literature contain any description of artificial flavouring compositions with a meaty taste comprising pyrrolidone carboxylic acid as taste-modifying agent.

It is known indeed that pyrrolidone carboxylic acid is found in a number of products of vegetable origin. Among other things, it forms a component of certain Japanese soybean sauces. Furthermore, a number of authors associate the so-called "off-flavour" of certain foodstuffs of vegetable origin with their content of pyrrolidone carboxylic acid. It appears that the compound is found in a number of sterilised products (beets, tomatoes, maize and cherries), whereas in fresh condition these products do not contain pyrrolidone carboxylic acid or contain it in a much lower concentration. In this connection it could be shown that under the influence of the sterilisation conditions employed the

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acid was formed from glutamine, whereas the glutamic acid was not converted under these conditions into pyrrolidone carboxylic acid.

It has been suggested in the literature to employ the hygroscopic properties of the salts of pyrrolidone carboxylic acid by adding these salts as agents for promoting moisture retention to products which tend to lose moisture when exposed to the air, such as cosmetics, emulsions and foodstuffs; in order to produce the desired effect these products should then contain at least 2, but preferably 4 to 10% by wt. of such a salt.

On the basis of the properties of pyrrolidone carboxylic acid described above, it is very surprising that this product can be applied as taste-modifying agent in flavouring compositions having a meaty taste.

Further, certain limitations should be made with respect to artificial flavouring compositions with a meaty taste to which glutamic acid or MSG, respectively, have been added as the flavouring component. Although, as stated before, in the sterilisation of vegetable foodstuffs containing glutamic acid no conversion of this product into pyrrolidone carboxylic acid can be established, it should still be taken into account, on the basis of the chemical properties of the said product, that such a conversion takes place, be it for a small percentage up to maximum of 2%. However, from taste tests it has appeared that in artificial flavourings compositions containing glutamic acid in combination with pyrrolidone carboxylic acid no taste improving effect can be established if the amount of pyrrolidone carboxylic acid is less than 2% by wt. of the glutamic acid present. So, as far as heating (e.g. for sterilisation purposes) would lead to the formation of pyrrolidone carboxylic acid, the amount of this acid is insufficient to produce the desired effect, so that for such glutamic acid containing flavouring compositions it remain necessary to add pyrrolidone carboxylic acid. For clarity's sake therefore, it is stated that the invention includes neither processes nor flavouring compositions in which the pyrrolidone carboxylic acid exclusively originates from glutamic acid.

If desired, other components than those already mentioned above may be incorporated in the flavouring compositions according to the invention. The first of such components to be considered are kitchen-salt, carboxylic acids other than those already mentioned, such as lactic acid and malic acid, and amino acids other than glutamic acid. By amino acids are understood here the building stones of proteins, such as alanine, histidine, arginine, threonine, methionine and leucine. As regards the mutual ratio of these amino acids the aim is preferably to approach an amino cadi composition such as that of meat broth.

The amino acid mixtures to be used for carrying out the invention can be obtained in a simple way by hydrolysis, autolysis or fermentation, or combinations thereof, of vegetable or animal proteins, such as soybean protein, gluten, casein and yeast, or of extracts of these products.

Further compounds or classes of compounds which can be applied advantageously in the flavouring compositions according to the invention are the following:—

1) Amino acids such as homo-cysteine acid, ornithine, oxyproline and β-hydroxy-glutamic acid.

2) Peptides, such as alanyl-alanine, alanyl-fenylalanine, ananyl-asparagine, carnosine and anserine.

3) 5'-ribonucleotides other than those already mentioned above, such as xanthose-5'-monophosphate (5'-XMP), uridine-5'-monophosphate (5'-UMP), cytidine-5'-monophosphate (5'-CMP), as well as their amides, desoxy derivatives.

4) Artificial sweetening substances.

5) Substances having the flavour of meat or broth, particularly sulphur containing compounds, such as compounds obtained by reaction of amino acids like cysteine/cystine with reducing sugars, ascorbic acid and the like, reaction products of hydrogen sulphide with lower aliphatic aldehydes or ketones (e.g. propionaldehyde, crotonaldehyde, methional, mercaptoacetaldehyde).

6) Other volatile sulphur compounds, such as H_2S, mercaptans, disulphides and sulphides, such as dimethyl sulphide and diallyl sulphide.

7) Guanidines, such as creatine and creatinine.

8) Salts, such as phosphates, particularly in connection with the pH, so-called acid phosphate like Na_2HPO_4, NaH_2PO or other alkali or ammonium phosphates and organic phosphates, such as phosphorus containing amino acids.

9) Nitrogen compounds, such as ammonia, amines, urea.

10) Saturated or unsaturated carboxylic acids having 2—12 carbon atoms.

11) Saturated or unsaturated higher hydroxycarboxylic acids and γ- and σ-lactones derived therefrom, such as deca- and dodeca-5-olides and 2,3-dimethyl-2,4-alkadiene-4-olides.

12) Lower saturated and unsaturated aldehydes, e.g. acetaldehyde; propionaldehyde, isobutyraldehyde and hepten-4-al.

13) Lower saturated and unsaturated ketones, such as acetone, butanone and diacetyl.

14) Tricholominic acid and ibotenic acid or their salts.

15) Aromatic or non-aromatic carbocyclic and/or heterocyclic compounds, such as ortho amino - acetophenone, N - acetonyl pyrrole, indole, skatole, maltol isomaltol, ethyl maltol,

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lentionine, hypoxanthine, guanine, inosine and guanosine.

16) Lower saturated and unsaturated alcohol, such as ethanol, glycerol and octenol.

17) Colouring substances, such as curcuma.

18) Thickening agents such as gelatin and starch.

The dosage of these optional ingredients depends on the kind of flavour one wishes to imitate and further on the nature of the foodstuff to which it is added and the other ingredients incorporated in it, such as herbs and spices.

The flavouring composition according to the invention may be prepared simply in solution or in the form of a paste. It is also possible to prepare a granulated, powdered or tablet-shaped product by using fillers such as kitchen salt, starch and gelatin. Further, it is possible to coat the powdered or granulated product with a substance such as fat.

The invention will now be illustrated by the following examples:

The L-pyrrolidone carboxylic acid used in the examples possessed the following characteristics:

Melting point:	160—162°C
Optical rotation $[\alpha]_D^{20}$:	−10.7° (C=6; H_2O).

Example 1

Two solutions were prepared by dissolving the following ingredients in water:

	Solution G	Solution H
Sodium chloride	1.0 g	1.0 g
Lactic acid	4.0 g	4.0 g
Succinic acid	0.20 g	0.20 g
L-pyrrolidone carboxylic acid	—	2.0 g

The pH of these solutions was adjusted at 5.5 and subsequently both solutions were diluted to 1 liter. After heating to 55°C the taste of both solutions was judged by 29 persons. The taste of solution H was preferred by 20 persons.

Example 2

Two solutions were prepared by dissolving the following ingredients in water:

	Solution K	Solution L
Sodium chloride	1.0 g	1.0 g
5'-IMP	0.15 g	0.15 g
5'-GMP	0.15 g	0.15 g
Lactic acid	8.0 g	8.0 g
Succinic acid	0.20 g	0.20 g
L-pyrrolidone carboxylic acid	—	2.0 g

The pH of these solutions was adjusted to 5.5 and subsequently both solutions were diluted to 1 litre. After heating to 55°C the taste of both solutions was judged by 28 persons. The taste of solution L, more resembling that of broth, was preferred by 23 persons.

Example 3

Two solutions were prepared by dissolving the following ingredients in water:

	Solution O	Solution P
Sodium chloride	1.0 g	1.0 g
5'-IMP	0.20 g	0.20 g
Lactic acid	7.0 g	7.0 g
Monosodium glutamate	2.0 g	2.0 g
Succinic acid	0.20 g	0.20 g
L-pyrrolidone carboxylic acid	—	2.0 g

The pH of both solutions was adjusted to 5.5 and subsequently both solutions were diluted to 1 litre. After heating to 55°C the taste of both solutions was judged by 28 persons. The fuller taste of solution P, a taste more resembling that of broth, was preferred by 22 persons.

Example 4

Two flavouring solutions were prepared by dissolving the following ingredients in water:

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	Solution Q	Solution R
Sodium chloride	1.0 g	1.0 g
5′-IMP	0.20 g	0.20 g
5′-GMP	0.15 g	0.15 g
Monosodium glutamate	0.5 g	0.5 g
Succinic acid	0.20 g	0.20 g
Casein hydrolysate	0.50 g	0.50 g
Pyrrolidone carboxylic acid	—	2.5 g

Both solutions were adjusted to pH 5.7, supplemented to 1 litre and subsequently heated up to 55°C. A panel of 18 persons unanimously preferred the taste of solution R.

EXAMPLE 5

Two solutions were prepared by dissolving the following ingredients in water:

	Solution S	Solution T
Sodium chloride	1.0 g	1.0 g
5′-IMP	0.20 g	0.20 g
5′-GMP	0.10 g	0.10 g
Monosodium glutamate	0.5 g	0.5 g
Lactic acid	5.0 g	5.0 g
Succinic acid	0.10 g	0.10 g
Phosphoric acid	1.5 g	1.5 g
Casein hydrolysate	0.5 g	0.5 g
L-pyrrolidone carboxylic acid	—	2.0 g

The pH of these solutions was adjusted to 5.5 and subsequently these solutions were diluted to 1 litre. After heating to 55°C the taste of both solutions was judged by 27 persons. Of this panel 21 persons preferred the taste, more resembling that of broth, of solution T.

EXAMPLE 6

A soup base was prepared by mixing the following ingredients and diluting them with water to 2 litres:

13.0 g sodium chloride
12.0 g lard
3.0 g onion powder
2.0 g celery salt
2.0 g casein hydrolysate
0.20 g dried parsley
0.04 g curcuma
0.12 g pepper
0.06 g laurel powder
0.04 g mace.

Two flavouring solutions were prepared by dissolving the following substances in water:

	Solution 1	Solution 2
Succinic acid	2.5 g	2.5 g
L-pyrrolidone carboxylic acid	—	25.0 g

The pH of both solutions was adjusted to 6.0, after which both solutions were diluted to 1 litre. Subsequently, two test samples were prepared by adding to 1 litre of the soup base described above 10 ml of solution 1 and solution 2, respectively. After cooking for 10 minutes the two test samples were appreciated by a panel of 18 persons. The fuller taste of the sample containing solution 2 was preferred by 15 persons of the panel.

EXAMPLE 7

A soup base was prepared by mixing the following ingredients and diluting them with water to 4 litres:

24.0 g sodium chloride
7.0 g casein hydrolysate
4.0 g monosodium glutamate
8.0 g Gistex (spray-dried yeast extract)
0.08 g curcuma
2.0 g onion powder
0.2 g parsley (dried)
0.25 g seasonings for soup.

At the same time two flavouring solutions were prepared by dissolving the following substances in water:

	Solution 3	Solution 4
Sodium chloride	10.0 g	10.0 g
5′-IMP	2.0 g	2.0 g
Lactic acid	15.0 g	15.0 g
Casein hydrolysate	8.0 g	8.0 g
Succinic acid	0.3 g	0.3 g
L-pyrrolidone carboxylic acid	—	4.0 g

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The pH of these solutions was adjusted to 6.0, after which both solutions were diluted to 1 litre. Subsequently two test samples were prepared by adding to 2 litres of the above soup base 200 ml solution 3, and 200 ml solution 4, respectively. After cooking for 10 minutes the samples were tasted in a triangle-test by 24 persons. Of this panel 15 persons correctly recognized the deviating sample.

EXAMPLE 8

A flavouring composition was prepared by dissolving the following ingredients in water:

10.0 g NaCl
10.0 g casein hydrolysate
10.0 g monosodium glutamate
15.0 g lactic acid
0.4 g succinic acid
0.5 g fumaric acid
4.0 g L-pyrrolidone carboxylic acid
0.6 g 5'-IMP
0.4 g 5'-GMP
1.0 g taurine
2.5 g carnosine

The pH of this solution was adjusted at 5.5 and the volume was made up to 1 litre. This solution will be referred to as solution 5.

A gravy base was prepared from the following ingredients:

4.0 g gelatine
0.1 g curcuma
6.0 g NaCl
1.0 g carrot powder
1.0 g onion powder
5.0 g tomato purée
0.3 g clove powder
0.04 g laurel powder
0.06 g pepper
1.0 g casein hydrolysate
15.0 g tallow
1.0 l water

The gelatin was soaked in part of the water. The rest of the water was heated and mixed with the other ingredients. Finally the gelatine solution was added.

To 1 litre of the above gravy base 100 ml of solution 5 was added. A second gravy was prepared by adding to 1 litre of the gravy base 5 g meat extract, dissolved in 100 ml water. After cooking for 10 minutes both gravy samples were organoleptically appreciated by a panel of 26 persons. Of this panel 19 persons preferred the gravy prepared with solution 5.

A third gravy, composed of 1 litre of gravy base, 2 g meat extract dissolved in 50 ml water and 50 ml of solution 5, was compared in an analogous way with the second gravy, composed of the gravy base and 5 g meat extract. It then appeared that also the partial replacement of meat extract by the flavouring composition resulted in a product which a test panel preferred to the second gravy, in which nothing of the meat extract had been replaced.

EXAMPLE 9

A ragout base was composed of the following ingredients:

40.0 g margarine
40.0 g flour
400.0 g water
0.01 g pepper
1.5 g monosodium glutamate
0.02 g curcuma
2.5 g NaCl
20.0 g veal

The molten margarine was mixed with the flour and the mixture obtained was stirred up with the heated water. The sauce was finished with the remaining ingredients. The meat was added to this mixture in a finely divided and well-done form.

At the same time the two flavouring solutions were prepared by dissolving the undermentioned substances in water:

	Solution 6	Solution 7
Succinic acid	1.0 g	1.0 g
L-pyrrolidone carboxylic acid	—	12.0 g

The pH of both solutions was adjusted to 5.8 and their volume was made up to 250 mls. in each case.

To the ragout base described 25 ml of solution 6 and 25 ml of solution 7, respectively, were added per 500 g of ragout base. After heating both ragouts were organoleptically judged by a panel of 22 persons. Of this panel 17 persons preferred the ragout prepared with solution 7.

EXAMPLE 10

Nasi goreng was prepared with the following ingredients:

200.0 g rice
8.0 g sodium chloride
1.2 g sambal
1.5 g casein hydrolysate
50.0 g pork
20.0 g red paprika
200.0 g onions (cut)
15.0 g lard
400.0 g water

The rice was cooked for 25 minutes in water with salt. In a frying pan the meat was fried in the fat, after which the onions, paprika, sambal and casein hydrolysate were

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added. All this was well mixed and fried until the onions had obtained a golden colour. Subsequently, the rice was added and fried with constant stirring.

To this nasi 40 ml of a flavouring composition were added which had been obtained by dissolving the undermentioned ingredients in water:

10.0 g casein hydrolysate
60.0 g lactic acid
1.0 g 5'-GMP
1.5 g 5'-IMP
12.0 g L-pyrrolidone carboxylic acid
1.0 g succinic acid.

The pH of this solution was adjusted at 5.5 and subsequently the volume was made up to 1 litre (solution 8).

A panel of 18 testers unanimously preferred the nasi with the flavouring composition 8, on account of its being full-flavoured and having a more meaty taste.

EXAMPLE 11

A powdered flavouring composition, suitable as sprinkling flavour, was obtained by spray-drying a 35% solution, containing NaCl, sodium lactate and dextrine maltose in a ratio of 3.5:2:1.

To 110 g of the powder thus obtained the following substances were added:

10.0 g NaCl
10.0 g casein hydrolysate
1.5 g 5'-IMP
1.0 g 5'-GMP
10.0 g monosodium glutamate
6.0 g L-pyrrolidone carboxylic acid Na salt
0.6 g succinic acid
6.0 g creatine
3.0 g taurine
1.6 g $Na_2HPO_4.2H_2O$.

A panel of 19 testers found that the addition of this flavouring composition, as a sprinkling flavour, to a soup already served improved the taste of this soup.

EXAMPLE 12

A powdered flavouring composition was prepared by mixing 450 g 60% sodium lactate solution with 700 g potato starch. After setting of the mixture it was dried and ground. To 500 g of the powder obtained the following substances were added:

40.0 g casein hydrolysate
3.0 g 5'-GMP
3.5 g 5'-IMP
2.5 g sucicnic acid
40.0 g NaCl
1.0 g Malic acid
30.0 g L-pyrrolidone carboxylic acid Na salt
5.0 taurine
7.0 g creatine

The mixture was thoroughly mixed and ground once more.

A dry soup was prepared by mixing 80 g of the above pulverized flavouring composition with the following ingredients:

25.0 g casein hydrolysate
5.0 g monosodium glutamate
60.0 g sodium chloride
50.0 g lard
60.0 g dried beef (cut)
0.2 g curcuma
2.0 g parsley
5.0 g celery salt
0.2 g thyme
0.2 g mace
0.2 g clove powder
0.2 g laurel powder
10.0 g onion powder
50.0 g vermicelli

A soup was prepared by cooking 35 g of the mixture thus obtained with 1 litre water for 10 minutes. On organoleptic judgement this product was qualified as a good beef soup.

EXAMPLE 17

A soup base was prepared by incorporating the following ingredients in 1 litre water:

15.0 g sodium chloride
1.25 g monosodium glutamate
6.25 g casein hydrolysate
2.5 g onion powder
1.25 g celery salt
0.05 g thyme
0.05 g mace
0.05 g clove powder
0.05 g laurel powder
0.5 g dried parsley
0.07 g curcuma
2.5 g gelatine
12.5 g lard

A flavouring solution was prepared by dissolving the undermentioned ingredients in water:

2.5 g sodium chlorine
2.5 g casein hydrolysate
3.5 g L-pyrrolidone carboxylic acid
0.25 g succinic acid
20.0 g lactic acid
0.6 g 5'-GMP

The pH of this solution was adjusted to 5.7, after which the solution was supplemented to 1 litre.

A concentrated soup was prepared by adding to 400 ml soup base 100 ml of the flavouring solution. After a sterilisation process the soup thus obtained was diluted with an equal volume of water (0.5 litres) and heated up to 55°C to yield a ready-for-use product.

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On organoleptic judgement this soup was qualified as very good.

If in the above-mentioned flavouring solution 3.5 g L-pyrrolidone carboxylic acid were replaced by 4 L-glutamine, further test conditions being the same, also a soup of very good quality was obtained.

The L-glutamine used in this case possessed the following characteristics:

Melting point:	183°—184°C (with decomposition)
Optical rotation $[\alpha]_D^{20}$:	31.8° (C=7; 1.37 N hydrochloric acid).

As stated above, processes and flavouring compositions in which the pyrrolidone carboxylic acid exclusively originates from glutamic acid form no part of this invention.

Subject to the foregoing disclaimer, what we claim is:—

1. An artificial flavouring composition comprising pyrrolidone carboxylic acid and succinic acid in which the weight ratio of the acids, calculated as the free acid, is pyrrolidone carboxylic acid 1 part to succinic acid 0.01 up to 5 parts.

2. An artificial flavouring composition as claimed in claim 1 in which the weight ratio of pyrrolidone carboxylic acid to succinic acid is 1 to 0.02 up to 1 part.

3. An artificial flavouring composition as claimed in claim 1 or claim 2 in which glutamic acid is also present and in which the weight ratio, calculated as free acid, of pyrrolidone carboxylic acid to glutamic acid is 1 to 0.02 up to 50 parts.

4. An artificial flavouring composition as claimed in claim 3 in which the weight ratio of pyrrolidone carboxylic acid to glutamic acid is 1 to 0.25 up to 25 parts.

5. An artificial flavouring composition as claimed in any one of the preceding claims in which a 5′-ribonucleotide is present and in which the weight ratio, calculated as free acid, of pyrrolidone carboxylic acid to 5′-ribonucleotide is 1 to 0.01 up to 10 parts.

6. An artificial flavouring composition as claimed in claim 5 in which the weight ratio of pyrrolidone carboxylic acid to 5′-ribonucleotide is 1 to 0.03 up to 5 parts.

7. An artificial flavouring composition as claimed in any one of the preceding claims in which the pyrrolidone carboxylic acid is L-pyrrolidone carboxylic acid.

8. An artificial flavouring composition as claimed in any one of the preceding claims in which the pyrrolidone carboxylic acid is introduced partly or completely in the form of a precursor.

9. An artificial flavouring composition as claimed in claim 8 in which the precursor is glutamine.

10. An artificial flavouring composition as claimed in claim 1 substantially as described herein with reference to any one of the examples.

11. A process of flavouring foodstuffs comprising incorporating into the foodstuff a quantity of an artificial flavouring composition as claimed in any one of the preceding claims such that a ready-to-use foodstuff will contain between 0.01 and 10 g. of pyrrolidone carboxylic acid per 1 kg. of ready-for-use foodstuff.

12. A process as claimed in claim 11 in which the ready-for-use foodstuff contains between 0.1 and 3 g. of pyrrolidone carboxylic acid per kg. of ready-for-use foodstuff.

UNILEVER LIMITED
Per: J. E. Farndon
Chartered Patent Agent,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1224989

1224989

NO DRAWINGS
(21) Application No. 43364/67 (22) Filed 22 Sept. 1967
(23) Complete Specification filed 17 Sept. 1968
(45) Complete Specification published 10 March 1971
(51) International Classification A 23 l 1/26
(52) Index at acceptance
A2B 6A 6G

(72) Inventor CHRISTIAAN HERMANN THEODOOR TONSBEEK

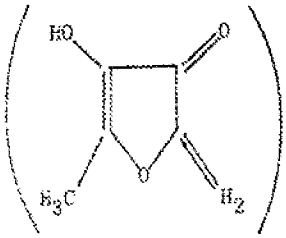
(54) MEAT FLAVOURED PRODUCTS

PATENTS ACT 1949

SPECIFICATION NO 1224989

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated 22 January 1974, this Specification has been amended under Section 14 in the following manner:-

Page 7, *after* line 46 *insert* No claim is made herein to a foodstuff containing 5-methyl-4-hydroxy-2,3-dihydrofuran-3-one

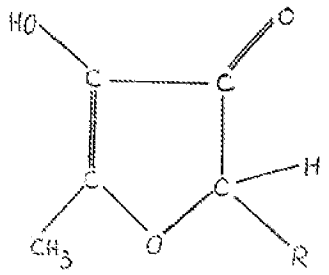


in the form of a colourless and Needle-like crystalline solid.

Subject to the foregoing disclaimer,

THE PATENT OFFICE
7 March 1974

R 74607/12



in which R represents —H or —CH_3. The dihydrofuranone may be incorporated as such, or in the form of precursors or reactants yielding the desired compound after completion of

to foodstuffs which contain meat or a meat simulating product or improving such flavour. Under such foodstuffs are to be understood here foods ready for consumption and concentrated foodstuffs in which a meaty flavour is desired such as soups including concentrated canned soup and dry soup mixes, preserved meals, rissoles, preserved meat e.g. canned ham, simulated meat gravy, gravy tablets or cubes, and "powdered flavour" such as that which may be sprinkled over meaty foodstuffs shortly before consumption.

Both the furanones involved show keto-enol tautomerism, but it appears that they normally occur in the structure represented in the structural formula given above.

This appears from infra red and nuclear magnetic resonance spectra and they also show

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(54) MEAT FLAVOURED PRODUCTS

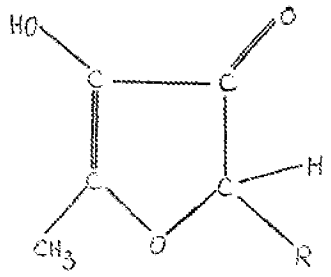
(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

The invention relates to processes for imparting a meaty flavour to certain foodstuffs or improving such flavour and to concentrated as well as ready-for-use foodstuffs obtained according to the process.

It has been proposed to improve the flavour of various foodstuffs which contain meat or a meat simulating product, by adding certain components such as protein hydrolysate, monosodium glutamate, 5'-nucleotides and organic carboxylic acids. Although the products thus obtained often possess a meaty taste, their odour usually is not satisfactory.

It has now been found that a meaty flavour can be enhanced or imparted to foodstuffs which contains meat or a meat simulating product by the incorporation of certain furanones.

Accordingly the present invention provides a foodstuff comprising a meat product or a meat simulating product and a 4-hydroxy-2,3-dihydrofuran-3-one of the general formula:—



in which R represents —H or —CH_3. The dihydrofuranone may be incorporated as such, or in the form of precursors or reactants yielding the desired compound after completion of the preparation of the foodstuff in a form ready for consumption.

The general formula covers two compounds, which are known in the literature viz. 2, 5 - dimethyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one and 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one.

A preparative method for the 2,5-dimethyl compound has been described in U.S. Specification 2,936,308 to John E. Hodge in Example 2 and Table 2, by conversion of L-rhamnose in the presence of piperidine and acetic acid.

A preparative method for 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one (II) has been described in Zeitschrift für Lebensmittel - Untersuchung und - Forshung, Volume 134 of 10th August, 1967, pages 230 to 232, by reaction of an aldopentose with primary amines in aqueous media.

An improved method of preparing these compounds as described in Dutch Patent Specification 6,712,748 filed 18th September, 1967, involves converting N . N - disubstituted glycosyl amines derived from an aldopentose or a 6-desoxy hexose by means of the action of a suitable organic carboxylic acid in a suitable solvent.

The process according to the invention relates as stated to imparting a meaty flavour to foodstuffs which contain meat or a meat simulating product or improving such flavour. Under such foodstuffs are to be understood here foods ready for consumption and concentrated foodstuffs in which a meaty flavour is desired such as soups including concentrated canned soup and dry soup mixes, preserved meals, rissoles, preserved meat e.g. canned ham, simulated meat gravy, gravy tablets or cubes, and "powdered flavour" such as that which may be sprinkled over meaty foodstuffs shortly before consumption.

Both the furanones involved show keto-enol tautomerism, but it appears that they normally occur in the structure represented in the structural formula given above.

This appears from infra red and nuclear magnetic resonance spectra and they also show

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the characteristic colour reaction with Fe III chloride. Theoretically however it may be expected that the substances occur in mixtures in which other structures such as the double keto, double enol and another keto-enol form play a role. By special techniques mixtures may be obtained in which these other forms occur predominantly. According to the present invention also these other tautomeric forms or mixtures thereof can be incorporated in foodstuffs as to obtain a meaty flavour.

In another embodiment precursors or reactants are incorporated, which during the preparation of the ready-for-use product are converted into the 2,3-dihydrofuran-3-one. Thus e.g. esters like the acetates may be used. Furthermore it has been found that after heating for prolonged periods as e.g. occurs during sterilization of canned soups the furan-3-one can be formed from e.g. pentose 5 phosphates and compounds such as pyrollidone carboxylic acid or taurine.

As the type of foodstuffs which can be improved as to flavour according to the invention varies widely, the concentrations in which the 2,3-dihydrofuran-3-ones are applied also ranges widely. When incorporating 5-methyl-4-hydroxy-2,3-dihydrofuran-3-one good results are obtained at levels varying from 0.5 to 100 parts per million calculated on the foodstuff in the ready-for-consumption form; best results are obtained in the range from 2 to 25 parts per million. When incorporating 2,5-dimethyl-4-hydroxy-2,3-dihydrofuran-3-one good results are obtained at levels varying from 0.05 to 50 parts per million; best results are obtained in the range from 0.1 to 20 parts per million. As this substance is a stronger flavouring agent than the monomethyl homologue it is quite possible to use it at lower concentrations as from 0.05 to 0.5 p.p.m. especially when combined with the other compound. As these concentrations apply in the case of foods ready for consumption it is obvious that where more concentrated foodstuffs such as e.g. canned concentrated soups, dry soup mixes and seasoning compositions are involved appreciably higher concentrations may be used, dependent on the degree of dilution they undergo during preparation.

The relative weight ratios where both compounds are used together also depends on the foodstuff involved but in the case of soup or soup products the dimethyl compound is generally used in quantities ranging from 1/10 to 9/10 of the quantity by weight of the monomethyl compound present.

Where precursors or reactants which are converted into the desired compounds are used the quantities incorporated are generally higher than those indicated above in order to overcome the effects of the reaction not taking place quantitatively.

The substances incorporated according to the invention are not quite stable against oxidative attack and oxidation and decomposition products may also contribute appreciably to the desired flavour. For storage it may therefore be desirable to prepare the 2,3-dihydrofuran-3-ones in a stabilised form as e.g. encapsulated or coated with another material. Also, operation in an inert atmosphere may be feasible.

In order to obtain products with a fuller meaty taste and flavour the 2,3-dihydrofuran-3-ones may be utilized together with other substances as e.g. one or more compounds from the following classes of substances. Preferred mixtures are combinations of compounds mentioned under classes I, II and III, together with a 4-hydroxy 2,3-dihydrofuran-3-one.

I. Amino acids. These may be obtained simply by hydrolysis, autolysis or fermentation or by combination of these from vegetable or animal proteins such as gluten, casein or soyabean protein.

II. Nucleotides, such as adenosine - 5' - monophosphate, guanosine - 5' - monophosphate, inosine - 5' - monophosphate, xanthosine - 5' - monophosphate, uridine - 5' - monophosphate, cytidine - 5' - monophosphate, and derivatives thereof, such as their amides, desoxy derivatives or salts. Combinations of several nucleotides as e.g. of guanosine - 5' - monophosphate and inosine - 5 - monophosphate are particularly suitable.

III. Carboxylic acids such as lactic acid, glycolic acid and β-hydroxy butyric acid on one hand and dicarboxylic acids as succinic acid or glutaric acid on the other hand. Preferred mixtures are those in which succinic acid and lactic acid occurred in weight ratios of 1:30 to 1:150.

IV. Pyrrolidone carboxylic acid or precursors thereof.

V. Peptide such as alanyl-alanine, alanyl-phenylalanine, alanyl-asparagine, carnosine or anserine.

VI. Sweetening substances, both artificial, like e.g. saccharine or cyclamates, and natural, particularly mono- and disaccharides.

VII. Substances with the flavour of meat or broth, particularly sulphur containing compounds, such as e.g. reaction products of amino acids like cysteine/cystine with reducing sugars, ascorbic acid etc., reaction products of hydrogen sulphide with lower aliphatic aldehydes and ketones (e.g. propionaldehyde, crotonaldehyde, methional, mercaptoacetaldehyde).

VIII. Other volatile sulphur compounds, such as H_2S, mercaptans, disulphides and sulphides, such as dimethyl sulphide and diallyl sulphide.

IX. Guanidines, such as e.g. creatine and creatinine.

X. Salts, such as e.g. NaCl and phosphates, particularly, in connection with the pH so-called acid phosphates like Na_2HPO_4, NaH_2PO_4 or other alkali metal or ammonium

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phosphates, and organic phosphates, such as e.g. phosphorus containing amino acids. However, it is by no means necessary to incorporate phosphates.

XI. Nitrogen compounds, such as ammonia, amines, urea, indole or skatole.

XII. Saturated or unsaturated carboxylic acids with e.g. 2 to 12 carbon atoms.

XIII. Saturated or unsaturated higher hydroxycarboxylic acids and γ and δ-lactones derived therefrom, such as deca- and dodeca - 5 - olide and 2, 3 - dimethyl - 2, 4 - alkadiene - 4 - olides.

XIV. Lower saturated and unsaturated aldehydes, e.g. acetaldehyde, propion-aldehyde, iso-butyraldehyde and hepten - 4 - al.

XV. Lower saturated and unsaturated ketones, such as acetone, butanone or diacetyl.

XVI. Trichlomic acid and ibotenic acid or their salts.

XVII. Optionally aromatic carboxylic and/or heterocyclic compounds, such as ortho amino - acetophenone, N - acetonyl pyrrole, maltol, isomaltol, ethyl maltol, lenthionine, hypoxanthine, guanine, inosine or guanosine.

XVIII. Lower saturated and unsaturated alcohols, such as ethanol, octanol.

XIX. Colouring substances, such as curcuma or caramel.

X. Thickening agents such as gelatin and starch.

The dosage of these optional ingredients is dependent on the kind of flavour one wishes to imitate and moreover on the nature of the foodstuff to which the ingredients are added and the other ingredients added, such as herbs and spices.

By way of illustration the following Examples are given to elucidate the invention.

Example 1

Two samples were prepared imitating broth. The first sample consisted of 7 g. sodium chloride and 5 g. commercial beef extract, dissolved in 1 litre water. The second sample was prepared in a similar way but contained also 0.010 g. 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one (m.p. 126.5—127.5°C). After heating both samples to the desired temperature a panel was requested to taste both compositions and to indicate a preference. The panel consisted of 18 persons, of which 15 preferred the composition which contained the 2,3-dihydrofuran-3-one.

Example 2

A flavouring composition imitating beef broth was prepared by dissolving the following ingredients in water:

2.00 g.	lactic acid
0.10 g.	inosine-5'-monophosphate
0.08 g.	succinic acid
4.00 g.	monosodiumglutamate
4.00 g.	casein hydrolysate
0.10 g.	tartaric acid
0.05 g.	creatine
26.00 g.	sodium chloride

Further water was added until a volume of slightly less than 4 litres was obtained and the pH of the solution was adjusted to 5.8 by means of adding 0.1 N sodium hydroxide.

The solution was divided into two parts, each equalling 2 litres and to one of these a quantity of 0.010 g. 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one m.p. 126.5—127.5°C (II) was added. Furthermore a reference beef broth sample was prepared by boiling 500 g. lean beef for 2.5 hours in two litres of water in which 13 g. sodium chloride had been dissolved. After cooling the beef was removed by filtration and a clear broth was obtained. The three samples described above were heated and a tasting panel consisting of 29 persons was requested to determine which of the two artificial mixtures resembled the beef broth sample more closely. 23 persons indicated that according to them the sample containing the dihydrofuranone resembled the flavour of beef broth most.

Example 3

A "concentrated" beef broth was prepared by boiling 1 kg. of shin of beef in 4 litres of water for 3 hours. After removal of the beef by filtration the broth was divided into three parts. The first part consisted of approximately 2 litres of "concentrated" broth and served as a reference sample in testing. The second part consisted of approximately 1 litre concentrated broth and was diluted with 1 litre of water. The third part consisted of approximately 1 litre concentrated broth, was diluted with 1 litre of water and 0.010 g. of 5 - methyl - 4 - hydroxy 2, 3 - dihydrofuran - 3 - one (II) (m.p. 126.5—127.5°C) was added.

The three samples described above were heated and a tasting panel of 28 persons was requested to determine which of the two diluted broth samples resembled as to their flavour the reference concentrated broth sample more closely. Twenty-two persons of the panel thought that the sample containing the furanone (II) resembled the concentrated broth more closely.

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EXAMPLE 4

Two artificial broth compositions were prepared by dissolving the following ingredients in water:

	Solution A	Solution B
Lactic acid	1.5 g.	1.5 g.
Casein hydrolysate	3.5 g.	3.5 g.
Monosodiumglutamate	2.0 g.	2.0 g.
Succinic acid	0.06 g.	0.06 g.
Phosphoric acid	0.6 g.	0.6 g.
Inosine-5'-monophosphate	0.05 g.	0.05 g.
Guanosine-5'-monophosphate	0.04 g.	0.04 g.
Sodium chloride	13.0 g.	13.0 g.
2,5-dimethyl-4-hydroxy-2,3-dihydro-furan-3-one	—	0.0006 g.

The pH of both solutions was adjusted to 5.7 by means of adding a sodium hydroxide solution after which to both A and B water was added until a volume of 2 litres was reached.

Furthermore a reference broth was prepared by boiling 500 g. beef in 2 litres water containing 13 g. sodium chloride for 2.5 hours. After allowing to cool the beef was removed by filtration and a clear broth obtained.

After heating the three broth samples to the desired temperature a panel consisting of 24 persons was requested to determine whether A or B resembled the beef broth best. Twenty members of the panel stated that they thought that B resembled beef broth more closely.

EXAMPLE 5

A basis for canned soups was prepared by adding the following ingredients to 4 litres water:

250 g.	chopped boiled well done beef
100 g.	tallow
250 g.	vermicelli
80 g.	sodium chloride
30 g.	dried cut carrots
25 g.	dried leek
15 g.	monosodiumglutamate
5 g.	casein hydrolysate
1.2 g.	pepper
0.2 g.	bay-leaf

An artificial broth composition was prepared by dissolving the following ingredients in water:

35.0 g.	lactic acid
0.8 g.	succinic acid
1.1 g.	inosine-5'-monophosphate
0.8 g.	guanosine-5'-monophosphate
4.5 g.	pyrrolidone carboxylic acid
1.0 g.	creatine
0.2 g.	2, 5 - dimethyl - 4 - hydroxy 2, 3 - dihydrofuran - 3 - one.

The pH of this solution was adjusted to 5.9 and water was subsequently added as to obtain a volume of 2 litres. Two samples of concentrated soup were prepared using the above mentioned basis for soups and the artificial broth. The first sample was prepared by adding to 400 ml. of the soup basis 20 ml. of the artificial broth and 80 ml. water. The second sample was prepared by adding to 400 ml. soup basis, 20 ml. artificial broth, 75 ml. water and 5 ml. of an aqueous solution containing 1.25 mg. 5 - methyl - 4 - hydroxy 2, 3 - dihydrofuran - 3 - one (m.p. 126.5—127.5°C) per ml. The mixtures thus obtained were canned in 0.5 litre tins and sterilized in an autoclave.

A soup ready for consumption was prepared by adding to the contents of each tin an equal volume water. After heating both soups were served to a panel consisting of 32 persons for organoleptic testing. Twenty-three members of the panel indicated a preference for the soup which contained both 2,3-dihydrofuran-3-ones.

EXAMPLE 6

In a similar way as described in the previous Example a basis for soups was prepared. Also a similar artificial broth composition was prepared, which contained 0.600 g. 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one instead of 0.2 g. of the 2,5-dimethyl homologue. The pH was adjusted to 5.8 and water was added to obtain a volume of 2 litres. The first sample was prepared by adding to 400 ml. soup basis 20 ml. artificial broth and 80 ml. water. The second sample by adding to 400 ml. soup basis 20 ml. artificial broth, 70 ml. water and 10 ml. of a solution containing 2, 5 dimethyl - hydroxy - 2, 3 - dihydrofuran - 3 - one in a quantity of 0.21 mg. per ml. The mixtures were canned in 0.5 litre tins and sterilized. Soups ready for consumption were prepared by adding to the contents of each tin an equal volume of water. After heating both soups were served to a panel consisting of 26 persons for organoleptic testing. Nineteen members of the panel indicated a preference for the soup which contained both 2,3-dihydrofuran-3-ones.

EXAMPLE 7

A basis composition of a dry soup mix was prepared by mixing.

90 g.	sodium chloride
20 g.	monosodiumglutamate
50 g.	tallow
200 g.	vermicelli
60 g.	dried beef
20 g.	casein hydrolysate
30 g.	dried onions
10 g.	dried carrots
4 g.	herbs

A preparation of 2, 3 - dihydrofuran - 3 - one (II) which can be dosed easily was prepared by dissolving 1 g. 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 -one (m.p.

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126.5—127.5°C) in 40 ml. of a 50% aqueous dextrine-maltose solution and freeze drying this solution. The powder thus obtained contains 2, 3 - dihydrofuran - 3 - one (II) and dextrine maltose in a weight ratio of 1:20.

Two samples were prepared subsequently. The first by mixing 100 g. of the dry soup mix with 2 litres of water and boiling after addition of 0.20 g. dextrine maltose. The second sample was prepared in the same way, however instead of dextrine maltose the powder containing furanone (II) and dextrine maltose was added in a quantity of 0.20 g. After heating the samples to the correct temperature they were compared as to flavour by a panel of 41 persons, of which 28 preferred the 2, 3 - dihydrofuran - 3 - one conaining soup.

EXAMPLE 8

A basis composition of a dry soup mix was prepared as described in the previous Example.

A preparation of 2, 5 - dimethyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one which can be dosed easily was prepared by dissolving 1 g. of the 2, 3 - dihydrofuran - one (m.p. 79.5—80.5°C) in 80 ml. of a dextrine maltose solution in water of 50% solids content. The solution was freeze-dried and the product contained the furanone and dextrine maltose in a weight ratio of 1:40.

Two samples were prepared subsequently. The first by mixing 100 g. of the above mentioned dry soup mix with 2 litres of water and boiling after addition of 0.120 g. dextrine maltose. The second one also from 100 g. soup mix and 2 litres of water and boiling after addition of 0.120 g. of the furanone dextrine maltose preparation. After heating the samples to the desired temperature they were compared as to flavour by a panel of 36 persons, of which 26 preferred the soup containing the 2, 5 - dimethyl - 4 - hydroxy - furan - 3 - one.

EXAMPLE 9

A beef broth was boiled from 250 g. beef and 1 litre water. After boiling for 2.5 hours and allowing to cool the beef was separated from the "concentrated" broth by filtration. The concentrated broth was divided into two equal parts, one of which was set aside for the preparation of a reference sample ragout whereas the other was diluted with an equal volume of water. Thus was 1 litre of dilute broth obtained, which was divided into two parts of each 500 ml. To one of these quantities of dilute broth 3.75 mg. of 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one dissolved in 3 ml. water were added.

From each of the 500 ml. portions of broth a ragout was prepared for which the following ingredients were used:

50 g.	margarine
50 g.	flour
10 g.	beef
3 g.	sodium chloride
1 g.	monosodiumglutamate
0.01 g.	pepper
0.02 g.	curcuma

The margarine was molten, the flour added and the mixture was stirred with the heated broth. The ragout was finished with the other ingredients. The beef was done well, chopped and added to the mixture. After heating the three ragouts were tested as to their organoleptic properties by a panel consisting of 24 persons. The members of the panel were requested to indicate which of the two ragouts prepared from diluted broth resembled more closely the ragout prepared from the concentrated broth. Nineteen members of the panel preferred the sample which contained the furanone (II).

EXAMPLE 10

A gravy was prepared from the following ingredients:

4.0 g.	gelatin
5.0 g.	tomato puree
15.0 g.	tallow
6.0 g.	sodium chloride
1.0 g.	powdered carrots
1.0 g.	powdered onions
1.0 g.	casein hydrolysate
0.1 g.	curcuma
0.06 g.	pepper
0.04 g.	bay-leaf
0.03 g.	clove
1 litre	water

The gelatin was soaked in part of the water. The remainder of the water was heated and the other ingredients added, and finally the dissolved gelatin was added. Thus a basis for gravy was obtained.

Furthermore a solution of the following ingredients in water was prepared:

10.0 g.	sodium chloride
10.0 g.	monosodiumglutamate
10.0 g.	casein hydrolysate
15.0 g.	lactic acid
0.4 g.	succinic acid
0.6 g.	inosine-5'-monophosphate
0.5 g.	fumaric acid
1.0 g.	taurine
0.5 g.	guanosin-5'-monophosphate
0.1 g.	5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one

The pH of this solution was adjusted to 6.0 and subsequently water was added to obtain a volume of 1 litre.

To the gravy basis mentioned earlier 100 ml. of the flavouring composition described above was added. After heating this gravy was tested organoleptically by a panel of 23 persons. The panel members almost unanimously

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stated that the gravy tasted like an excellent beef gravy.

EXAMPLE 11

A gravy was prepared from the following ingredients:

4.0 g.	gelatin
5.0 g.	tomato puree
25.0 g.	tallow
6.0 g.	sodium chloride
1.5 g.	powdered carrots
1.5 g.	powdered onions
2.0 g.	casein hydrolysate
0.1 g.	curcuma
0.05 g.	pepper
0.04 g.	bay-leaf
0.04 g.	cloves
1 litre	water

The gelatin was soaked in part of the water. The remainder of the water was heated and the other ingredients added and finally the dissolved gelatin was added. Thus a basis for gravy was obtained.

Furthermore a solution of the following ingredients in water was prepared:

10.0 g.	sodium chloride
15.0 g.	monosodiumglutamate
10.0 g.	casein hydrolysate
20.0 g.	lactic acid
0.3 g.	succinic acid
0.6 g.	inosine-5'-monophosphate
0.5 g.	guanosine-5'-monophosphate
0.022 g.	2, 5 - dimethyl - 4 - hydroxy - 2, 3 - dihydro - furan - 3 - one

The pH of this solution was adjusted to 6.0 by addition of sodium hydroxide solution and subsequently water was added to a volume of 1 litre.

To the gravy basis mentioned earlier 100 ml. of the flavouring composition described above was added. After heating this gravy was tested organoleptically by a panel and was qualified as an excellent gravy.

EXAMPLE 12

A mixture of flavouring compounds in powder was prepared by mixing the following ingredients:

20 g.	casein hydrolysate
35 g.	monosodiumglutamate
1.3 g.	inosine-5'-monophosphate
1.1 g.	guanosine-5'-monophosphate
0.8 g.	monosodium succinate
20.0 g.	sodium chloride

The mixture thus obtained served as the basis for seasoning compositions.

Finally 1 g. of 5 - methyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one were added to the mixture. This compound was added in the form of a powdered mixture of dextrine maltose and the 2, 3 - dihydrofuran - 3 - one (II) weight ratio 20:1) cf. Ex. 7. After mixing thoroughly the composition was finely ground and put in sprinklers. A panel of 32 persons were of the opinion that the addition of this seasoning improved both the taste and odour of soups and gravies.

EXAMPLE 13

A basis for seasoning compositions was prepared as described in the previous Example. To this mixture was added 0.5 g. of 2, 5 - dimethyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one (m.p. 79,5—80.5° C) in the form of a dried mixture with dextrine maltose (weight ratio furanon: dextrine maltose 1:40). After mixing thoroughly the mixture was finely ground and put in sprinklers. A panel was unanimously of the opinion that the addition of this seasoning improved both taste and flavour of soups.

EXAMPLE 14

Fibres spun from soya protein were thoroughly washed and cut into pieces. The pieces thus obtained were chopped and mixed with water in a household mixer and subsequently boiled with water for 15 minutes. After cooling excess water was removed and the product pressed in a cloth. To 100 g. of this product were added:

20 g.	pasteurized egg white
1 g.	sodium chloride
0.25 g.	caramel dye
0.050 g.	casein hydrolysate
0.200 g.	monosodiumglutamate
0.300 g.	sodium lactate
0.005 g.	succinic acid
0.010 g.	inosine-5'-monophosphate
0.008 g.	guanosine-5'-monophosphate
0.015 g.	dextrine maltose

Another sample of synthetic meat was prepared in the same way, however also adding 0.020 g. of the dextrine maltose-dihydrofuran-3-one composition described in Example 7.

Each of the samples was subsequently pressed into an artificial sausage casing and coagulated by boiling in water for 30 minutes. Both samples were then tested for their organoleptic properties by a panel consisting of 26 persons of which 18 persons preferred the 2,3-dihydrofuran-3-one containing synthetic meat.

EXAMPLE 15

A synthetic meat from soyabean protein was prepared as described in the previous Example without adding a 2,3-dihydrofuran-3-one.

In a similar way a second sample of synthetic meat was prepared, to which instead of 0.015 g. dextrine maltose 0.010 g. of a quantity of a composition consisting of dextrine

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maltose and 2, 5 - dimethyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one was added.

Each of the two samples was subsequently pressed into an artificial sausage casing and coagulated by boiling in water for 30 minutes. Both samples were then tested for their organoleptic properties by a panel consisting of 24 persons of which 18 indicated a preference for the 2, 3 - dihydrofuran - 3 - one containing synthetic meat.

EXAMPLE 16

An Indonesian rice dish called nasi goreng was prepared from the following ingredients:

1,000 g.	rice
2 litres	water
625 g.	cut onions
300 g.	pork
80 g.	red paprica
125 g.	tallow
40 g.	sodium chloride
10 g.	casein hydrolysate
6 g.	sambal (an Indonesian spicing)

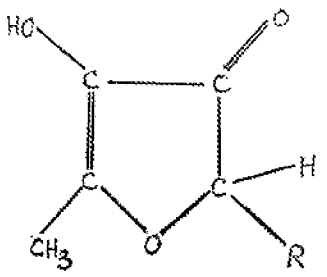
The rice was boiled for 25 minutes in water to which the salt and casein hydrolysate had been added. The pork was fried in the fat after which the onions, pepper and sambal were added and the mixture was fried until the onions turned golden yellow. Subsequently the dry cooked rice was added to the mixture and the mixture was fried under constant stirring and nasi goreng was obtained.

A sample for organoleptic testing was prepared from the thus obtained nasi goreng by adding to 1,000 g. nasi goreng 10 ml. water, whereas a second sample was prepared by adding to another 1,000 g. nasi goreng 10 ml. of an aqueous solution containing 1.15 mg. 2, 5 - dimethyl - 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one (m.p. 79.5—80.5°C) per ml.

After heating both mixtures to the desired temperature they were tasted by a panel consisting of 36 persons. Twenty-seven members of the panel indicated a preference for the nasi goreng which contained the 2, 3 - dihydrofuran - 3 - one.

WHAT WE CLAIM IS:

1. A foodstuff comprising a meat product or a meat simulating product and a 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one of the general formula:—



in which R represents —H or —CH_3.

2. A foodstuff as claimed in Claim 1 in which R in the furanone represents —CH_3 and the quantity of the furanone present, calculated on the weight of ready-for-use foodstuff, is from 0.05 to 50 parts per million.

3. A foodstuff as claimed in Claim 1 in which R in the furanone represents —H and the quantity of the furanone present, calculated on the weight of ready-for-use foodstuff, is from 0.5 to 100 parts per million.

4. A foodstuff as claimed in any one of the preceding claims in which the 4 - hydroxy - 2, 3 - dihydrofuran - 3 - one is added to the foodstuff in the form of a precursor.

5. A foodstuff flavouring composition comprising a furanone as defined in Claim 1 and at least one substance selected from each of classes I, II and III as hereinbefore defined.

6. A meaty foodstuff substantially as claimed in Claim 1 and as described herein with reference to the Examples.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1232719

1232719

NO DRAWINGS

(21) Application No. 35172/69 (22) Filed 11 July 1969
(31) Convention Application No. 48689 (32) Filed 11 July 1968 in
(33) Japan (JA)
(45) Complete Specification published 19 May 1971
(51) International Classification A 23 l 1/26
(52) Index at acceptance A2B 6A

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(54) IMPROVEMENTS IN OR RELATING TO FLAVOURING COMPOSITIONS AND THEIR PREPARATION

(71) We, AJINOMOTO CO. INC., a corporation organized under the laws of Japan, of No. 7, 1-chome, Takara-cho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flavouring compositions which have an aroma and taste similar to that of meat and which may be used for enhancing the flavour of foodstuffs, and to their preparation.

The beef flavour in many processed foods, e.g. soups and gravies, may be obtained by the incorporation therein of a product known as beef extract. However, the supply of beef extract is limited in spite of the large increase in demand by the processed foods industry, because it is prepared from an expensive raw material by a time-consuming and expensive process which generally comprises acid hydrolysis of meat tissue. The processors of food have long sought ways of overcoming these problems.

It has been reported that flavouring substances capable of imparting a savoury smell and taste to foodstuffs, particularly resembling those of cooked meat, may be obtained by the reaction of a monosaccharide with cysteine and/or cystine in the presence of water at an elevated temperature. It has been also reported that certain materials, e.g. creatinine, 5'-inosinic acid, 5'-guanylic acid and hydroxyproline, have a flavour similar to that of meat. However, we have found that the flavour and aroma of a mixture of these materials, was significantly different from the flavour and aroma of beef or any other meat.

It is an object of the present invention to provide a flavouring composition which has a favourable aroma and taste similar to that of a meat extract and which is stable.

According to one aspect of the present invention, there is provided a flavouring composition comprising a mixture of a first ingredient prepared by heating at least one amino acid and a reducing sugar in water, and a second ingredient prepared by heating cystine and/or cysteine and a reducing sugar in a fat or oil.

According to another aspect of the present invention, there is provided a process for preparing a flavouring composition, which comprises mixing a first ingredient prepared by heating at least one amino acid and a reducing sugar in water, and a second ingredient prepared by heating cystine and/or cysteine and a reducing sugar in a fat or oil.

Preferably, the first ingredient is one prepared by heating a mixture of amino acids, containing at least glutamic acid, threonine, valine, lysine, alanine (or glycine), leucine (or isoleucine), methionine and proline, and a reducing sugar in water. The second ingredient is, as stated above, prepared by heating cystine and/or cysteine and a reducing sugar in a fat or oil. The mixture prepared by mixing the first and second ingredients may be employed in, for example, paste form or as a powder.

Though it has been known that the Maillard reaction products obtained by heating a mixture of a sulphur-containing amino acid and a reducing sugar have a characteristic flavour similar to some extent to meat, there are some defects in respect of the preparation and the quality of the product. For example, as the solubility of cystine or cysteine in water of neutral pH is very small, the velocity of the Maillard reaction under these conditions is very slow; to complete the Maillard reaction between cysteine and/or cystine and a reducing sugar within a few hours, it is necessary to keep the pH of the solution greater than 9.5 but then the aroma of the product becomes too stimulative; and when the Maillard reaction is carried out in water, most of the volatile materials of lower molecular weight which have an aroma and which are produced during the reaction, e.g. aldehydes, ketone, amines and alcohols, are easily driven off.

However, we have found that the combina-

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tion of the first ingredient and the second ingredient, according to the present invention is important for preparing a flavouring composition having a meat-like aroma and taste.

The first ingredient provides a flavour and aroma based on comparatively high molecular weight substances and increases the savoury flavour known as "mouthfulness" which is specific to meat or beef extract.

The first ingredient may be prepared by heating the amino acid mixture preferably containing at least glutamic acid, threonine, valine, lysine, alanine (or glycine), leucine (or isoleucine), methionine and proline, and reducing sugar in solution in water at from 60° to 100°C., preferably from 80° to 90°C. for 0.5 to 2 hours. The above-mentioned amino acid mixture may contain other amino acids apart from the eight specified, but the total weight of the seven, excluding glutamic acid, should preferably be more than 15% by weight of the total quantity of all amino acids.

The eight amino acids are selected by a comparative study of the free amino acids included in meat extract, based on their resolving degree upon heat treatment and their contribution to the aroma. The precise quantitative balance between these seven amino acids cannot be readily determined but, according to our experiments, it is desirable that the amount of proline constitutes 1—10% of the total weight of the seven amino acids, the weight of methionine constitutes 0.1—2%, and the weight of valine constitutes 10—20%.

Examples of the reducing sugars employed include xylose, ribose and glucose. Any monosaccharide, including other pentoses, hexoses and alcohols, e.g. sorbitol, are also employable.

The amount of water in the Maillard reaction should preferably be 30 to 60% based on the weight of the solid materials.

The second ingredient is prepared by heating cystine and/or cysteine, together with other amino acids if desired, with a reducing sugar in a fat or oil, generally at 100°—200°C., preferably 140°—160°C., for 5 minutes to 2 hours. The weight of the mixture of cystine and/or cysteine and the reducing sugar employed for the present reaction, is preferably 0.1—10%, based on the weight of the fat or oil. The weight ratio between the reducing sugar and the sulphur-containing amino acids generally depends upon the reaction conditions. However, the reducing sugar should normally be added in 0.01—100 parts based on one part of amino acid by weight.

The fats and oils employed in the present invention include fats and oils of vegetable and animal origin, including the common edible, as well as other, fats and oils, e.g. lard, tallow, fish oil, chrysalis oil, linseed oil, corn oil, sesame oil and peanut oil. Similar effects are also obtained with phospholipids, and glycerides of fatty acids containing at least 11 carbon atoms.

The reducing sugars employed in the preparation of the second ingredient are the same as those mentioned for use in the preparation of the first ingredient.

Most of the volatile materials produced in the Maillard reaction in fats and oils are kept stably, compared with those produced in the Maillard reaction in water. These volatile materials, together with other fragrant materials derived from the fats and oils themselves, are very important for realizing a meat-like flavour and aroma. The fats and oils in which the Maillard reaction has been carried out may remain unreated in the second ingredient, or the residues formed during the Maillard reaction may be removed from the fat or oil before the second ingredient is mixed with the first.

The amount of the second ingredient used for preparing the flavouring composition of the present invention is normally less than 2% by weight of the first ingredient.

The mixture of the first and second ingredients is normally in a paste, but it may be dried to a powder by spray-drying method. The mixture may also contain a third ingredient, e.g. known seasoning materials or organic acids.

The present invention will now be illustrated by the following Examples.

EXAMPLE 1.

The following substances in parts by weight were mixed with stirring in a reaction vessel:

Monosodium glutamate	40
Alanine	2
Glycine	5
Lysine	5
Isoleucine	4
Threonine	2
Valine	3
Methionine	0.1
Serine	3
Glucose	10
Water	45
Proline	1.5

The pH of the solution was adjusted to 9.0 with 2N NaOH and the solution was heated at 80°C. for 1.5 hours. The reacted solution was then adjusted to pH 5.5 with 2N HCl. This solution was designated the first ingredient.

The second ingredient was prepared by heating a mixture containing, in parts by weight, 2 parts of cysteine, 1 part of xylose and 50 parts of hardened oil, at 150°C. for 15 minutes.

2 Parts by weight of the second ingredient were added to the first ingredient, and the

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resulting mixture was designated "Sample". A control, flavouring material, designated "Control", was prepared in the same manner as mentioned above except that the mixture used in preparing the first ingredient also contained 0.2 part by weight of cysteine.

An organoleptic test in order to determine the strength of the meat-like aroma and the preference of the flavour and aroma between the Sample and the Control, was performed with a panel of 50 members. The Sample and the Control were offered for testing as a 1% by weight solution. The results are shown in the following Table 1:

TABLE 1

	Number of Persons who selected Sample	Number of Persons who selected Control
The strength of the meat-like aroma	40	10
The preference	35	15

0.5 Part of disodium inosinate, 10 parts of calcium lactate, 0.5 part of monosodium succinate, 0.2 part of creatinine, 5 parts of K_2HPO_4 and 1 part of KCl were added to the Sample prepared as above, the parts being parts by weight.

The resulting modified flavouring composition and a beef extract available on the market were subjected to an organoleptic test. A preference test with respect to the flavour and aroma was carried out by a panel of 50 persons. The results were shown in the following Table 2:

TABLE 2

	Number of Persons who selected modified flavouring composition	Number of Persons who selected beef extract on the market
Preference of aroma	24	26
Preference of flavour	22	28
Preference as a total	24	26

Note: The test was performed with a 1% by weight solution. NaCl was added to the modified flavouring composition so that its content became equivalent to that of the beef extract.

EXAMPLE 2

The following substances in parts by weight were mixed with stirring in a reaction vessel and heated at 85°C. for 40 minutes:—

Monosodium glutamate	50
Alanine	2
Lysine	8
Leucine	2
Threonine	4
Valine	4
Methionine	0.1
Proline	1
Xylose	5
Water	35

To the reacted mixture were added 3 parts by weight of a second ingredient prepared by heating 1 part by weight of cystine and 1 part by weight of ribose in 100 parts of lard at 140°C. for 20 minutes. The resulting mixture was found to have a favourable flavour and aroma similar to that of meat.

This mixture was then diluted with 10 times its amount of water, and the resulting solution was mixed with dextrine in an amount equivalent to that of the all solid materials and 2% (by weight) of bone extract of beef. The resulting solution was dried to a powder in a spray-dryer of the nozzle type, the temperature at inlet of which was 200°C. and that at the outlet was 80°C. The resulting powder was found to be an excellent flavouring material, having a flavour and aroma similar to that of meat.

WHAT WE CLAIM IS:—

1. A flavouring composition comprising a mixture of a first ingredient prepared by heating at least one amino acid and a reducing sugar in water, and a second ingredient prepared by heating cystine and/or cysteine and a reducing sugar in a fat or oil.

2. A composition as claimed in Claim 1, wherein the first ingredient is prepared by heating a mixture of at least glutamic acid, threonine, valine, lysine, alanine or glycine,

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leucine or isoleucine, methionine and proline, with a reducing sugar in water.

3. A composition as claimed in Claim 1 or 2, wherein the reducing sugar of either or both of the first and second ingredients is a hexose or a pentose.

4. A flavouring composition as claimed in Claim 1, substantially as described in either of the foregoing Examples.

5. A process for preparing a flavouring composition, which comprises mixing a first ingredient prepared by heating at least one amino acid and a reducing sugar in water, and a second ingredient prepared by heating cystine and/or cysteine and a reducing sugar in a fat or oil.

6. A process according to Claim 5, wherein the first ingredient is prepared by heating a mixture of at least glutamic acid, threonine, valine, lysine, alanine or glycine, leucine or isoleucine, methionine and proline, with a reducing sugar in water.

7. Process according to Claim 6, wherein the combined weight of threonine, valine, lysine, alaninine or glycine, leucine or isoleucine, methionine and proline is more than 15% by weight of the amino acid mixture.

8. Process according to Claim 7, wherein proline constitutes 1 to 10%, methionine constitutes from 0.1 to 2% and valine constitutes from 10 to 20% by weight of said combined weight.

9. A process according to any one of Claims 5 to 8, wherein the reducing sugar, of the first and/or second ingredient, is a hexose or a pentose.

10. A process according to any one of Claims 5 to 9, wherein the first ingredient is prepared by heating an aqueous solution containing the amino acid(s) and reducing sugar at from 60° to 100°C. for from 0.5 to 2 hours.

11. Process according to Claim 10, wherein the aqueous solution is heated at from 80 to 90°C.

12. Process according to Claim 10 or 11, wherein the weight of water in the aqueous solution is from 30 to 60% based on the weight of the solid materials.

13. A process according to any one of Claims 5 to 12, wherein said second ingredient is prepared by heating cystine and/or cysteine and the reducing sugar in a fat or oil at from 100° to 200°C. for from 5 minutes to 2 hours.

14. Process according to Claim 13, wherein the cystine and/or cysteine and the reducing sugar is heated at from 140 to 160°C.

15. A process according to Claim 13 or 14, wherein, after cystine and/or cysteine is heated with a reducing sugar in a fat or oil, any residue formed in the fat or oil is removed before the first and second ingredients are mixed.

16. A process according to any one of Claims 5 to 15, wherein the composition obtained by mixing the first and second ingredients is dried to a powder.

17. Process according to Claim 5, substantially as described in either of the foregoing Examples.

18. A flavouring composition whenever prepared by the process claimed in any one of Claims 5 to 17.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 234 927

DRAWINGS ATTACHED

1 234 927

(21) Application No. 50794/69 (22) Filed 15 Oct. 1969
(31) Convention Application No. 767 705 (32) Filed 15 Oct. 1968 in
(33) United States of America (US)
(45) Complete Specification published 9 June 1971
(51) International Classification A 23 l 1/26 1/325
(52) Index at acceptance
A2B 1D 6A

(54) IMITATION MEAT EXTRACT

(71) We, RALSTON PURINA COMPANY, of 835 South 8th Street, St. Louis, Missouri 63199, United States of America, a Corporation organized and existing under the laws of the State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an imitation meat extract intended to simulate the taste of beef.

It is well known to use meat extracts, such as beef extracts, as ingredients in gravies, bouillons, soups and other foods. The method normally used for producing a beef extract is to cook beef muscle tissue in boiling water, yielding a rich-flavoured beef broth which is then further boiled so as to precipitate hot water-insoluble proteins and is further processed to remove its fat content. The product of such a process is a clear broth having the essence of the beef flavour and containing approximately 2% by weight meat solids. This broth is concentrated under carefully controlled conditions so as to give the finished extract. The cost of producing a beef extract by such a method is very high since it necessarily involves using beef muscle tissue.

The present invention makes it possible to produce a simulated beef extract from fish by-products much more cheaply than by the conventional methods, whilst still imparting to food products the flavour characteristics of a conventional beef extract.

Edible fish proteins, after hydrolysis either by enzymes or by acids, have been used for flavourings in the food art, for example chocolate flavouring. Unfortunately, such a hydrolysis treatment converts the insoluble as well as the soluble proteins to amino acids, which is not desirable in making a beef-flavoured product.

In accordance with the present invention, undesirable constituents such as lipids, insoluble proteins and volatile amines are substantially eliminated from a fish liquor, whilst soluble proteins and other soluble constituents are not hydrolysed but are combined with a reducing sugar under controlled conditions, to give a product having a beef-like flavour.

The invention consists in a process for producing simulated beef extract, which comprises heating a solution of substantially de-fatted fish solubles at a temperature from 180 to 205°F, at a pH from 6 to 9, under agitation and in the presence of a reducing sugar, so as to develop a beef-like flavour therein.

The solution of fish solubles, used as the starting material for the process of the invention, is conveniently obtainable from a by-product in the processing of fish; the by-products used may suitably comprise cooker juice from tuna-like fish and/or fishmeal rendering press-water, using fish such as albacore, bluefin, bonito, skipjack, yellowfin, yellowtail, mackerel, anchovies and herring.

It is highly preferred that the fish solubles used in the invention should have a content of natural fish fat not exceeding 0.5% by weight (based on total solids), since a greater fish fat content can result in a residual fishy flavour in the final product. However, other fats, such as beef fat, can be added to the fish solubles without impairing the flavour of the final product, suitably up to a maximum of 5.0% by weight (on solids). It is also preferred that the solution of fish solubles used for "cooking" with the reducing sugar should have a solids content of approximately 50% by weight; although this is not critical and a greater amount of water in the solution will merely require a longer cooking time.

A satisfactory method of obtaining a solution of substantially de-fatted fish solubles having the properties described in the preceding paragraph comprises acidulating fish cooker juice or fishmeal rendering press-water with a mineral acid, heating the acidulated liquor, removing sedimented proteins and fish oil from the liquor (for example, using centrifuges), and concentrat-

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ing the liquor to the desired solids content, which is preferably about 50% solids by weight.

It is preferred to use not more than 10% by weight of reducing sugar, on the basis of the total mixture (including the liquid), since higher amounts give rise to an undesirable sweetness in the final product. Although the solution of fish solubles should preferably have a pH of approximately 7 when heated with the reducing sugar, a pH range from 6 to 9 is satisfactory. The mixture of de-fatted fish solubles and reducing sugar is heated until a browning reaction occurs, the volatile amines which impart the fish-like flavour and odour are driven off and beef-like flavour develops. Preferably, the mixture is heated and agitated for a sufficiently long time to give a total solids content of 70 to 80% by weight; and a minimum "cooking" time of 4 hours is normally required. The product is then ready for packaging and use as a simulated meat extract.

The invention will be further described with reference to the accompanying drawing, which shows a flow diagram for producing a simulated meat extract according to the invention. Referring now to the drawing, cooker juice from vat 1, obtained as a by-product from the pre-cooking operation in the processing of canned tuna or other fish, and/or fishmeal rendering press-water from vat 3, is pumped to the heat-exchanger 2. On the way to the heat-exchanger, the pH of the cooker juice and/or fishmeal press-water is lowered to within the range of 4.0 to 4.8, and preferably to a valve of about 4.3, by means of acid fed from tank 4 through the metering pump 5. Suitable acids include hydrochloric, sulphuric and phosphoric acids; and sulphuric acid is particularly preferred. In the heat-exchanger 2, the acidulated liquor is continuously heated indirectly with steam, reaching a final temperature of approximately 200°F. The hot acidulated liquor then passes to a de-sludging centrifuge 6, which removes most of the unwanted protein sediment. The centrifuge liquid is then passed through a two-phase centrifugal separator 7, in which the free fish oil is removed as a by-product. The liquid obtained is then finally clarified in a high-gravity centrifuge 8, which removes the last traces of lipoprotein sediment, leaving a substantially fat-free liquid with a composition typically as follows:

Total solids	5%	by weight
Protein	4%	by weight
Total lipid less than	0.05%	by weight
Water	95%	by weight

The clarified, substantially fat-free aqueous fish extract is then led to a triple-effect vacuum evaporator 9, of a type well known in this art and comercially available from suppliers such as Blaw-Knox and Majonnier. The liquid entering the evaporator 9 will normally have a total solids concentration from 4 to 15% by weight; and, on leaving the evaporator, it will normally have a final solids content of approximately 50% by weight. This product, termed de-fatted condensed fish solubles, will typically have a composition as follows:

Total solids	50%	by weight
Protein	40%	by weight
Fish fat less than	0.5%	by weight
Other substances (such as sodium, potassium and chloride ions)	7.65%	by weight
pH	=4—4.8	

The de-fatted condensed fish solubles are pumped from the evaporator 9 into a steam-jacketed kettle 10, of a type commercially available from suppliers such as Grooen Manufacturing Co. and Oscar Krenz Co. The kettle 10 is equipped with a mechanical agitator or stirring paddles 11, used to keep the solution of fish solubles thoroughly stirred. A solution 12 is added to the condensed fish, in order to adjust the pH to a value from 6 to 9 and, most preferably, to approximately pH 7: it is preferred to use a solution of sodium hydroxide for this purpose although other alkaline reagents, such as potassium hydroxide or calcium hydroxide, may also be used. A solution of reducing sugar 13 is added to the fish solubles in the kettle: for reasons already explained, it is preferred that the reducing sugar should not amount to more than 10% by weight of the mixture, and approximately 2.5% by weight is generally suitable. Any food-grade reducing sugar may be used for this purpose, for example glucose, galactose, mannose, lactose, maltose, and invert sucrose and ribose; however, glucose is generally preferred.

The mixture in the kettle is stirred and heated to a temperature from 180 to 205°F, more preferably from 195 to 200°F, for a minimum period of 4 hours. During this operation, volatile amines, such as trimethyl amines, and moisture are driven off from the mixture; and, simultaneously, a browning or Maillard-type reaction occurs between the glucose (or other reducing sugar) and the amino-constituents of the protein present, to form a soluble brown-coloured product. In the course of this reaction, the fish flavour and odour disappear and a beef-like, meaty flavour is developed in the product. When the total solids content of the mixture amounts to

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70 to 80% by weight, the entire batch is discharged from the kettle and may be packaged for use as a simulated meat extract.

Instead of using the condensed fish solubles at a concentration of about 50% solids by weight, it is possible to dilute it with water, with a corresponding prolongation of the cooking time: this longer cooking time will allow more of the volatile amines to be driven off. The amount of water added at this stage will depend upon the length of cooking time desired; but the addition of up to 100% by weight of water to the condensed fish solubles has been found to work satisfactorily.

The invention is further illustrated by the following Examples.

EXAMPLE 1.

500g of condensed de-fatted fish solubles (containing 50% by weight total solids) obtained from tuna cooker juice were diluted with 500g of water. The resulting diluted fish solubles were adjusted to a pH of approximately 7.0 with 50% sodium hydroxide. 5% by weight of glucose, based on the dry solids content of the diluted condensed fish solubles, was then added (12.5g glucose/250g dry solids). The resulting mixture was evaporated in an open porcelain dish placed on a boiling water-bath. The mixture was agitated periodically throughout the eight-hour period required to bring the solids to 81.3% by weight total solids. The resulting product had a beef-like flavour and no trace of fish taste or odour.

EXAMPLE 2.

500g of condensed de-fatted fish solubles obtained from tuna cooker juice derived from the yellowfin species was adjusted to a pH of approximately 7.2 with 50% sodium hydroxide. 10% of glucose was added to the neutralised mixture containing approximately 50% by weight total solids (25g glucose/250g dry solids). The resulting mixture was heated with periodic agitation in a porcelain dish heated on a boiling water-bath. The maximum temperature attained by the mixture was 193°F and the time required to reach 70% total solids was 4 hours. The resulting mixture had a definite beef-like flavour and a very rich dark brown colour.

EXAMPLE 3.

15 gallons (approximately 150 lbs.) of de-fatted condensed fish solubles, obtained from cooker juice and containing 50% by weight total solids, were placed in a 25 gallon steam jacketed stainless-steel kettle. The fish solubles solution was diluted to a volume of 20 gallons and the pH was adjusted to 7.5. The resulting mixture was heated and agitated for 6.5 hours at a temperature of 190 to 200°F. No sugar was present other than the naturally-occurring glucose and ribose (approximately 1% dry basis). The resulting mixture had a beef-like flavour but was somewhat chicken-like in odour and medium dark-brown in colour.

Meat extract made in accordance with the preceding description and Examples has been used to make a spray-dried consommé, using the following formula:

Meat extract (from tuna-like fish)	70%	by weight
Monosodium glutamate	2%	by weight
Sugar	7.0%	by weight
Salt	20.68%	by weight

Misc. amount of flavour-enhancers.

25 lbs. of the above formula were dissolved in 6 gallons of distilled water and then spray-dried under the usual drying conditions. The product was a free-flowing powder of small round hollow spheres. The product was very hygroscopic; and, when the powder was dissolved in water, the aroma was released and re-constituted beef consommé was produced.

WHAT WE CLAIM IS:—

1. A process for producing a simulated beef extract, which comprises heating a solution of substantially de-fatted fish solubles at a temperature from 180 to 205°F, at a pH from 6 to 9, under agitation and in the presence of a reducing sugar, so as to develop a beef-like flavour therein.

2. A process according to claim 1, in which said fish solubles have a content of natural fish fat not exceeding 0.5% by weight (based on total solids).

3. A process according to claim 1 or claim 2, in which said fish solubles have been obtained from fish cooker juice or fish-meal rendering press-water.

4. A process according to any preceding claim, in which the amount of reducing sugar does not exceed 10% by weight of the total mixture.

5. A process according to claim 4, in which the amount of reducing sugar used is approximately 2.5% by weight of the total mixture.

6. A process according to any preceding claim, in which the reducing sugar used is glucose.

7. A process according to any preceding claim, in which said solution of fish solubles has a total solids content of approximately 50% by weight.

8. A process according to any preceding claim, in which the solution of fish solubles is subjected to heating and agitation for a period of at least 4 hours.

9. A process according to claim 1, substantially as herein described with reference to the accompanying drawing.

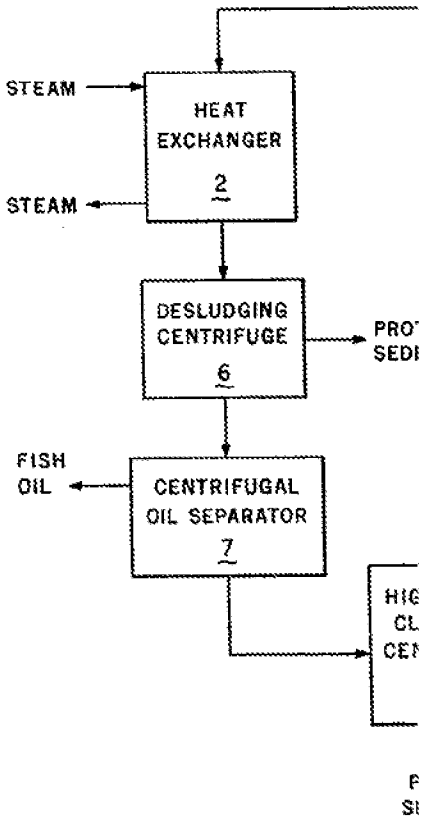
10. A process according to claim 1, substantially as herein described in any of the foregoing Examples.

11. A simulated beef extract when produced by the process of any preceding claim.

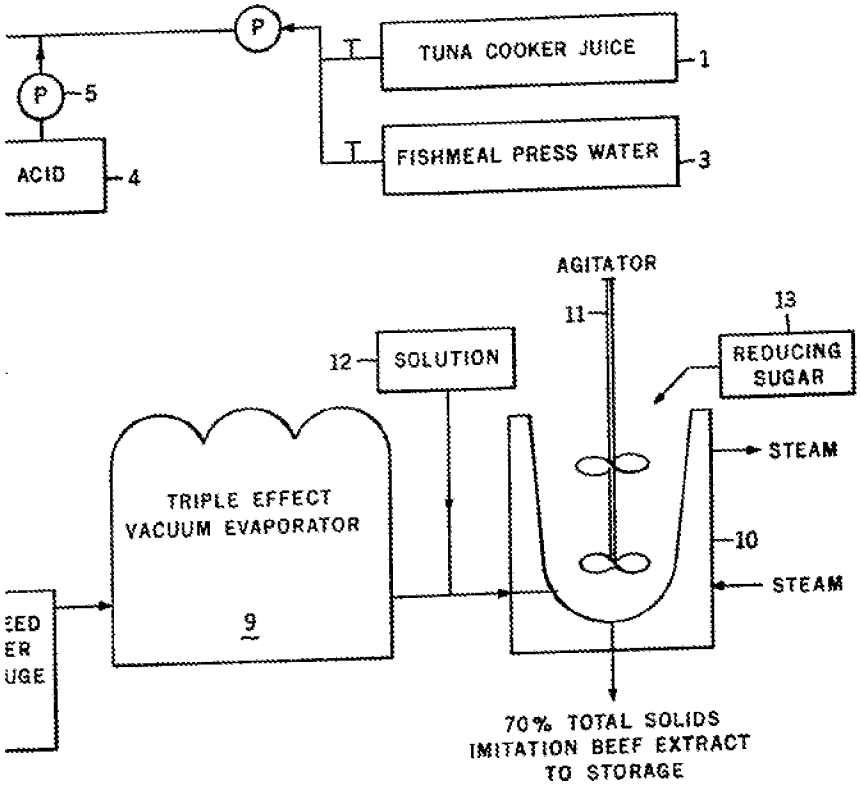
12. A food product comprising a beef extract according to claim 11.

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Agents for the Applicants.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1971.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.


STEAM
HEAT EXCHANGER
2
STEAM
DESLUDGING CENTRIFUGE
6
FISH OIL
CENTRIFUGAL OIL SEPARATOR
7

1234927 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*



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LOW DIAGRAM FOR SIMULATED MEAT EXTRACT

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FLOW DIAGRAM FOR SIMULATED MEAT EXTRACT

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PATENT SPECIFICATION (11) 1256462

1256462

NO DRAWINGS

(21) Application No. 5602/70 (22) Filed 5 Feb. 1970
(31) Convention Application No. 796923 (32) Filed 5 Feb. 1969
(31) Convention Application No. 864227 (32) Filed 6 Oct. 1969 in
(33) United States of America (US)
(45) Complete Specification published 8 Dec. 1971
(51) International Classification C 07 d 5/04 5/10 5/16 A 23 l 1/26
(52) Index at acceptance
C2C 175—193—286 176—199—275 177—271—279 215 247 253 25Y 292 29Y 30Y 313 318 31Y 339 366 367 370 371 373 37Y 394 39Y 420 422 42Y 551 560 600 614 775 799 QG QM
A2B 6A 6G

(72) Inventor WILLIAM JOHN EVERS

(54) SULFUR-CONTAINING COMPOUNDS, A PROCESS FOR THEIR PREPARATION AND COMPOSITIONS CONTAINING THEM

(71) We, INTERNATIONAL FLAVORS AND FRAGRANCES INC., a Corporation organised under the laws of the State of New York, United States of America, of 521 West 57th Street, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to certain furan derivatives, a process for their production, and compositions containing them.

Artificial flavoring agents for foodstuffs have received increasing attention in recent years. In many areas, such food flavoring agents are preferred over natural flavoring agents, at least in part because of the uniform flavor that may be so obtained. For example, natural food flavoring agents such as extracts, essences, concentrates and the like are often subject to wide variation due to changes in the quality, type, and treatment of the raw materials. Such variation can be reflected in the end product and results in unreliable flavor characteristics and uncertainty as to consumer acceptance and cost. Additionally, the presence of the natural product in the ultimate food may be undesirable because of increased tendency to spoil. This is particularly troublesome in convenience and snack food usage where such products as dips, soups, chips, prepared dinners, canned goods, sauces, gravies, and the like are apt to be stored by the consumer for some time prior to use.

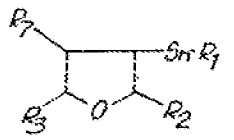
The fundamental problem in preparing artificial flavoring agents is that of achieving as nearly as possible a true flavor reproduction. This generally proves to be a difficult task since the mechanism for flavor development in many foods is not understood. This is notable in products having meaty and roasted flavor characteristics.

Reproduction of roasted and meat flavors and aromas has been the subject of a long and continuous search by those engaged in the production of foodstuffs. The severe shortage of foods, especially protein foods, in many parts of the world has given rise to the need for utilizing non-meat sources of proteins and making such proteins as palatable and as meat-like as possible. Hence, materials which will closely simulate or exactly reproduce the flavor and aroma of roasted products and meat products are required.

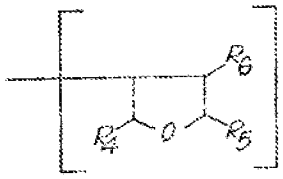
Moreover, there are a great many meat-containing or meat-based foods at present distributed in a preserved form, examples being condensed soups, dry soup mixes, dried meats, freeze-dried or lyophilized meats, packaged gravies, and the like. While these products contain meat or meat extracts, the fragrance, taste, and other organoleptic factors are very often impaired by the processing operations, and it is desirable to supplement or enhance the flavors of these preserved meat foods.

The present invention relates to materials having desirable meat, roast meat, and roasted fragrance and flavors. These materials are organic oxygen-containing heterocyclics wherein the second carbon atom from the oxygen atom contains a sulfur substituent. Thus the present invention provides a flavoring composition comprising a furan derivative having the formula:

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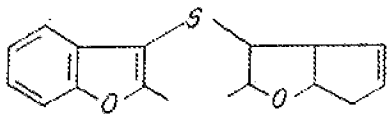


wherein n is one to four; R_1 is hydrogen, alkyl, alkenyl, alkadienyl, or a moiety of the formula

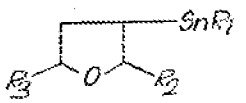


R_2, R_3, R_4, R_5, R_6, and R_7 ar hydrogen, alkyl, alkenyl, or alkadienyl, or taken together R_5 and R_6 and/or R_3 and R_7 form cyclialkyl, cyclialkenyl, cyclialkadienyl, benzo, thieno, dihydrothieno, tetrahydrothieno, furano, dihydrofurano, or tetrahydrofurano rings; and the dashed lines represent single or double carbon-to-carbon bonds, together with a suitable vehicle or carrier, which may be, for example, an auxiliary flavoring adjuvant.

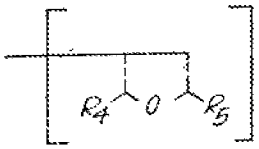
When R_2, R_3, R_4, R_5, R_6 and R_7 represent alkyl, alkenyl, or alkadienyl groups, it is desirable that they be lower alkyl, alkenyl or alkadienyl groups having up to five carbon atoms. Thus, for example, these groups can be methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, pentyl, vinyl, allyl, isopropenyl, butenyl, butadienyl, isopentenyl, pentenyl, pentadienyl, isopentadienyl, and the like. When R_5 and R_6 and/or R_3 and R_7, taken together form cyclialkyl or cyclialkenyl or cyclialkadienyl rings, it is preferred that they be 5- or 6-membered rings. Thus, for example, the following fused ring compound is representative of one of such ring materials:



The particularly preferred compounds according to the present invention for imparting desirable meat, roast meat, and roasted fragrance and flavor notes include furan derivatives having the formula:



wherein n is one and R_1 is hydrogen or n is one, two, three or four and R_1 is a moiety of the formula:



or n is two or three and R_1 is alkyl, and wherein R_2 and R_3 are alkyl, R_4 and R_5 are hydrogen or alkyl, and the dashed lines represent single or double carbon-to-carbon bonds. These compounds are novel. In the above formula, when R_2, R_3, R_4, and R_5 represent alkyl groups it is desirable that they be lower alkyl groups having up to five carbon atoms. Thus, the alkyl groups can be methyl, ethyl, propyl, isopropyl, butyl, secondary butyl, pentyl, and the like. It is especially preferred that the alkyl groups be methyl or ethyl.

It has been found that when both dashed lines represent double bonds, that is, when the ring is a furyl ring, the compounds have a desirable pronounced meat flavor and aroma characteristic. When the furan ring is more highly saturated, and particularly when the ring is dihydrofuryl, a roasted flavor and aroma characteristic is more dominant.

The compounds of the present invention are oily liquids or crystalline solids and are, in general, characterized by pronounced pleasant meat, roasted meat and/or roasted food flavor and aroma at the concentrations envisaged herein. The dominant note is one of roasted protein with a notable absence of any pungency or lachrymose factor.

It will be understood that some of the compounds of this invention can exist in various isomeric forms, and the formulae given herein include such isomers. By way of example, the 2 - methyl - [2,3H] - dihydrofuran - 3 thiols exist as geometric isomers and as optical isomers. A representation of one of the isomers of this compound is as follows:



Another isomer is:



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Exemplary of 3-sulfur substituted furans contemplated herein are:

bis-(2-methyl-3-furyl) tetrasulfide
2-methylfuran-3-thiol
2-methyldihydrofuran-3-thiol
2-methyltetrahydrofuran-3-thiol
2-ethylfuran-3-thiol
2-ethyldihydrofuran-3-thiol
2-ethyltetrahydrofuran-3-thiol
2-propylfuran-3-thiol
2-isopropylfuran-3-thiol
2-isopropyldihydrofuran-3-thiol
2-isopropyltetrahydrofuran-3-thiol
2-propyldihydrofuran-3-thiol
2,5-dimethylfuran-3-thiol
2,5-dimethyldihydrofuran-3-thiol
2,5-dimethyltetrahydrofuran-3-thiol
2,5-diethylfuran-3-thiol
2,5-diethyldihydrofuran-3-thiol
2,5-diethyltetrahydrofuran-3-thiol
2-ethyl-5-methylfuran-3-thiol
2-methyl-5-ethylfuran-3-thiol
2-ethyl-5-methyldihydrofuran-3-thiol
2-ethyl-5-methyltetrahydrofuran-3-thiol
2,5-dipropylfuran-3-thiol
2,5-diisopropylfuran-3-thiol
5-isopropyl-2-methylfuran-3-thiol
2-butylfuran-3-thiol
2-ethyl-5-propyltetrahydrofuran-3-thiol
bis(2-methyl-3-furyl) sulfide
bis(2-methyl-3-furyl) disulfide
bis(2-ethyl-3-furyl) sulfide
bis(2-ethyl-3-furyl) disulfide
bis(2,5-dimethyl-3-furyl) sulfide
bis(2,5-dimethyl-3-furyl) disulfide
bis(2-methyl-3-dihydrofuryl) sulfide
bis(2-methyl-3-tetrahydrofuryl) sulfide
bis(2-methyl-3-tetrahydrofuryl) disulfide
bis(2-methyl-3-dihydrofuryl) disulfide
bis(2,5-diethyl-3-dihydrofuryl) sulfide
bis(2,5-diethyl-3-furyl) sulfide
bis(2-ethyl-5-methyl-3-furyl) disulfide
bis(2,5-diethyl-3-furyl) disulfide
bis(2,5-dipropyl-3-furyl) disulfide
bis(2,5-dipropyl-3-furyl) sulfide
bis(2,5-dibutyl-3-furyl) disulfide
bis(5-ethyl-2-methyl-3-dihydrofuryl) disulfide
bis(2-isopropyl-3-furyl) sulfide
bis(2-isopropyl-3-furyl) disulfide
bis(2-isopropyl-3-dihydrofuryl) sulfide
bis(2-isopropyl-3-tetrahydrofuryl) disulfide

It will be understood from the present disclosure that the derivatives of dihydrofuran can be 2,3H or 4,5H. Thus, 2 - methyldihydrofuran - 3 - thiol includes 2 - methyl - [4,5H] - dihydrofuran - 3 - thiol and 2 - methyl - [2,3H] - dihydrofuran - 3 - thiol, and bis(5 - ethyl - 2 - methyl - 3 - dihydrofuryl) disulfide includes bis[5 - ethyl - 2 - methyl - 3 - ([4,5H] - dihydrofuryl)] disulfide and bis[5 - methyl - 2 - methyl - 3 - ([2,3H] - dihydrofuryl)] disulfide.

In accordance with the invention, the novel sulfur compounds can be utilized singly, in admixture, or in combination with other edible materials to impart a meaty or roasted organoleptic impression to foods or edible materials. Thus, the compounds herein described can comprise flavouring compositions and flavor-enhancing compositions. The compositions of the invention comprise the compounds together with a suitable carrier. The term carrier is to be construed broadly to cover any other edible ingredient that can be admixed with the compounds to form a flavoring or flavor-enhancing composition. It will be understood herein that a flavoring composition is one capable of imparting a definite flavor to a tasteless or bland foodstuff, and a flavor-enhancing composition is one capable of reinforcing one or more flavor notes of a natural or other material with is deficient in flavor. A flavor-enhancing composition would be useful for improving the flavor of, say, a canned meat product, the flavor of which was diminished or undesirably altered by the processing. It will accordingly be understood that the disclosed sulfur-containing compounds can be mixed with other flavoring ingredients, vehicles and the like to form compositions suitable for imparting a flavor to, enhancing the flavor in, or altering the flavor of, a food composition, and such food compositions and the methods for preparing them are included in this disclosure. The furyl monosulfides, disulfides, and mercaptans of this invention generally impart a meat or cooked meat flavor and aroma. The dihydrofuryl sulfides, disulfides, and mercaptans impart a roasted flavor and odor which is even redolent of roasted sesame seeds in some instances. Their flavor characteristics are sufficiently pronounced and persistent that a desirable flavor and odor can be developed by simply using the undiluted compound or compounds; for example, by addition of the undiluted compound to a processed fish meal.

When the sulfur compounds of this invention are used in flavoring compositions to enhance existing flavors in, or to provide the entire flavor impression to, a foodstuff, they can be combined with organic acids including fatty, saturated, unsaturated and amino acids, alcohols, including primary and secondary alcohols, esters, carbonyl compounds including aldehydes and ketones, lactones, cyclic organic materials including benzene derivatives, alicyclics, heterocyclics such as furans, pyridines, pyrazines and the like, sulfur-containing materials including thiols, sulfides, disulfides and the like, proteins, lipids, carbohydrates, and so-called flavor potentiators such as monosodium glutamate, guanylates, inosinates, natural flavering materials such as vanillin, and the like. It will be appreciated

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that the types and amounts of materials selected from the foregoing groups of materials will depend upon the precise organoleptic character desired in the finished product and, especially in the case of flavoring compositions used to enhance other flavors, will vary according to the foodstuff to which the flavor and aroma are to be imparted. Inorganic materials such as sodium chloride and freshness preservers such as butylated hydroxyanisole, butylated hydroxytoluene and propyl gallate can be added for their adjuvant or preservative effects on the flavoring composition or on the final food composition itself.

As carriers for the composition of the invention there may be used, for example, gum arabic and carrageenen. Vehicles, such as ethyl alcohol, water or propylene glycol may be present. When the carrier is an emulsion, the flavoring composition can also contain emulsifiers such as mono- and diglycerides of fatty acids and the like. With these carriers or vehicles the desired physical form of the composition can be prepared. It will be understood that the compounds of this invention can be used in spray-dried, liquid, encapsulated, emulsified and other forms in which flavorings are added to foodstuffs. The compounds can be so used alone or in combination with the other ingredients set forth therein. In the case of a foodstuff which is prepared from a combination of ingredients the furyl sulfur derivatives, flavor enhancers and flavoring compositions of this invention can be added to one of the ingredients and thereby be incorporated into the composition as a whole.

The amount of sulfur-containing compound or compounds used should be sufficient to impart a meaty or roasted flavor and aroma note to the ultimate foodstuff in which they are used. Thus, a small but effective amount of 3-sulfur substituted furan sufficient to provide the meaty flavor note in or to round out the meat, roasted, or other flavor note in the ultimate foodstuff is used. The amount will vary depending upon the ultimate food composition to be flavored: for example, more may be required in producing a full, rounded meat flavor in an unflavored material and less may be required when this invention is used to enhance a meat or roasted foodstuff or flavoring material which is deficient in natural flavor or aroma.

Those skilled in the art will appreciate that the amount of furyl sulfur derivatives according to this invention can be varied over a range to provide the desired flavor and aroma. The use of too little of the derivative or derivatives will not give the full benefit, while too much will make the flavor compositions and foodstuffs needlessly costly, and in extreme cases will unbalance the flavor and aroma so that optimum results are not obtained.

It is accordingly preferred that the ultimate food composition contain at least about 1.0 part per billion (as defined in U.S.) of the sulfur derivatives, based on total composition, and it is not generally desirable to use more than about 500 parts per million (ppm) in the finished composition. Thus, the desirable range for use in the practice of this invention is from 0.001 to 500 ppm of the furyl sulfur compound or compounds. When these compounds are added to the foodstuff in the form of a meat flavor composition, the amount should be sufficient to impart the requisite flavor and/or aroma not to the composition so that the flavor and aroma will be balanced in the finished foodsuff. Accordingly, the flavoring compositions of this invention preferably contain from 0.0001% to 10% of sulfur derivatives based on the total weight of said flavoring composition. Unless otherwise indicated, all parts, proportions, percentages, and ratios herein are by weight.

The flavoring compositions of this invention can be added to the foodstuffs by conventional methods known in the art. The flavor material of this invention together with any other liquids if desired, can be admixed with a carrier, such as gum arabic, gum tragacanth, carrageenen and the like, and spray-dried to obtain a particulate solid flavoring material. Where a powdered prepared flavor mix is being made, the dried solids and flavoring compositions or furyl sulfur derivatives of this invention are mixed together in a dry blender to attain uniformity.

When liquid materials are involved in the preparation of foodstuffs, the flavoring materials of this invention can be combined with either the liquid to be used in the finished composition, or alternatively they can be added with a liquid carrier in which they are dissolved, emulsified, or otherwise dispersed.

It has been found that the bis(2,5 - dialkyl - 3 - furyl) sulfide can readily be prepared by reacting a 2,5 - dialkyl furan with the appropriate sulfur chloride preferably in the presence of a catalyst. Thus, a bis(2,5 - dialkyl - 3 - furyl) sulfide is produced by the reaction of a 2,5 - dialkyl furan with sulfur dichloride, SCl_2, and a bis(2,5 - dialkyl - 3 - furyl) disulfide can be obtained by the reaction of such a 2,5 - dialkyl furan with sulfur mono - chloride, that is, S_2Cl_2.

While the reaction can be carried out in the absence of catalysts, it is preferred to use as catalysts Lewis acids including metal salts such as stannic chloride, ferric chloride, ferric bromide, zinc chloride, boron trifluoride, and boron trifluoride complexes such as boron trifluoride diethyl etherate, and the like.

It has been found that the time of reaction for obtaining suitable results is between 15 minutes and 2 hours; that the desirable temperature range is between −30°C and

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+50°C; that a reaction vehicle is preferable for controlling the reaction, and that such reaction vehicle can be a hydrocarbon solvent such as hexane, cyclohexane, and the like or dimethyl furan used in large excess. The reactant proportions are such that the dimethyl furan compound is used in large molar excess over the particular sulfur chloride. The reaction is preferably run at atmospheric pressure.

It has also been discovered that furan - 3 - thiols and alkyl - substituted furan - 3 - thiols can be produced by the reaction of an appropriate dihydrofuranone - 3 or tetra - hydrofuranone - 3 with hydrogen sulfide under acidic conditions, preferably in the presence of anhydrous hydrogen chloride at temperatures of −60 to −100°C. This reaction provides furan - 3 - thiols; dihydrofuran - 3 - thiols; and tetrahydrofuran - 3 - thiols as well as alkyl - substituted derivatives thereof.

The reaction of the di - or tetrahydro - furanone - 3 or alkylated counterparts with hydrogen sulfide in the presence of gaseous hydrogen chloride will take plate in from about 5 up to about 25 hours at temperatures of about −60° down to about −100°C. The reaction vehicle can be any polar solvent having a melting point below about −100°C and a viscosity such that the reaction mass can be turbulently mixed at that temperature. Desirable polar solvents having the above properties are Diglyme, tetrahydrofuran, methanol, ethanol and the like. The hydrogen sulfide reactant is preferably in about a 5 - to 10 - fold excess over the furanone - 3.

It will be understood that the thione can readily be converted to the corresponding thiol with a reducing agent such as lithium aluminum hydride, diethoxy aluminum hydride, ethoxy aluminum dihydride and the like. The vehicle for this reduction can be an oxygenated solvent such as diethyl ether, tetrahydrofuran, Diglyme (dimethyl ether of diethylene glycol), and the like. The temperature of the reaction can vary from about 0°C up to the reflux temperature of the reaction medium. Although the reaction can be carried out over a range of pressures, it is preferred that the pressure be atmospheric. The reducing agent is preferably in excess molar proportion relative to the thione.

It will be understood that the corresponding bis(3 - furyl), bis(3 -dihydrofuryl), and bis(3 - tetrahydrofuryl) disulfides can be produced by oxidizing the corresponding thiols under mild oxidizing conditions. Thus the thiols can be oxidized with an air stream bubbled through them at 20°C and 760 mm Hg pressure for 8 hours. Stirring of the reaction mass with use of baffles during the bubbling is adequate to maintain suitable contact between the reactants. Other suitable mild oxidising agents include ferric chloride, iodine - potassium iodide, dimethyl disulfide, dimethylsulfoxide and the like.

The time of this mild oxidation reaction will vary from substantially instantaneous up to 20 hours at temperatures from about 10°C to 50°C and atmospheric pressure. The pH of the reaction mass depends upon the nature of the oxidizing agent; as does the time of reaction which is a function of the net oxidation reduction potential of the reactants and the concentrations and relative proportions of the reactants. It is preferred that stoichiometric quantities of thiol and oxidizing materials be used unless such easy-to-remove oxidizing agents as dimethyl sulfoxide, dimethyl sulfide and the like are employed, in which case an excess of such oxidizing agents can be utilized.

In another process contemplated herein a 2 - alkyl - 5 - furoic acid, 2 - alkyl - 5 - cyanofuran, or a 2 - alkyl - 5 - halofuran is treated with oleum (fuming sulfuric acid) to produce the corresponding 3 - sulfofuran derivative, the 5 - substituent is then removed by "Known methods" to obtain 2 - alkyl - 3 - sulfofuran, and the sulfofuran is reacted with thionyl chloride to form 2 - alkyl - 3 - (chloro sulfo) furan, and the (chloro - sulfo) furan reduced to produce 2 - alkyl furan - 3 - thiol.

When the 5 - furoic acid is used in the above process, after the treatment with oleum the barium salts of the resulting acid are then obtained by treatment of the acid with barium carbonate which is used in excess so as to eliminate any unreacted sulfuric acid. The barium salt is converted to the sodium salt which is then decarboxylated with an equivalent amount or an excess of mercuric chloride in a refluxing aqueous solution. The resulting sodium sulfonate is reacted with a 7—8 fold excess of thionyl chloride, the excess of thionyl chloride being used as a solvent in the presence of a trace of dimethyl formamide. In place of excess thionyl chloride, other inert solvents may be used, for example, benzene, hexane or diethyl ether. The resulting 3 - chlorosulfo group is reduced to the thiol (—SH) group by reaction with a reducing agent used in excess to insure total reduction. Agents such as lithium aluminum hydride, mono - alkoxy aluminum dihydride, dialkyl hydride or zinc in hydrochloric acid wherein each of these reducing agents is in a vehicle can be used. Such a reduction can be carried out at room temperature to reflux under atmospheric pressure. The vehicles carrying the reducing agent can be oxygenated vehicles such as diethyl ether, tetrahydrofuran, Diglyme and the like.

Saturated furan - 3 - thiols can also be produced by treating alkyl - 3 - halotetra - hydrofurans with sodium hydrosulfide under reflux conditions in the presence of ethanol, methanol, or like vehicles.

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The mercaptans of this invention can, if desired, be reacted with various chlorosulfur compounds to obtain di - or tri - or tetrasulfides. Thus, a thiol such as 2 - alkyl - 3 - furan thiol can be reacted with preferably an equimolar amount of alkyl disulfur chloride, at a temperature of from —60°C up to about 0°C to produce alkyl (2 - alkyl - 3 - furyl) trisulfide. Preferably, 2 - methyl - 3 - furan thiol is reacted with methyl disulfur chloride to produce methyl (2 - methyl - 3 - furyl) trisulfide. This reaction can be carried out in a solvent such as diethyl ether, cyclohexane, hexane, carbon tetrachloride, benzene and the like. Similarly, a thiol such as 2 - alkyl - 3 - furanthiol can be reacted with preferably an equimolar amount of alkyl sulfur chloride, to produce alkyl (2 - alkyl - 3 - furyl) disulfide, for example 2 - methyl - 3 - furanthiol can be reacted with methylsulfur chloride (CH_3SCl) to produce methyl (2 - methyl - 3 - furyl) disulfide. This reaction also can be carried out in a solvent such as diethyl ether, cyclohexane, hexane carbon tetrachloride, benzene and the like. The reaction temperature is preferably from —60°C up to 0°C at atmospheric pressure.

The di- and tetrahydro materials according to this invention are also conveniently prepared directly from the appropriate alkyl or dialkyl di- or tetrahydrofurans, under reaction conditions similar to the conditions used in the analogous reactions described heretofore.

The bis(2 - methyl - 3 - furyl) disulfide and 2 - methyl - 3 - furan thiol of this invention can also be obtained by: (a) forming a mixture of thiamine, cysteine, hydrolyzed vegetable protein and water and heating the mixture to reflux for a period of from about 2 to about 10 hours as shown in United States Patent 3,394,016; (b) removing the distillate at intervals; (c) treating the distillate in an extractive process using as an extractant a low boiling solvent such as methylene chloride and the like, whereby the bis(2 - methyl - 3 - furyl) disulfide and 2 - methyl - 3 - furan thiol of this invention are obtained; (d) separating the furyl sulfur compounds from the mixture by means of, for example, a gas-liquid chromatographic column or column chromatographic techniques.

The following examples are given to illustrate the invention.

Example I

Preparation of bis(2,5 - Dimethyl - 3 - furyl) sulfide and bis(2,5 - Dimethyl - 3 - furyl) disulfide

Into a 1-liter, three-neck, round bottom flask equipped with addition funnel and magnetic stirrer are introduced 175 g of 2,5 dimethylfuran and 0.4 g of stannic chloride. After cooling to —20°C 75.3 g of sulfur dichloride, SCl_2, is added during 33 minutes while maintaining a temperature of —20°C. The reaction mixture is stirred for 1 hour and 40 minutes and allowed to warm to +34°C. Pouring the reaction mixture into 1 liter of ice-water, and extraction with hexane gives, after drying with sodium sulfate and solvent removal, 64.8 g of residue. Column chromatography of the residue on 1625 g of silicic acid with 5% diethyl ether in hexane gives 14.4 g of a mixture of mono- and disulfides. Distillation of 11.0 g of mixture provides 3.8 g of bis(2,5 - dimethyl - 3 - furyl) sulfide, b.p. 81—85°C at 0.15 mm Hg, and 5.1 g of bis(2,5 - dimethyl - 3 - furyl) sulfide, b.p. 112—116°C at 0.45 mm Hg.

Repeating the above experiment using 98.5 g of sulfur monochloride, S_2Cl_2, in place of sulfur dichloride produces a 54.2 g residue. Chromatography on 1355 g of silicic acid with 5% ether in hexane yields 13.9 g of mono- and disulfide. Distillation of 11.0 g of the mixture gives 1.96 g of a 40/60 mixture, as determined by proton magnetic resonance (PMR) of mono- and disulfide and 6.6 g of bis(2,5 - dimethyl - 3 - furyl) disulfide, b.p. 115°C at 0.45 mm Hg.

The data on the bis(2,5 - dimethyl - 3 - furyl) sulfide are as follows:

Protion Magnetic Resonance
In carbon tetrachloride:
2.2 (singlet, 6 protons)
2.3 (singlet, 6 protons) and
5.78 (singlet, 2 protons) ppm.

Infra-red:

λmax.	Interpretation
3.22	CH stretch or aromatic ring
6.21, 6.36	C=C stretch of aromatic furan ring
7.26	Methyl group
12.05	CH bond of aromatic ring.

Mass Spectrum

Ratio of Mass to Charge	Net Peak Height	Pattern Intensity %
43	1100.—	100.01
53	130.—	11.8
95	140.—	12.7
96	280.—	25.56
126	390.—	35.53
127	310.—	28.25
128	220.—	20.0
179	320.—	29.14
207	210.—	19.1
222	800.—	72.72

Both compounds impart a distinct meaty flavor to a soup base at a concentration of 0.2 ppm. The bis(2,5 - dimethyl - 3 - furyl) disulfide is preferred and both 3 - furyl sulfides are preferred over bis(5 - methyl - 2 - furyl) disulfide which is found to have only a chemical, rubbery taste and aroma under the same conditions.

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EXAMPLE II

Preparation of bis(2,5 - Dimethyl - 3 - furyl) Monosulfides.

Into a 25 ml three-neck, round-bottom flask equipped with an addition funnel, magnetic stirrer and ice bath are introduced 9.6 g of 2,5 - dimethylfuran and 1.104 g of stannic chloride. At a temperature of 0°C 2 g of sulfur dichloride, SCl_2, is added during 33 minutes. The reaction mixture is then poured into 50 cc of ice-water slurry, and the reaction mass is extracted twice with 20 cc of isopentane and once with 40 cc of diethyl ether. About three grams of brown oil is recovered after solvent removal. This brown oil has an odor of roast meat Column chromatography on 50 g of silicic acid with 5% ether in hexane gives 0.6 g of material having a roast meat aroma. Rechromatography of this material on 25 g of silicic acid initially using hexane and then 1% ether in hexane as eluent gives 0.22 g of a mixture of 2,5 - dimethyl - 3 - furyl monosulfide and 2,5 - dimethyl - 3 - furyl disulfide.

The resulting mixture of bis(2,5 - dimethyl - 3 - furyl) sulfide and disulfide is recovered after the combined solvent extracts have been evaporated. The sulfide and disulfide have a meat aroma and a cooked meat taste.

EXAMPLE III

Preparation of bis(2,5 - Dimethyl - 3 - furyl) Disulfide

Into a 500 cc three-neck, round bottom flask equipped with a thermometer and addition funnel, and immersed in an acetone-dry ice bath are added 78.6 g 2,5 - dimethyl - furan, 0.1 g anhydrous stannic chloride, and 100 cc hexane. Over a period of one hour, 27 cc of sulfur monochloride, S_2Cl_2, is added while the pot temperature is maintained between —22°C and 0°C. During the last 20 minutes a vacuum is applied to the reaction flask to remove the hydrogen chloride gas which evolves.

At the end of the reaction the reaction mass is poured onto 200 cc of a water-ice slurry. Hexane-insoluble solids are then filtered and the aqueous layer is separated from the hexane layer. The hexane layer is washed with one volume of 10% aqueous sodium bicarbonate and then with 100 cc of water. This is followed by washes with 200 cc water, 5% aqueous sodium carbonate and 200 cc water. The hexane solution is then dried over anhydrous sodium sulfate and filtered, and the hexane is evaporated to produce 21.9 g of a dark oil. This dark oil, on standing, deposits a solid. The residual oil is taken up in 50 cc hexane and the hexane solution is washed twice with 50 cc and one with 100 cc of water. After drying over sodium sulfate and solvent removal, 11.4 g of oil is recovered.

Ten grams of this crude oil is dissolved in 5% of diethyl ether in hexane and subjected to column chromatorgraphy using a 5.5×78 cm column packed with 200 g of silicic acid and the diethyl ether-hexane mixture as eluent. Analysis of the 5.3 g of product recovered from the column by means of proton magnetic resonance and infra-red and mass spectroscopy confirms the production of bis(2,5 dimethyl - 3 - furyl) disulfide. This material has a roasted-meat aroma and a cooked-meat taste.

Analytical data are obtained as follows:

Infra-red:

λmax.	Interpretation
3.22	Aromatic CH stretch
6.21, 6.38	Aromatic ring C=C stretch
7.23	Methyl group
12.55	CH bond of aromatic ring

Proton Magnet Resonance:
In carbon tetrachloride:
2.1 (singlet, 6 protons),
2.27 (singlet, 6 protons), and
6.0 ppm (singlet, 2 protons).

Mass Spectrum:
Base Peak 43, Molecular Peak 254. Other peaks in descending order: 127, 128, 85.

EXAMPLE IV

Production of Furan - 3 - Thiol Derivatives

A 250 ml flask fitted with a mechanical stirrer, gas inlet tube, calcium chloride drying tube, thermometer, and Y-tube is charged with 50 ml of distilled Diglyme, and the Diglyme is saturated with gaseous hydrogen chloride at 0—5°C with constant stirring.

The flask is then immersed in a dry ice-isopropanol bath at —80°C. The cooled flask is charged with 14.0 g (0.14 mole) of 2 - methyl - 3 - tetrahydrofuranone, and 28.5 g (0.84 mole) of hydrogen sulfide which has been chilled to —80°C is slowly warmed and allowed to boil over into the reaction flask.

About one-half hour after the beginning of the hydrogen sulfide addition a pink-red color begins to appear in the reaction mixture. By the end of the 2.5 hours required for the addition of all the hydrogen sulfide, the reaction mixture is orange in color. At this time stirring is stopped, and the reaction mixture is permitted to stand 16 hours.

A one-liter Erlenmeyer flask is charged with sufficient sodium bicarbonate to cover the bottom of the flask and is placed into a dry ice-isopropanol bath. The reaction mixture is then poured slowly over the sodium bicarbonate to minimize foaming. Additional sodium bicarbonate is added until all foaming ceases. The neutralized mixture is treated with 200 ml of water and quickly extracted with 100 ml of methylene chloride. The organic solution so obtained is dried and con-

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centrated to provide 39.5 grams of an oil. The oil is distilled under vacuum to provide a first cut taken at 73—80°C at 57 mm Hg and a second cut at 80—83°C at the same pressure.

The 25 ml of the second portion is dissolved in 100 ml of ethyl ether and extracted four times with 5 ml of 5% aqueous sodium hydroxide to remove the pink color. The basic fraction so obtained is acidified with 11.2 cc of hydrochloric acid and extracted twice with 10 ml of ethyl ether, dried over sodium sulfate, and concentrated.

This concentrate is then chromatographed to separate the 2 - methylfuran - 3 - thiol and 2 - methyl - [2,3H] - dihydrofuran - 3 - thiol produced. These thiols have a roast meat aroma with the aroma of the furan - 3 - thiol being very similar to that of the disulfide produced in Example III.

The analytical data on the 2 - methylfuran - 3 - thiol are:

Infra-red:

λmax.	Interpretation
3.92	S—H group conjugated with aromatic ring
7.40, 6.60	Aromatic ring C=C bond
7.26	Methyl group
13.58	C—H bond of aromatic ring

Proton Magnetic Resonance:
In carbon tetrachloride:
2.12 (doublet, 3 protons),
2.23 (doublet, 1 proton),
6.08 (doublet, 1 proton) and
7.04 ppm (doublet, 1 proton).

Mass Spectrum:
Base Peak 43, Molecular Peak 114. Other peaks in descending order: 41, 45, 85, 47, 113, 71, 75, 74.

Example V

Preparation of bis(2 - Methyl - 3 - furyl) disulfide

The thiol produced in Example III is oxidized under mild conditions by dissolving 5 g of the thiol in 100 cc of hexane. The solution is placed in a 250 cc flask equipped with a sparger supplied by an air source, a stirrer, and a heater. Air is bubbled in at room temperature at a rate of 20 ml/minute during 20 hours. Solvent is replaced as required in order to maintain the original volume of solution. At the end of the reaction period the solvent is flash-evaporated and the resulting mixture is purified by column chromatography to yield 3 g of bis(2 - methyl - 3 - furyl) disulfide.

The purified bis(2 - methyl - 3 - furyl) disulfide has a full meat flavor and a cooked meat aroma when used in soup base at a concentration of 0.2 ppm. In a comparison 5 - methyl - 2 - furyl disulfide is also used in soup base at a concentration of 0.2 ppm and is found to have only a chemical, rubbery taste and aroma.

The analytical data for the 3-furyl disulfide follow:

Infra-red

λmax.	Interpretation
3.22	Aromatic C—H stretch
6.32, 6.60	Aromatic C=C stretch
7.22	Methyl group
11.28	Furanic ring vibration
13.6	C—H out-of-plane bend of a 2,3-disubstituted furan.

Proton Magnetic Resonance
In carbon tetrachloride:
7.14 (doublet, 2 protons),
6.25 (doublet, 2 protons), and
2.07 ppm (singlet, 6 protons).

Mass Spectrum
Base Peak 113; Molecular Peak 226; Other peaks in descending order: 43, 45, 51, 114, 85.

Example VI

The following ingredients are homogeneously admixed at 25°C:

Ingredient	Amount (g)
2-Methylfuran-3-thiol	2.0
2-Methyl-[4,5-H]-dihydrofuran-3-thiol	0.5
bis(2-Methyl-3-furyl) disulfide	93.0
bis(2-Methyl-3-furyl) monosulfide	4.0
bis(2-Methyl-3-furyl) trisulfide	0.5

The mixture has an excellent roasted-meat flavor when used in a soup base at 10 ppm.

Example VII

The monosulfide prepared in Example I is dissolved in propylene glycol to provide a 0.1% solution. This solution in the amount of 0.966 g is added to 7.3 g of a soup base consisting of:

Ingredient	Amount (Parts/100 total)
Fine ground sodium chloride	35.62
Hydrolyzed vegetable protein	27.40
Monosodium glutamate	17.81
Sucrose	10.96
Beef fat	5.48
Sethness caramel color (powder B & C)	2.73

The resulting mixture is added to 12 ounces of boiling water to obtain a soup having an excellent meat flavor.

The composition of Example VI (.005 g)

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when added to the above soup base also provides a soup having a good roasted-meat flavor. Similar results are obtained when the bis(2 - ethyl - 3 - furyl) sulfide or bis(2 - propyl - 3 - furyl) disulfide is used.

Example VIII

One-half gram of the soup base mixture of Example VII is emulsified in a solution containing 100 g gum arabic and 300 g water. The resultant emulsion is spray-dried with a Bowen Lab Model Drier utilizing 250 cfs of air with an inlet temperature of 500°F, an outlet temperature of 200°F, and a wheel speed of 50,000 RPM.

Twelve grams of the spray-dried material is mixed with 29.2 g of the soup base set forth in Example VII. The resulting mixture is then added to 12 ounces of boiling water, and an excellent roasted-meat flavored soup is obtained.

Example IX

The following ingredients are selected and mixed as described in Example VI to yield compositions having excellent meat flavor:

MIXTURE A

Ingredient	Amount (Parts/100 total)
2-Methylfuran-3-thiol	5.
2-Methyl-3-thiol-[4,5H]-dihydrofuran	5.
bis(2-Methyl-3-furyl) disulfide	1.
bis(2-Methyl-3-furyl) monosulfide	89.

MIXTURE B

bis(2-Methyl-3-furyl) trisulfide	15.
bis(4-Methyl-3-furyl) trisulfide	5.
bis(4-Propyl-[4,5H]-dihydro-3-furyl) monosulfide	5.
bis(2,5-Dimethyl-3-furyl) monosulfide	25.
Corn oil	50.

MIXTURE C

2-Ethylfuran-3-thiol	9.
2-Butylfuran-3-thiol	9.
bis(2-Pentyl-3-furyl) trisulfide	30.
bis(2-Ethyl-5-isopropyl-[2,3H]-dihydro-3-furyl)trisulfide	1.
bis(2-Butyltetrahydro-3-furyl) monosulfide	1.
Gum arabic	50.

Example X

Isolation of bis(Furyl) Disulfides from a Reaction Mixture

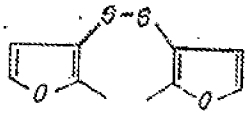
A 4,000-pound batch having the following composition:

	parts
Thiamine hydrochloride	8.8
L-Cysteine hydrochloride	8.8
Maggi (Registered Trade Mark) 4 BE protein hydrolysate	309.6
Water	672.8
	1,000.0

is heated at reflux for four hours. After the first 45 minutes of reflux a total of 40 gallons of condensate is removed uniformly over the next 3 hours and 15 minutes. Each gallon of condensate is extracted with 400 ml portions of methylene chloride. After removal of the methylene chloride under very mild vacuum, a 50 ml residue is obtained which possesses an extremely powerful roast-meat aroma.

Preparative thin-layer chromatography ($8 \times 8'' \times 1.25$ mm, silica-gel G, 200 λ/plate) of approximately 2.4 g gave 0.066 g of a pure compound having a good basic roast-meat aroma upon proper dilution. The mass spectrum of this compound is as follows: m/e (rel. intensity 226 (9.6), 227 (1.9), 228 (1.7), 113 (10.0), 43 (4.7), 114 (4.4), 45 (3.6), 85 (3.1), 51 (2.9), 69 (17.6). Proton magnetic resonance in carbon tetrachloride shows 2.07 (singlet, 2—$\overset{|}{C}C\overset{|}{H_3}$), 6.25 (doublet, 2 furyl protons), and 7.14 ppm (doublet, 2 furyl protons).

The above data are in excellent agreement with the proposed structure of bis(2 - methyl - 3 - furyl) disulfide:



When the crude extract is analyzed by preparative gas/liquid chromatography a compound having a very intense pot roast odor is obtained. This compound has been identified as 2 - methyl - furan - 3 - thiol.

Example XI

Preparation of 2-Methyl-3-Furanthiol

A 500 cc three-neck round-bottom flask is fitted with a Y-tube, thermometer, and stirrer and is then charged with 32 g of fuming sulfuric acid (oleum) containing 20% SO_3. The temperature is maintained at 24.28°C, and 40 g (0.318 mol) of 5 - methyl - 2 - furoic

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acid is slowly added to the oleum during a period of 45 minutes. After addition is complete, the reaction mixture is stirred for an additional 2-1/4 hours and then held for 16 hours.

The reaction mixture is thereupon poured over 600 cc of ice-water mixture and neutralized to pH 5 with 430 g of barium carbonate, during which neutralization a thick paste forms. After addition of 500 cc of water, the paste is boiled and then vacuum-filtered while hot. The barium sulfate-containing solids which remain after filtration are boiled with 700 cc of water, and the mixture is vacuum-filtered while hot. Both filtrates are combined and refrigerated for two days to form crystals which are recovered. The filtrate is evaporated to a volume of about 500 cc and cooled in ice to recover further crystals. The remaining filtrate is evaporated to a volume of 50 cc, 100 cc of methanol is added, and the liquid is chilled to obtain crystals. The yield of solids (barium - 2 - methyl - 3 - sulfo - 5 - furoic acid) from the three crystallizations is 93.5 g.

Barium - 2 - methyl - 3 - sulfo - 5 - furoic acid in the amount of 98.2 g and 1800 cc of distilled water is charged to a flask, and the flask is heated in a steam bath to 70°C until all the solids are dissolved. Then, 116 g of 20% aqueous sulfuric acid is gradually added to precipitate barium sulfate. The decanted liquid is cooled in ice and filtered. The water is evaporated from the filtrate, and the remainder is evaporated under high vacuum at room temperature to obtain 35.1 g of yellow oil which crystallizes after being held in a desiccator overnight.

The sodium salt of the sulfo furoic acid is prepared by dissolving 33.1 g of the crystallized oil (sulfo furoic acid) in 100 cc of water and gradually adding 6.75 g of sodium bicarbonate. After drying in a steam bath and then in a vacuum desiccator, 37.4 g of the sodium salt containing water of crystallization is obtained.

The sodium salt is decarboxylated by charging 13.2 g of mercuric chloride ($HgCl_2$) in 60 cc of water to a 500 cc three-neck round-bottom flask fitted with a condenser having a gas outlet and with a Y-tube, a nitrogen inlet, a stirrer, and a heating mantle. Then 11.1 g of the sulfo furoic acid sodium salt in 80 cc of water is charged to the flask, and this is followed by 1.95 g of sodium hydroxide in 20 cc of water. The mixture is refluxed for 2 hours and 40 minutes while the pH is maintained at 4—5 by addition of aqueous sodium hydroxide or hydrochloric acid as required, and carbon dioxide evolves. The mixture is then cooled to room temperature and filtered. The filtrate is adjusted to pH 7—8 with 10% aqueous sodium bicarbonate, and hydrogen sulfide is bubbled through the mixture to precipitate mercuric sulfide. The mercuric sulfiide is separated by filtration and the filtrate is concentrated in a rotary evaporator. About 30 cc of water is added to dissolve all the solids after concentration and the mixture is cooled to crystallize out 4.93 g of 2 - methyl furan - 3 - sulfonic material. The crystals are filtered from the supernatant and dried.

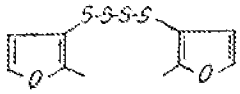
The sulfonic acid derivative is converted to the sulfonyl chloride derivative by treatment of 1.3 g of the sulfonic acid with 33 g of thionyl chloride and two drops of dimethyl formamide for 75 minutes at 25°C. The excess thionyl chloride is removed on a rotary evaporator, the residue is washed with benzene., and the benzene is stripped off to obtain 0.88 g of amber oil having a sharp, meaty odor.

The amber oil so obtained is then reacted with 0.8 g of lithium aluminum hydride in 30 cc of diethyl ether. The reaction is carried out by adding the hydride to 20 cc of ether, filtering, adding the oil in 10 cc of ether at reflux during a period of eight minutes. The reflux is then continued for 75 minutes. After reflux the remaining hydride in the mixture is reacted with methanol in ether, and the product so obtained is poured into ice water, acidified to pH 1 with hydrochloric acid, and extracted with ether to obtain an oil. This oil is dried, filtered, and stripped of ether to obtain 0.27 g of a yellow oil having a good meaty aroma.

Proton magnetic resonance of the major peak obtained from this oil by gas-liquid chromatography shows a thiol. Mass spectroscopy of this material shows peaks at 114 and 113. These results confirm the production of the 2 - methyl - 3 - furanthiol.

Example XII

Preparation of bis - (2 - methyl - 3 - furyl) tetrasulfide



To a flask containing a solution of 2 - methyl - 3 - furanthiol (1.65 g) in ethyl ether (10 ml.) and solid sodium bicarbonate (3.0 g) cooled to —30°C was added dropwise a solution of sulfur monochloride (1.01 g) in ethyl ether (10 ml). After standing 45 minutes the reaction mixture is poured into water (75 ml), the upper layer is separated and washed with water (25 ml). After back-extracting the aqueous washings with ethyl ether (25 ml.) the ether solutions are combined and washed with water (2×30 ml.) until the pH of the wash is about 5. Drying the ether solution with anhydrous sodium

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sulfate followed by solvent removal *in vacuo* gives 1.6 g. of crude bis(2 - methyl - 3 - furyl) tetrasulfide.

Column chromatography of the amber oil on 60 g. of silicic acid packed in hexane followed by elution with hexane gives 1.1 g. of analytically pure bis(2 - methyl - 3 - furyl) tetrasulfide as a light yellow oil. The purified bis(2 - methyl - 3 - furyl) tetrasulfide has a full meat flavor and brothiness when used in soup base at a concentration of 0.2 ppm.

Infra-red
λmas
3100
2900
1570
1510
1435
1380
1225
1122
1086
938
887
730
645 cm^{-1}

Proton Magnetic Resonance
in carbon tetrachloride.
2.37 (singlet, 6 protons)
6.38 (doublet, J=2Hz, 2 protons)
7.20 (doublet, J=2Hz, 2 protons)

Mass Spectrum
Base Peak 43; Molecular Peak 290. Other peaks in descending order 113, 45, 226, 114, 51, 85, 69.
Elemental analysis:

Calculated for $C_{10}H_{10}O_2S_4$;
C, 41.35; H, 3.47; S, 44.16.
Found: C, 41.52; H, 3.38; S, 43.77.

EXAMPLE XIII

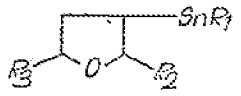
The following ingredients are homogeneously admixed at 25°C:

Ingredient	Amount (g.)
2-Ethylfuran-3-thiol	9
2-Butylfuran-3-thiol	9
bis(2-Pentyl-3-furyl) trisulfide	30
bis(2-Ethyl-5-isopropyl-[2,3H]-dihydro-3-furyl) trisulfide	1
bis(2-Butyltetrahydro-3-furyl) monosulfide	1
bis(2-Methyl-3-furyl) tetrasulfide	5
Gum arabic	45
Total	100

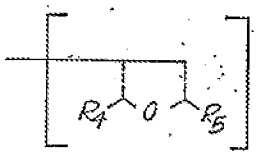
The mixture has an excellent roasted-meat flavor and may be added to a soup base at 10 ppm.

WHAT WE CLAIM IS:—

1. Furan derivatives having the formula:



wherein n is one and R_1 is hydrogen or n is one, two, three, or four and R_1 is a moiety of the formula:



or n is two or three and R_1 is alkyl, and wherein R_2 and R_4 are alkyl, R_3 and R_5 are hydrogen or alkyl, and each dashed line represents a single or double carbon-to-carbon bond.

2. Furan derivatives as claimed in claim 1, wherein the alkyl groups are methyl or ethyl groups.

3. Furan derivatives as claimed in claims 1 or 2 wherein, in the general formula, both dashed lines represent double bonds.

4. bis(2-Methyl-3-furyl) disulfide.

5. 2-Methylfuran-3-thiol.

6. bis(2,5-Dimethyl-3-furyl) sulfide.

7. bis(2,5-Dimethyl-3-furyl) disulfide.

8. 2-Methyl-[4,5H]-dihydrofuran-3-thiol.

9. bis(2-Methyl-3-furyl) tetrasulfide.

10. Furan derivatives as claimed in claim 1 and substantially as described in any one of the Examples herein, excluding those compounds specifically claimed in claims 4—9.

11. A process for the production of furan derivatives which comprises reacting a 2,5 - dialkylfuran with sulfur monochloride or sulfur dichloride and forming bis(2,5 - dialkyl - 3 - furyl) disulfide or bis(2,5 - dialkyl - 3 - furyl) sulfide respectively.

12. A process as claimed in claim 11, wherein the reaction is carried out in the presence of a Lewis' acid as catalyst.

13. A process as claimed in claims 11 or 12, wherein the reaction is carried out for a period of time between 15 minutes and 2 hours.

14. A process as claimed in any one of claims 11—13, wherein the reaction temperature is within the range from −30°C to +50°C.

15. A process as claimed in any one of claims 11—14, wherein the proportions of the reactants are such that the dimethyl furan compound is used in large molar excess over the particular sulfur chloride used.

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16. A process for the production of furan - 3 - thiols and alkyl-substituted furan - 3 - thiols which comprises reacting an appropriate dihydrofuranone-3 or tetrahydrofuranone-3 with hydrogen sulfide under acidic conditions to give furan - 3 - thiols, dihydrofuran - 3 - thiols, tetrahydrofuran - 3 - thiones or alkyl-substituted derivatives thereof.

17. A process as claimed in claim 16, which comprises reacting a 2 - alkyltetrahydro - furanone - 3 with hydrogen sulfide under acidic conditions to form alkylfuran - 3 - thiol and alkyldihydrofuran - 3 - thiol.

18. A process as claimed in claims 16 or 17, wherein the reaction is carried out in the presence of anhydrous hydrogen chloride at a temperature within the range from −60 to −100°C.

19. A process as claimed in any one of claims 16—18, wherein at least one of the thiols is oxidized under mild conditions to produce the corresponding disulfide.

20. A process as claimed in claim 19, wherein the thiols are oxidised by passing an air stream through them at 20°C and 760 mm Hg pressure for 8 hours.

21. A process as claimed in claim 19, wherein the thiols are oxidised with a mild oxidising agent selected from ferric chloride, iodine-potassium iodide, dimethyl disulfide or dimethylsulfoxide.

22. A process for the production of furan derivatives which comprises reacting a 2 - alkyl - 3 - halotetrahydrofuran with sodium hydrosulfide to form 2 - alkyltetrahydro - furan - 3 - thiol.

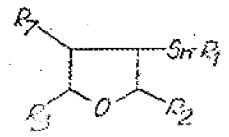
23. A process as claimed in claim 22, wherein the reaction is carried out under reflux conditions in the presence of a vehicle.

24. A process for the production of a furan derivative which comprises reacting a 2 - alkyl - 5 - furoic acid, a 2 - alkyl - 5 - cyanofuran, or a 2 - alkyl - 5 - halofuran with oleum to produce the corresponding 3 - sulfofuran derivative, removing the 5 sub - stituent by known methods to obtain 2 - alkyl - 3 - sulfofuran, reacting the sulfofuran with thionyl chloride to form 2 - alkyl - 3 - (chlorosulfo)furan, and reducing the (chloro - sulfo)furan to produce 2 - alkylfuran - 3 - thiol.

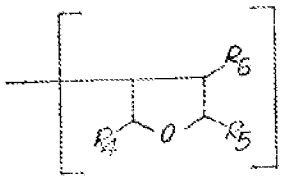
25. A process as claimed in claim 24, wherein the 5 furoic acid is used as starting material and, after the treatment with oleum, the barium salt of the resulting acid is obtained by treatment of the acid with excess barium carbonate and the barium salt is converted to the sodium salt which is then decarboxylated with an equivalent amount or excess of mercuric chloride in a refluxing aqueous solution, and the resulting sodium sulfonate is reacted with a 7—8 fold excess of thionyl chloride to form the 2 - alkyl - 3 - (chlorosulfo) furan.

26. A process as claimed in claims 24 or 25, which comprises reacting the 2 - alkyl - furan - 3 - thiol with alkyl disulfur chloride to produce alkyl(2 - alkyl - 3 - furyl) tri - sulfide or with alkyl sulfur chloride to produce alkyl(2 - alkyl - 3 - furyl)disulfide.

27. A flavoring or flavor enhancing composition comprising a furan derivative having the formula:



Wherein n is one to four; R_1 is hydrogen, alkyl, alkenyl, alkadienyl, or a moiety of the formula:



and R_2, R_3, R_4, R_5, R_6 and R_7 are hydrogen, alkyl, alkenyl, or alkadienyl, or taken together R_5 and R_6 and/or R_5 and R_7 form cycli-alkyl, cyclialkenyl, cyclialkadienyl, benzo, thieno, dihydrothieno, tetrahydrothieno, furano, dihydrofurano, or tetrahydrofurano rings; and the dashed lines represent single or double carbon-to-carbon bonds, together with a suitable vehicle or carrier.

28. A composition as claimed in claim 27, comprising a furan derivative as claimed in claim 1.

29. A composition as claimed in claim 27, comprising a furan derivative as claimed in any one of claims 2—10.

30. A composition as claimed in claim 27, comprising a furan derivative prepared by a process claimed in any one of claims 11—26.

31. A composition as claimed in any one of claims 27—30, wherein an auxiliary flavoring adjuvant is present.

32. A composition as claimed in claim 27, wherein 0.0001% to 10% by weight of furan derivative is present based on the total weight of the composition.

33. A food composition comprising a foodstuff and a compound as claimed in claim 1, in sufficient quantity to impart a roasted meat flavor to the composition.

34. A process for flavoring a foodstuff which comprises admixing an effective amount of a composition as claimed in claim 27 with the foodstuff.

35. A process for the production of a

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furan derivative substantially as hereinbefore described in any of Examples I—V, XI or XII.

36. Furan derivatives when produced by the process claimed in any one of claims 11—26.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1283913

1283913

NO DRAWINGS

(21) Application No. 34141/69 (22) Filed 1 July 1968
(23) Complete Specification filed 1 July 1969
(45) Complete Specification published 2 Aug. 1972
(51) International Classification C07G 17/00 A23L 1/26
(52) Index at acceptance
C2C 30Y 782 783 789 799 XX
A2B 6A

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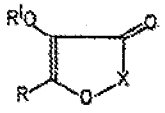
(54) FLAVOURING SUBSTANCES PREPARED BY REACTION OF HETEROCYCLIC KETONES WITH HYDROGEN SULPHIDE

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the preparation of artificial flavouring substances and their use in the flavouring of foodstuffs. In particular, the invention is concerned with the preparation of substances capable of imparting a savoury flavour, for example a flavour resembling that of roast or fried meat, to foodstuffs. When the foodstuff is of a type which already has a savoury flavour, then such a flavour may be improved by judicial incorporation of these substances.

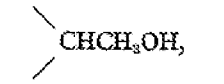
We have discovered that certain heterocyclic ketones are capable of reacting with certain organic or inorganic sulphur-containing compounds with the formation of a reaction mixture which has aroma and flavour characteristics remarkably similar to that of cooked meat.

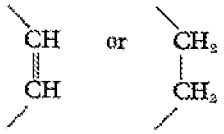
Accordingly, the invention provides a process for the preparation of a flavouring substance in which process a heterocyclic ketone having the structure:



where X is one of the groupings:







and where R is an alkyl radical having from 1—4 carbon atoms, and where R′ is hydrogen or an acyl radical having from 2—7 carbon atoms or an alkyl radical having from 1—4 carbon atoms,

is reacted in the presence of water with hydrogen sulphide or other sulphur-containing compound which is capable of liberating hydrogen sulphide under the reaction conditions

The ketones thus comprise a class of compounds which are substituted furanones or pyrones, especially those wherein the alkyl radical denoted by R in the above structural formula is a methyl, ethyl, n-propyl, iso-propyl or n-butyl radical and wherein R′ is hydrogen.

Although the radical R′ is preferably hydrogen, we have found that certain organic radical substituents react in a similar manner to form flavouring substances according to the invention. Thus, for example, R′ may alternatively be an acyl radical such as acetate, propionate, n-butyrate, iso-butyrate and benzoate, or an alkyl radical such as methyl, ethyl, n-propyl, iso-propyl and n-butyl.

Certain of these compounds show keto-enol tautomerisation, but from analytical data including infra-red and nmr-spectra, it is believed that under normal conditions they are present in the enol form represented by the above structural formula.

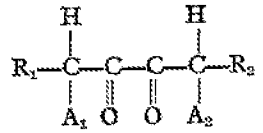
Preferred examples of the furanones which may be reacted with hydrogen sulphide according to the invention are:

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4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one
4 - hydroxy - 2,5 - dimethyl - 2,3 - dihydrofuran - 3 - one
4 - hydroxy - 2 - methyl - 5 - ethyl - 2,3-dihydrofuran - 3 - one
4 - hydroxy - 5 - methyl - 2 - ethyl - 2,3-dihydrofuran - 3 - one
4 - hydroxy - 2,5 - diethyl - 2,3 - dihydrofuran - 3 - one
4 - hydroxy - 2 - hydroxymethyl - 5-methyl - 2,3 - dihydrofuran - 3 - one
4 - acetoxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one
4 - methoxy - 2,5 - dimethyl - 2,3 - dihydrofuran - 3 - one

Of these furanones, the first three named examples are the most preferred.

The alkyl substituted furanones which are used according to the present invention can be prepared by heating and reacting a diketo diester of the general formula:



in which R_1 and R_2 represent a hydrogen atom or an alkyl radical containing 1 or 2 carbon atoms, with the provision that the number of carbon atoms of R_1 and R_2 together is at least one and A_1 and A_2 represent acid radicals. The acid radicals may be derived from carboxylic acids, especially from lower aliphatic carboxylic acids. Preferred ester groups are those derived from acetic and propionic acid.

The reaction is carried out in an aqueous acidic medium which contains at least 50 percent by volume, preferably at least 75 percent of water, the remainder being a water-miscible polar solvent as, for example a lower aliphatic alcohol such as methanol and ethanol.

The acidic compound available in the aqueous acidic medium may comprise an inorganic acid, a carboxylic acid, or, for example, an organic sulphonic acid. Suitable acids include hydrobromic or hydrochloric acid, sulphuric acid, phosphoric acid, formic acid, acetic acid, propionic acid, and p-toluene sulphonic acid. Polycarboxylic acids and hydroxycarboxylic acids are less suitable. The use of strong acids, showing a pK value below 5 or rather below 4, is particularly preferred.

The amount of acid in the aqueous medium is not particularly critical and may vary widely. Good results have been obtained with amounts of 0.1—5 equivalents of acid per litre medium. Also the concentration of the diketo diester in the aqueous medium may vary widely. Generally, less than 200g of diketo diester are dissolved per litre of medium. For practical reasons, in particular to reduce the volume of the reaction mixture, the use of too dilute solutions is avoided. A practical range is from 10—100g of diketo diester per litre medium.

The reaction temperature and time of reaction are related. For convenient reaction periods in the range of 0.5—10, preferably from 1—5 hours, it is preferred to conduct the reaction at temperatures above 75°C, preferably at boiling temperature at atmospheric pressure. It is however possible to obtain a satisfactory conversion at lower temperatures, for example of about 50°C, provided the reaction period is suitably adjusted to at least 20 hours.

After termination of the reaction the aqueous reaction mixture is allowed to cool and the desired furanone derivative is isolated in a conventional way. This could be done, for example, by extraction with ether, drying of the etheral solution and evaporation of the solvent. Undesired polymeric contaminants are removed by distillation of the product under diminished pressure.

Esterification or etherification of the hydroxyl group in the 4-position may be achieved by conventional methods.

The diketo diester starting materials for the process according to the invention can be prepared in various ways. A convenient method is via acetylenic compounds.

Step 1—Preparation of an alkyne diol

Acetylene was coupled with two moles of aldehyde using two moles of a Grignard compound. This method is described in Bull. Soc. Chim.—France 425 (1956). Alternatively a 1-alkyne-3-ol could be coupled with formaldehyde as described in Annalen 596 525 (1955) or by coupling a 1-alkyne-3-ol and other aldehydes or ketones (as described in Bull Soc. Chim. supra).

Step 2—Esterification of the alkyne diol

The diacetates were conveniently prepared by reacting with acetic anhydride in the presence of e.g. pyridine or sodium acetate.

Step 3—Oxidation of the alkyne diester

The alkyne diester was oxidized with dilute aqueous potassium permanganate at a low temperature yielding the diketo diester. This method has been described in Bull. Soc. Chim. (France) 789 (1949).

Preferred examples of the pyrones which may be reacted with hydrogen sulphide according to the invention are:

3 - hydroxy - 2 - methyl - 1,4 - pyrone (maltol)
3 - hydroxy - 2 - ethyl - 1,4 - pyrone (ethyl maltol)

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The sulphur containing compound with which the furanone or pyrone is reacted is hydrogen sulphide, in the form of a gas, liquid or solution, or an organic or inorganic compound which is capable of liberating hydrogen sulphide, either in gaseous or nacent form, under the reaction conditions.

Suitable examples of organic sulphur-containing compounds are cysteine, or a peptide containing cysteine such as glutathione, cystine, mercaptoacetamide, thioacetamide or salts, for example potassium or sodium salts, hydrochlorides, esters or other simple derivatives of these sulphur-containing compounds.

Suitable examples of inorganic sulphur-containing compounds are sulphides or hydrosulphides of alkali metals, alkaline earth metals or ammonia, such as sodium sulphide, potassium sulphide, ammonium sulphide, calcium sulphide or the corresponding hydrosulphides. Also, other inorganic metallic sulphides, for example ferrous sulphide, may be used.

The reaction mixture comprising at least one ketone and hydrogen sulphide or a sulphur-containing compound as herein defined which react to form the flavour substances according to the invention, may optionally also contain other ingredients which improve or enhance the character of the flavour which subsequently is produced. These optional ingredients may be added before, during or after the ketone and hydrogen sulphide or sulphur-containing compound react.

Thus it is possible to include in the reaction mixture amino acids, the preferred amino acids being one or more of the following: arginine, glutamic acid, proline, glycine, α-alanine, β-alanine, threonine, lysine, leucine, iso-leucine, serine, valine, histidine, cysteine and cystine or a salt thereof. Cysteine and cystine may of course serve in the reaction as sulphur-containing compounds according to the invention.

It is also possible to include in the reaction mixture as an optional ingredient a monosaccharide or a carbohydrate which is capable of being hydrolysed to a monosaccharide under the conditions of the reaction. The most suitable monosaccharides are hexoses, such as glucose, and pentoses, such as ribose, xylose, rhamnose and arabinose.

It is also possible to conduct the reaction in the presence of C_{12}—C_{18} aliphatic fatty acid, for example, palmitic acid or oleic acid or a salt, ester or glyceride thereof.

The proportions of the ketone to hydrogen sulphide or sulphur-containing compound which are present in the reaction mixture may vary widely. Thus it is possible to use proportions on a weight basis of from 1 part ketone and 50 parts hydrogen sulphide or sulphur-containing compound to 50 parts 1 part hydrogen sulphide or sulphur-containing compound. Preferred weight proportions are between 1 part ketone and 10 parts hydrogen sulphide or sulphur-containing compound to 10 parts ketone and 1 part hydrogen sulphide or sulphure-containing compound.

Where the reaction conditions are such that excess hydrogen sulphide remains after the reaction is complete, it is advisable to allow the reactants to stand, or to apply ventilation or other means to remove the excess hydrogen sulphide, otherwise the flavour substance may be objectionable due to residual hydrogen sulphide.

The reaction should be conducted under conditions in which at least a trace amount of water is present in the reaction mixture; suitably the amount of water present should be at least equal by weight to the amount of hydrogen sulphide or the sulphur-containing compound. It is however preferred for reasons of convenience that the weight of water should be at least equal to that of the reactants, so that intimate mixing of the ingredients is thereby facilitated. In general it is not necessary that the weight of water present should exceed 100 times that of the reaciants, primarily to facilitate subsequent concentration of the flavouring substances which are the products of the reaction. It is also possible to conduct the reaction where the water is bound in the form of water of crystallisation. As an example, sodium sulphide nonahydrate may be employed in the reaction to act both as a sulphur containing compound and as a source of water.

The rate at which the ketone and hydrogen sulphide or sulphur-containing compound react is dependent on the temperature of the reaction mixture, higher temperatures in general resulting in a faster rate of reaction. However, we have found that it is possible to obtain the flavour substances according to the invention by employing a reaction temperature of between 0° and 150°C, but for practical purposes it is preferred and is more convenient to employ a temperature in excess of 60°C, and most preferably between about 90° and 110°C. This is particularly applicable when the reaction is carried out by refluxing at atmospheric pressure.

It is necessary to apply a pressure above that of atmospheric pressure when aqueous systems are heated at a temperature above the boiling point of the system at atmospheric pressure. It has also been found advantageous to employ superatmospheric pressures when one of the reactants is a gas, for example when gaseous hydrogen sulphide is employed.

When the reaction is conducted in the presence of more than a trace amount of water, the pH of the reaction mixture may vary over a wide range of values. The reaction thus may be conducted at pH values ranging from 2 to 10, but values between 4 and 7 are preferred.

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The duration of the reaction may vary considerably and is, of course, dependent on other parameters which control the rate of reaction. We have, for example, found that the flavour substances are produced within a few minutes of commencing the reaction and continue to build up in the reaction mixture for several days. As a general guide, we have found that for a reaction temperature of 100°C, a reasonable reaction time is from 1 minutes to 15 hours, whereas at room temperature, the flavour composition may be produced in as little as 3 minutes to as long as 30 days. It is, however, preferred to restrict the reaction time to between 1 and 6 hours.

According to a preferred embodiment of the invention, a ketone and a sulphur-containing compound giving rise to hydrogen sulphide are reacted together in the presence of water by boiling or simmering under reflux at a temperature slightly in excess of 100°C for about 3 hours. The aqueous reaction mixture may subsequently be concentrated to a paste or dried to powder, care being taken to ensure that the loss of volatile components of the flavouring substance so produced is kept to a minimum.

The flavouring substances prepared according to the invention may thus be employed in liquid or semi-liquid form, for example as solutions, emulsions or pastes, or in dried form, for example as a powder. Drying of the reaction products may be accomplished for example by freeze-drying which has been found to be most suitable for optimum retention of flavour volatiles.

The flavouring substances thus prepared may be blended with a further quantity of a ketone as herein defined, which itself is capable of imparting a savoury taste to a foodstuff, or with one or more compounds from the following classes of substances:

I. Amino acids which may be obtained by hydrolysis, autolysis or fermentation or by combination of these from vegetable or animal proteins such as gluten, casein, or soyabean protein.

II. Nucleotides, such as adenosine-5'-monophosphate, guanosine - 5' - monophosphate, inosine - 5' - monophosphate, xanthosine - 5' - monophosphate, uridine - 5' - monophosphate, cytidine - 5' - monophosphate, or their amides, desoxy derivatives or their salts. Combinations of nucleotides, for example guanosine - 5' - monophosphate and inosine-5-monophosphate are particularly suitable.

III. Carboxylic acids such as lactic acid, glycolic acid and γ-hydroxy butyric acid on one hand and discarboxylic acids such as succinic acid and glutaric acid on the other hand, and especially mixtures of carboxylic acids in which succinic acid and lactic acid occur in weight ratios of 1:30 to 1:150.

IV. Pyrrolidone carboxylic acid or precursors thereof.

V. Peptides such as alanyl-alanine, alanyl - phenylalanine, alanyl - asparagine, carnosine and anserine.

VI. Sweetening substances, both artificial, such as saccharine and cyclamate, and natural, particularly mono- and disaccharides.

VII. Substances with the flavour of cooked or roast meat or of meat broth, (other than those which result from the reaction of a ketone with a sulphur-containing compound as hereinbefore defined), for example the reaction products of amino acids such as cysteine or cystine with reducing sugars, or ascorbic acid, or the reaction products of hydrogen sulphide with lower aliphatic aldehydes and ketones, such as propionaldehyde, crotonaldehyde, methional, mercapto-acetaldehyde.

VIII. Volatile sulphur compounds, such as hydrogen sulphides, mercaptans, disulphides and sulphides, such as dimethyl sulphide and diallyl sulphide.

IX. Guanidines, such as creatine and creatinine.

X. Salts such as sodium chloride, disodium hydrogen phosphate, monosodium dihydrogen phosphate or other alkali or ammonium phosphates and organic phosphates, such as phosphorus-containing amino acids.

XI. Nitrogen-containing compounds, such as ammonia, amines, urea, indole and skatole.

XII. Saturated or unsaturated carboxylic acids for example those containing from 2 to 12 carbon atoms in the molecule.

XIII. Saturated or unsaturated higher hydroxycarboxylic acids and γ and δ-lactones derived therefrom, such as deca- and dodeca-5-olide and 2,3-dimethyl-2,4-alkadiene-4-olides.

XIV. Lower saturated and unsaturated aldehydes, for example acetaldehyde, propionaldehyde, iso-butyraldehyde and hepten-4-al.

XV. Lower saturated and unsaturated ketones, such as acetone, butanone and diacetyl.

XVI. Tricholomic acid and ibotenic acid or their salts.

XVII. Aromatic and/or heterocyclic compounds, such as ortho amino-acetophenone, N-acetonyl pyrrole, iso-maltol, lenthionine, hypoxanthine, guanine, inosine and guanosine.

XVIII. Lower saturated and unsaturated alcohols, such as ethanol and octanol.

XIX. Colouring substances, such as curcuma and caramel.

XX. Thickening agents such as gelatin and starch.

XXI. Unsaturated C_{12}—C_{18} aliphatic fatty acids and their glycerides or saturated glycerides.

The proportions of these optionally added substances used is dependent on the kind of flavour desired and also on the nature of the foodstuff to which they are added together with other ingredients, such as herbs and spices.

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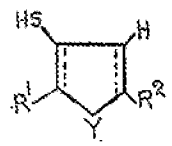
In addition to preparing flavouring substances for subsequent addition for foodstuffs, by reacting together a ketone and hydrogen sulphide as herein described, it is also possible to add the unreacted starting materials to the foodstuff so that the flavouring substances may subsequently develop in the foodstuff before consumption. Thus, for example, it is possible to add a ketone and a sulphur-containing compound capable of producing hydrogen sulphide to the ingredients of a soup which is subsequently canned and heat sterilised. A desirable roast meat-like flavour may thereby be developed within the soup after heat sterilisation in the sealed can.

The flavouring substances prepared according to the invention may otherwise be incorporated into foodstuffs, such as soups, sausage, reformed comminuted meat, simulated meat products, such as textured vegetable protein, and pastry products, in an amount sufficient to impart or enhance the desired flavour. Thus, flavouring amounts will vary according to the individual palate and according to the nature of the foodstuffs. As a general guide, the flavouring substances in amounts of from 1 ppm to 8,000 ppm have been incorporated in foodstuffs, these proportions being expressed on a weight basis.

As an illustration of suitable quantities of the flavouring substances that may be added to specified types of foodstuffs, we have found that as little as 1 ppm to 10 ppm w/w is sufficient to impart a pleasant roast meat flavour to soups which are bland other otherwise lightly flavoured. On the other hand, when incorporating a similar roast meat flavour to already flavoured foodstuffs such as those based on vegetable protein, it may be necessary to incorporate larger amounts, for example from 600 to 8,000 ppm w/w of the flavouring substance in order to obtain a desirable flavour.

When the flavour substances prepared according to the invention are added to a foodstuff, it is believed that further reaction in situ in the foodstuff contributes to the development of the desired flavour characteristic. It would thus appear likely, for example, that sulphydryl groupings present in or derived from protein present in the foodstuff react further with the ketone derivatives in the flavour substance to produce compounds having improved flavour properties.

Our copending application 31378/68 claims a compound of the general formula



in which Y represents an oxygen or sulphur atom and R^1 and R^2 a hydrogen atom, a methyl group or an ethyl group, the total number of carbon atoms of R^1 and R^2 together being at least one, and in which no more than one of the dotted lines between carbon atoms 2 and 3, or 4 and 5 represents either an additional carbon to carbon bond between these atoms, or that instead these carbon atoms carry each a hydrogen atom.

The invention is illustrated by the following examples.

Example 1

A beef flavoured composition was prepared by adding 250 ml of water to a mixture of 5.7g of 4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one and 25.0g of cysteine and heating the mixture at about 100°C for 2½ hours. The resulting mixture was cooled and quantities of between 0.2 and 2.0 ml of the reaction mixture were sprayed over 100g portions of dehydrated textured vegetable protein containing no meat. An excellent roast meat flavour was thereby imparted to this material as assessed by eleven out of a total panel of twelve expert tasters.

Dextrin-maltose was added to a portion of the flavoured mixture which resulted from the reaction described above in an amount which provided a composition containing about 70 parts by weight of dextrin-maltose to each part of the substance calculated on a solid basis. The composition was freeze dried and a beef flavoured product was obtained.

Example 2

To 6.4g of 4 - hydroxy - 2,5 - dimethyl-2,3 - dihydrofuran - 3 - one in a buffer solution containing about 35g sodium acetate, about 14g of acetic acid and 400 ml of water (pH 5.0), a solution of 12g of sodium sulphide ($Na_2S \cdot 9H_2O$) in 200 ml of water was added over a period of 30 minutes. The mixture was then boiled under reflux conditions at atmospheric pressure for 2 hours and allowed to cool. The pH was then 6.6. The reaction mixture so obtained had a good roasted meat flavour.

Example 3

A mixture of 7.2g of 4 - hydroxy - 2-hydroxymethyl - 5 - methyl - 2,3 - dihydrofuran - 3 - one, 12g of sodium sulphide ($Na_2S \cdot 9H_2O$) and 300 ml of water was heated in a round-bottomed flask fitted with reflux condenser for 2 hours at a temperature of 110°C. The reflux condenser was then removed and the contents cooled to room temperature. The resulting solution had a taste resembling that of roasted meat.

Example 4

6.3g of 3-hydroxy-2-methyl-1,4-pyrone, 3.8g of thioacetamide and 100 ml of water

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were heated together in a round-bottomed flask at 100°C for 2½ hours. The reaction mixture was then allowed to cool (pH 4.3) and it was shown to have an excellent roast beef flavour.

EXAMPLE 5

A roast beef-flavoured composition was prepared by adding 200 ml of water to a mixture of 7.0 g of 3-hydroxy-2-ethyl-1,4-pyrone and 4.6g of mercaptoacetamide and heating the mixture to 100°C for 5 hours. A product having a good roasted meat flavour was obtained. Before use in conjunction with the foodstuff, the pH was adjusted to 5.5 by the addition of sodium hydroxide solution.

EXAMPLE 6

3.0g of a 70/30 mixture of 4 - hydroxy-2 - methyl - 5 - ethyl - 2,3 - dihydrofuran-3 - one and 4 - hydroxy - 5 - methyl - 2-ethyl - 2,3 - dihydrofuran - 3 - one, 9.0g of cysteine and 60 ml of water were heated in a round bottom flask fitted with reflux condenser for 2 hours at 100°C. The reflux condenser was then removed and the contents cooled to room temperature. The resulting solution had a good roasted meat flavour.

EXAMPLE 7

A composition with a meat-like flavour was prepared by adding 100 ml of water to a mixture of 4.0g of 4 - hydroxy - 2,5 - diethyl - 2,3 - dihydrofuran - 3 - one and 20.0g of cysteine and heating the mixture at 95—100°C for 4 hours.

EXAMPLE 8

A mixture of 1.5g of 4 - hydroxy - 5-methyl - 2,3 - dihydrofuran - 3 - one and 1.5g of cysteine in 30 ml of water was heated at about 100°C for 2½ hours. To the resulting solution was added 33g of malto-dextrin. The solution thus obtained was carefully freeze dried. The powder obtained was used as a good beef flavour in soup or gravy.

EXAMPLE 9

A gravy was prepared from the following ingredients:

	grams
potato starch	15
onion powder	2.5
monosodium glutamate	3
beef tallow	20
flour	15
caramel	1.6
pepper	0.02
bayleaves	0.02
clove	0.02
sodium chloride	8
protein hydrolysate	4
beef extract powder	2
tomato powder	1
	72.16

The potato starch and flour were added to the molten beef tallow at 60°C under continuous stirring. The other ingredients were well blended and likewise added to the beef tallow. The whole mixture was boiled in 1 litre of water.

The gravy so obtained was divided into two portions of 500 ml. In the first portion 250mg of malto-dextrin was dissolved; in the second portion 250mg of the flavour powder prepared according to Example 8. Both gravies were assessed in a paired comparison test by a panel consisting of 12 persons.

The gravy containing the flavour powder was preferred by 10 out of the 12 tasters because of its more pronounced fried meat flavour.

EXAMPLE 10

A basic composition for a dry beef soup was obtained by mixing the following ingredients:

	grams
onion powder	0.5
spice mix	0.5
fat	4
dried soup vegetables	1
MSG	2
modified potato starch	3
noodles	20
salt	8

One litre of water was added to the mixture and the whole was boiled for 5 minutes. The soup so obtained was divided in two portions of 500 ml. In the first portion 150 mg of malto-dextrin was dissolved and in the section portion 150 mg of the flavour powder prepared according to Example 8.

Both soups were assessed in a paired comparison test by a panel consisting of 8 persons. The soup containing the flavour powder had a characteristic beef flavour and was preferred by 7 out of the 8 tasters.

EXAMPLE 11

6.3g of 3 - hydroxy - 2 - methyl - 1,4-pyrone, 10.5g of sodium sulphide (Na_2S9H_2O) and 100 ml of water were heated together in a round-bottomed flask at 100°C for 2½ hours.

To the reaction mixture was added 117g of malto-dextrin. The resulting solution was spray-dried immediately. The powder thus obtained proved to have a good beef flavour.

EXAMPLE 12

1 litre gravy was prepared according to the method described in Example 10. This gravy was divided into two portions of 500 ml each. To the first portion 125mg of malto-dextrin was added and to the second portion 125mg of the flavour powder prepared according to Example 11. Subsequently both gravies were

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boiled for 5 minutes and judged afterwards by a panel consisting of 9 expert tasters. Of these, 7 persons preferred the gravy with the aroma powder, while the other 2 expressed no preference. A fuller flavour and a more meaty taste were given as reasons for the preference.

EXAMPLE 13

100g of textured vegetable protein (T.V.P.) was boiled for 15 minutes in 500 ml of water together with:

	grams
MSG	1.85
Salt	4.0
protein hydrolysate	1.1
spices	0.45
flavour powder prepared according to Example 12	6.0

The T.V.P. thus obtained was compared with the product in which the flavour powder was replaced by 6.0g of malto-dextrin. Both T.V.P. products were assessed in a paired comparison test. The product with the flavour powder was generally preferred. A fuller flavour and a more meaty taste were given as reasons for this preference.

EXAMPLE 14

5.0g of 4 - hydroxy - 2,5 - dimethyl - 2,3-dihydrofuran - 3 - one, 0.5g of hydrogen sulphide and 100 ml of water were placed in an autoclave and heated for 2 hours at 100°C. To the resulting solution was added 100g of malto-dextrin. The solution thus obtained was carefully freeze dried. The powder obtained was used as a beef flavour in soup.

EXAMPLE 15

Minced meat was prepared from the following ingredients:

	grams
sausage meat	825
salt	10
whole egg	82.5
bread-crumbs	82.5
	1000

The minced meat so obtained was divided into two portions of 500g each. To the first portion was added a mixture of 10g of bread-crumbs and 0.25g malto-dextrin, and to the second portion a mixture of 10g of bread-crumbs and 0.25g of the flavour powder prepared according to Example 14. Meat balls prepared from each portion were fried in margarine for 30 minutes. The meat balls of both portions were assessed in a paired comparison test by a panel consisting of 8 persons. A unanimous preference was shown for the meat balls containing the flavour powder, because of the more pronounced fried meat flavour.

EXAMPLE 16

1.6g of 4 - hydroxy - 2,5 - dimethyl - 2,3-dihydrofuran - 3 - one, 8.0g of glutathione and 50 ml of water were heated for 1½ hours at 100°C in a round-bottomed flask fitted with a reflux condenser. To the resulting solution was added 5.0g cysteine, and the mixture was again heated for 2 hours at 100°C. The resulting solution had a good roasted meat flavour.

EXAMPLE 17

A basis for canned beef soup was prepared by adding the following ingredients to 4 litres of water:

	grams
noodles	160
herbs and spices	1.6
tallow	80
vegetables	400
MSG	16
protein hydrolysate	16
meat extract	16
salt	64
raw meat	400

The total amount was divided into two portions, each of 2 litres. 1.4g of the flavoured solution prepared according to Example 16 was added to one of the portions. The second portion which was used without further addition, served as a control. The mixtures thus obtained were canned in half litre tins and sterilised in an autoclave. A soup ready for consumption was prepared by adding to the contents of each tin an equal volume of water. After heating, both soups were served to a panel consisting of 19 people for organoleptic testing. The soup with the flavour solution was preferred by 15 persons, because of its more meaty flavour.

EXAMPLE 18

One litre of gravy was prepared according to the method described in Example 9. This gravy was divided into two portions of 500 ml each. To one of the portions was added 0.2g of the flavoured solution obtained in Example 16, while the other was used without further addition. Both gravies were judged by a panel consisting of 9 persons. Of these 8 persons preferred the gravy with the flavour solution. A more meaty taste and a fuller flavour were given as reasons for the preference.

EXAMPLE 19

A mixture of 4g of powdered casein hydrolysate, 2g of cysteine, 1g of xylose, 1g of 4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one and 50 ml of water was

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heated in a flask with stirring for 2½ hours at 95°C. The solution thus obtained proved to have a good beef flavour.

EXAMPLE 20

One litre of gravy was prepared according to the method described in Example 9. This gravy was divided into two portions of 500 ml each. To the first portion was added 0.5g of the flavoured solution prepared according to Example 19, and to the second portion, 0.5g of a solution prepared according to the method described in Example 20 except that the 1g of 4 - hydroxy - 2,3 - dihydrofuran-3 - one had been omitted. Both gravies were assessed in a paired comparison test by a panel consisting of 9 persons. The gravy portion containing the flavoured solution prepared using all the ingredients of Example 19 was significantly preferred because of its more pronounced meat flavour.

EXAMPLE 21

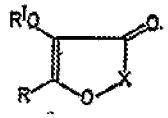
One litre of gravy was prepared according to the method described in Example 9. The gravy was divided into two portions of 500 ml each. To the first portion was added 250mg of the flavour powder prepared according to the method described in Example 8, and to the second portion was added 12.5mg of 4 - hydroxy - 5 - methyl - 2,3 - dihydrofuran - 3 - one. Both gravies were assessed in a paired comparison test by a panel consisting of 16 expert tasters. The gravy containing the flavour powder was preferred by 12 out of 16 persons because of its more pronounced fried meat flavour.

EXAMPLE 22

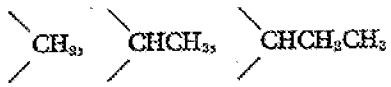
A mixture of 1.0g of 4 - acetoxy - 5-methyl - 2,3 - dihydrofuran - 3 - one, 2.0g of thioacetamide and 20ml of water were heated together in a round bottom flask at 100°C for 4 hours. The reaction mixtured was then allowed to cool. It had a good roast beef flavour.

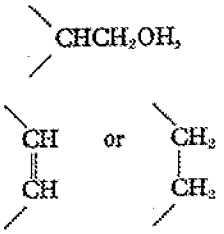
WHAT WE CLAIM IS:—

1. A process for the preparation of a flavour substance, in which process a heterocyclic ketone having the structure:



where x is one of the groupings:





and where R is an alkyl radical having from 1—4 carbon atoms, and where R' is hydrogen, or an acyl radical having from 2—7 carbon atoms or an alkyl radical having from 1—4 carbon atoms,

is reacted in the presence of water with hydrogen sulphide or other sulphur-containing compound which is capable of liberating hydrogen sulphide under the reaction conditions.

2. A process according to claim 1, in which the ketone is 4 - hydroxy - 5 - methyl - 2,3-dihydrofuran - 3 - one.

3. A process according to claim 1, in which the ketone is 4 - hydroxy - 5 - methyl - 2,3-dihydrofuran - 3 - one.

4. A process according to claim 1, in which the ketone is 4 - hydroxy - 2 - methyl - 5-ethyl - 2,3 - dihydrofuran - 3 - one.

5. A process according to claim 1, in which the ketone is 4 - hydroxy - 5 - methyl - 2-ethyl - 2,3 - dihydrofuran - 3 - one.

6. A process according to claim 1, in which the ketone is 4 - hydroxy - 2,5 - diethyl-2,3 - dihydrofuran - 3 - one.

7. A process according to claim 1, in which the ketone is 4 - hydroxy - 2 - hydroxymethyl-5 - methyl - 2,3 - dihydrofuran - 3 - one.

8. A process according to claim 1 in which the ketone is 4 - acetoxy - 5 - methyl - 2,3-dihydrofuran - 3 - one.

9. A process according to claim 1, in which the ketone is 4 - methoxy - 2,5 - dimethyl-2,3 - dihydrofuran - 3 - one.

10. A process according to claim 1, in which the ketone is 3-hydroxy-2-methyl-1,4-pyrone.

11. A process according to claim 1, in which the ketone is 3-hydroxy-2-ethyl-1,4-pyrone.

12. A process according to any one of claims 1—11, in which the sulphur-containing compound is cysteine.

13. A process according to any one of claims 1—11 in which the sulphur-containing compound is mercaptoacetamide or thioacetamide.

14. A process according to any one of claims 1—11, in which the sulphur-containing compound is a sulphide or hydrosulphide of an alkali metal, alkaline earth metal or ammonia.

15. A process according to any preceding claim, in which, in addition to the ketone and hydrogen sulphide or sulphur-containing com-

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pound, there is present in the reaction mixture at least one amino acid having no sulphur atom in the molecule.

16. A process according to any one of claims 1 to 15, in which, in addition to the ketone and hydrogen sulphide or sulphur-containing compound, there is present in the reaction mixture at least one pentose or hexose monosaccharide.

17. A process according to any preceding claim, in which the amount of weight of water present is at least equal to the weight of hydrogen sulphide or sulphur-containing compound.

18. A process according to any preceding claim, in which the reaction is conducted at a pressure above atmospheric pressure.

19. A process according to any preceding claim and as herein described with reference to any specific Example.

20. A flavour substance prepared in accordance with the process as claimed in any preceding claim.

21. A seasoning composition comprising the product according to claim 20 in admixture with other substances as herein disclosed and described.

22. A method of preparing a flavoured foodstuff, which comprises incorporating in a foodstuff a flavouring amount of the flavouring substance according to claim 20.

23. A method of preparing a flavoured foodstuff, which comprises incorporating in a foodstuff a mixture containing a heterocyclic ketone as defined in claim 1 and a sulphur-containing compound capable of giving rise to hydrogen sulphide, the mixture providing on subsequent reaction a flavouring amount in the foodstuff of the flavouring substance according to claim 20.

24. A flavoured foodstuff prepared according to the method claimed in claim 22 or 23.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 284 357

NO DRAWINGS

1 284 357

(21) Application No. 27262/70 (22) Filed 5 June 1970

(45) Complete Specification published 9 Aug. 1972

(51) International Classification A23L 1/26

(52) Index at acceptance
A2B 6A

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(71) We, NESTLE'S PRODUCTS LIMITED, a company incorporated in the Bahamas, of Nestle House, Collins Avenue, Nassau, Bahamas, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a flavouring composition having a taste resembling that of roasted beef.

Various synthetic flavourings are known which are inteded to reproduce the taste of cooked meats. In general, however, these products give only an approximate imitation of the natural taste and aroma of cooked meat and frequently develop "off" flavours on storage.

An object of the present invention is to provide a stable composition capable of imparting the natural flavour of beef to a broad range of food products.

Another object of the invention is to provide a process for preparing a flavouring composition starting from readily available natural materials.

According to the invention, a process for preparing a flavouring composition comprises the following successive steps: heating, at a temperature of from 60 to 90°C for 3 to 5 hours a mixture of from 40 to 50 parts by weight (dry matter) of yeast autolysate containing from 1 to 6% by weight of reducing substances (as hereinafter defined), at least 3% by weight of amino-nitrogen and at least 7% by weight of total nitrogen, from 30 to 40 parts by weight (dry matter) of vegetable protein hydrolysate, from 3 to 6 parts by weight (dry matter basis) of enzymatically hydrolysed meat extract, from 0.9 to 2.7 parts by weight of lactic acid and from 10 to 30 parts by weight of water, holding the mixture at ambient temperature for from 8 to 12 days, adjusting the pH of the mixture to a value of 6.0 to 6.5 and the water content of the mixture to from 25 to 35% by weight, heating the mixture to a temperature of 60 to 90°C, holding the mixture at a temperature within this range for 1 to 3 hours, adjusting the pH to a value of 6.5 to 7.0 and maintaning the mixture at a temperature of 60 to 90°C for 1 to 3 hours.

The yeast autolysate preferably contains from 1 to 2.5% by weight of reducing substances. The term "reducing substances" as used in the present specification means substances which reduce Fehling's solution, such as ribose or glucose. Any commercially available yeast autolysate meeting the above specifications may be used; it is conveniently employed as a paste containing about 80% by weight of dry matter.

The hydrolysed vegetable protein may be obtained by conventional acid hydrolysis of any plant protein. The aqueous product obtained by hydrolysis is preferably decolorised after filtration by treatment with active charcoal and it may be evaporated to a paste containing about 80% by weight of dry matter.

It has been found that commercial extracts of beef and and whale meat, produced by aqueous extraction, are particularly satisfactory sources of extract and are readily available. The extract may be hydrolysed by treatment with proteolytic enzymes, for example papain or an enzyme composition known as "Rhozyme P 11" (Röhm & Haas G.m.b.H., Darmstadt). Hydrolysis is preferably carried out under optimum conditions of temperature and pH for the enzyme used. Thus, for example, when papain is used the extract, diluted to about 15% by weight of solids content, may be heated with papain, in an amount of about 5% by weight of the amino-nitrogen in the extract, for about one hour at about

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65°C, followed by heating at 100°C for 5 to 10 minutes to inactivate the enzyme, and evaporation to a dry matter content of about 80% by weight.

The lactic acid preferably contains at least 72% by weight of free lactic acid.

Preferably, after the pH has been adjusted to 6.5 to 7.0, one to two parts by weight of a 5'-nucleotide are added whilst the temperature is maintained within the range 60 to 90°C. The nucleotide selected should contain at least 50% by weight of inosinic acid or inosinate, and it may conveniently be added as a mixture of substantially equal quantities of sodium inosinate and sodium guanylate. The pH adjustments during the reaction may be made by adding alkali such as sodium hydroxide.

The reaction mixture obtained by the process of the invention is in the form of a paste containing 30 to 40% by weight of water. It may be further concentrated, for example by evaporation, if desired under reduced pressure, to a moisture content of 12 to 20% by weight. The vapours liberated during concentration may be condensed and a portion of the condensate returned to the concentrated paste, desirably after fractionation.

The concentrated paste may be dried, for example to a moisture content of 2 to 6% by weight. Vacuum drying, preferably at 50 to 80°C, is preferred but other techniques such as belt-, spray- or freeze-drying may be used. The dried material may be ground to any desired particle size.

The flavouring composition according to the invention may be used either in dry form or as a paste, in a wide range of food products, such as, for example, soups, sauces, condiments and bouillons.

It will be seen from the foregoing that the flavouring composition according to the invention is prepared from readily available starting materials by a procedure which does not require specialised equipment or processing techniques.

The following Examples, in which all parts and percentages are by weight, are given by way of illustration only.

Example 1

55 parts of yeast autolysate (about 80% dry matter, 1.8% reducing substances, 7.2% total nitrogen, 3.5% amino-nitrogen), are mixed with 45 parts hydrolysed peanut protein containing about 80% dry matter which has been decolorised with two parts of active charcoal, 4 parts of enzymatically hydrolysed beef extract containing about 80% dry matter, and 2 parts of lactic acid (containing 90% of free lactic acid). The mixture is heated to 90°C for 4 hours, cooled to ambient temperature and stored at ambient temperature for 10 days.

Thereafter, the water content is adjusted to 30% and the pH to 6.3 by addition of sodium hydroxide, and the mixture is heated to 90°C and held at this temperature for 3 hours. The pH is then adjusted to 6.8 (NaOH) and the mixture is again held at 90°C for 3 further hours before being evaporated to a paste having a moisture content of 16-17%. The paste is finally dried in a vacuum oven at 80°C to a final moisture content of about 3%. Alternatively, the final mixture may be diluted to 50% solids and spray-dried.

The dry product is brown in colour, and it may be ground to a powder having any desired particle size. It is soluble in hot or cold water, giving a solution having a flavour close to that of a broth prepared from roasted beef. The product also has an enhancing effect on the flavour of various other foodstuffs, such as vegetables and mushrooms.

The dry product can be stored for at least 1½ years at 20°C without any significant alteration in flavour.

Example 2

The procedure of Example 1 is repeated, except that after adjusting the pH to 6.8, 2 parts of a blend (50/50) of sodium inosinate and sodium guanylate are added whilst the mixture is maintained at 80°C.

The final product is recovered as a paste containing 15% moisture. It may be stored at ambient temperature for at least 1 year without deterioration.

Example 3

The basic procedure is followed as described in Example 1, but the final evaporation is carried out under vacuum at 40°C and the vapours are fractionated and condensed. A portion of the condensed vapours is incorporated in the evaporated product which is recovered as a paste containing 15% moisture.

WHAT WE CLAIM IS:—

1. A process for preparing a flavouring composition comprising the following successive steps: heating, at a temperature of from 60 to 90°C for from 3 to 5 hours, a mixture of from 40 to 50 parts by weight (dry matter) of yeast autolysate containing from 1 to 6% by weight of reducing substances (as hereinbefore defined), at least 3% by weight of amino-nitrogen and at least 7% by weight of total nitrogen, from 30 to 40 parts by weight (dry matter) of vegetable protein hydrolysate from 3 to 6 parts by weight (dry matter) of enzymatically hydrolysed meat extract, from 0.9 to 2.7 parts by weight of lactic acid and from 10 to 30 parts by weight of water, holding the mixture at ambient temperature for from 8 to 12 days, adjusting the pH of the mixture to a value of 6.0 to 6.5 and the water content of the mixture to from 25

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to 35% by weight, heating the mixture to a temperature of 60 to 90°C, holding the mixture at a temperature within this range for 1 to 3 hours, adjusting the pH to a value of 6.5 to 7.0 and maintaining the mixture at a temperature of 60 to 90°C for 1 to 3 hours.

2. A process according to claim 1, in which the hydrolysed vegetable protein is hydrolysed peanut protein.

3. A process according to claim 1 or claim 2, in which the meat extract is beef extract or whale meat extract.

4. A process according to any one of the preceding claims, in which the hydrolysed meat extract is prepared by heating for about 1 hour at a temperature of about 65°C an aqueous solution of meat extract containing about 15% by weight of total solids with a quantity of papain corresponding to about 5% by weight of the amino-nitrogen present in the extract.

5. A process according to any one of the preceding claims, in which 1 to 2 parts by weight of a 5′-nucleotide containing at least 50% by weight of inosinic acid or an inosinate are added to the mixture after the pH has been adjusted to a value in the range 6.5 to 7.0.

6. A process according to any one of the preceding claims, in which the yeast autolysate contains 1.0 to 2.5% by weight of reducing substances.

7. A process according to any one of the preceding claims, in which the flavouring composition is concentrated to a paste having a moisture content of 12 to 20% by weight.

8. A process according to claim 7, in which the composition is concentrated by evaporation under vacuum and the vapours removed during evaporation are fractionated and condensed and a portion of the condensate is returned to the composition.

9. A process according to any one of the preceding claims, in which the flavouring composition is dried to a moisture content of 2 to 6% by weight.

10. A process according to claim 1, substantially as herein described with reference to any one of the Examples.

11. A flavouring composition prepared by a process according to any one of the preceding claims.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1972.
Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY from which copies may be obtained.

PATENT SPECIFICATION (11) 1302525

1302525

NO DRAWINGS

(21) Application No. 15561/69 (22) Filed 25 March 1969
(61) Patent of Addition to No. 1224989 dated 17 Sept. 1968
(23) Complete Specification filed 23 March 1970
(44) Complete Specification published 10 Jan. 1973
(51) International Classification A23L 1/26
(52) Index at acceptance A2B 6A

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(54) EDIBLE PRODUCTS

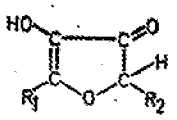
(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain of Port Sunlight, Wirrall, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to processes for imparting a meaty flavour to certain foodstuffs or improving such flavour and to concentrated as well as ready-for-use foodstuffs obtained according to the process.

It has been proposed to improve the flavour of various foodstuffs which contain meat or meat simulating product, by adding certain components such as protein hydrolysate, monosodium glutamate, 5'-nucleotides, and organic carboxylic acids. Although the products thus obtained often possess a meaty taste, their odour usually is not satisfactory.

It has now been found that a meaty flavour can be enhanded or imparted to foodstuff which contains meat or a meat simulating product by the incorporation of certain furanones.

Accordingly the present invention provides a foodstuff comprising a meat product or a meat simulating product and a 4 - hydroxy - 2,3 - dihydrofuran - 3 - one of the general formula:—

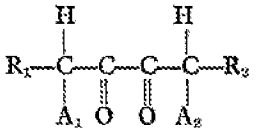


in which R_1 and R_2 represent an alkyl group containing 1 or 2 carbon atoms, and in which the sum of the carbon atoms of R_1 and R_2 together is from 3—4. The dihydrofuranone may be incorporated as such, or in the form of precursors or reactants yielding the desired compound after completion of the preparation of the footstuff in a form ready for consumption.

The general formula covers two compounds, viz. 2 - methyl - 5 - ethyl - 4 - hydroxy - 2,3 - dihydrofuranone - 3 and 2,5 - diethyl - 4 - hydroxy - 2,3 - dihydrofuranone - 3. The compounds mentioned above show keto-enol tautomerism, but is has appeared that normally the compounds predominantly occur in the structure represented in the structural formula given above. This appears inter alia from the infrared and n.m.r. spectra. Theoretically, however, it may be expected that the compound occurs in various other tautomeric forms such as the diketo and the dienol forms which, however, are then again converted into the indicated form.

By special techniques other tautomeric forms or mixtures thereof can be isolated from the hydroxydihydrofuranones mentioned above, which, however, are then again converted into the indicated form. According to the present invention also these other tautomeric forms or mixtures thereof can be incorporated into foodstuffs which contain meat or a meat simulating product.

The hydroxydihydrofuranones which are used according to the present invention can be prepared by heating and reacting a diketo diester of the general formula:



in which R_1 and R_2 represent an alkyl group containing 1 or 2 carbon atoms, with the provision that the number of carbon atoms of R_1 and R_2 together is from 3—4 and A_1 and A_2 represent acid radicals. The acid radicals may be derived from carboxylic acids, especially from C_1—C_4 aliphatic carboxylic acids. Preferred ester groups are those derived from acetic and propionic acid.

The reaction is carried out in an aqueous acidic medium which contains at least 50 percent by volume, preferably at least 75 per-

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cent by volume of water, the remainder being a water-miscible polar solvent such as a C_1—C_4 aliphatic alcohol for example methanol or ethanol.

The acidic compound present in the aqueous acidic medium may comprise an inorganic acid, a carboxylic acid or an organic sulphonic acid. Suitable acids include hydrobromic or hydrochloric acid, sulphuric acid, phosphoric acid, formic acid, acetic acid, propionic acid and p-toluene sulphonic acid. Polycarboxylic acids and hydroxycarboxylic acids are less suitable. The use of strong acids, producing a pH-value below 5 or better below 4, is particularly preferred.

The amount of acid in the aqueous medium is not particularly critical and may vary widely. Good results have been obtained with amounts of 0.1—5 equivalents of acid per litre of medium. Also the concentration of the diketo diester in the aqueous medium may vary widely. Generally, less than 200 grams of diketo diester are dissolved per litre of medium. For practical reasons, in particular to reduce the volume of the reaction mixture, the use of too dilute solutions is avoided. A practical range is from 10—100 grams of diketo diester per litre of medium.

The reaction temperature and time reaction are related. For convenient reaction periods in the range of 0.5—10 hours, preferably from 1—5 hours, it is preferred to conduct the reaction at temperatures above 75°C, preferably at boiling temperature at atmospheric pressure. It is however possible to obtain a satisfactory conversion at lower temperature e.g. of about 50°C, provided the reaction period is suitably adjusted to at least 20 hours.

After termination of the reaction the aqueous reaction mixture is allowed to cool and the desired dihydrofuranone derivative is isolated in a conventional way. This could be done by extraction with ether, drying of the etheral solution and evaporation of the solvent. Undesired polymeric contaminants are removed by distillation of the product under diminished pressure.

The diketo diester starting materials for the process according to the invention can be prepared in various ways. A convenient method is via acetylenic compounds.

Step 1—Preparation of an alkyne diol.

Acetylene was coupled with two moles of aldehyde using two moles of a Grignard compound. This method is described in Bull. Soc. Chim.—(France) 425 (1956). Alternatively a 1 - alkyne - 3 - ol could be coupled with aldehydes or ketones (as described in Bull. Soc. Chim. supra).

Step 2—Esterification of the alkyne diol.

The diacetates were prepared by reacting with acetic anhydride in the presence of e.g. pyridine or sodium acetate.

Step 3—Oxidation of the alkyne diester.

The alkyne diester was oxidized with dilute aqueous potassium permanganate at a low temperature yielding the diketo diester. This method has been described in Bull. Soc Chim. (France) 789 (1949).

Experiment 1

This example describes the preparation of 2,5 - diethyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one.

2 moles of propionaldehyde were coupled with 1 mole of acetylene under the influence of ethylmagnesium bromide according to Bull. Soc. Chim. (France) 425 (1956) and 4 - octyne - 3,6 diol (b.p. 120°C at 4 mm) was obtained in 50% yield.

The alkyne diol (14.2 g or 0.1 mole) was acetylated by gently refluxing for two hours with acetic anhydride (20.4 g) in the presence of freshly molten sodium acetate (0.82 g). After cooling the reaction mixture was poured into a flask containing 200 g of crushed ice. The reaction mixture was extracted with ether and the organic layer separated. After washing repeatedly with small quantities of 5 percent aqueous sodium bicarbonate the etheral solution was dried over anhydrous sodium sulphate and the ether evaporated off. The residual liquid was distilled under vacuum and 4 - octyne - 3,6 - diacetate (b.p. 103—105°C at 2, 3 mm) was obtained in 95% yield.

5.16 g (0.02 mole) of 4 - octyne - 3,6 - diacetate were dissolved in 500 ml ethanol-water (90:10 by volume). To this solution which was cooled to —20°C were slowly added 17.5 g of potassium permananate and 25 g of magnesium sulphate heptahydrate dissolved in 500 ml water. During this addition which took 2 hours the temperature was maintained at —20°C. After stirring for an additional 2 hours at the same temperature 200 ml of water were added and the brown reaction mixture was extracted three times with 200 ml portions of cold chloroform. The chloroform solutions were combined and dried over anhydrous sodium sulphate. Chloroform was evaporated off, and 60% of octane - 4,5 - dione - 3,6 diacetate were obtained.

5.16 g of octane - 4,5 - dione - 3,6 - diacetate was heated with 1500 ml of 0.5 N aqueous hydrochloric acid for 3 hours at a temperature of 100°C. After extracting with ether and combining the extracts, washing and drying took place. The solvent was evaporated and 4 g of an orange coloured residue were obtained. The residue was distilled at diminished pressure and the distillate was investigated by means of gas-liquid chromatography which showed only one peak.

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A sample was further investigated by preparative thin-layer chromatography and checked by infrared and mass spectrometry. 2,5 - diethyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one (m.p. −5°C) was found present in a yield of 35%. The smell of the product closely resembled that of the corresponding dimethyl compound.

Experiment 2

This example describes the preparation of 5 - ethyl - 2 - methyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one.

1 mole of 1 butyne - 3 - ol was coupled with 1 mole of propionaldehyde under the influence of ethylmagnesium bromide according to Bull. Soc. Chim. (France) 425 (1956) and 3 - heptyne - 2,5 - diol (b.p. 109—110°C at 2 mm) was obtained in 60% yield. The alkyne diol was acetylated as described in Experiment 1 and 3 - heptyne - 2,5 - diacetate (b.p. 103—105°C at 3 mm) was obtained in 95% yield. The alkyne diacetate was oxidised with aqueous potassium permanganate as described in Experiment 1, also at a temperature of −20°C and heptane 3,4 - dione - 2,5 - diacetate was obtained in 90% yield.

2.44 g of heptane - 3,4 - dione - 2,5 - diacetate was added to 750 ml of 0.5 N aqueous hydrochloric acid and the mixture was refluxed for 2 hours. After extracting with ether and combining the extracts, washing and drying took place. The solvent was evaporated and 2 g of a dark yellow residue were obtained. Gas-chromatography showed two peaks very close together. Further attemps to separate the two peaks failed. Infrared and mass spectrometry suggest that 5 - ethyl - 2 - methyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one, possibly together with 2 - ethyl - 5 - methyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one, is present. The boiling point of the product estimated from gas-liquid chromatography volatility is 208—210°C. The yield of this product was 28%.

The process according to the invention relates, as stated, to imparting a meaty flavour to foodstuffs which contain meat or a meat simulating product or improving such flavour. Under such foodstuffs are to be understood here foods ready for consumption and concentrated foodstuffs in which a meaty flavour is desired, such as soups, including concentrated canned soup and dry soup mixes, preserved meals, rissoles, preserved meat such as canned ham, simulated meat gravy, gravy tablets or cubes, and "powdered flavour" such as that which may be sprinkled over meaty foodstuffs shortly before consumption.

In another embodiment precursors or reactants are incorporated, which during the preparation of the ready-for-use product are converted into the 2,3 - dihydrofuran - 3 - one. For example esters such as the acetate may be used. Furthermore enol-esters and ketals derived from the compounds may also be used.

The type of foodstuffs which can be improved as to flavour according to the invention varies widely, the concentrations in which the 2,3 - dihydrofuran - 3 - ones are applied also range widely. When incorporating 4 - hydroxy - 2,3 - dihydrofuran - 3 - ones good results are obtained at levels varying from 0.1 to 30 parts per million calculated on the foodstuff in the ready-for-consumption form; best results are obtained in the range from 0.5 to 10 parts per million.

The use of the compounds at levels below their individual threshold values of about 0.5 parts per million may take place where two or more substituted isomeric 4 - hydroxy - 2,3 - dihydrofuran - 3 - ones are used together and such a combination may result in a more favourable taste than could be obtained with the compounds separately. As these concentrations apply in the case of foods ready for consumption, it is obvious that where more concentrated foodstuffs, such as canned concentrated soups, dry soup mixes and seasoning compositions are involved appreciably higher concentrations may be used, dependent on the degree of dilution they undergo during preparation.

Where precursors or reactants which are converted into the desired compounds are used the quantities incorporated are generally higher than those indicated above in order to overcome the effects of the reaction not taking place quantitatively.

The substances incorporated according to the invention are not quite stable against oxidative attack and oxidation and decomposition products may also contribute appreciably to the desired flavour. For storage it may therefore be desirable to prepare the 2,3 - dihydrofuran - 3 - ones in a stabilized form as e.g. encapsulated or coated with another material. Also, operation in an inert atmosphere may be feasible.

In order to obtain products with a fuller meaty taste and flavour the 2,3 - dihydrofuran - 3 - ones may be utilized together with other substances such as one or more compounds from the following classes of substances. Preferred mixtures are combinations of compounds mentioned under classes I, II and III, together with a 4 - hydroxy - 2,3 - dihydrofuran - 3 - one as previously defined.

The dihydrofuranones as previously defined may be used together with the dihydrofuranones as defined under IV below.

I. Amino acids which may be obtained simply by hydrolysis, autolysis or fermentation or by combination of these from vegetable or animal proteins such as gluten, casein and soyabean protein.

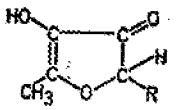
II. Nucleotides, such as adenosine - 5' -

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monophosphate, guanosine - 5′ - monophosphate, isosine - 5′ - monophosphate, xanthosine - 5′ - monophosphate, uridine - 5′ - monophosphate, cytidine - 5′ - monophosphate, and their amides, desoxy derivatives and salts. Combinations of several nucleotides such as guanosine - 5′ - monophosphate and isosine - 5′ - monophosphate are particularly suitable.

III. Carboxylic acids such as lactic acid, glycolic acid and β-hydroxy butyric acid on one hand and dicarboxylic acids as succinic acid and glutaric acid on the other hand, and especially mixtures in which succinic acid and lactic acid occur in weight ratios of 1:30 to 1:150.

IV. A substituted 5 - methyl - 4 - hydroxy - 2,3 - dihydro - furan - 3 - one of the general formula:



in which R represents —H or —CH_3.

V. Pyrrolidone carboxylic acid or precursors thereof.

VI. Peptides such as alanyl-alanine, alanyl-phenylalanine, alanyl-asparagine, carnosine, anserine.

VII. Sweetening substances, both artificial, like saccharine or cylamates*, and natural, particularly mono- and disaccharides.

VIII. Substances with the flavour of meat or broth, particularly sulphur containing compounds, such as reaction products of amino acids like cysteine/cystine was reducing sugars, such as ascorbic acid, reaction products of hydrogen sulphide with lower aliphatic aldehydes and ketones (e.g. propionaldehyde, crotonaldehyde, methional, mercapto-acetaldehyde).

IX. Other volatile sulphur compounds, such as H_2S mercaptans, disulphides and sulphides, such as dimethyl sulphide and diallyl sulphide.

X. Guanidines, such as creatine and creatinine.

XI. Salts, such as NaCl and phosphates, particularly, in connection with acid phosphates such as Na_2HPO_4, NaH_2PO_4 or other alkali or ammonium phosphates and organic phosphates, such as phosphorus containing amino acids. However, it is by no means necessary to incorporate phosphates.

XII. Nitrogen compounds, such as ammonia, amines, urea, indole, and skatole.

XIII. Saturated or unsaturated carboxylic acids with from 2 to 12 carbon atoms.

XIV. Saturated or unsaturated higher hydroxycarboxylic acids and α and δ-lactones derived therefrom, such as deca and dodeca - 5 - olide; 2,3 - dimethyl - 2,4 - alkadiene - 4 - olides.

XV. Lower saturated and unsaturated aldehydes, e.g. acetaldehyde, proion-aldehyde, isobutyraldehyde and hepten - 4 - al.

XVI. Lower saturated and unsaturated ketones, such as acetone, butanone and diacetyl.

XVII. Tricholomic acid and ibotenic acid or their salts.

XVIII. Optionally aromatic carboxylic and/or heterocyclic compounds, such as ortho amino-acetophenone, N-acetonyl pyrrole, maltol, iso maltol, ethyl maltol, lenthionine, hypoxanthine, guanine, inosine and guanosine.

XIX. C_2—C_{10} saturated and unsaturated alcohols, such as ethanol, octanol.

XX. Colouring substances, such as curcuma, caramel.

XXI. Thickening agents such as gelatin and starch.

The dosage of these optional ingredients is dependent on the kind of flavour one wishes to imitate and moreover on the nature of the foodstuff to which the ingredients are added and the other ingredients added, such as herbs and spices.

By way of illustration the following Examples are given to elucidate the invention.

Example 1

A gravy was prepared from the following ingredients:

	g
Potato starch	15
Onion powder	2.5
Monosodium glutamate	3
Tallow	20

* We are aware of The Artificial Sweeteners in Food Regulations 1969, and in so far as this invention relates to a process for the preparation of food for sale in the United Kingdom and/or the sale of food in the United Kingdom so prepared, we make no claim to the use of the invention in contravention of the law.

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Wheat flour	15
Caramel dye	1.6
Pepper	0.02
Bay leaf powder	0.02
Clove	0.02
Salt	8
Protein hydrolysate	4
Meat extract	2
Tomato powder	1

The tallow was melted and potato starch and wheat flour were added whilst stirring. The remaining ingredients were then thoroughly mixed and added to the mixture containing the tallow, after which the resulting mixture was added to 1 litre of water and boiled.

The gravy thus obtained was divided into two parts of approximately 500 ml and to one of the samples 0.8 mg of 2,5 - diethyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one were added. The samples were evaluated against each other in a pair test by a panel consisting of 15 persons; 13 persons preferred the sample containing the furanone and indicated that the taste and flavour were more meat-like.

Example 2

An imitation meat broth was prepared by dissolving 70 g sodium chloride and 50 g commercial meat extract in 10 litres of water. The meat broth thus obtained was divided into two quantities of approximately 5 litres and to one of these a quantity of 5 mg 2 - methyl - 5 - ethyl - 4 - hydroxy - 2,3 dihydrofuran - 3 - one was added.

After heating both samples they were evaluated against each other in a pair test by a panel consisting of 23 persons; 18 persons expressed a preference for the sample which had been aromatized with 2 - methyl - 5 - ethyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one and some indicated that this mixture had a taste characteristic of true meat broth.

Example 3

A dry soup mix was obtained by mixing the following ingredients:

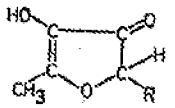
	g
Sodium chloride	90
Vermicelli	200
Monosodium glutamate	20
Tallow	50
Dried meat	60
Casein hydrolysate	20
Dried onion	30
Dried carrots	10
Mixed spices	4

5 litres of water were added to 250 g of the dry soup mix mentioned above and the mixture was boiled and separated into two portions of each about 2½ litres. To one of these 0.2 g dextrin-maltose was added and to the other one 0.2 g of a powder consisting of 1 part of 2,5 - diethyl - 4 - hydroxy - 2,3 - dihydrofuran - 3 - one and 40 parts of dextrin-maltose.

Both samples were then heated to the boil and evaluated against each other by means of a triangle panel test. The difference between both samples was noted by a significant number of the 21 persons of the panel and the majority preferred the soup containing the dihydrofuran - 3 - one, because it was considered more reminiscent of beef broth.

WHAT WE CLAIM IS:—

1. A foodstuff comprising a meat product or a meat simulating product and a 4 - hydroxy - 2,3 - dihydrofuran - 3 - one of the general formula:



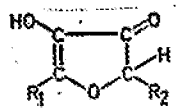
in which R_1 and R_2 represent alkyl groups containing 1 or 2 carbon atoms, with the provision that the number of carbon atoms of R_1 and R_2 together is 3 or 4.

2. A foodstuff as claimed in claim 1, in which the quantity of the furanone present, calculated on the weight of ready-for-use foodstuff, is from 0.1 to 30 parts per million.

3. A foodstuff as claimed in claim 1, in which the quantity of the furanone present, calculated on the weight of ready-for-use foodstuff is from 0.5 to 10 parts per million.

4. A foodstuff as claimed in any preceding claim, in which the 4 - hydroxy - 2,3 - dihydrofuran - 3 - one is added to the foodstuff in the form of an ester, enolester or ketal precursor.

5. A foodstuff flavouring composition comprising a 4 - hydroxy - 2,3 - dihydrofuran - 3 - one as defined in claim 1 and a substituted 5 - methyl 4 - hydroxy - 2,3 - dihydrofuran - 3 - one of the general formula:



in which R represents —H or —CH_3.

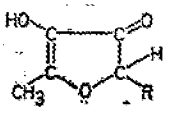
6. A foodstuff flavouring composition comprising a furanone as defined in claim 1 and a mixture of substances selected from classes I, II and III as hereinbefore defined.

7. A meaty foodstuff substantially as claimed in claim 1 and as described herein with reference to the Examples.

8. Process for preparing a meat product or meat simulating product which comprises incorporating in the product a 4 - hydroxy - 2,3 - dihydrofuran - 3 - one of the general formula:

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in which R_1 and R_2 represent alkyl groups containing 1 or 2 carbon atoms, with the provision that the total number of carbon atoms of R_1 and R_2 together is 3 or 4.

9. Process according to claim 8, characterised in that the quantity of the furanone incorporated is from 0.1 to 30 parts per million calculated on the weight of the ready-for-use product.

10. Process according to claim 8, characterised in that the quantity of the furanone incorporated is from 0.5 to 10 parts per million calculated on the weight of the ready-for-use product.

11. Process according to any one of the claims 8 to 10, characterised in that the 4 - hydroxy - 2,3 - dihydrofuran - 3 - one is incorporated in the form of an ester, enolester or ketal precursor.

UNILEVER LIMITED
per J. E. Farndon
Chartered Patent Agent
Agent for the Applicants

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1311638

1311638

NO DRAWINGS

(21) Application No. 59556/71 (22) Filed 22 Dec. 1971
(31) Convention Application No. 019 071 (32) Filed 23 Dec. 1970 in
(33) Switzerland (CH)
(44) Complete Specification published 28 March 1973
(51) International Classification A23L 1/26
(52) Index at acceptance A2B 6A



(54) SYNTHETIC MEAT AROMA

(71) We, L. GIVAUDAN & CIE SOCIETE ANONYME, a Swiss company, of Vernier-Geneve, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to synthetic meat aromas. More particularly, the invention is concerned with a process for the manufacture of synthetic meat aromas, with foodstuffs, delicacies and feedstuffs containing said aromas and with a method for the aromatization of foodstuffs, delicacies and feedstuffs by means of said aromas.

According to the process provided by the present invention, synthetic meat aromas are manufactured by heating a mixture containing proline, cysteine, methionine, a pentose and a polyalcohol which is a trihydric alcohol or a glycol.

The amino-acids aforesaid can be employed as such or in the form of derivatives or salts thereof which form the free amino-acids under the conditions of the process. Cysteine hydrochloride, for example, can be employed instead of cysteine. In addition to proline, cysteine and methionine, the mixture can contain other amino-acids; for example, smaller amounts of the amino-acids known to occur in meat such as, for example, alanine, arginine, cystine, glycine, histidine, isoleucine, leucine, lysine, serine, threonine, valine, anserine, carnosine or taurine.

The amount of the amino-acids proline, cysteine and methionine present in the mixture expediently amounts to 2 to 40%, preferably 5 to 30 wt.%. If less than 2 wt.% of amino-acids are present, no powerful aroma is obtained and, indeed, it can even be markedly weak. If more than 40 wt.% are present, undesired side-reactions can occur.

According to a preferred embodiment of the present process, proline is employed as the main component of the three amino-acids aforesaid. The use of a mixture in which over 50 wt.% of the amino-acid ingredients consists of proline is preferred. On the other hand, however, this amount should not exceed 85 to 90%, since otherwise the aroma which is obtained is reminiscent of bread.

Ribose is preferably employed as the pentose, although other pentoses such as, for example, arabinose or xylose can also be employed. Mixtures of such pentoses can also be be employed. The amount of pentose present expediently amounts to 0.4 to 18 wt.% and preferably 1 to 10 wt.%.

As polyalcohols there are employed trihydric alcohols such as glycerine, or glycols such as, for example, propylene glycol. The polyalcohol can be present in the mixture in an amount of 9 to 90 wt.%, preferably 40 to 90 wt.%.

Suitable proportions of the main components of the mixture used in accordance with the present invention are given in the following Table:

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TABLE

	Per cent by weight
proline	1.0 — 55%
cysteine	0.1 — 30%
methionine	0.1 — 16%
pentose	0.4 — 18%
polyalcohol	9.0 — 90%

As a rule, the desired meat aroma is formed when the mixture used as the starting material is heated to temperatures of 90°—170°C, in particular to about 110°—130°C. The heating time is normally inversely proportional to the heating temperature; it expediently amounts to about 15 minutes to 2 hours.

Besides the aforementioned main components, there can also be present in the mixture other ingredients such as aroma enhancers [e.g. 0.1—200% by weight monosodium glutamate, 0.1—100% by weight disodium inosine - 5' - monophosphate (IMP) and disodium guanosine-5-phosphate (GMP)], fats (e.g. groundnut oil) or special aroma substances (e.g. butter or synthetic butter composition).

The products obtained after the heating are highly concentrated synthetic meat aromas which may be diluted or distributed in edible materials in a manner known per se. They can be converted according to methods which are known per se into the usual forms of presentation such as solutions, pastes or powders. The product can be spray-dried, vacuum-dried or lyophilised. As carrier materials there can be used, for example, gum arabic, salts or brewers yeast or similar adsorbancies. Indoles, maltol, dienals, spice oleoresins or smoke aromas can also be added as flavour-improvers.

The thus formulated products can serve for the aromatization of many kinds of foodstuffs, delicacies and feedstuffs; for example, meat-like products manufactured from natural or synthetic proteins as well as chips.

The following Table gives a basis for suitable concentrations of the synthetic meat aromas in various forms of presentation.

TABLE

Form of presentation	General	Preferred
solutions	1 — 100%	10 — 60%
pastes	1 — 100%	10 — 90%
spray-dried powder	3 — 60%	15 — 35%
lyophilised vacuum-dried powder	2 — 30%	8 — 18%

The following Examples illustrate the present invention:

Example 1

An intimate mixture containing:

proline	1.5 g
cysteine	1.25 g
methionine	0.3 g
ribose	0.8 g
butter aroma	0.2 g
glycerine	20 ml

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is heated with constant stirring to 120°C and held at this temperature for 1 hour. The resulting product has a powerful meat aroma. By dilution with hot water (2 g to 1 litre), there is obtained a clear broth with a marked meat aroma.

Example 2

An intimate mixture containing:

proline	16 g
cysteine	2.5 g
methionine	0.6 g
ribose	2.5 g
glycerine	40 ml
butter	0.2 g
groundnut oil	20 ml
IMP	20 g

is cautiously heated with stirring to 120°C and with constant further stirring held at this temperature for 1 hour. Addition of 0.2% by weight of this product to a sauce imparts to the latter a marked aroma of boiled meat.

Example 3

An intimate mixture containing:

proline	6.0 g
cysteine	5.0 g
methionine	1.2 g
ribose	3.2 g
glycerine	5 ml
butter	0.6 g
guanylic acid	20 g
GMP	15 ml

is cautiously heated with stirring to 120°C and then held at this temperature for 1 hour. The product has a flavour of boiled meat with a fatty note. By mixing this product with 0.1—5%, preferably 6%, by weight of an artificial smoke aroma, there results a product with marked ham note which can be used for aromatizing broths, meat substitutes from protein-containing materials, crackers or potato crisps.

Example 4

An intimate mixture of:

proline	30 g
cysteine	7 g
methionine	2 g
ribose	7 g
glycerine	100 g
water	50 ml

is cautiously heated with stirring to 120°C and held at this temperature for 1 hour. The product has marked roast beef flavour. It can, for example, be used in amounts of 0.2—4% by weight for imparting the typical roast beef flavour to purely synthetic fibrous meat substitute.

Example 5

An intimate mixture of:

proline	7 g
cysteine	4.0 g
methionine	0.4 g
xylose	3.5 g
glycerine	50 ml
butter aroma	0.25 g
GMP	10 g
groundnut oil	50 ml
water	15 ml

is cautiously heated with stirring to 120°C and held at this temperature for 1 hour. The product can be added to a waffle filling to which it imparts a delicious flavour of roast liver in amounts of about 1.5% by weight.

Example 6

An intimate mixture of:

proline	28.0 g
cysteine	6.6 g
methionine	1.6 g
ribose	6.8 g
glycerine	57.0 ml
water	50.0 ml

is cautiously heated with stirring to 120°C and held at this temperature for 1 hour. The product has a marked roast beef flavour and can be used for the manufacture of a "dip" for potato crisps.

Example 7

A potato crisp dip is manufactured according to the following process:

product of Example 6	5.8 g
edible curd	200 g
whipped cream	100 g
salt	2 g
paprika	0.1 g
pepper	0.1 g
chives (fresh)	1.5 g

The edible curd is firstly stirred to a fine mass and the whipped cream is cautiously admixed therewith. The spices are added to the resulting homogeneous mass.

WHAT WE CLAIM IS:—

1) A process for the manufacture of synthetic meat aromas, which process comprises heating a mixture containing proline, cysteine, methionine (or a derivative or salt of proline, cysteine or methionine which forms free proline, cysteine or methionine respectively under the conditions of the process), a pentose and a polyalcohol which is a trihydric alcohol or a glycol.

2) A process according to claim 1, wherein the said amino-acids are present in the mixture in an amount of 2 to 40 wt.%.

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3) A process according to claim 2, wherein the said amino-acids are present in the mixture in an amount of 5 to 30 wt.%.

4) A process according to claim 1, claim 2 or claim 3, wherein proline, cysteine and methionine are the only amino-acids present in the mixture.

5) A process according to any one of claims 1 to 4 inclusive, wherein over 50% of the amino-acid ingredients consists of proline.

6) A process according to any one of claims 1 to 5 inclusive, wherein the mixture contains 0.4 to 18% of a pentose.

7) A process according to claim 6, wherein the mixture contains 1 to 10% of a pentose.

8) A process according to any one of claims 1 to 7 inclusive, wherein the pentose is ribose.

9) A process according to any one of claims 1 to 8 inclusive, wherein the mixture contains 9 to 90% of the polyalcohol.

10) A process according to claim 9, wherein the mixture contains 40 to 90% of the polyalcohol.

11) A process according to any one of claims 1 to 10 inclusive, wherein the polyalcohol is glycerine.

12) A process according to any one of claims 1 to 11 inclusive, wherein the mixture contains, by weight, 1 to 55% proline, 0.1 to 30% cysteine, 0.1 to 16% methionine, 0.4 to 18% of a pentose and 9 to 90% of the polyalcohol.

13) A process according to any one of claims 1 to 12 inclusive, wherein the mixture also contains water.

14) A process according to any one of claims 1 to 13 inclusive, wherein the mixture is heated to a temperature of 90°C to 170°C.

15) A process according to claim 14, wherein the mixture is heated to a temperature of 110°C to 130°C.

16) A process for the manufacture of a synthetic meat aroma, substantially as hereinbefore described with reference to the foregoing Examples.

17) A synthetic meat aroma, when manufactured according to the process claimed in any one of claims 1 to 16 inclusive.

18) A foodstuff, delicacy or feedstuff which contains a synthetic meat aroma in accordance with claim 17.

19) A method for the aromatization of foodstuffs, delicacies or feedstuffs which comprises adding a synthetic meat aroma in accordance with claim 17 to foodstuffs, delicacies or feedstuffs.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1313830

1313830

NO DRAWINGS

(21) Application No. 42089/72 (22) Filed 14 May 1971
(62) Divided out of No. 1304293
(31) Convention Application No. 37305 (32) Filed 14 May 1970
(31) Convention Application No. 135337 (32) Filed 19 April 1971 in
(33) United States of America (US)
(44) Complete Specification published 18 April 1973
(51) International Classification A23L 1/26
(52) Index at acceptance
A2B 6A 6G

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(54) SULFUR CONTAINING FLAVOR MODIFYING COMPOSITIONS

(71) We, INTERNATIONAL FLAVORS & FRAGRANCES INC., a corporation organized under the laws of the State of New York, of 521, West 57th Street, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates in general to compositions and processes useful in altering the organoleptic characteristics of a foodstuff. More particularly, this invention has to do with the use of certain branched-chain alkanethiols to alter the flavor of foodstuffs.

The term "alter" in its various forms is used herein to mean the supplying or imparting a flavor character or note to an otherwise bland, relatively tasteless substance, or augmenting an existing flavor characteristic where the natural flavor is deficient in some regard, or supplementing the existing flavor impression to modify its quality, character or taste.

The term "foodstuff" as used herein includes both solid and liquid ingestible materials which usually do, but need not, have nutritional value. Thus, foodstuffs includes meats, gravies, soups, convenience foods, beverages, dairy products, candies, vegetables, cereals, soft drinks and snacks.

Reproduction of roasted and meat flavors and aroma has been the subject of a long and continuing search by those engaged in the production of foodstuff. The acute shortage of foods, especially protein foods, in many parts of the world has given rise to the need for utilizing non-meat sources of proteins and making such proteins as palatable and as meat-like as possible. Hence, materials which are capable of closely simulating or even exactly reproducing the flavor and aroma of roasted products and meat products are highly desirable, if not necessary.

The use of certain mercaptans and other sulfur-containing materials in foodstuffs is known. For example, allyl mercaptan has been used in spice flavors for soup and meat, n-butyl mercaptan has been used in vegetable soup flavors, and n-propyl mercaptan has been utilized in onion flavors.

Mercaptans such as thienyl mercaptan have been stated to have an odor faintly resembling coffee in extremely high dilutions. Moreover, recent work reported by Grey et al in *Chemical Abstracts 67*, 20711n; Gumbmann et al in *Chemical Abstracts* 61, 12552c; Brennan et al, *Chemical Abstracts 61*, 11247b; Merrit, *Chemical Abstracts 61*, 15260c; and Libbey et al, *Chemical Abstracts 61*, 1175b, suggest the presence of unbranched thiols, respectively in chicken tissue, potato volatiles, canned beef headspace, irradiated foods and cheddar cheese volatiles. Ronald et al in *Chemical Abstracts 62*, 6843f suggest the presence of primary and other thiols in oyster volatiles.

In accordance with this invention, it has been found that novel foodstuff and flavoring compositions having desirable meat, roasted meat flavor and aroma notes may be readily provided by the utilization of at least one compound which is: a branched-chain alkanethiol having the formula

$$R_1R_2CH—(CH_2)_n—CR_3R_4—SH$$

wherein R_1, R_2, R_3 and R_4 are the same or different alkyl groups or hydrogen, at least two or R_1, R_2, R_3 and R_4 being alkyl, at least one of R_1, R_2, R_3 and R_4 being hydrogen; and n is 0 or 1.

Branched-chain alkanethiols having this formula can be used to impart roasted flavor

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and aroma notes to consumable materials such as foodstuffs and the like. Certain of the alkanethiols according to this invention are particularly suited to the production of meat and roasted meat flavors and aromas in foodstuffs, and the lower alkyl groups contemplated in the formula given above are those having from one to three carbon atoms in the alkyl groups. These desirable alkyl groups can be methyl, ethyl, propyl, and isopropyl.

The alkanethiols according to the present invention are accordingly suited for use in processes which comprise adding a relatively small amount of the thiol or thiols to the foodstuff in an amount effective to alter the flavor and/or aroma properties of the foodstuff. The thiols are also well-suited to the production of flavouring compositions comprising in addition to the thiol or thiols, monosodium glutamate, sulfur containing amino acid such as cysteine or the like, hydrolyzed protein materials such as hydrolyzed vegetable protein or hydrolyzed fish protein, or tetramethylpyrazine or a combination or reaction product of two or more of such additional ingredients to provide a roasted meat flavour to proteinaceous and other products.

A particularly preferred thiol according to the present invention is 2-methyl-3-butanethiol, that is, the alkanethiol according to the above formula wherein R_1, R_2, and R_4 are methyl and R_3 is hydrogen and n is zero. This compound, which is commercially available, has a powerful braised beef, roasted meat, pot roast aroma and taste, and is a very potent flavor chemical. Another preferred alkanethiol according to the present invention is 2-methyl-1-butanethiol, that is, a thiol according to the formula given above wherein R_1 is ethyl, R_2 is methyl, R_3 and R_4 are hydrogen and n is zero. This material has sweet and roasted aroma and flavor notes at levels somewhat above the threshold level, the character changing toward roasted meat and pot roast at higher usage levels.

An alkanethiol which can also be used in the present invention is 3-methyl-1-butanethiol, that is a thiol according to the formula given above wherein R_1 and R_2 are methyl, R_3 and R_4 are hydrogen, and n is 1. At the 1 ppm level in water this material has a rendered pork fat or chicken fat character which is suitable for pork, chicken, and fatty flavor notes in foodstuffs. A further alkanethiol is 2-methyl-2-propanethiol, that is, a material according to the above formula wherein R_1 and R_2 are hydrogen, R_3 and R_4 are methyl and n is zero. A 1% ethanolic solution of this material has a sweet light fat, rendered pork aroma with character of roasted onions. The taste in water at 1 ppm has interesting meat flavour notes and an onion character. Another compound according to the formula given above wherein R_1 and R_3 are methyl, R_2 and R_4 are hydrogen, and n is zero, is 2-butanethiol. A 1 ppm solution in water has a boiled meat flavor character with onion notes which are useful in the formulation of meat gravy flavoring compositions.

Alkanethiols as utilized herein can be prepared by a number of reaction routes. One route which has proved to be effective is preparation of the thiol from the corresponding halo compound wherein the halo is chloro, bromo or iodo. The bromo compounds are generally preferred. The halo compound is reacted with thiourea or a substituted thiourea to provide the iso-thiuronium salt. This phase of the preparation is carried out at temperatures from about 60°C to 100°C and is preferably carried out at 70°C—80°C. It is desirable to utilize a reaction vehicle, for instance, a glycol ether such as thiethylene glycol. The halo compound is preferably added slowly to the reaction vehicle containing the thiourea with continuous agitation.

After the first phase of the reaction is completed, a polyamine, such as tetraethylene pentamine, is added to cleave the isothiuronium salt and produce the alkanethiol corresponding to the haloalkane. The reaction with the amine is carried out under the same conditions of temperature and pressure and in the presence of the same reaction vehicles as are utilized for the first phase of the reaction. The pressures utilized can be subatmospheric or superatmospheric, but ordinary atmospheric pressures are generally desirable for preparing the alkanethiols.

It will be understood according to the present invention that the intermediate and the final products prepared herein can be neutralized, washed, and dried to purify and cleanse the desired substance. The alkanethiols can be obtained in purer form or in substantially pure form by conventional purification techniques. Thus, the intermediate and the product can be purified and/or isolated by distillation, extraction, crystallization, filtration or preparative chromatographic techniques.

It will be understood from the present description that the usage levels of the alkanethiols are controlled to provide the desirable flavor and aroma properties to foodstuffs and other consumable materials. Thus, the materials can be utilized in foodstuffs from their threshold levels which are on the order of 0.0005 ppm (parts per million) up to levels where the effect of the alkanethiol becomes overwhelming and unbalances the flavor properties of the composition. All parts, percentages, proportions, and ratios herein are by weight unless otherwise stated.

It will be appreciated from the present disclosure that the alkanethiols according to the present invention can be used to alter, vary, fortify, modify, enhance, or otherwise improve the flavor of a wide variety of materials which

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are ingested, consumed, or otherwise organoleptically sensed.

The alkanethiols and mixtures thereof are accordingly useful in flavoring compositions. A flavoring composition is taken to mean one which contributes a part of the overall flavor impression by supplementing or fortifying a natural or artificial flavor in a material as well as one which supplies substantially all the flavor and/or aroma character to a consumable article.

The flavouring compositions described herein can be prepared according to conventional techniques well known in the art for such purposes. Thus, liquid products can be formulated by merely admixing the involved ingredients within the proportions stated in a suitable blender to obtain the desired consistency and homogeneity of dispersion.

The nature of the co-ingredients included with the alkanethiol in formulating the product composition will, of course, depend primarily upon the ultimate use contemplated, i.e. as a foodstuff *per se* or alternatively as a flavoring composition adapted to be added to a foodstuff at some subsequent point of time. In any event, such compounds serve to alter the organoleptic characteristics of the ultimate foodstuff treated therewith. Preferred compositions are those formulated with a protein hydrolysate, thiamine, sodium glutamate, 5-ribonucleotides and amino acids such as cysteine, glutamic acid, polypeptides and mixtures thereof.

Substances suitable for use herein as co-ingredients or flavoring adjuvants are well known in the art for such use being extensively described in the relevant literature. Apart from the requirement that any such material be "ingestibly" acceptable, and thus non-toxic or otherwise non-deleterious, nothing particularly critical resides in the selection thereof. Accordingly, such materials, which may in general be characterized as flavoring adjuvants or vehicles comprise broadly, stabilizers, thickeners, surface active agents, conditioners, flavorants and flavor intensifiers.

Stabilizer compounds include preservatives, e.g., sodium chloride, antioxidants, e.g., calcium and sodium ascorbate, ascorbic acid, butylated hydroxyanisole (mixture of 2 and 3 tertiary butyl-4-hydroxyanisole), butylated hydroxy toluene (2,6-di-tertiary-butyl-4-methyl phenol) and propyl gallate, and sequestrants, e.g., citric acid.

Thickener compounds include carriers, binders, protective colloids, suspending agents and emulsifiers, e.g., agar-agar; carrageenan; cellulose and cellulose derivatives such as carboxymethyl cellulose and methyl cellulose; natural and synthetic gums such as gum arabic, gum tragacanth; gelatin, proteinaceous materials; lipids; carbohydrates; starches; pectins, and emulsifiers, e.g., mono- and diglycerides of fatty acids.

Surface active agents include emulsifying agents, e.g., fatty acids such as capric acid, caprylic acid, palmitic acid and myristic acid, mono- and diglycerides of fatty acids, lecithin, and defoaming and flavor-dispersing agents such as sorbitant monostearate, potassium stearate and hydrogenated tallow alcohol.

Conditions include compounds such as bleaching and maturing agents, e.g., benzoyl peroxide, calcium peroxide and hydrogen peroxide; starch modifiers such as peracetic acid, sodium chlorite, sodium hypochlorite, propylene oxide and succinic anhydride; buffers and neutralizing agents, e.g., sodium acetate, ammonium bicarbonate, ammonium phosphate, citric acid, lactic acid and vinegar; colorants, e.g., carminic acid, cochineal, tumeric and curcumin; firming agents such as aluminum sodium sulfate, calcium chloride and calcium gluconate; texturizers; anti-caking agents, e.g., aluminum calcium sulfate and tribasic calcium phosphate; enzymes; yeast foods, e.g., calcium lactate and calcium sulfate; and nutrient supplements, e.g., iron salts such as ferric phosphate, ferric pyrophosphate, ferrous gluconate, riboflavin, vitamins, and zinc sources such as zinc chlorides and zinc sulfate.

Flavorants and flavor intensifiers include organic acids, e.g., fatty saturated, unsaturated and amino acids; alcohols, e.g., primary and secondary alcohols; esters; carbonyl compounds including aldehydes and ketones, lactones; cyclic organic materials including benzene derivatives; alicyclics, heterocyclics such as furans, particularly 2-acetylfuran, pyridines and pyrazines, and sulfur-containing materials including thiazoles, thiols, sulfides and disulfides; so-called flavor potentiators such as monosodium glutamate, guanylates, inosinates, and natural and synthetic flavorants such as vanillin, and natural gums; spices, herbs, essential oils and extractives including anise, anise oil, alkanet root extract, bay leaves and capsicum extract.

The specific flavoring adjuvant selected for use may be either solid or liquid, depending upon the desired physical form of the ultimate product, i.e. foodstuffs, whether simulated or natural, and should, in any event, be capable of providing an environment in which the alkane thiol can be dispersed or admixed to provide a homogeneous medium. In addition, selection of one or more flavoring adjuvants as well as the quantities thereof will depend upon the precise organoleptic character desierd in the finished product; thus, in the case of flavouring compositions, ingredient selection will vary in accordance with the foodstuff to which the flavor and aroma are to be imparted. In contra-distinction, in the preparation of solid products, e.g., simulated foodstuffs, ingredients capable of providing normally solid compositions should be selected such as various cellulose derivatives.

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It will be understood by those skilled in the art that the alkanethiols can be added to the materials to be flavored at any convenient point in the production of the finished product. Thus, when the alkanethiol is used to alter or otherwise vary the flavor of a foodstuff, it can be added in the original mixture, dough, emulsion or batter, for example, prior to any cooking or heating operation. Alternatively, it can be added at a later stage of processing if volatilization losses would be excessive during the earlier processing. The quantity of alkanethiol utilized should be sufficient to impart the desired roasted or meat flavor characteristic to the product, but on the other hand, the use of an excessive amount of such alkanethiols is not only wasteful and uneconomical, but too large a quantity unbalances the flavor of the product consumed. Moreover, at too high a level in flavoring compositions (and also in foodstuffs) the roasted character of the alkanethiols will be lost.

The quantity used will vary depending upon the ultimate foodstuff, or other consumable product; the amount and type of flavor initially present in the product; the further process or treatment steps to which the product will be subjected; regional and other preference factors; the type of storage, if any, to which the product will be subjected; and the pre-consumption treatment, such as baking or frying, given to the product by the ultimate consumer. Accordingly, the terminology "effective amount" and "sufficient amount" is understood in the context of the present invention to be quantitatively adequate to alter the flavor of the foodstuff, tobacco, or other consumable material.

It is accordingly highly desirable that the ultimate compositions contain from about 0.005 parts per million (ppm) to about 5.0 ppm of the thiol or thiols. More particularly, in food compositions it is preferred to use from about 0.01 to about 1.0 ppm. The higher usage levels up to about 0.9 ppm are for veterinary products, such as dog food.

The amount of alkanethiol to be utilized in flavoring compositions can be varied over a wire range depending upon a particular quality to be added to the foodstuff or other consumable material. Thus, amounts of the thiol according to the present invention from about 0.1 percent up to 80 or 90 percent can be incorporated in such compositions.

It is generally found to be desirable to include from about 0.5 to about 25 percent of the thiol in such compositions.

The following examples serve to illustrate embodiments of the invention as it is now preferred to practice it. It will be understood that these examples are illustrative and the invention is to be considered restricted thereto only as indicated in the appended claims.

EXAMPLE I

Preparation of 2 - Methyl - 1 - butanethiol

A one-liter flask fitted with a magnetic stirrer, a thermometer, a dropping funnel and a 14-inch glass helix-packed column having a variable reflux stillhead is charged with 125 ml of triethylene glycol and 83.8 g of thiourea, the temperature is raised to 75°C, and 100 g of 2-methyl-1-bromobutane is added dropwise with stirring. After the bromobutane addition is complete, the reaction mixture is stirred for an additional 15 minutes at 75°C, and 94.6 g of tetraethylene pentamine is added through the dropping funnel. The reaction product is stirred for an additional hour at 75°C.

The two-phase reaction product is transferred to a separatory funnel, and the lower layer is drawn off and discarded. Gas chromatography of the upper layer shows peaks corresponding to the mercaptan and the monosulfide. The upper layer is dissolved in 500 ml of 4N potassium hydroxide, and the layer is then extracted thrice with 80 ml volumes of diethyl ether to remove the monosulfide and other impurities.

The resulting aqueous mixture is acidified with hydrochloric acid and extracted with ether to remove the mercaptan. The ether extract is dried over sodium sulfate and concentrated on a rotary evaporator. The concentrate so obtained is chromatographed on a 5% Carbowax TPA-terminated column, and peaks corresponding to the ether and 2-methyl-1-butanethiol are found.

GC (gas chromatographic) analysis indicates that the 11 g of material obtained is 99.395% pure, and the structure is confirmed by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The methylbutanethiol so prepared has sweet, roasted flavor notes redolent of roasted nuts at the 0.0001% level in ethanol. At the 0.005 ppm level it has a strong roasted aroma and a roasted meat, pot roast taste; at 0.001 ppm, it has a very characteristic roasted aroma. In sugar water the roasted meat notes are somewhat depressed. It is suitable for roasted flavor notes in meat, nuts, caramel, and vegetable flavors. Its threshold level is below 0.0001 ppm.

EXAMPLE II

A 0.1% solution in propylene glycol of the methylbutanethiol produced in Example I is prepared, and a powdered shaker composition is prepared with the following formulation:

Ingredient	Amount (g)
Ham Spices	2.5
Monosodium Glutamate, fine grind	2.5
Salt, fine grind	55.0
Solution of thiol prepared above	0.02

When the powdered material is used on

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ham, it is found that the ham flavor is enhanced and improved. (An alcoholic solution can be similarly used.)

EXAMPLE III

A beef noodle soup mix concentrate is prepared by admixing the following ingredients:

Ingredient	Amount (g)
Salt	5.00
Aqueous solution of 3-methyl-2-butanethiol (0.1%)	0.03
Gelatin (180 bloom)	1.00
Monosodium glutamate	.40
Caramel Color	.40
Garlic powder	.10
White pepper, ground	.06
Mixed vegetable pieces	36.00

The foregoing composition is made into bouillon-type cubes weighing from 4 to 5 grams. When one cube is dissolved in 6 ounces of boiling water a soup having excellent, rich, meat broth flavor is obtained.

Similar results are obtained when 2-methyl-1-butanethiol is substituted for the aforementioned 3-methyl material.

EXAMPLE IV

A gravy flavor composition is prepared by admixing the following ingredients:

Ingredient	Amount (g)
Corn starch	10.50
Ethanolic solution of 2-methyl-1-butanethiol (0.1%)	0.03
Ethanolic solution of 3-methyl-2-butanethiol (0.1%)	0.03
Caramel color	0.30
Garlic powder	0.05
White pepper	0.05
Salt	1.92
Monosodium glutamate	0.20

The foregoing composition is added to 100 g of water and brought to a boil. The resulting gravy has an excellent pot roast flavor.

EXAMPLE V

Cysteine hydrochloride in the amount of 8.8 g is refluxed at 125°F under atmospheric pressure for four hours with a mixture of 309 g of hydrolyzed vegetable protein and 674 g of water. Subsequent to the reflux, the mixture is cooled and 8.8 g of 4-methyl-5-(beta-hydroxyethyl) thiazole and 0.08 g of 2-methyl-2-propanethiol are added and intimately admixed with the refluxed composition. The mixture so obtained has an excellent roast beef flavor.

WHAT WE CLAIM IS:—

1. A flavor altering composition comprising an ingestibly acceptable flavoring adjuvant and at least one sulfur containing compound which is an alkane thiol of the formula

$$R_1R_2CH—(CH_2)_n—CR_3R_4—SH$$

wherein R_1, R_2 R_3 and R_4 are the same or different alkyl groups or hydrogen, at least two of R_1, R_2, R_3 and R_4 being alkyl, and at least one of R_1, R_2, R_3 and R_4 being hydrogen, and n is 0 or 1, said thiol being present in amounts sufficient to alter the flavor of a foodstuff in which it is incorporated.

2. A composition according to claim 1 wherein the alkyl groups contain from one to three carbon atoms.

3. A composition according to claim 1, where R_1, R_2 and R_3 are methyl, R_4 is hydrogen and n is zero.

4. A composition according to claim 1, wherein R_1 is ethyl, R_2 is methyl, R_3 and R_4 are each hydrogen, and n is zero.

5. A composition according to claim 1 wherein R_1 and R_3 are methyl, R_2 and R_4 are hydrogen, and n is 1.

6. A composition according to claim 1, wherein R_3 and R_4 are methyl, R_1 and R_2 are hydrogen, and n is zero.

7. A composition according to any preceding claim, wherein there is additionally added at least one of monosodium glutamate, hydrolyzed protein, or tetramethylpyrazine as a meat-flavoring ingredient.

8. A composition according to claim 1, substantially as described in any of the foregoing Examples.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1318460

1318460

NO DRAWINGS

(21) Application No. 45546/71 (22) Filed 30 Sept. 1971
(31) Convention Application No. 78591 (32) Filed 6 Oct. 1970 in
(33) United States of America (US)
(44) Complete Specification published 31 May 1973
(51) International Classification A23L 1/26
(52) Index at acceptance
A2B 6A 6G

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(54) BEEF FLAVOUR

(71) We, NESTLE S.A., of La Tour-de-Peilz, Switzerland, a Swiss company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with novel flavouring substances having a flavour and aroma similar to roasted beef.

It is generally believed that the development of the basic meaty flavour common to all meat is produced by non-enzymatic browning of the precursors present in the water-soluble fractions of fresh meat.

Various materials having the flavour and aroma of roasted meats are described in the literature, and the preparation of these substances is essentially based on the Maillard reaction which takes place when amino acids or proteinaceous substances are heated in the presence of mono or polysaccharides. The heating causes browning of the reactants accompanied by the development of aromatic components.

A particular role in flavour development has been ascribed to cystine, cysteine or peptides containing these amino acids, but other amino acids such as phenylalanine and methionine have been excluded from the reaction as they are believed to give rise to undesirable flavours.

Despite the voluminous literature which exists in this field, no really satisfactory meat flavours have apparently been produced.

An object of the present invention is to provide a flavouring agent having a strong and characteristic roast beef flavour and aroma.

Another object of the invention is to provide a flavouring agent superior in flavour and keeping quality to substances prepared from cystine or cysteine.

A further object of the invention is to provide a roast beef flavouring material which can be prepared from readily-available starting materials.

The present invention provides a process for preparing a flavouring agent which comprises reacting together, by heating in an aqueous medium, a mixture comprising about 20 to 40 parts by weight of protein hydrolysate free of cystine or cysteine about 0.09 to 1.5 parts by weight of methionine and about 0.5 to 6 parts by weight of saccharide (mono or poly-saccharide), the amount of water present in the medium being about 1 to 4 times the total weight of solids.

The principal starting material is a protein hydrolysate obtained, for example, by acid hydrolysis of a vegetable protein followed by neutralisation. Such hydrolysates may be obtained from various proteinaceous materials, for example wheat germ, corn gluten, soy protein, linsed protein, peanut press cake and the like. Typical preferred vegetable protein hydrolysates contain 25 to 35% of amino acids, with no cystine or cysteine. Apart from vegetable proteins, hydrolysates of animal or fish proteins may also be used.

The saccharide should preferably be lactose or a pentose such as ribose, xylose or arabinose, or a hexose such as glucose. A mixture of mono and polysaccharides may also be used as starting material, and this may conveniently be provided in the form of an acid hydrolysate of a carbohydrate material such as coffee chaff, oats, rye or barley, and particularly of spent coffee grounds (obtained as a by-product in the manufacture of coffee extract). The hydrolysate may be prepared by heating these materials with about 3% of concentrated sulphuric acid for 6 to 10 hours, preferably at reflux temperature. The resulting hydrolysate contains about 5 to 15% of monosaccharide.

It has, surprisingly, also been found that such hydrolysates may be reacted directly with a protein hydrolysate, in the absence of added methionine, to provide beef-flavoured products.

According to this aspect the invention provides a process for preparing a beef flavouring agent which comprises reacting together, by heating in an aqueous medium, a mixture

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comprising about 20 to 40 parts by weight of protein hydrolysate containing methionine but free of cystine or cysteine, and 2 to 12 parts by weight of an acid hydrolysate of a carbohydrate-containing material, the amount of water present in the medium being about 1 to 4 times the total weight of solids.

The reaction leading to the formation of the flavouring agent should preferably be effected by heating the reactants in water for about 2 to 3 hours, desirably under reflux at the boiling temperature of the reaction medium which is about 90 to 100°C. The reaction medium may contain up to about 80% of water, and usually about 60 to 75%.

Preferred compositions may be prepared by reacting a mixture of 20 to 40 parts by weight of protein hydrolysate, 0.09 to 1.5 parts by weight of methionine (either isomer), about 0.5 to 6.0 parts by weight of saccharide suspended in water. When a hydrolysate of a carbohydrate material is used as saccharide source, this reactant may be present in the medium at a level of 2 to 12 parts by weight, the amount of protein hydrolysate being within the limits given.

In addition to the principal reactants (protein hydrolysate, methionine and saccharide), the reaction medium may also contain minor amounts of a carboxylic acid which, it has been found, confers desirable flavour notes to the product. Lower carboxylic acids, such as lactic, malic or succinic acid, as well as fatty acids (e.g. plamitic, stearic or oleic acid) may be used, either singly or as mixtures, preferably at a total level betwen about 0.3 and 3.0% by weight of the reaction medium. One or more 5′-nucleotides, such as sodium inosinate or sodium guanylate, may also be added, in an amount between 0.3 and about 1% by weight of the medium. Alternatively, the nucleotide may be added to the product after reaction.

Specific flavour notes may be obtained by addition of yeast autolysate, either to the reactants prior to heating or to the finished product. It has been found that particularly preferred beef flavourings are obtained when the quantity of yeast added corresponds to 20 to 50% of the protein hydrolysate.

The flavouring agent may be provided in liquid, paste or dry form, the reaction medium being concentrated and/or dried by conventional methods. No separate isolation step is necessary, and the final product is water-soluble and has a strong beef flavour.

The invention is illustrated by the following examples, in which the parts and percentages are by weight.

Example 1

The following substances are refluxed at about 100°C for 2½ hours with stirring:—

	parts
Hydrolysed plant protein (cysteine-free)	22.0
Sodium guanylate	0.64
Malic acid	0.38
Methionine	0.31
Xylose	0.57
Water	76.10

After reaction the product is vacuum dried, providing 23 parts of a brown powder having the flavour of roast beef. The sodium guanlyate may alternatively be added to the dry powder rather than to the reaction medium.

Example 2

The following substances are heated at about 100°C under reflux for 3 hours:—

	parts
Hydrolysed plant protein (cysteine-free)	26.55
Sodium guanylate	0.47
Lactic acid	0.28
Palmitic acid	0.47
Succinic acid	0.19
Methionine	0.28
Xylose	0.71
Water	71.07

After reaction the product is concentrated to a paste containing 45% solids and may be used directly as a beef flavouring for various foodstuffs.

Example 3

The following substances are refluxed for 2½ hours:—

	parts
Hydrolysed plant protein (cysteine-free)	28.95
Stearic acid	0.44
Sodium inosinate	0.22
Sodium guanylate	0.22
Hydrolysed spent coffee grounds	4.38
Water	65.79

The resulting product is vacuum dried and is particularly suitable for imparting a beef flavour to soups and gravies.

If the stearic acid is omitted a slightly less mild-flavoured product is obtained. The inosinate and guanylate may alternatively be blended with the dried product after reaction.

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Their presence is desirable as these substances confer a pleasant mouthfeel to the finished flavouring.

Example 4

3 beef flavours are prepared by refluxing the listed ingredients for about 2½ hours:—

	parts		
	A	B	C
Hydrolysed plant protein* (cysteine-free)	18.61	18.54	18.54
Autolysed yeast	—	5.93	—
Methionine	0.09	0.37	0.22
Xylose	0.55	0.64	0.74
Water	74.43	74.15	74.18

* Obtained from 60/40 mixture of corn gluten and wheat germ. After reaction the water is evaporated and the residues are dried. The resulting powders have good beef flavour. Particular flavour notes may be obtained by adding 0.37 parts of a 5′-nucleotide mixture to the dry flavouring. Yeast autolysate (about 6 parts) may be added to compositions A and C.

Example 5

Two beef flavouring agents are prepared from the ingredients and by the procedures described in Examples 1 and 2, but with the xylose being replaced by, respectively, 0.76 and 0.95 parts of lactose. The products have good roasted beef flavour.

WHAT WE CLAIM IS:—

1. A process for preparing a flavouring agent which comprises reacting together, by heating in an aqueous medium, a mixture comprising about 20 to 40 parts by weight of protein hydrolysate free of cystine or cysteine, about 0.09 to 1.5 parts by weight of methionine and about 0.5 to 6 parts by weight of saccharide, the amount of water present in the medium being about 1 to 4 times the total weight of solids.

2. A process according to claim 1 in which the reaction medium contains autolysed yeast in an amount corresponding to 20 to 50% of the protein hydrolysate.

3. A process according to claim 1 or claim 2 in which the saccharide is xylose and/or lactose.

4. A process for preparing a beef flavouring agent which comprises reacting together, by heating in an aqueous medium, a mixture comprising about 20 to 40 parts by weight of protein hydrolysate containing methionine but free of cystine or cysteine, and 2 to 12 parts by weight of an acid hydrolysate of a carbohydrate-containing material, the amount of water present in the medium being about 1 to 4 times the total weight of solids.

5. A process according to claim 4 in which the carbohydrate-containing material is selected from the group consisting of coffee chaff, oats, rye, barley or spent coffee grounds.

6. A process according to any one of the preceding claims in which the reaction medium also contains a carboxylic acid.

7. A process according to claim 6 in which the reaction medium contains about 0.3 to 3.0% by weight of a carboxylic acid.

8. A process according to claim 6 or claim 7 in which the carboxylic acid is lactic, malic, succinic, palmitic, stearic and/or oleic acid.

9. A process according to any one of the preceding claims in which upon completion of the reaction the medium is concentrated to provide the flavouring agent in paste form.

10. A process according to any one of the preceding claims in which upon completion of the reaction the flavouring agent is recovered in powdered form by removing the water from the medium.

11. A process for preparing a flavouring agent substantially as herein described with reference to any one of the Examples.

12. The flavouring agent obtained by the process of any preceding claim.

13. The beef flavouring agent obtained by the process of claim 4 or claim 5.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 325 335

NO DRAWINGS

1 325 335

(21) Application No. 33550/70 (22) Filed 10 July 1970 (19)

(44) Complete Specification published 1 Aug. 1973

(51) International Classification A23L 1/26 C07D 51/50

(52) Index at acceptance
A2B 6A
C2C 173—198—289 178—196—274 247 250 252 253 25Y 30Y 321 32Y 351 352 360 362 366 368 36Y 781 782 XX
C2P 2L13 2L15 2L19F 2L19G 2L26B 2L30C 2L33 5B 7

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(54) FLAVORING SUBSTANCES AND THEIR PREPARATION

(71) We, H. KORNSTAMM & COMPANY, INC., a New York Corporation, 161 Avenue of the Americas, New York, New York, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of a meat-flavor.

In general, it has been known in the prior art how to prepare artificial flavouring substances which impart a savory taste or smell to foodstuffs and particularly those flavors which impart a meat-like flavor. It has been disclosed in U.S. Patents 2,934,436, 2,934,435 and 2,918,376, to react various materials to obtain a meat-like flavor. For example, it is suggested by the disclosure of U.S. Patent 2,934,436 to react an amino acid such as cystine or cysteine with glyceraldehyde in the presence of water and at elevated temperatures in order to obtain a flavor product. To achieve flavors having a particular resemblance to beef, certain pentoses, such as ribose, are generally included in the reaction to hasten or catalyze amino acid degradation.

In the reaction of low molecular weight aldehydes, or aldehydes that represent sugar fragments (such as glyceraldehyde and the like) with amino acids to degrade the latter, the reaction frequently yields final products having an undesirable off-flavor due to their dehydration or polymerization resulting in partially reacted or unreacted end products of undesirable flavor. When sugars such as pentoses, hexoses or polysaccharides are added to assist in the catalysis of the amino acid reactant, burnt or caramel-like flavors are frequently developed as a result of sugar decomposition products formed therein as well as caramelisation. These side reactions limit the use of the flavor and detract from the basic meaty flavor or character of the product. The caramelisation side reaction has particularly been for a very long time a stumbling block in attempts at development of meaty flavors, since the off-flavor development resulting therefrom almost always imposes strict limitations on the techniques employed for the control of flavor development.

It is an object of the present invention to provide a technique of flavor development free of such side reactions.

The present invention provides a process for the production of a meat-flavor which comprises reacting a ribonucleotide reactant or mixtures of the same with an amino acid reactant which is cystine or cysteine. The optimum ratio of the two reactants is from 1:2 to 3:1 parts by weight respectively of nucleotide to amino acid.

The method of preparation of the flavor product basically involves reacting the aforesaid ingredients with or without the presence of water at an elevated temperature until a flavoring substance having the aroma and taste of cooked meat is obtained. The amount of water involved in the reaction, when employed, is of sufficient quantity to wet the reactants but comprises varying amounts of water for each part of amino acid present in the reaction mixture or none at all for a flat soluble flavor preparation. The minimum ratio of water to amino acid reactant is preferably 5:1 by weight and the minimum ratio of water to ribonucleotide reactant is preferably 5:1.5 by weight whereas the optimum ratio of water to amino acid is 19:1 by weight. The reaction is generally carried out at elevated temperature, preferably from 60°C to 200°C. For fat soluble flavors the reaction temperature will go as high as 235°C. The reaction will normally

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proceed until all of the water initially present has been removed and the flavour product is present in the reaction vessel as a dried friable mass.

If desired the flavour reaction may be conducted in an oil or fat to develop a fatty flavor. When this is done water is excluded from the reaction vessel and the preferred range of reaction temperatures is from 150°C to 235°C and a time of about 5 to 15 minutes is generally adequate to complete the reaction.

In accordance with the present invention it has been found possible to produce flavouring substances capable of imparting to foodstuffs a savory meat-like aroma and taste, especially resembling that of cooked meat.

The amino acid reactant is cystine and/or cysteine, although for the development of certain types of meat flavors, additional amino acids may be added for example in the form of commercial synthetic amino acids or naturally occuring protein hydrolysates, which will release amino acids in the course of the reaction.

The ribonucleotide reactant which is involved in the preparation of the flavor product may be derived from a naturally occurring product containing ribonucleotides or other ribose-radical-containing complexes, for example it may be selected from a large number of materials such as inosinates, guanylates, other ribonucleotides, combinations of these or products containing such nucleotides or combinations of natural products containing nucleotides as well as synthetic nucleotide materials.

Cysteine, cysteine-derivatives or amino acid mixtures having a high percentage of cysteine are the preferred source of amino acid. A particularly preferred flavor is obtained when cysteine or derivatives such as the hydrochloride salt thereof predominates in the amino acid mixture if, in fact, a mixture of amino acids is employed.

It has been found that the ratio of the ribonucleotide reactant to amino acid reactant is a determining factor in the development of optimum flavor and, in general, the useable ratio of ribonucleotide broadly defined ranges from 0.1—4.0 parts by weight of ribonucleotide reactant to one part by weight of the primary amino acid reactant. By varying the ratios of reactive ingredients employed, the ultimate flavor character changes. This result is a distinct advantage of the invention as one is able to thereby approximate the particular flavor of various types and species of meat as may be desired in the particular situation. In many instances, as little as 0.5 to 1.5 parts of ribonucleotide for one part of cysteine is sufficient to develop a savory or meat-like flavor in the ultimate product. The excess of ribonucleotide may, however, be added for its own inherent flavor. It is the inherent flavor-enhancing properties of the nucleotides that is partly responsible for the development of its superior flavor by the application of the improved process of the invention as contrasted with those methods of the prior art which employed those known amino acid degradation agents such as the pentoses, hexoses and aldehydes as noted above. An ideal ratio, for example, of cysteine to ribonucleotide reactant when used alone has been found to be 1.0 part of cysteine hydrochloride monohydrate to 2.3 parts by weight of a 50/50 mixture of various nucleotides such as 5'-inosinate and 5'-guanylate or 2.3 parts of either 5'-inosinate or 5'-guanylate alone. It must be understood that the nucleotide reactant of the reaction mixture may be added *per se*, or as part of a natural product, containing the same, which will release the nucleotide "in situ" during the course of the reaction.

The reaction which comprises the development of the present flavor material will generally take place in the presence of a large amount of water of the order of 30 parts of water for each one part of the amino acid reactant under generally elevated temperature and normal or elevated pressure conditions. The reaction time involved will depend to some extent upon the temperature and pressure of the reaction. A preferred range of reaction temperatures will generally extend between 60°C and 200°C and reaction will proceed until the reaction is complete and the water present has been evaporated. In this case the liquid is dissipated and a virtually dry friable material remains in the reaction vessel.

The flavor developing reaction may also take place in the presence of the food product in which the savory meat-like flavor is sought to be developed. In this particular instance, the cystine-containing or cysteine-containing amino acid reagent and the ribonucleotide and/or natural materials containing the ribonucleotide will act as precursors in the reaction, which ultimately will involve reaction between the ribose moiety of the ribonucleotide and the amino acid to form the ultimate savory meat-like product or flavor. In this case the ribonucleotide reactant may be present in the food product which is merely reacted with the amino acid reactant to impart a meat flavour to the food product.

An example of the use of the products of this invention may be as part of a seasoning mixture added to various meat products where a supplementary meat or savory flavor is desired. In addition, the flavor ingredient obtained according to the invention may be added to processed proteins which have no meat flavor of their own and in which a meat or savory flavor is

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desired. A very common use is in the canning industry to flavor food products that have been or are to be sterilized or autoclaved, which may result in a loss of some of their natural flavor. Under these conditions the meat-like flavor is developed in the processing the food product. There are, moreover, food products which are processed by the final user such as dry soup mixes, gravy mixes, and a host of other similar materials wherein the flavor ingredient is incorporated in the mix and upon preparation of the mix, the desirable meat flavor is imparted thereto.

By way of explanation of the function of the formation of the meat flavor of the invention, it may be stated generally that cysteine, cystine and other amino acids are degraded to form aromatic materials having a meat-like flavor. The aromatics particularly derived from cysteine will give a basic meat flavor, while the other amino acids such as glycine, alpha or beta alanine, arginine, iso-leucine, threonine, proline, glutamic acid, lysine, aspartic acid, tyrosine, leucine, histidine and valine to mention a few of these will impart a particular meat flavor therein. While it is preferred to use single amino acids in those instances where it is desired to supplement the basic meat flavor of the product, combinations of more than one amino acid may also be used, and the synthetic racemic mixture as well as the naturally occurring dextro or levo forms of the acid may be employed. In some instances, depending upon the particular food product being treated, the supplemental amino acid ingredient may be added in the form of its hydrochloride, or bound up in proteins or polypeptides which will, under proper conditions, generate the desired amino acids under the conditions of reaction.

As noted above, the reaction involved in the invention may be carried out if desired by simply adding the reagents to a selected food product in which it is desired to develop a meat flavor and then heating the product to effect reaction. One conventional way of proceeding is simply to place the food to be flavored and the flavor reactants in an autoclave and reacting until a proper flavor is attained.

The reaction products of the invention may be separately prepared and subsequently converted to dry powders by such conventional techniques as lyophilization or spray drying. As a flavor additive they may be added to food products in a wide range of proportions extending from 0.1 to 10.0 per cent of the total weight of the food product to which they are added depending upon the nature of the product and the other circumstances which dictate the level of flavor desired.

The flavoring substances of the invention, when independently prepared and incorporated into a wide array of food products may be added as either solutions or dry powders as convenience dictates. These may be used to impart a meaty flavor to artificial food products or may be used to enhance the natural flavor of fresh meat products. The supplemental amino acids give varying specific flavors which are in addition to the basic meat flavors imparted to the food product by the reaction product of ribonucleotide and the cysteine.

The flavor produced according to the invention may be enhanced by the addition of a mixture of 2,4 decadienal, 2,6 nonadienal, undecanal and methyl sulphide or up to 3 p.p.m. of an aldehyde.

The following Examples illustrate the invention, the amounts of ingredients employed being in parts by weight unless otherwise designated.

EXAMPLE NO. 1

3.90 grams of cysteine hydrochloride monohydrate and 30.0 grams of hickory smoked torula yeast were thoroughly stirred in 100 parts of water.

The reaction mixture, in a glass plate, was placed in an oven and the ingredients were allowed to heat between 130°—135°C for 2½ hours. The yield of crude material was 30.0 grams. The powdered residue had a ham-like taste.

EXAMPLE NO. 2

30 parts of a 50:50 (% by weight) mixture of commerical disodium guanosine 5¹-monophosphate and disodium inosine 5¹-monophosphate, 20 parts of cysteine hydrochloride monohydrate, and 100 parts of hickory smoked torula yeast were thoroughly stirred in 400 parts of water. The contents were poured into a large glass plate in an oven set at 130°—135°C. The material was heated until the residue could be powdered. The yield of crude material was 149.0 parts of meat flavor base.

EXAMPLE NO. 3

To a mixture of 40 parts of water, 7.54 parts of cysteine hydrochloride monohydrate and 17.20 parts of a 50:50 (% by weight) mixture of commercial, disodium guanosine 5¹-monophosphate and disodium inosine 5¹-monophosphate, was added an emulsion of 40 parts of gum acacia in 100 parts of water. The combination was well-mixed in a blender and spray dried in a commercially available spray drier unit.

The inlet temperature of the atomizer varied from 190°—235°C. The air flow pressure varied from 3 to 5 kg. per square inch.

A yield of 40.2 parts of white powder was

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obtained which had a savory, chicken-like odor. An aqueous solution of the material had a mouth-watering, chicken-meat flavor.

EXAMPLE NO. 4

To a 4000 ml. vessel equipped with a stirrer was added 1550 parts of water, 162 parts of commercial disodium inosine 5'-monophosphate, 108 parts of commercial L-cysteine hydrochloride monohydrate and 540 parts of hickory smoked tortula yeast.

This medium was then added to a large tray and placed in an oven set at 130°—135°C.

After several hours of heating, the dried residue was powdered, giving a yield of 732 parts of material which when dissolved in water produced, a savory, meat-like odor and flavor.

EXAMPLE NO. 5

The following combination:

10 parts 2,4 decadienal
1 part 2,4 nonadienal
1 part undecanal
1 part methyl sulfide

at a level of 0.25—1.0 ppm imparts a "chicken fat" flavor to the meat flavor already prepared in the previous Examples.

The addition of proper seasonings (celery, onion, pepper, etc.) and other flavor materials round off or give a roasted character. The following Examples 6 to 8 illustrate reaction in an oil or fat to produce a fatty flavor.

EXAMPLE NO. 6

A mixture of 6.5 g. disodium 5'-inosinate, 4.3 g. of L-cysteine hydrochloride and 21.6 g. of hickory smoked torula yeast was added to 432 g. of stirred coconut oil at 370—375°C. The total heating time was eight minutes. The suspension while stirring was cooled to room temperature and the insoluble material removed by centrifugation or filtration to give a clear, golden brown liquid with a nutty or burned meat aroma and flavor.

EXAMPLE NO. 7

To 268 g. (240 ml) of stirred, melted butter oil at 380—385°C was added a ground mixture of 2.2 g. of L-cysteine hydrochloride monohydrate and 5.0 g. of disodium 5'-inosinate. Total heating time was seven minutes. Upon cooling down to 50°C the clear liquid was centrifuged or passed through cheese cloth to remove coarse particles and thne allowed to solidify to a yellow brown semi-solid with a savory, roasted beef aroma and taste.

EXAMPLE NO. 8

A ground mixture of 1.0 g. of L-cysteine hydrochloride and 2.0 g. of disodium 5'-inosinate was added to 300 g. of lard previously melted and heated to 195°C. The mixture was heated further for one minute, cooled to 150°C. and 1800 ml wood smoke distillate added. The mixture was shaken well and the oil layer separated. Salt, protein hydrolysates, additional flavouring materials can be added to the fat to prepare a complete bacon or smoked ham type flavor.

WHAT WE CLAIM IS:—

1. A process for the production of a meat-flavor which comprises reacting a ribonucleotide reactant with an amino acid reactant which is cysteine or cystine until a meat-flavor develops.

2. A process as claimed in claim 1 wherein the ribonucleotide is derived from a naturally occuring product containing ribonucleotides or is a synthetic ribonucleotide.

3. A process as claimed in claim 1 or 2 wherein the ratio of ribonucleotide to amino acid is from 1:2 to 3:1 parts by weight.

4. A process as claimed in any of claims 1 to 3 carried out at elevated temperature.

5. A process as claimed in any of claims 1 to 4 wherein the reaction is carried out in the presence of water.

6. A process as claimed in claim 5 wherein the minimum ratio of water to amino acid is 5:1 by weight and the minimum ratio of water to ribonucleotide reactant is 5:1.5 by weight.

7. A process as claimed in any of claims 1 to 4 wherein the reaction is carried out in the absence of water.

8. A process as claimed in claim 7 wherein the reaction is carried out in an oil or fat at a temperature of from 150°C. to 235°C.

9. A process as claimed in any of claims 1 to 8 wherein the amino acid reactant also contains at least one supplemental amino acid.

10. A process as claimed in any of claims 1 to 9 wherein a mixture of 2,4 decadienal, 2,6 nonadienal, undecanal and methyl sulphide is added to the flavoring substance produced.

11. A process as claimed in any of claims 1 to 9 wherein up to 3 p.p.m. of an aldehyde is added to the flavoring substance produced.

12. A process as claimed in any of claims 1 to 11 wherein the ribonucleotide reactant is present in a food product which is reacted with the amino acid reactant to impart a meat flavour to the food product.

13. A process for the production of a meat-flavor substantially as hereinbefore described with reference to any of Examples 1 to 8.

14. A flavoring substance when produced

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by a process as claimed in any of claims 1 to 11 and 13.

15. A method of imparting a meat flavor to a food product which comprises admixing with the food product a minor proportion of a flavoring substances as claimed in claim 14.

16. A method as claimed in claim 15 wherein the food product contains a ribonucleotide as part of its normal composition.

17. A food product when prepared by a process as claimed in any of claims 12, 15 and 16.

18. A method of imparting a meat flavor to a food product containing naturally occuring ribonucleotides which comprises adding cysteine and/or cystine and heating the mixture in the presence of water.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1973.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

Espacenet

Bibliographic data: GB1357091 (A) — 1974-06-19

FLAVOURING AGENT

Inventor(s):

Applicant(s): NESTLE SA + (NESTLE SA)

Classification: **- international:** ***A23L27/21;*** (IPC1-7): A23L1/26
- cooperative: **A23L27/215**

Application number: GB19730013279 19730320

Priority number (s): US19720241431 19720405

Also published as: CA999852 (A) CH563726 (A5) DE2316896 (A1) DE2316896 (B2) DE2316896 (C3) more

Abstract of GB1357091 (A)

1357091 Flavouring NESTLE SA 20 March 1973 [5 April 1972] 13279/73 Heading A2B Meat-like flavourings are prepared by reacting S-acetyl-mercaptosuccinic acid or its anhydride with a vegetable protein hydrolysate and/or autolysed yeast. Flavour enhancers such as nucleotides may also be present. The reaction may be effected in an aqueous medium.

PATENT SPECIFICATION (11) 1382335

1382335

(21) Application No. 16512/72 (22) Filed 10 April 1972
(44) Complete Specification published 29 Jan. 1975
(51) INT CL[2] A23L 1/227 1/228 1/231
(52) Index at acceptance
A2B 6A 6G

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(54) FLAVOURING AGENTS

(71) We, C.P.C. INTERNATIONAL INC., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of International Plaza, City of Englewood Cliffs, State of New Jersey 07632, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a flavouring agent having a flavour similar to that of a meat extract, and relates to a process for preparing such a flavouring agent.

It is known that flavouring agents can be prepared by a reaction referred to as the Maillard Reaction. This reaction takes place when substances containing saccharides and amino acids or proteins are heated together. Generally a great deal of browning occurs and certain flavours are formed, depending on the mixture, accompanied by the reduction of sugars and amino acids. The importance of the Maillard Reaction in the flavour of baked foods is well recognised and various specific formulations subjected to Maillard Reaction conditions have been used for the production of specific flavours.

In accordance with the invention a process for preparing a flavouring agent having a flavour similar to that of a meat extract, comprises performing a Maillard reaction at elevated temperature between at least one saccharide, an amino acid component as hereinafter defined, and an egg component selected from the group comprising egg white, egg yolk, and whole egg dispersion.

The saccharide may conveniently comprise or include a monosaccharide selected from the group comprising arabinose, xylose, ribose, glucose, mannose, fructose and sorbose.

If desired, the saccharide may comprise or include a disaccharide selected from the group comprising lactose and maltose.

The saccharide content in the reaction mixture may be any suitable quantity. The maximum quantity which can be added is governed by the point where it starts to interfere unduly with the flavour.

The proportion by weight of saccharide in the reaction mixture may be less than 10%. Conveniently the proportion of saccharide in the reaction mixture may be between ½% and 10% by weight.

It will be appreciated that any saccharide, such as a poly-saccharide, which can be broken down under the specific reaction conditions, to yield a saccharide or saccharides which will undergo a Maillard Reaction, may be used.

The process may be carried out in the presence of water. The proportion of water in the reaction mixture may conveniently be at least 10% by weight.

The term amino acid component as used herein refers to an amino acid or mixture of amino acids which will undergo a Maillard reaction but excludes the egg component.

The proportion of amino acid component in the reaction mixture may conveniently be between 40% and 50% by weight.

The amino acid component may, for example, comprise a suitable acid hydrolysed protein. The protein may conveniently be a vegetable protein. Thus, for example, it may be a protein derived from sun flower or soya beans.

If desired, the protein hydrolysate may be fortified with monosodium glutamate. The proportion of monosodium glutamate in the reaction mixture may be between 25% and 30% by weight.

The egg component may be used in its unhydrolysed or in its hydrolysed form. Where the egg component is used in its hydrolysed form, the egg component may be hydrolysed by means of a suitable enzyme. The enzyme may, for example, be selected from the group comprising papain, bromolain, ficin trypsin, fungal proteases and bacterial proteases.

We have found that where egg white or whole egg is hydrolysed, the reaction tends to proceed faster than the reaction where they are unhydrolysed. In fact the reaction

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rate appears to approach the rate at which the reaction takes place when the egg component is not present in the reaction mixture.

We have further found that egg yolk alone is not effective as egg white or whole egg, although it does have a beneficial effect on the flavour of the end product.

The proportion of egg component in the reaction mixture may be between 2% and 50% by weight. Conveniently the proportion of egg component in the reaction mixture may be between 6% and 20% by weight.

The reaction mixture may include a sulphide component which may be a plant juice, for example, a juice derived from cabbages or onions.

The proportion of juice in the reaction mixture may be between 5% and 30% by weight. When the juice is present in the reaction mixture, the juice may replace any or some of the water which would have been included in the reaction mixture.

It has been found that, in a number of cases, the reactants of the mixture react vigorously while large amounts of gas are evolved. The end product of the reaction is usually dark brown in colour and can have a greater flavour intensity than a Maillard Reaction end product which has been made by reacting the same amino acids with the same mono-saccharides. Furthermore, it has been found that the flavour obtained can closely approach a meat-like flavour as opposed to the flavour obtained by reacting the same amino-acids with the same mono-saccharides without the addition of an egg component.

The invention further extends to a flavouring agent having a flavour similar to that of a meat extract, whenever prepared by any process as described herein.

The following non-limiting examples are illustrative of the invention. The control examples which do not include an egg component, illustrate the effect of the egg component in the reaction.

EXAMPLE 1

Reaction Mixture	Percentage by Weight
Commercial hydrolysed protein sold under the trade name "Protex" by Messrs. Frederick Boehm.	48%
Monosodium Glutamate	27%
Water	19%
Dextrose	6%

The mixture was heated in a water bath to 95°C until evolution of gas had ceased and the reaction was obviously completed. The total reaction time at 95°C was about 20 minutes. The flavour of the product was dull and uninteresting.

EXAMPLE 2

Reaction Mixture	Percentage by Weight
Protex	44%
Monosodium Glutamate	24%
Dextrose	4%
Fresh egg white	10%
Water	18%

Procedure:
As for example 1.
Temperature: 90—95°C.
Reaction time: ~3 hours
The resultant product had an excellent meat extract-like flavour.

EXAMPLE 3

Reaction Mixture	Percentage by Weight
Protein hydrolysate	44%
Monosodium glutamate	24%
Dextrose	4%
Fresh whole egg	10%
Water	18%

Procedure:
As for example 1.
Temperature: 90—95°C
Reaction time: ~4 hours
The resultant product had an excellent meat extract-like flavour.

EXAMPLE 4

Reaction Mixture	Percentage by Weight
Protein hydrolysate	44%
Monosodium glutamate	24%
Fructose	4%
Fresh onion juice	18%
Water	10%

Procedure:
As for example 1.
Reaction time: ~20 minutes
The resultant product had a pronounced onion flavour.

EXAMPLE 5

Reaction Mixture	Percentage by Weight
Protein hydrolysate	44%
Monosodium glutamate	26%
Fructose	4%
Egg white	10%
Onion juice	18%

Procedure:
As for example 1.
Reaction time: ~4 hours
The end product had an excellent meat extract-like flavour that could not be identified with onion.

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EXAMPLE 6

Reaction Mixture	Percentage by Weight
Protein hydrolysate	44%
Monosodium glutamate	26%
Dextrose	4%
Cabbage juice	16%
Water	10%

Procedure:
As for example 1.
Reaction time: ~20 minutes
The end product of the reaction mixture had a flavour, a large part of which could be identified as cooked cabbage.

EXAMPLE 7

Reaction Mixture	Percentage by Weight
Protein hydrolysate	46%
Monosodium glutamate	24%
Dextrose	4%
Egg white	10%
Cabbage juice	16%

Procedure:
As for example 1
Reaction time: ~4 hours
The flavour of the resultant product was excellent, but could not be identified with cabbage.

EXAMPLE 8

Reaction Mixture	Percentage by Weight
Protex	44%
Monosodium Glutamate	24%
Dextrose	4%
Proteolitic enzyme hydrolised egg white	10%
Water	18%

Procedure:
As for example 1.
Temperature: 90—96°C
Reaction time: ~30 minutes
The resultant product has a good meat extract-like flavour.

WHAT WE CLAIM IS:—

1. A process for preparing a flavouring agent having a flavour similar to that of a meat extract, which comprises performing a Maillard reaction at elevated temperature between at least one saccharide, an amino acid component, as hereinbefore defined, and an egg component selected from the group comprising egg white, egg yolk, and whole egg dispersion.

2. A process according to claim 1, in which the saccharide is a monosaccharide selected from the group comprising arabinose, xylose, ribose, glucose, mannose, fructose, and sorbose.

3. A process according to claim 1, in which the saccharide is a disaccharide selected from the group comprising lactose and maltose.

4. A process according to any of claims 1 to 3, in which the proportion by weight of saccharide in the reaction mixture is less than 10%.

5. A process according to claim 4, in which the proportion of saccharide in the reaction mixture is between ½% and 10% by weight.

6. A process according to any one of the preceding claims, which is carried out in the presence of water.

7. A process according to claim 6, in which the proportion of water in the reaction mixture is at least 10% by weight.

8. A process according to any one of the preceding claims, in which the proportion of amino acid component in the reaction mixture is between 40% and 50% by weight.

9. A process according to any one of the preceding claims, in which the amino acid component comprises an acid hydrolysed protein.

10. A process according to claim 9, in which the protein is a vegetable protein.

11. A process according to claim 9 or claim 10, in which the protein hydrolysate is fortified with monosodium glutamate.

12. A process according to claim 11, in which the proportion of monosodium glutamate in the reaction mixture is between 25% and 30% by weight.

13. A process according to any one of the preceding claims, in which the egg component is used in hydrolysed form.

14. A process according to claim 13, in which the hydrolysed egg component is an enzyme hydrolysed egg component.

15. A process according to any one of the preceding claims, in which the proportion of egg component in the reaction mixture is between 2% and 50% by weight.

16. A process according to claim 15, in which the proportion of egg component in the reaction mixture is between 6% and 20% by weight.

17. A process according to any one of the preceding claims, in which the reaction mixture includes a sulphide component comprising a plant juice.

18. A process according to claim 17, in which the juice is a juice derived from cabbages or onions.

19. A process according to claim 17 or claim 18, in which the proportion of juice in the reaction mixture is between 5% and 30% by weight.

20. A process as claimed in any one of claims 1 to 19 substantially as described herein.

21. A process as claimed in any one of claims 1 to 19, substantially as described with

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reference to any one of examples 2, 3, 5, 7 and 8.

22. A flavouring agent having a flavour similar to that of a meat extract, whenever prepared by the process as claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1384332

1384332

(21) Application No. 44539/72 (22) Filed 27 Sept. 1972
(31) Convention Application No. 14114/71 (32) Filed 28 Sept. 1971 in
(33) Switzerland (CH)
(44) Complete Specification published 19 Feb. 1975
(51) INT CL² A23L 1/231
(52) Index at acceptance
A2B 6A 6G

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(19)

(54) FLAVOURING AGENT

(71) We, NESTLE S.A., of La Tour-de-Peilz, Switzerland, a Swiss company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with the preparation of substances having the aroma and flavour of cooked meat.

In accordance with the invention, there is provided a process for preparing a meat flavouring which comprises adding enzymes present in fresh meat to an aqueous solution containing yeast autolysate and a hexose, the total dry matter content and the hexose content of the solution not exceeding, respectively, 25 and 1.5% by weight and the yeast autolysate being present in an amount of at least 15 times the weight of hexose, subjecting the resulting mixture to a treatment which comprises maintaining the pH of the solution between 4.0 and 7.0, and its temperature at below 37°C if the pH is between 4.0 and 6.0, or at below 15°C if the pH is between 6.0 and 7.0, thereafter concentrating the solution to a dry matter content not exceeding 65% by weight, adjusting the pH of the resulting concentrated solution to a value of 6.0 to 6.4 and finally heating the solution at a temperature of 90 to 100°C for at least 15 minutes.

The fresh meat enzymes used in the process according to the invention may be added, for example, as finely subdivided fresh, raw meat or as an extract of such meat. By "fresh meat" is meant raw meat obtained from the carcass of an animal slaughtered not more than 24 hours before use, or which has been preserved at low temperatures (deep-frozen) under conditions such that on thawing it is in all respect similar to the meat obtained from a carcass less than 24 hours after slaughter. In particular, the meat must possess enzyme activity by virtue of the presence of enzymes of the following 3 groups:—

proteolytic enzymes, particularly katepsins
enzymes degrading nucleotides such as adenosine triphosphate
enzymes capable of converting carbohydrates, particularly hexoses, into hexose phosphates, pentose phosphates and lactates.

Preferably, the amount of fresh meat used is between 1 and 15% by weight of the autolysate/hexose solution, or a quantity of extract corresponding to such an amount of fresh meat. An extract may be prepared using water or a solution of a salt such as sodium or potassium chloride. The meat is advantageously lean beef, and amounts within the range 3—5% by weight are highly satisfactory. Subdivision by colloid milling is particularly preferred.

The yeast autosylate preferably contains on a dry matter by weight basis, less than 2% of reducing substances. Among hexose glucose and fructose are preferred, and the dry matter content of the solution is advantageously around 20% by weight.

The treatment at pH 4 to 7 is of particular significance, and it is generally desired to maintain the enzyme/substrate mixture under these conditions for at least 48 hours. Particularly preferred treatment temperatures are 12°C and below, and the mixture may be maintained at these temperatures for 60 to 70 hours. It should, on the other hand, be noted that the treatment temperature is adjusted having regard to the pH, rather than vice versa, which means that if the temperature is maintained below 15°C, the pH may vary within the broad range of 4 to 7, whereas a pH of 4 to 6 is required if a temperature between 15 and 37°C is chosen. The pH adjustments may be made by addition of appropriate amounts of alkali, such as sodium hydroxide, or an organic or mineral acid, for example lactic acid, glutamic acid, aspartic acid or hydrochloric acid.

According to one particularly preferred em-

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bodiment of the invention, the pH may be varied during the treatment, within the defined limits. Furthermore, when the pH is between 4.0 and 6.0, the temperature may be raised above 15°C, which has a favourable effect on the kinetics of the enzyme reaction and allows the total treatment time to be shortened.

Upon completion of the treatment, and before concentration, the pH of the solution is preferably adjusted to a value of 4.8 to 5.5, desirably 5.0—5.2. This pH adjustment is desirable because loss of volatile aromas may be reduced in the subsequent concentration step, especially if evaporation is employed. Insoluble matter present in the solution may be removed before or after the pH adjustment. Concentration of the solution, desirably to about 60% by weight of dry matter, may be effected by classical techniques, such as evaporation, reverse osmosis or flashing.

The concentrated solution is then heated at 90—100°C for at least 15 minutes, preferably 40 minutes at 90°C, its pH having first been adjusted to a value between 6.0 and 6.4, e.g. 6.2. After heating, the concentrated solution may be dried, or used directly as a paste. If the paste is to be dried (spray or drum for example) its pH is advantageously lowered to 5.5 or below whereby aroma losses may be diminished. The concentrate may also be dried with a support or carrier such as corn syrup, starch or a gum.

The finished product has the characteristic flavour and aroma of roasted meat, and may be used in various foodstuffs, including soups, bouillons, prepared dishes, canned or frozen food items, snacks and the like, as well as for flavouring textured protein products obtained by spinning or extrusion of vegetable or microbial proteins.

A product having the aroma and flavour or a stock or bouillon prepared from fresh meat may be obtained by addition of a fat to the concentrated solution before it is heated. Depending on the flavour desired, beef or chicken fat may be added, at a level of 2.5 to 5.0% by weight of the solution.

Furthermore, extracts of vegetables such as celery, carrot or leek may also be added before heating. Such extracts may be prepared by conventional procedures, involving cooking, stripping, separation of insolubles and combination of stripped aromas with concentrated extract. The concentrated extracts may also be dried with a support such as malto-dextrin.

Finally, it is also possible to add various flavour precursors to the concentrated solution before heating, such as the following, expressed in parts per thousand of the dry matter content of the concentrated solution:—

cysteine	0.1—0.3
methionine	0.1—0.3
thiamine	0.05—0.2

Each of these substances may be added singly or in combinations of two or all three, if desired together with the optional ingredients noted previously (fats, vegetable extracts). Nucleotides such as inosine or guanosine monophosphate may be added to the finished product, at a level of 1—2% by weight on dry matter.

The invention is illustrated by the following examples, in which the percentages are by weight.

Example 1

An aqueous solution is prepared containing 1% of glucose and 20% dry matter of a yeast autolysate having the following composition:—

Total nitrogen	7.7%
Amino nitrogen	4.3%
Reducing substances	1.1%
NaCl	17.0%
P_2O_5	3.9%
Ash	22.6%
Glutamic acid	4.3%
Dry matter	79.5%

4% of fresh beef, ground in a colloid mill, are added to the solution, the mixture is cooled to 10—12°C and maintained at these temperatures, with stirring, for 60 hours. The pH is maintained at 5.

At the end of the treatment, insoluble solids are filtered off and the solution is concentrated by evaporation to about 60% solids. The pH of the concentrated solution is then raised to 6.2 and it is heated at 90°C for 40 minutes. The pH is then adjusted to 5.0 and the solution is spray-dried.

The resulting product has a strong flavour and aroma of roast beef.

Example 2

An aqueous solution of glucose and yeast autolysate is prepared as in Example 1, and 4% of fresh beef, ground in a colloid mill, are added. The mixture is cooled to 10—12°C and maintained at these temperatures, with stirring, for 60 hours. During this time the pH is adjusted periodically to different values, as shown in the table. It should be noted that between any two adjustments, the pH will itself have a tendency to decrease, so that the actual pH may be below the lowest adjusted value, particularly between 4.5 and 5.0 which is the most favourable range for the action of katepsins.

TABLE

Time (hours)	pH adjusted to
0 (start)	7.0
18	6.0
24	5.5
42	5.0
48	6.0
60	end of treatment

At the end of the treatment, insoluble matter is removed by centrifugation and the

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pH of the clarified solution adjusted to 5.1. The solution is then concentrated by evaporation to about 60% solids.

The pH of the concentrated solution is adjusted to 6.2 and 3% beef fat and 1% inosine monophosphate are added. The mixture is heated for 40 minutes at 90°C, the pH then adjusted to 5.0 and it is spray-dried.

The resulting product has the flavour and aroma of a bouillon prepared from fresh beef.

Example 3

An aqueous solution of glucose and yeast autolysate is prepared as described in Example 1, and 4% fresh beef, ground in a colloid mill, are added. The mixture is cooled with stirring to 10—12°C and maintained for 66 hours with periodic pH adjustment in accordance with the programme set out below:—

Time (hours)	pH adjusted to
0 (start)	7.0
18	6.0
24	5.5
42	5.0
56	6.0
66	end of treatment

Insoluble mater is then filtered off and the resulting solution is treated as described in Example 2.

The product has the flavour and aroma of a bouillon prepared from fresh beef, with a more meaty note than the product of Example 2.

It should be observed that the pH programme in the present example is such that, by reason of its own tendency to decrease, the pH of the mixture remains below 5.0 for 14 hours (42 to 56) which is particularly favourable for the action of katepsins, whereas in Example 2 the pH remains within this range for only 6 hours. This difference, resulting in a flavour improvement, emphasizes the significance of pH programming.

Example 4

An aqueous solution of glucose and yeast autolysate is prepared as described in Example 1. 4% of fresh beef, ground in a colloid mill are added. The mixture is cooled with stirring to a temperature of 10—12°C, and temperature and pH are adjusted periodically to different values in accordance with the programme set out below:—

Time (hours)	pH	Temperature
0 (start)	7.0	10—12
18	6.0	10—12
24	5.5	37
28	5.0	37
36	6.0	10—12, maintained until end of the treatment
48	end of treatment	

At the end of the treatment, the pH of the mixture is adjusted to 5.1 and insoluble matter removed by centrifugation.

The resulting solution is then concentrated by evaporation to about 60% solids.

The pH is adjusted to 6.2 and 0.25% parts per thousand cysteine, 0.25% parts per thousand methionine and 0.15% parts per thousand thiamine are added to this solution. This mixture is then heated at 90°C during 40 minutes and its pH is adjusted to 5.0.

The resulting product has the flavour and aroma of roast beef.

The features of the treatment described in this example are its duration, which is shorter than in the previous examples, and the temperature profile which has a maximum of 37°C during 12 hours. This raising of the temperature permits a reduction of the treatment time.

Example 5

20 g of fresh beef are ground in a colloid mill and suspended in 10 ml of a 2% solution of sodium chloride in distilled water. This suspension is maintained at 10°C for 3 hours with stirring, and insoluble matter is then removed by centrifugation. The insoluble matter is re-suspended at 10°C for 3 hours, with stirring, in 10 ml of 2% aqueous sodium chloride solution. After removal of insoluble matter, the two solutions are mixed, providing an extract of fresh meat.

The extract is added to 500 ml of an aqueous solution of glucose and yeast autolysate prepared as described in Example 1. The resulting solution is cooled and maintained at a temperature of 10—12°C and a pH of 5.0 for 60 hours.

At the end of the treatment, the pH is adjusted to 5.1, and the solution is concentrated by evaporation to about 60% solids. The pH is adjusted to 6.2 and 15 g of beef fat, 3 g of dried leek extract and 2 g of dried carrot extract are then added to the concentrated solution. The resulting mixture is then heated at 90°C for 40 minutes, the pH is adjusted to 5.0, and it is spray-dried.

The resulting powdered product has the flavour and aroma of a bouillon prepared from fresh beef.

WHAT WE CLAIM IS:—

1. A process for preparing a meat flavouring which comprises adding enzymes present in fresh meat to an aqueous solution containing yeast autolysate and a hexose, the total dry matter content and the hexose content of the solution not exceeding, respectively 25 and 1.5% by weight and the yeast autolysate being present in an amount of at least 15 times the weight of hexose, subjecting the resulting mixture to a treatment which comprises maintaining the pH of the solution between 4.0 and 7.0, and its temperature at below 37°C if the pH is between 4.0 and 6.0, or at below

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15°C if the pH is between 6.0 and 7.0, thereafter concentrating the solution to a dry matter content not exceeding 65% by weight, adjusting the pH of the resulting concentrated solution to a value of 6.0 to 6.4 and finally heating the solution at a temperature of 90 to 100°C for at least 15 minutes.

2. A process according to claim 1, in which the yeast autolysate has a content of reducing substances not exceeding 2% by weight on dry matter.

3. A process according to claim 1 or claim 2, in which the hexose is glucose or fructose.

4. A process according to any one of the preceding claims, in which the treatment is effected at a temperature below 12°C.

5. A process according to any one of the preceding claims, in which the enzymes are added to the solution of yeast autolysate and hexose, by mixing, as fresh, raw, subdivided meat.

6. A process according to claim 5, in which the amount of fresh meat added is 1 to 15% by weight of the solution.

7. A process according to any one of claims 1 to 4, in which the enzymes are added to the solution of yeast autolysate and hexose in the form of an aqueous extract prepared from fresh, raw meat.

8. A process according to any one of the preceding claims, in which the treatment is effected during at least 48 hours.

9. A process according to any one of the preceding claims, in which after the treatment and before concentration, the pH is adjusted to a value of 4.8 to 5.5.

10. A process according to any one of the preceding claims, in which before heating, the pH of the concentrated solution is adjusted to 6.2.

11. A process according to any one of the preceding claims, in which 2.5% to 5% by weight of fat are added to the concentrated solution before heating.

12. A process according to any one of the preceding claims, in which a vegetable extract is added to the concentrated solution before heating.

13. A process according to any one of the preceding claims, in which at least one of the following substances is added to the concentrated solution in the specified amounts:—

cysteine	0.1 to 0.3	parts per thousand on weight of dry matter in concentrated solution.
methionine	0.1 to 0.3	
thiamine	0.05 to 0.2	

14. A process according to any one of the preceding claims in which, after heating, the concentrated solution is dried.

15. A process according to claim 14 in which after heating and before drying, the pH of the concentrated solution is adjusted to a value not exceeding 5.5.

16. A process for preparing a flavouring agent substantially as herein described with reference to any one of the Examples.

17. A flavouring agent prepared by a process according to any one of the preceding claims.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1447730

1447730

(21) Application No. 12096/74 (22) Filed 19 March 1974
(31) Convention Application No. 342360 (32) Filed 19 March 1973 in
(33) United States of America (US)
(44) Complete Specification published 25 Aug. 1976
(51) INT CL² A23L 1/231 1/227 1/229
(52) Index at acceptance
A2B 6A

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(19) THE PATENT OFFICE LONDON

(54) EDIBLE COMPOSITIONS HAVING A MEAT FLAVOR AND PROCESSES FOR MAKING SAME

(71) We, INTERNATIONAL FLAVORS & FRAGRANCES INC., a corporation organised and existing under the laws of the State of New York, United States of America, having an office at 521 West 57th Street, New York, New York, 10019 United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

Background of the Invention

This invention relates to flavoring foodstuffs, to compositions for flavoring foodstuffs, and to the products so obtained.

Much attention has been devoted to improving the flavor of foodstuffs and particularly the flavors of meat products, fruits and confectioneries. There is also a need to provide compositions and processes for improving the flavors of meat products such as pâtés containing beef, lamb, chicken, duck or turkey meat, of for providing savory meat or poultry flavors to foods containing a low level of meat products originally having only a low level of flavor.

A substantial number of investigations have been carried out relating to reacting such materials as amino acids, hydrolysed vegetable proteins, sugars, sulfur-containing compounds (e.g., cysteine and hydrogen sulfide) and ribonucleotides in an effort to produce meaty tasting products including poultry meat tasting products, or ingredients therefor. Thus, for example, the following publications set forth such reaction products and methods for preparing same.

Publication	Reactants
(1) U.S. Patent 3,394,017	Poultry meat flavor produced by reacting thiamine and a mixture of amino acids.
(2) U.S. Patent 3,519,437	Poultry flavor produced by reacting thiamine and 2 - aminoethane sulfonic acid.
(3) U.S. Patent 3,532,514	Cysteine, sugar, fatty acid material.
(4) Belgian Patent 740,221	Reducing sugar and fish product extract.
(5) U.S. Patent 3,645,753	Enzymatic digest of meat extract hydrolysed vegetable protein and yeast autolysate.
(6) U.S. Patent 3,394,015	Sulfur-containing compound and hydrolysed vegetable protein (sugar-free).
(7) U.S. Patent 3,394,016	Thiamine and an aliphatic carboxylic acid.
(8) German Offen. 1,932,800	Hydrogen sulfide and a 4 - hydroxy - 2,3 - dihydrofuran - 3 - one.
(9) U.S. Patent 2,918,376	Fish protein hydrolysate and cysteine.
(10) U.S. Patent 2,887,387	Fish protein hydrolysate and saccharide.

However, none of the foregoing references, disclosing processed food flavoring materials, discloses the production of a natural meat-flavored material from reactants containing no egg product and having low protein levels and wherein one of the reactants is a meat enzymatic digest and another of the key reactants is a sulfur-containing compound. Although the above-mentioned U.S. Patent 3,645,753 describes reaction products wherein one reactant is an enzymatic digest of meat extract, and another reactant is a mixture of amino acids, e.g., hydrolysed vegetable protein, the reaction product disclosed does not have the full bodied meaty flavor with the substantially authentic mouthfeel of the flavors of this invention, and no sulfur-containing compound is set forth as one of the reactants. In addition, thiamine or a salt thereof or a precursor thereof is not included as one of the reactants.

The reaction product of cysteine and a hydrolysed vegetable protein of U.S. Patent 3,394,015 is different in kind from a reaction product produced under conditions disclosed in U.S. Patent 3,394,015 except that the hydrolysed vegetable protein is replaced with an enzymatic meat digest.

Copending British Application 51903/73 discloses a reaction product wherein all of the above-mentioned reactants are used to form such a reaction product except that meat enzymatic digest is not disclosed as one of the reactants and egg products are not omitted as reactants. The inclusion of egg products and the omission of enzymatic meat digest in this copending patent application gives rise to reaction products which are different in kind from those of our invention as set forth herein.

Copending British Application 51903/73 (Serial No. 1,444,793) also discloses a meat-flavored product produced by means of a heat reaction of (i) an egg product (e.g., egg yolk) which may or may not be enzymatically digested (ii) a meat product which may or may not be enzymatically digested and (iii) a sulfur compound such as cystine. The inclusion of an egg product in this copending patent application gives rise to reaction products which are different in kind from those of our invention as set forth herein. Furthermore the inclusion of an egg product may in several instances be detrimental where the individual ingesting the product is allergic to one or more of the chemical components of the egg.

This invention relates to novel meat (including poultry meat) flavoring compositions and to processes for preparing them.

The term "meat" in this disclosure is intended to include such edible animal protein as various types of beef, veal, pork, lamb chicken, turkey, and duck meat. Thus, the term "meat-like" is intended herein to not only include "beef-like" but also "poultry meat like".

Food products enhanced with meat-like flavorings are well known and have long been used. There is considerable demand for meat flavored and poultry flavored products wherein there is little if any actual beef, veal, pork, lamb or poultry meat and where larger quantities of such meats are either unnecessary or are actually undesirable. Thus, for example, in the preparation of sauces, gravies and purees a beef, veal, pork, lamb or poultry flavor is desired, but it is necessary to cook the desired meat and then remove said meat by straining or using some similar operation to obtain the final product ready for use.

Additionally, where weight, space and/or storage capacity are problems, e.g., when a convenience food is prepared, the presence of relatively large quantities of the actual meat may be undesirable because of deterioration problems in storage. Moreover, there are occasions when sterilising or otherwise preserving relatively larger concentrations of the natural product is extremely deleterious to the flavor of the natural materials and the desired natural flavor is lost.

United States Patents 3,394,015; 3,394,016; 3,394,017 and 3,519,437 as well as copending British Application 51903/73 in part, provide solutions to the aforementioned problems by providing methods for the production of poultry and other meat flavors which contain a substantial number of the notes of natural poultry and other meat flavors but which do not contain any actual meat products. However, these several patents and patent applications do not teach techniques for producing *highly intensified* and controlled meat or poultry flavors having mouthfeel and flavor nuances closely resembling those properties attributable to the actual natural meat and poultry meat flavors. Furthermore, the above-mentioned patents and copending patent application do not disclose our highly refined technique for reproducibly duplicating a specific desired meat or poultry flavor, (1) without including very substantial quantities of the actual meat, the flavor of which is desired to be duplicated in the initial reaction mass, and still (2) providing such highly intensified controlled meat or poultry flavors having mouthfeel and flavor nuances closely duplicating those of the said desired natural flavor. The term "controlled" is intended to mean the determination, in advance, of the specific quality of the flavor desired to be produced, (e.g., "reacted beef", "veal", "pork", "lamb", "duck meat", "white turkey meat", and "chicken meat") by using the appropriate reactants in the proper proportion.

Although the aforementioned publications and patent applications give rise to general meat flavor applications, the high degree of

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control of quality taken together with the high intensity and an ability to duplicate mouthfeel and substantially all of the flavor nuances of the various meat flavors is not taught therein.

Furthermore, although copending British Application 51903/73 (Serial No. 1,444,793) also disclosed processes for producing highly intensified controlled meat flavors having mouthfeel and flavor nuances closely resembling those properties attributable to actual natural meat flavors, the process encompassed by said earlier filed case (i) gives rise to meat flavors which are different in *kind* from those created by the process of our invention and (ii) require the use of an egg product or enzymatic digest thereof, specifically excluded from the process of our invention.

Accordingly, this invention provides specific reproducibly controlled beef, veal, pork, lamb and poultry flavors as desired, not only insofar as their flavor nuances are concerned but also insofar as the mouthfeel of such flavors are concerned produced without the need for using any egg components.

This invention also provides essentially natural particularly controlled meat flavored products which are suitable for incorporation into a wide range of foodstuffs.

According to the invention there is provided a process for preparing a flavoring composition comprising forming an intimate mixture of:—

(1) an enzymatic digest of meat; and

(2) a sulfur-containing compound selected from sulfur-containing amino-acids and salts thereof other than thiamine, thiamine precursors or salts thereof, alkyl mercaptans, alkyl sulfides, alkyl disulfides, aminoalkane sulfonic acids and salts thereof, hydrogen sulfide, and inorganic sulfur compounds of the general formula MSx (in which M is an alkali or alkaline earth metal or ammonium and Sx is sulfide, polysulfide, or hydrosulfide);

and heating the mixture in the absence of any egg product to produce a meat flavored composition.

The edible reaction products produced by the process of our invention are meat flavoring materials or bases. Accordingly, edible compositions having enhanced flavor and which comprises a food and the aforesaid reaction product are further within the scope of our invention. In addition, other reactants are used to modify or augment the particular meat flavor without changing, in kind, the resulting specific meat flavor produced. Thus, for example, acid salts of thiamine in the reaction mixture will give rise to a more natural intense meaty flavor but will not bring about a change in the specific nature of the meat flavor produced. Other materials that can be added in addition or in lieu of thiamine are thiazole alkanols (which are, for example, thiamine precursors) such as those described in United Statements Patent 3,681,088 and other free amino acids and polypeptides.

The enzymatic digest of meat such as enzymatic digest of turkey meat is produced by mixing said meat, preferably in the form of powder in aqueous media with an enzyme which has the ability to effect selective cleavage of the peptide bonds located in the molecular structure of the meat protein. The enzymes used in digesting the meat protein are as follows:

(1) Papain
(2) Pilzprotease S (produced by Roehm G.M.B.H., Darmstadt Germany)
(3) Rhozyme P 11 (produced by Rohm & Haas G.M.B.H., Darmstadt Germany)
(4) Bromelin
(5) Pepsin
(6) Trypsin
(7) J-25 (produced by Rohm & Hass Inc. of Philadelphia, Pa.)
(8) Protease 62 (produced by Rohm & Haas Inc. of Philadelphia, Pa.)
(9) HT Proteolytic 200 (produced by Marschall Division of Miles Laboratories, Inc. Elkhart, Indiana)
(10) Fungal Protease (produced by Marschall Division of Miles Laboratories, Inc. Elkhart, Indiana)
(11) Prolase MT-7820 (produced by Wallerstein Laboratories of Martin Grove, Illinois)
(12) Molsin (produced by Seishin Pharmaceuticals Ltd. Noda Shiba, Japan)
(13) Mylase
(14) Baktierian Protease N (produced by Roehm G.M.B.H., Darmstadt (Germany)
(15) Protease enzymes produced according to the processes set forth in German Offen. 2,063,988, published on July 28, 1972 and assigned to Henkel & Cie G.M.B.H.

Of all of the above mentioned enzymes, the most preferred for digesting meat protein from both a commercial standpoint and organoleptic standpoint for the purpose of this invention are pepsin and mylase.

Furthermore, when producing the enzymatic digest of the above mentioned meat protein material, it is preferred to mix the enzyme with the meat material at a temperature of from 40°C up to 75°C in aqueous media for a period of time from 10 hours up to 150 hours. Periods of time greater than 200 hours and/or temperatures higher than 75°C will give rise to a product which is less desirable for the purpose of subsequent reaction with the sulfur-containing compound. On the other hand, temperatures below 40°C and/or times of mixing below

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10 hours will give rise to only a partially enzymatically digested meat product which would not give rise to a product having predictable flavor nuances, mouthfeel and texture properties. Furthermore, in producing the above mentioned enzymatic digest, it is important that proper pH adjustments be made on the enzyme-protein material-water mix, prior to incubation. Suitable pH ranges vary from 3 up to 6 and constant pH's are obtainable by using appropriate buffers, e.g. sodium citrate and sodium diacid phosphate of a pH of 4.6.

The term "sulfur-containing compounds" is intended to mean sulfur-containing amino acids and salts thereof which have the ability to liberate hydrogen sulfide when reacted, or alkyl mercaptans, or alkyl sulfides, or alkyl disulfides, or amino alkane sulfonic acids or salts thereof, e.g. the sodium salts of amino ethane sulfonic acid (taurine). The term "sulfur-containing compounds" may also include an inorganic sulfur compound or hydrogen sulfide itself, each of which is adapted to liberate a flavor under heating with the enzymatic digest. Such inorganic sulfur compounds are designated herein as having the formula MS_x, wherein M is selected from the group consisting of an alkali metal (e.g. sodium or potassium), an alkaline earth metal (e.g. calcium or magnesium) and ammonium and S. is selected from the group consisting of sulfide, polysulfide and hydrosulfide.

When hydrogen sulfide or a alkyl mercaptan is used, it is necessary to control the amount used so as to avoid overpowering the aroma of the product with the aroma of the mercaptan or the hydrogen sulfide. The alkyl mercaptans and sulfides preferably contain from 1 up to 6 carbon atoms. The alkyl disulfides preferably contain 1 to 3 carbon atoms. Cysteine and methionine and their salts, such as cysteine hydrochloride, are especially preferred sulfur-containing amino acids or salts thereof. Especially preferred products resembling natural flavor and having the natural texture and mouthfeel attributable to such natural flavor are produced by means of first producing a mylase enzymatic digest of powdered chicken meat and then heating a mixture of such enzymatic digest with cysteine hydrochloride in the absence of any egg products.

Cysteine and cystine are sulfur-containing amino acids readily available as free amino acids or as salts, both acid and basic. Preferably, the acid salts, especially the halogen acid salts, such as the hydrochloride, are utilized. The inorganic sulfur-containing compounds mentioned above include sodium hydrosulfide and sodium sulfide. Instead of sodium compounds, corresponding compounds of potassium, calcium and ammonium may be used. Any such compound employed must be capable of reacting to give the desired specific natural meat note.

Other organic sulfur-containing compounds useful in the practice of our invention include methyl mercaptan, ethyl mercaptan and propyl mercaptan, dimethyl sulfide, dimethyl disulfide and methyl ethyl sulfide.

The term "sulfur-containing compounds" as used herein is not intended to include thiamine or thiamine precursors or acidic or basic salts of thiamine. Such thamine salts or precursors of thiamine or thiamine per se are used preferably *in addition* to the "sulfur-containing compounds" of our invention in the reaction mass.

Additional flavor nuances may be introduced into the reaction product of our invention by incorporating into the reaction mass prior to or during the heat reaction, thiazole derivatives, such as, for example, thiamine hydrochloride and/or 4 - methyl - 5 - (β - hydroxyethyl) - thiazole. Instead of using thiamine hydrochloride, the thiamine may be used as a free base; but it is preferably employed as an acid salt and, indeed, the hydrochloride is especially suitable. In addition, free amino acids, such as alanine, leucine, valine, glutamic acid and/or various polypeptides including dipeptides and tripeptides may also be added to the reaction mass prior to or during the heat reaction process. In addition, quantities of nucleotides may be added prior to, during or subsequent to the reaction between the sulfur-containing compound and meat powder enzymatic digest. The preferred nucleotides used in the practice of this invention are mixtures of disodium inosinate and disodium guanylate. In addition, prior to or during the reaction between the sulfur-containing compound and the enzymatic meat digest, a quantity of a saccharide material such as d-xylose, ribose, sucrose, and dextrose may be added in order to modify the resulting meat type flavor.

When producing specific poultry meat flavors, alkyl carbonyl materials, such as ketones and alkyl aldehydes can be mixed into the reaction system during or subsequent to the heating step. It is generally preferred to add these materials after heating the reaction mass since they are generally volatile, and losses thereof may occur during the heating. The ketonic materials used in this aspect of the invention are preferably alkanones and hydroxy-substituted alkanones containing from 4 to 8 carbon atoms such as diacetyl, acetyl-methylcarbinol and acetylpropionyl. The alkyl aldehydes are preferably the aldehydes containing from 5 up to 12 carbon atoms. Especially preferred are n-pentanal, n-hexanal, n-heptanal, 2,4-nonadienal, 2,4-decadienal, and 2,4-undecadienal. Conveniently, these aldehydes and/or ketones are

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employed at levels ranging from 0.01 up to 0.1 times the weight of the meat powder enzymatic digest used.

The reaction between the sulfur-containing compound and the meat powder enzymatic digest is preferably carried out at reflux conditions (usually over 100°C) at pressures of between 1 and 10 atmospheres for periods of times of from 0.2 up to 10 hours. It is to be emphasized that, generally, temperatures above 400°C make the reaction difficult to control and may well produce uncharacteristic burnt notes even with very short reaction times (e.g. of the order of 10—20 minutes). Accordingly, it is preferred to carry out the reaction at temperatures of from 100°C up to 350°C; until the desired flavor development is achieved. As stated above, the heating periods may range from about 0.2 hours up to about 10 hours depending upon the heating method used.

Where it is desired, the process can be carried out on a batch basis in small quantities of, for example, 50 to 100 grams or it can be carried out batchwise, semi-continuously, or continuously on much larger quantities of 500 kilograms or more.

In preparing the enzymatic meat digest a preferred ratio of enzyme to meat material (e.g. turkey powder) is from 0.1% up to 1%; preferably from 0.1% up to 0.4%. The weight percent of sulfur-containing compound based on enzymatic meat digest is from 15% up to 20%; preferably between 2% and 5%. Where it is desired to use thiazole derivatives for the purpose of introducing additional flavor nuances into the product of our invention, the weight ratio of thiazole derivatives (e.g. thiamine hydrochloride) to sulfur-containing compounds is between 0.25:1 and 1:1; preferably 0.5:1. Where it is desired to use a saccharide material in the reaction mass in order to introduce still additional flavor nuances into the product of our invention, the weight ratio of saccharide to sulfur-containing compound is between 1:100 and 1:3; preferably 1:6.

It should be noted that the presence of the saccharides in the reaction mass gives rise to a reaction product having somewhat intense sweet meat flavor characteristics (e.g. poultry or sweet port nuances). Care should be exercised in utilizing such saccharides, however, since they may tend to contribute some burnt notes to the ultimate reaction product. When used, suitable results are obtained at levels ranging up to about 25% by weight based on the total weight of the reaction mass. Preferably the range is from 0.5 to 5 weight percent of the overall reaction mass. This range is further limited by the preferred ratio of saccharide to sulfur-containing compound.

Preferably, but not necessarily, a large weight excess of water or other reaction medium (e.g., beef fat, vegetable fat, chicken fat, duck fat, and fatty acid glycerides, such as "Neobee M-5" produced by the Drew Chemical Division of U.S. Filter Corporation or fish oil or mixtures of such fats and oils with water either in emulsified or non-emulsified forms) is used in preparing the enzymatic meat digest used in practising our invention, although such excess is not essential. Varying amounts of water or fat or fish oil, for example from about 1:1 up to about 10:1 by weight based on the total weight of the remainder of the enzymatic meat digest can be used. In the case of aqueous mixtures after mixing of the enzymatic meat digest with the sulfur-containing compound and after the subsequent reaction with the sulfur-containing compound the water can be at least partially evaporated to produce a solid or a semi-solid edible composition. When using triglyceride fats, the fatty acids predominantly range in carbon chain length from 20 carbon atoms to 22 carbon atoms. The term "triglyceride fat" will be understood to mean both fats and oils. It is preferred that the triglyceride fats be refined, bleached and deodorized. They can be in their natural form or they can be hydrogenated.

The quantity of reaction product utilized in the practice of our invention when added to a foodstuff can be varied to provide a wide range of meaty flavors. At levels as low as 0.1%, the reaction product begins to impart a very light, almost undefinable sensation in aqueous solution. As the level is increased to 0.2%, a different pleasant meaty like character is imparted to an aqueous solution. As the level reaches 0.5% a definite, good characteristic beef, veal, pork, lamb or poultry meat like flavor and aroma is obtained and this level persists up to levels of 2% and beyond, where the substance leaves a light, lingering after taste. At levels higher than 1% not only is the specific meat flavor indistinguishable from the natural meat flavors but the mouthfeel and texture provided by the reaction product of our invention are substantially identical to those properties provided by the natural meat flavor desired. All parts, proportions, percentages and ratios herein are by weight unless otherwise indicated.

The reaction product of our invention can be added in pure form to foodstuffs or in admixture with other flavors and/or aroma imparting ingredients and/or in admixture with other non-toxic edible solvents (e.g. water, ethanol, wines and liqueurs), thickeners (e.g. starch paste) carriers and extenders (e.g. bread crumbs). The resulting mixtures may be used as such or may be further processed as by heating.

It will be understood by those skilled in the art that regardless of the purity of the

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reactants used they should contain no noxious or noisome components which would interfere with the flavor conferred on foodstuffs or on its safety for use in edible materials.

It is contemplated herein that foodstuffs flavored according to this invention include both solid and liquid preparations for oral consumption by human beings and by animals particularly warm-blooded domestic animals, such as are used for pets or raised for consumption.

The products of our invention may be provided as dry solids, in liquid mixtures or in pastes. Preferably, they are prepared by heating, in the absence of any egg products such as egg yolk, the meat powder enzymatic digest in conjunction with the sulfur-containing compound wherein at least one of the foregoing materials is mixed with its equal weight of water. The resulting end product may be used as such, or it may be concentrated for use. If solid products are desired, the same may be obtained by drying the liquid mixtures. The aqueous compositions are dehydrated by spray-drying although drum-drying, freeze-drying and other drying procedures are also applicable to the reaction product of our invention. A solid carrier is often added to the liquid mixture before drying.

When carrying out the spray-drying process which is the preferred drying process, we have found that carriers are useful in extending the flavor of our products when so prepared. These carriers do not diminish the quality of the flavor, but they stabilize it and increase the shelf life of the product. Polysaccharides having relatively complex structures such as gum arabic, gum tragacanth, gum karaya and guar gum and mixtures of same are useful, as are cellulose derivatives such as methyl cellulose and carboxy methyl cellulose or partially hydrolysed starch such as dextrin.

In a preferred process, an aliquot of the liquid composition is dried and the flavor solids content of the composition determined. An amount of carrier substantially equal to the calculated solids content of the liquid composition is added thereto and the mixture dried, preferably by spray-drying. Alternatively, an amount of carrier substantially equal to the combined weight of the meat enzymatic digest and sulfur-containing compound is added to the liquid composition after reaction of the ingredients and the mass is then dried. The preferred amounts of carrier are from 0.2:1 up to about 2:1 based on the solids content of the liquid mixture.

The following examples, with the exception of examples A to G which illustrate the process for producing enzymatic digests for use in other examples, illustrate the invention. In the examples, the various ingredients are listed in parts by weight.

EXAMPLE A

Into a 300 m l flask equipped with stirrer, thermometer and heating mantle the following materials are placed:

50 grams—ground raw beef burger meat (ground chuck)
100 ml—water
0.20 grams—Mylase enzyme

The pH of the contents of the flash is adjusted to exactly 5.0 by addition thereto of phosphoric acid. The contents of the flask is prepasteurized for 30 minutes at 60°C. The contents of the flask are then incubated at 50°C using agitation (250 RPM) for a period of 120 hours. The resulting enzymatic beef digest is used in the reaction flavoring as set forth in the several examples following.

EXAMPLE B

The procedure of Example A is repeated except using ground raw pork meat instead of ground raw beef burger meat. The resulting enzymatic pork digest is used in the reaction flavoring as set forth in the several examples following.

EXAMPLE C

The procedure of Example A is repeated except using ground raw leg of lamb instead of ground raw beef burger meat. The resulting enzymatic lamb digest is used in the reaction flavoring as set forth in the several examples following.

EXAMPLE D

The procedure of Example A is repeated except using ground raw turkey meat instead of ground raw beef burger meat. The resulting enzymatic turkey digest is used in the reaction flavoring as set forth in the several examples following.

EXAMPLE E

The procedure of Example A is repeated except using ground raw chicken meat instead of ground raw beef burger meat, and only 0.10 grams of Mylase enzyme are added. The resulting enzymatic chicken digest is used in the reaction flavoring as set forth in the several examples following.

EXAMPLE F

The procedure of Example D is carried out using the following quantities of turkey meat paste and enzymes except that the pH of each of the mixtures is first adjusted to 4.6. using a buffer which is a one molar solution of sodium citrate and sodium diacid phosphate:

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Quantity of Turkey Powder	Enzyme and Quantity
100 gms.	0.1 gms. prolase
100 gms.	0.1 gms. bromelain
100 gms.	0.1 gms. papain
100 gms.	0.1 gms. pilzprotease S
75 gms.	0.1 gms. rhozyme P 11
75 gms.	0.1 gms. bromelin
50 gms.	0.1 gms. pepsin
50 gms.	0.1 gms. trypsin
50 gms.	0.1 gms. J-25
50 gms.	0.1 gms. protease 62
50 gms.	0.1 gms HT proteolytic 200
40 gms.	0.1 gms. fungal protease
25 gms.	0.1 gms. prolase MT-7820
25 gms.	0.1 gms. molsin
25 gms.	0.1 gms. mylase
20 gms.	0.1 gms. bakterien
20 gms.	0.1 gms. protease

Each of the resulting enzymatic turkey meat digests are used, separately, in the reaction flavoring as set forth in the several examples following.

EXAMPLE G

The procedure of Example E is carried out using the following quantities of chicken meat paste and enzymes except that the pH of each of the mixtures is first adjusted to 4.6 using a buffer which is a one molar solution of sodium citrate and sodium diacid phosphate:

Quantity of Chicken Meat paste	Quantity of Enzyme
100 gms.	0.1 gms. prolase
100 gms.	0.1 gms. bromelain
100 gms.	0.1 gms. papain
100 gms.	0.1 gms. pilzprotease S
75 gms.	0.1 gms. rhozyme P 11
75 gms.	0.1 gms. bromelin
50 gms.	0.1 gms. pepsin
50 gms.	0.1 gms. trypsin
50 gms.	0.1 gms. J-25
50 gms.	0.1 gms. protease 62
40 gms.	0.1 gms. HT proteolytic 200
25 gms.	0.1 gms. fungal protease
25 gms.	0.1 gms. prolase MT-7820
25 gms.	0.1 gms. molsin
20 gms.	0.1 gms. mylase
20 gms.	0.1 gms. bakterien

Each of the resulting enzymatic chicken digests are used separately in the reaction flavoring as set forth in the several examples following.

EXAMPLE 1

32 Grams of the enzymatic turkey meat digest from Example D, 1500 grams of water, 8.8 grams of cysteine hydrochloride and 29.4 grams of thiamine hydrochloride are intimately mixed. The resulting mixture is refluxed at atmospheric pressure for a period of four hours with stirring. The resulting slurry is then cooled and filtered. 1.4 kilograms of the filtrate is then intimately mixed with 623 grams of a 45% aqueous gum arabic solution and the resulting mixture is spray-dried. The resulting solid spray-dried material has an excellent natural-like turkey meat flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 2

The procedure of Example 1 is repeated except using the enzymatic lamb meat digest from Example C. The resulting solid spray-dried material has an excellent natural-like lamb meat flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 3

The procedure of Example 1 is repeated except using the enzymatic pork meat digest from Example B. The resulting solid spray-dried material has an excellent natural-like pork meat flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 4

The procedure of Example 1 is repeated except using the enzymatic beef meat digest from Example A. The resulting solid spray-dried material has an excellent natural-like beef meat flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 5

0.704 Kilos of cysteine hydrochloride, 0.19 kilos enzymatic chicken meat digest from Example E and optionally 0.352 kilos of thiamine hydrochloride is added to a pressurised scraped wall "Giusti" reaction vessel and the reaction vessel is operated for a period of 30 minutes at a temperature of 130°C and at a pressure in the range of from 2 up to 3 atmospheres. The reaction mass is then cooled yielding a product having an excellent chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 6

Separately, each of the enzymatic turkey meat digests from Example F are mixed with 8.8 grams cysteine hydrochloride, 29.4 grams of thiamine hydrochloride and 400 grams of water. Each of the resulting mixtures is refluxed at atmospheric pressure for periods of four hours with stirring. Each of the resulting slurries is then cooled and filtered. 250 Grams of each of the filtrates is

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then mixed with 125 grams of a 45% aqueous gum arabic solution and each of the resulting mixtures is spray-dried. Each of the resulting solid spray-dried materials has an excellent natural turkey meat flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 7

The procedure of Example 6 is repeated except using each of the enzymatic chicken meat digests from Example G. Each of the resulting solid spray-dried materials has an excellent natural chicken meat flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 8

150 Grams of the enzymatic chicken meat digest from Example E, 400 grams of water, 26.25 grams of cysteine hydrochloride, 13.25 grams of thiamine hydrochloride and 4.4 grams of d-xylose are intimately mixed. The resulting mixture is then refluxed at atmospheric pressure for a period of four hours with stirring. The resulting product has an excellent intense chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 9

The procedure of Example 8 is carried out except using 1000 grams of Neobee M-5 instead of water. The resulting product has an excellent chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 10

68 Grams of cysteine hydrochloride, 500 grams of water, 30 grams of the enzymatic chicken meat digest from Example E and 34 grams of thiamine hydrochloride are intimately mixed. The resulting slurry is then heated to reflux and maintained at reflux with stirring for a period of four hours. The resulting slurry is filtered yielding 0.51 kilograms of filtrate. An aliquot of the filtrate is withdrawn and dried. Based on the weight of the dry product obtained, sufficient gum arabic is added to the filtrate to provide a composition containing one part by weight of flavor solids and one part by weight of gum arabic. The composition is then spray-dried to produce a dry product with an intense chicken flavor having a very close resemblance to natural chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 11

12.75 Grams of cysteine hydrochloride, 800 grams Neobee M-5, 20 grams of the enzymatic chicken meat digest from Example G and 6.375 grams of thiamine hydrochloride are intimately mixed. The resulting mixture is refluxed for a period of four hours with stirring. 0.8 Kilograms of the resulting flavor is then mixed with 0.356 kilograms of a 45% aqueous gum arabic solution and the resulting mixture is spray-dried yielding 315 grams of a product having a flavor closely resembling natural chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 12

80 Grams of the enzymatic chicken meat digest from Example E, 8.8 grams of cysteine hydrochloride, 4.4 grams of thiamine hydrochloride and 1030 grams of water are intimately mixed. The resulting slurry is then heated to reflux at one atmosphere absolute pressure and maintained at reflux with stirring for a period of four hours. The resulting slurry is divided into two equal portions; portion A and portion B. Portion A is filtered. An aliquot of the filtrate is withdrawn and dried. Based on the weight of the dry product obtained, sufficient gum arabic is added to the filtrate to provide a composition containing one part by weight of flavor solids and one part by weight of gum arabic. The composition is then spray-dried to produce a dry product with an intense chicken flavor having a very close resemblance to natural chicken flavor (Product A) insofar as flavor nuances, mouthfeel and texture are concerned. Product B (portion B produced supra) also has an intense chicken flavor having a very close resemblance to natural chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 13

300 Grams of the enzymatic chicken meat digest from Example E, 500 grams of water, 68 grams of 2-amino ethane sulfonic acid sodium salt (taurine) and 34 grams of thiamine hydrochloride are intimately mixed. The resulting slurry is then heated to reflux and maintained at reflux with stirring for a period of four hours. The resulting slurry is filtered yielding 0.50 kilograms of filtrate. An aliquot of the filtrate is withdrawn and dried. Based on the weight of the dry product obtained, sufficient gum arabic is added to the filtrate to provide a composition containing one part by weight of flavor solid and one part by weight of gum arabic. The composition is then spray-dried to produce a dry product with an intense chicken flavor having a very close resemblance to natural chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 14

44 Grams of cysteine hydrochloride, 600 grams of water, 70 grams of the enzymatic

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chicken meat digest from Example E and 22 grams of thiamine hydrochloride are intimately mixed. The resulting mixture is then heated at reflux for a period of four hours. To 1/2 kilogram of the resulting product 2.22 kilograms of a 45% aqueous gum arabic solution is added. The resulting mixture is spray-dried to produce an excellent chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 15

200 Grams of the enzymatic turkey meat digest from Example D, 2000 grams of water, 58.8 grams of cysteine hydrochloride and 29.4 grams of thiamine hydrochloride are intimately mixed. The resulting mixture is refluxed at atmospheric pressure for a period of four hours with stirring. The resulting slurry is then cooled and filtered. 1.4 Kilograms of the filtrate is then intimately mixed with 623 grams of a 45% aqueous gum arabic solution and the resulting mixture is spray-dried. The resulting solid spray-dried material has an excellent natural-like turkey meat flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 16

0.45 Kilos of the enzymatic chicken meat digest from Example E, 1 kilo of Neobee M-5, 128 grams of cysteine hydrochloride and optionally 64 grams of thiamine hydrochloride are intimately mixed. The resulting mixture is refluxed for a period of four hours with stirring. 0.9 Kilograms of the resulting flavor is then mixed with 0.356 kilograms of a 45% aqueous gum arabic solution and the resulting mixture is spray-dried yielding 315 grams of a product having a flavor closely resembling natural chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 17

Into a pressurised scraped wall "Giusti" reaction vessel the following materials are introduced; 0.704 kilos of cysteine hydrochloride, 0.704 kilos of the enzymatic chicken meat digest from Example E and 0.352 kilos of thiamine hydrochloride. The reaction vessel is operated for a period of 30 minutes at a temperature of 130°C and at a pressure in the range of from 2 up to 3 atmospheres. The reaction mass is then cooled yielding a product having an excellent chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 18

58 Grams of the enzymatic chicken meat digest from Example E, 800 grams of Neobee M-5, 68 grams of 2-amino ethane sulfonic acid sodium salt (taurine) and 34 grams of thiamine hydrochloride are intimately mixed. The resulting slurry is then heated to reflux and maintained at reflux with stirring for a period of four hours. The resulting slurry is filtered yielding 0.51 kilograms of filtrate. An aliquot of the filtrate is withdrawn and dried. Based on the weight of the dry product obtained, sufficient gum arabic is added to filtrate to provide a composition containing one part by weight of flavor solid and one part by weight of gum arabic. The composition is then spray-dried to produce a dry product with an intense chicken flavor having a very close resemblance to natural chicken flavor insofar as flavor nuances, mouthfeel and texture are concerned.

EXAMPLE 19

A chicken soup is prepared by mixing together

Ingredient	Grams
Salt	5.00
The spray dried flavoring of Example 1	6.00
Gelatin (180 bloom)	1.00
Monosodium glutamate	.40
Caramel color	.40
Garlic powder	.10
White pepper, ground	.06
Mixed vegetable pieces	36.00

Three cups of water are added to the above mixture; and the mix is brought to a full boil, simmered for five minutes, and is then ready to serve.

The spray dried flavor of Example 1 may be replaced by any one of the spray dried flavorings produced from Examples 6, 7, 11, 14, or 16, or either of products A or B produced from Example 12 to prepare soup.

EXAMPLE 20

The following ingredients are admixed to form a chicken soup concentrate:

Ingredients	Grams
Salt	312
Hydrogenated peanut oil	260
Monosodium glutamate	155
Chicken flavoring produced by Example 8	—78
Turmeric extract in 10% ethyl alcohol	5.2
Spices	26
Hydrolysed vegetable protein	156
Dried parsley leaf	5.2

20 grams of the foregoing concentrate is admixed with one litre of water at a temperature of 85°C. The resulting mixture is refluxed for a period of three minutes yielding a flavorful chicken soup.

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The chicken flavor produced from Example 8 may be replaced by the flavoring product from Example 9 to prepare soup concentrate.

WHAT WE CLAIM IS:—

1. A process for preparing a flavoring composition comprising forming an intimate mixture of:—

(1) an enzymatic digest of meat; and

(2) a sulfur-containing compound selected from sulfur-containing amino-acids and salts thereof, other than thiamine, thiamine precursors or salts thereof, alkyl mercaptans, alkyl sulfides, alkyl disulfides, aminoalkane sulfonic acids and salts thereof, hydrogen sulfide, and inorganic sulfur compounds of the general formula MSx (in which M is an alkali or alkaline earth metal or ammonium and Sx is sulfide, polysulfide or hydrosulfide);

and heating the mixture in the absence of any egg product to produce a meat flavored composition.

2. The process of claim 1 in which the mixture comprises also at least one thiazole derivative.

3. The process of claim 2 in which the thiazole derivative is thiamine or a salt thereof.

4. The process of claim 3 in which the thiazole derivative is thiamine hydrochloride.

5. The process of claim 2 in which the thiazole derivative is thiazole alkanol.

6. The process of any of claims 2 to 5 in which the at least least one thiazole derivative is present in a weight ratio of 0.25:1 to 1:1 based on the sulfur-containing compound.

7. The process of any preceding claim in which the mixture comprises also at least one free amino acid or polypeptide apart from the sulfur-containing compound.

8. The process of any preceding claim in which the mixture comprises also at least one nucleotide.

9. The process of claim 8 in which the mixture comprises, as the said at least one nucleotide, a mixture of disodium ionsinate and disodium guanylate.

10. The process of any preceding claim in which the mixture comprises also at least one saccharide.

11. The process of claim 10 in which the saccharide is d-xylose, sucrose, or dextrose.

12. The process of claim 11 in which the weight ratio of saccharide to sulfur-containing compound in the mixture is between 1:100 and 1:3 and the saccharide is present in an amount of 0.5—5 wt% of the total mixture.

13. The process of any preceding claim in which the meat digest is of chicken meat with papain.

14. The process of any of claims 1 to 12 in which the meat digest is of raw turkey meat with mylase.

15. The process of any of claims 1 to 12 in which the meat digest is of meat with one of the enzymes hereinbefore specifically mentioned in description.

16. The process of any preceding claim, comprising also the prior step of preparing the meat digest by digesting meat with the enzyme at 40—75°C. in an aqueous medium at pH 3—6 for 10—150 hours.

17. The process of claim 16 in which the meat is digested with 0.1 to 1.0% of its own weight of enzyme.

18. The process of any one of claims 1 to 17 in which the sulfur-containing compound is cysteine, methionine, or an acid salt thereof.

19. The process of claim 18 in which the sulfur-containing compound is L-cysteine hydrochloride.

20. The process of any preceding claim in which the mixture contains 1 to 20 wt% of the sulfur-containing compound, based on the meat digest.

21. The process of claim 20 in which the mixture contains 2 to 5 wt% of the sulfur-containing compound based on the meat digest.

22. The process of any preceding claim in which the mixture is heated under reflux in an aqueous medium at 100—350°C and 1—10 atmospheres pressure for 0.2 to 10 hours.

23. The process of any preceding claim in which, during or after heating, an alkyl carbonyl compound is added to the mixture.

24. The process of claim 23 in which the said carbonyl compound is an alkanone or hydroxy-substituted alkanone containing 4—8 carbon atoms or an alkyl aldehyde containing 5 to 12 carbon atoms, and is added in an amount of 0.01 to 0.1 times the weight of digest.

25. The process of any of claims 1 to 24 in which, after heating, the composition is mixed with a carrier and spray-dried.

26. The process of claim 25 in which the carrier is gum arabic.

27. The process for the production of a flavoring composition substantially as hereinbefore described in any of Examples 1 to 18.

28. A flavoring composition whenever produced by the process of any of claims 1 to 27.

29. Foodstuffs comprising a nutritious material and an organoleptically modifying amount of a composition of claim 28.

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30. The foodstuff of claim 29 containing 0.1—2 wt% of the said composition.

31. A foodstuff containing an organoleptically modifying amount of flavoring composition substantially as hereinbefore described in Examples 19 or 20.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 471 907

1 471 907

(21) Application No. 36053/74 (22) Filed 15 Aug. 1974
(31) Convention Application No. 48/093 194
(32) Filed 20 Aug. 1973 in
(33) Japan (JA)
(44) Complete Specification published 27 April 1977
(51) INT CL² A23L 1/231
(52) Index at acceptance A2B 6A 6G
(72) Inventors KYOSUKE ISHIGURO and TAKEHIKO ICHIKAWA

(19) 

(54) FLAVOURING AGENTS AND PROCESS FOR THEIR PRODUCTION AND USE

(71) We, AJINOMOTO CO., INC., a corporation organized under the laws of Japan, of No. 6, 1-chome, Kyobashi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flavouring agents, more particularly those capable of imparting a beef-like flavour to food; and to processes for the production and use of such agents.

Many flavouring agents are known to impart a meat-like flavour to other food products. Examples of such agents are meat extract, hydrolyzed vegetable protein, yeast extract and mixtures of amino acids. Such agents are widely used in the food processing industry, but supply cannot keep up with increasing demand because of a lack of raw materials.

It is known from British Patent Specification No. 1,126,889 that ribose 5-phosphate reacts with amino acids, particularly lysine, at a temperature of from 100° to 250°C to produce a meat-flavoured composition. It has now been found that much stronger flavour more similar to that of beef can be obtained by the reaction at from 60° to 250°C of ribose or ribose 5-phosphate with protein having a relatively high molecular weight, and that the blood plasma of animals is a readily available, inexpensive source of such protein.

Accordingly, one aspect of the present invention provides a flavouring agent capable of being produced by heating a mixture of ribose or ribose 5-phosphate and a protein of animal origin at a temperature in the range from 60° to 250°C until the mixture assumes the flavour of cooked beef.

Another aspect of the present invention provides a process for producing a flavouring agent, which comprises heating a mixture of ribose or ribose 5-phosphate and a protein of animal origin at a temperature in the range from 60° to 250°C until the mixture assumes the flavour of cooked beef.

The mixture can be dispersed in, for example, water or liquid fat or oil, during the heating.

As beef or pig blood is readily available at low cost, these particular animal blood plasma solids are preferred.

Another aspect of the present invention, provides a process for imparting a beef-like flavour to an edible material. This can be effected by incorporating the flavouring agent in the material while the latter is being cooked.

The reaction between ribose or ribose 5-phosphate and protein in the form of blood plasma solids of animal blood occurs more readily and in the best yield when conducted in the presence of water, but does not appear to involve hydrolysis of the protein prior to reaction with the ribose or ribose 5-phosphate, because the flavour produced by reacting the hydrolyzation products of the same protein with the ribose or ribose 5-phosphate is not a comparably strong meat flavour.

Other proteins of animal origin react with ribose or ribose 5-phosphate in the same manner as blood plasma solids, but are not so economically attractive at this time. The flavouring agent of the present invention may be produced *in situ*, that is directly in the edible liquid or solid that it is desired to flavour providing that the edible material undergoes processing at a temperature and for a period sufficient to perform the reaction between protein and the ribose or ribose 5-phosphate. If the plasma solids (or other protein solids) are reacted with ribose or ribose 5-phosphate in an aqueous medium, the reaction product may be recovered as a powder by spray drying or freeze drying. It has the characteristic flavour of boiled meat, particularly boiled beef, and imparts such flavour to food to which it is added. When a mixture of blood plasma solids and ribose or ribose 5-phosphate is heated in the presence of fat, a

flavour closely similar to that of broiled or fried beef is obtained.

The ratio of ribose or ribose 5-phosphate to protein may be varied over a wide range, for example 0.01 part to 10 parts by weight ribose or ribose 5-phosphate per part by weight of protein, but best results are usually achieved within the narrower range of 0.1 part to 3 parts by weight ribose or ribose 5-phosphate per part by weight of protein. The temperature and time for obtaining the desired flavour are inversely related in the usual manner. The temperature may be selected from the range from 60° to 250°C. At temperatures of 100°C or less, the necessary processing time is generally between ten minutes and three hours; at higher temperatures, during frying or broiling, the necessary time varies between 15 seconds and 30 minutes, and factors other than temperature may affect optimum timing.

The flavouring agents of the present invention are compatible with known seasoning agents and may be used jointly with such agents. The flavouring agents of the present invention may be added to food as a dry powder, in the manner of salt or pepper; as a concentrated liquid in which water, an edible organic solvent or an edible oil provides the liquid phase; or as a semi-solid paste in combination with other ingredients which may have flavouring effects on their own.

A strong meat flavour may be imparted to non-meat food or to meat of poor quality by the flavouring agents of the present invention whether the latter are prepared separately or directly in admixture with the edible material.

The following Examples are further illustrative of the present invention.

EXAMPLE 1.

Beef cattle blood was centrifuged to remove cells and other solids, and the supernatant was diluted with an equal volume of 95% ethanol. The protein which precipitated was centrifuged to remove adherent liquid as far as possible, and then dried in a vacuum. 10 Grams of cattle plasma powder thus prepared and 5 g of disodium ribose 5-phosphate were added to one litre of water, and the mixture was boiled for 80 minutes to produce a first broth.

A second broth was prepared in the same manner from (a) 10g protein hydrolyzate obtained by complete hydrolysis of lean beef with hydrochloric acid, neutralization of the hydrolysis mixture with sodium hydroxide and spray drying, and (b) 5 g disodium ribose 5-phosphate.

A third broth was prepared from 5 g of disodium ribose 5-phosphate and from 8.9 g of a mixture of 0.5 g serine, 0.5 g glutamic acid, 0.2 g proline, 1.0 g glycine, 4.0 g alanine, 0.4 g valine, 0.1 g methionine, 0.2 g isoleucine, 0.4 leucine, 0.2 g ornithine, 0.2 g lysine, 0.6 g aspartic acid, 0.4 g threonine, and 0.2 g arginine; the mixture closely resembles the composition of a beef protein hydrolyzate.

The three broths were presented in blind, organoleptic tests to a panel of 20 experienced tasters who were requested to state which broth had the strongest flavour of boiled beef, and which broth tasted closest to beef soup. A large majority of the tasters chose the first broth in both tests (17 and 18 respectively), and but one taster ascribed the strongest boiled meat flavour to the third broth. Two tasters preferred the second broth in both tests.

EXAMPLE 2.

In a procedure otherwise identical to that described with reference to the first broth in Example 1, pig's blood was substituted for cattle blood, and the fourth broth thus produced was set before the same panel, together with the three broths of Example 1 for a comparison test.

Their verdict was as to the second and third broths was the same, but they were spilt approximately equally with respect to the first and fourth broths, 9 preferring the boiled meat flavour of the first broth, and 8 choosing the fourth broth. The flavour most closely resembling beef soup was found in the first broth by 9 tasters and in the fourth broth by the same number.

EXAMPLE 3.

3.5 Litres of water were mixed with 15 g cattle plasma powder prepared as in Example 1, 15 g ribose, 150 g carrots, 230 g onions, 70 g turnips, 100 g welsh onions, 380 g celery stems, 16 g salt and 0.5 g beef fat. The mixture was quickly heated to the boil and simmered for two hours, whereupon it was filtered through cheese cloth. 3 Grams of monosodium glutamate, 0.1 g of disodium inosinate, and some pepper were added to the filtrate.

A control was prepared in a similar manner, but the plasma powder and ribose were replaced by 800 g of lean beef.

The two liquids were presented, as consomme, to a panel of 10 tasters, and they were requested to state a preference. Only six preferred the genuine beef consomme, while four selected the soup flavoured according to the present invention.

EXAMPLE 4.

A liquid composition was prepared by mixing 200 ml soy sauce, 20 ml "Worcestershire sauce" (registered Trade

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Mark), 20 ml distilled spirits (known in Japan as Shochu), 70 ml vinegar, 70 ml sweet Japanese rice wine (Mirin), 10 g sugar, 30 g millet jelly, 3 g monosodium glutamate, 0.08 g disodium inosinate, 0.08 g disodium guanylate, 15 g corn starch, some onion, garlic and white pepper powder, 2 ml sesame oil, 50 g egg white, and 20 g disodium ribose 5-phophate.

A control composition was prepared from the same ingredients except for the omission of the egg white and of the ribose 5-phosphate.

Soy bean curd (textured, purified soy protein) was dipped in the first composition and then fried in purified beef fat at 220°C for one minute. Slices of beef were dipped in the control composition and fried in the same manner. The fried products were subjected to an organoleptic test by a panel of seven tasters.

Six of the seven preferred the texture of the fried beef, but only four of the seven preferred the taste of the fried beef; the other three preferred the taste of the soy protein.

EXAMPLE 5.

Baker's yeast was subjected to autolysis and concentrated to produce a yeast extract of pasty consistency. The paste was mixed intimately with one litre of a broth prepared in the same manner as the first broth in Example 1. The mixture was partly evaporated in a vacuum to a water content of 35% by weight. There was obtained 750 g seasoning paste having a strong and pleasant beef flavour.

Beef cattle and pigs are the only practical sources of animal blood from which the plasma powder of the present invention may be prepared under industrial conditions in developed countries. Sheep and goat blood may be mixed with other blood to the extent that it does not add an undesired flavour of its own to the seasoning composition of the present invention. Blood of other animals, such as horses, useful in itself, is not normally available in adequate quantities.

The term "animal" is used herein in the broad sense to include birds as well as ground-bound creatures, and is used in contrast to the broad term "vegetable".

WHAT WE CLAIM IS:—

1. A flavouring agent capable of being produced by heating a mixture of ribose or ribose 5-phosphate and a protein of animal origin at a temperature in the range from 60° to 250°C until the mixture assumes the flavour of cooked beef.

2. A flavouring agent capable of being produced by heating a mixture of ribose or ribose 5-phosphate and, as protein, blood plasma solids of animal blood at a temperature in the range from 60° to 250°C until the mixture assumes the flavour of cooked beef.

3. A flavouring agent produced by heating a mixture of ribose or ribose 5-phosphate and, as protein, blood plasma solids of animal blood at a temperature in the range from 60° to 250°C until the mixture assumes the flavour of cooked beef.

4. A flavouring agent according to claim 1, 2 or 3, wherein in the mixture there are from 0.01 to 10 parts by weight of ribose or ribose 5-phosphate per part by weight of protein.

5. A flavouring agent according to claim 4, wherein in the mixture there are from 0.1 to 3 parts by weight of ribose or ribose 5-phosphate per part by weight of protein.

6. A flavouring agent according to any preceding claim, wherein the mixture is heated at a temperature of up to 100°C for from 10 minutes to 3 hours.

7. A flavouring agent according to any one of claims 1 to 5, wherein the mixture is heated at a temperature in excess of 100°C for from 15 seconds to 30 minutes.

8. A flavouring agent as claimed in any preceding claim, in powder form.

9. A flavouring composition comprising a flavouring agent as claimed in any one of claims 1 to 7, and a liquid phase therefore selected from water, an edible organic solvent or an edible oil.

10. A flavouring agent according to claim 1, substantially as described in any one of the foregoing Examples.

11. A process for producing a flavouring agent, which comprises heating a mixture of ribose or ribose 5-phosphate and a protein of animal origin at a temperature in the range from 60° to 250°C until the mixture assumes the flavour of cooked beef.

12. A process according to claim 11, wherein the protein of animal origin is blood plasma solids of animal blood.

13. A process according to claim 12, wherein the blood plasma solids are derived from the blood of beef cattle or pigs.

14. A process according to claim 11, 12 or 13, wherein the mixture is dispersed in water during the heating.

15. A process according to claim 11, 12 or 13, wherein the mixture is dispersed in liquid fat or oil during the heating.

16. A process according to any one of claims 11 to 15, wherein the mixture also contains an edible solid or liquid other than the protein of animal origin, and the flavour is imparted to the edible solid or liquid during heating.

17. A process according to any one of claims 11 to 16, wherein in the mixture there are from 0.01 to 10 parts by weight of

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ribose or ribose 5-phosphate per part by weight of protein.

18. A process according to claim 17, wherein in the mixture there are from 0.1 to 3 parts by weight of ribose or ribose 5-phosphate per part by weight of protein.

19. A process according to any one of claims 11 to 18, wherein the mixture is heated at a temperatue of up to 100°C for from 10 minutes to 3 hours.

20. A process according to any one of claims 11 to 18, wherein the mixture is heated at a temperature in excess of 100°C for from 15 seconds to 30 minutes.

21. A process according to claim 11, substantially as described in any one of the foregoing Examples.

22. A flavouring agent whenever produced by a process according to any one of claims 13 to 16 and 21, or to any one of Claims 17 to 20 when appendant to any one of claims 13 to 16.

23. A process for imparting a beef-like flavour to an edible material, which comprises incorporating in the edible material a flavouring agent according to any one of claims 1 to 10 and 22.

24. A process for imparting a beef-like flavour to an edible material, which comprises heating the edible material with a mixture of ribose or ribose 5-phosphate and protein of animal origin, at a temperature in the range from 60°C to 250°C.

25. A process according to claim 24, wherein the mixture is as defined in claim 2, 4 or 5.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 515 961

1 515 961

(21) Application No. 25707/76 (22) Filed 21 June 1976
(31) Convention Application No. 9744/75
(32) Filed 25 July 1975 in
(33) Switzerland (CH)
(44) Complete Specification published 28 June 1978
(51) INT CL² A23L 1/231, 1/227, 1/228
(52) Index at acceptance A2B 1B 1C 1JY 1L 1X 6A
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(54) FLAVOURING

(71) We, SOCIÉTÉ DES PRODUITS NESTLÉ S.A. of Vevey, Switzerland, a Swiss body corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing a flavouring agent, more especially a flavouring agent with a taste similar to that of cooked meat.

Various synthetic flavouring agents with a flavour reminiscent of cooked meat have been produced by carrying out a Maillard reaction in the presence of a substance containing sulphur in sulphide form. The Maillard reaction is a non-enzymatic browning reaction which occurs when substances such as amino acids, peptides or proteins are heated with saccharides and leads to the formation of substances with an aromatic character.

Most of the efforts made in this field are directed either towards a better choice of the amino acids, peptides or proteins, which explains why for example protein hydrolysates or yeast autolysates are readily used, or towards a better choice of the saccharides, which explains why it is generally preferred to use pentoses, such as ribose or arabinose.

An object of the present invention is above all to provide flavouring agents of the type commonly known as "meat aromas" of high quality and low price from readily available vegetable materials, even waste vegetables.

The present invention provides a process for the production of a flavouring agent having a taste similar to that of cooked meat, which comprises subjecting a polysaccharide containing acid groups or vegetable material rich in polysaccharides containing acid groups to hydrolysis with a dilute strong acid or to an equivalent enzymatic hydrolysis reaction, and subsequently reacting the hydrolysate obtained with at least one substance containing sulphur in sulphide form and at least one substance containing nitrogen in amino form at elevated temperature and at a pH-value in the range from pH 5 to pH 7.

The hydrolysate is preferably freed from the solids present in it either before it is reacted with the substances defined above or afterwards so as to obtain a homogeneous flavouring agent.

Polysaccharides containing acid groups exist in the natural state. They are encountered in abundance throughout the vegetable world, generally as a filling or supporting material. Thus, pectins, algins and alginates, gums, for example gum arabic, gum tragacanth, gum ammoniac, gamboge, are polysaccharides containing acid groups. Vegetable materials rich in polysaccharides of this type include fruits and tubers, generally rich in pectins, algae rich in algins and alginates, and plants from which various types of gum are extracted. Rather than using whole fruits or tubers, it is preferred to use residues and lees, such as pomace and marcs of other fruits of the same kind, lees of citrus fruits, residues from the refining of sugar (waste and pulps of sugar beet, cossettes), either as such or after purification (in which case they are known as apple pectin or beet pectin).

Other polysaccharides containing acid groups are, for example, the celluloses and oxidised starches, especially those obtained from celluloses and ordinary starches by oxidation with chlorine or with nitric acid.

In the content of the invention, an "equivalent enzymatic hydrolysis reaction" is an enzymatic hydrolysis reaction which has the same effect as hydrolysis with a dilute strong acid, for example hydrochloric acid or sulphuric acid, i.e. which breaks most of the glycosidic bonds and converts the polysaccharide containing acid groups into a mixture of monosaccharides containing acid groups or uronic acids. An enzymatic hydrolysis reaction such as this may be carried out with aid of a suitable enzyme, for example a pectinase in the case of pectin. In other words, the hydrolysate obtained contains uronic acids which are generally found to contain other saccharides, such as pentoses and hexoses, either because these other saccharides are already present in monomeric or polymeric form in the starting vegetable fraction alongside the polysaccharide containing acid groups,

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or because they partly enter the constituent chain of the polysaccharide. For example, a hydrolysate of gum arabic contains in addition to glucuronic acid significant quantities of arabinose, rhamnose and galactose. Similarly, a hydrolysate of gum tragacanth contains, in addition to galacturonic acid, fructose, arabinose, xylose and galactose. The presence of these hexoses and pentoses, for example arabinose, is of purely secondary importance. Thus, a hydrolysate of apple pectin, which contains at least 85% of galacturonic acid and little or no hexoses and pentoses, gives an excellent aromatising product. The same applies in cases where an alginate which is substantially polymannuronic acid in pure form, is used. The determining factor is the presence, even in small proportions, of these uronic acids.

As already known, the substances containing sulphur in sulphide form and nitrogen in amino form may be selected from mineral or organic substances, such as for example:

— hydrogen sulphide
— sulphides or polysulphides of sodium or ammonium
— methionine, cysteine, cystine, gluthatione, thiamine
— vegetable materials rich in sulphur-containing derivatives
— alkaline hydrolysates of vegetable materials rich in sulphur-containing derivatives
— ammonia or ammonium chloride
— amino acids, peptides, i.e. protein hydrolysates and yeast autolysates
— proteins

some of these substances being able to perform the double function of a substance containing sulphur in sulphide form and a substance containing nitrogen in amino form. Preferred substances containing sulphur in sulphide form, i.e. sulphur in a negative degree of oxidation, are organic substances in which the sulphur is in the —SH form or organic substances capable of readily producing —SH groups during a Maillard reaction. Substances of this type are, in particular cysteine, cystine and the alkaline hydrolysates of vegetable materials rich in sulphur-containing compounds for example those which are obtained by the alkaline hydrolysis of cabbages, onions, or garlic, or of juices or extracts thereof.

Our co-pending Application No. 25708/76 (Serial No. 1 515 962) describes and claims a process for the production of a flavouring agent having a taste similar to that of cooked meat, which comprises subjecting a vegetable material containing sulphur-containing compounds to hydrolysis with an alkaline agent, and subsequently reacting the hydrolysate obtained with at least one saccharide and at least one substance containing nitrogen in amino form at elevated temperature and at a pH in the range from pH 5 to pH 7. In the process of the present invention, unhydrolysed sulphur-containing vegetable material can be used as well, although this is less desirable.

The conditions under which the polysaccharide containing acid groups or the vegetable material rich in polysaccharides containing acid groups are hydrolysed by a dilute strong acid or by a suitable enzyme are the usual conditions for a hydrolysis reaction of this type and are not intended to be the subject of particular developments. Similarly, the conditions under which the reaction between the hydrolysate and the substance(s) containing sulphur in sulphide form and nitrogen in amino form is carried out are the usual conditions for the Maillard reaction. If desired, reference may be made to the preferred embodiment described hereinafter for indicative values of the reaction times and the reaction temperatures of the hydrolysis reaction or the Maillard reaction.

In one preferred embodiment of the process according to the invention, a polysaccharide or a vegetable material selected as follows is subjected to hydrolysis with 1.5% to 30% hydrochloric or sulphuric acid by heating under reflux for variable periods:

vegetable fraction	hydrolysis time
apple pectin	from 2 to 5 h
beet pectin	from 0.5 to 4 h
alginate	from 1 to 4 h
gum arabic	from 1 to 5 h
gum tragacanth	from 1 to 4 h
oxidised starch	from 2 to 5 h

Hydrolysis with a dilute strong acid may be replaced by an enzymatic hydrolysis reaction. For example, pectin may be hydrolysed by a pectinase, such as Spark-L-enzyme (a product of Miles Laboratories Inc.), Pectinex R (a product of Schweiz. Ferment A. G., Basle) or Ultrazyme 20 (a product of Dr. Schubert A.G.).

After hydrolysis, the solids present are eliminated by filtration of the reaction medium to obtain a homogeneous medium, followed by the addition to the filtrate of a hydrolysate of vegetable proteins, especially wheat gluten (in a quantity of from 200 to 800 g/l), cysteine or an alkaline hydrolysate of vegetable materials rich in sulphur-containing derivatives (in a quantity of from 5 to 40 g/l) and beef fat (in a quantity of from 5 to 30 g/l), at a pH-value kept in the range from pH 5 to pH 7, advantageously around pH 5.8, by the addition of sodium hydroxide. This is followed by heating under reflux for 1 to 4 hours, preferably for 2 hours, during which time the pH value may if desired be kept at its initial value by adding sodium hydroxide.

In one variant of this preferred embodiment, the solids are only separated after reaction of

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the hydrolysate of polysaccharides containing acid groups with the hydrolysate of vegetable proteins and cysteine.

In another variant of this preferred embodiment, the hydrolysate of polysaccharides containing acid groups is treated with active carbon before it is reacted.

The flavouring product obtained is in the form of a dark-coloured liquid having a strong odour and a pronounced taste of cooked meat. It may be concentrated or dried, for example by freeze-drying, to form a paste or a powder which may be redissolved without difficulty. This product is stable and may be stored in air for at least six months.

It may be directly used for providing a food product with a meat taste in quantities governed both by its concentration and by the type of food product in question. It may also be used for modifying the taste of a food product or for enhancing its meat taste. This product may be used either on its own or in conjunction with other agents which improve taste, such as monosodium glutamate or inosine-5'-phosphate.

Finally, the flavouring agent may be used for enhancing or modifying the taste of food-grade aromas which will subsequently be used as aromatising agents.

The process according to the invention is illustrated by the following Examples, in which the ratios and percentages quoted represent values by weight unless otherwise stated.

EXAMPLES 1 to 5.

5 g of a polysaccharide containing acid groups or its equivalent in the form of a vegetable material are suspended in 100 ml of 2 N HCl, followed by heating under reflux (104°C), as shown in the following Table:

Example No.	Vegetable material	Oxidised polysaccharide equivalents	refluxing time in h
1	15 g of pomace	5 g of pectin	4
2	15 g of beet pulp	5 g of pectin	0.5
3	—	5 g of alginate	2
4	—	5 g of gum arabic	1
5	—	5 g of gum tragacanth	2

After cooling, the reaction medium is filtered to eliminate the solids, followed by the addition to the filtrate of 100 g of a dry wheat gluten hydrolysate obtained by acid hydrolysis, 20 N sodium hydroxide to adjust the pH to 5.8, 2.5 g of cysteine and 2 g of beef fat. The mixture is then heated under reflux for 2 hours (104°C), the pH-value being kept at pH 5.8 by the addition of sodium hydroxide. The liquid obtained after cooling represents the flavouring product having a taste similar to that of cooked meat. It is in the form of a brown to dark brown liquid with the odour of cooked meat.

The flavouring products of Examples 1 and 3 to 5 have more of a "roasted" note whereas the product of Example 2 tends towards the "smoked" note.

Comparison Tests

In a first comparison test, a flavouring product is prepared in the same way as described above except that an equivalent quantity of arabinose is used instead of the hydrolysate of polysaccharides containing acid groups. It is found that, although the flavouring product thus obtained is similar to the flavouring products prepared as described in the above Table, the latter being judged to be "more rounded".

In a second comparison test, the procedure is as described above except that the apple pectin is hydrolysed with a base (2 N sodium hydroxide, refluxing for 4 hours) rather than with an acid. It is found that the flavouring product obtained in this way is not worthy of the name.

In a third comparison test, the procedure is as described above except that an autolysate of pomace (auto-hydrolysis of pectin at pH 8 by the enzymes present in the pomace) is used instead of an acid hydrolysate of pomace. In this case, too, the flavouring product obtained is not worthy of the name.

EXAMPLE 6.

The procedure is as in Example 2, except that the beet pectin hydrolysate obtained is treated with active carbon in a quantity of 50% by weight relative to the dry matter in the hydrolysate for a period of 2 hours at a temperature of 20°C. The flavouring product obtained is clearer than that of Example 2. It has a pleasant meat taste without a "smoked" or "caramelised" note.

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EXAMPLE 7.

An oxidised starch is prepared as follows from a potato starch:

5 g of potato starch with a residual moisture content of 5% are suspended in 18 ml of a 2:1 mixture of fuming nitric acid and water. After the suspension has been left to react while stirring for 30 minutes at 15°C, 1.2 ml of 80% formic acid are added dropwise. This is followed by stirring for 8 hours at 15°C, after which 5 ml of methanol are added. The mixture is then poured into 50 ml of methanol, after which the medium is filtered to recover the precipitate. After washing with methanol, a white powder of oxidised potato starch is thus obtained in a quantity of approximately 5 g.

The oxidised starch thus prepared is then hydrolysed and treated in the same way as described in Example 1, giving a flavouring product comparable with the product of Example 1, but less intense.

EXAMPLE 8.

An apple pectin is enzymatically hydrolysed as follows:

2 g of apple pectin are dissolved in 100 ml of water followed by the addition to the resulting solution of 10 ml of a solution of pectinase (Spark-L, a product of Miles Laboratories Inc.). The pH is adjusted to 5.2 by the addition of 2 N sodium hydroxide, after which the mixture is left to react while stirring for 15 hours at a temperature of 20°C. The reaction medium is then freed from the solids present in it and the filtrate is collected and treated in the same way as described in Example 1. A flavouring product comparable with that of Example 1 is obtained.

EXAMPLE 9.

5 g of onion powder are suspended in 30 ml of 2 N NaOH, after which the suspension is heated under reflux (104°C). for 2 hours. After cooling, the medium is filtered and the filtrate collected.

25 g of a wheat gluten hydrolysate obtained by acid hydrolysis are added to the filtrate, after which the pH is adjusted to pH 5.8 by the addition of 37% HCl. 5 g of beet pulp hydrolysate prepared as described at the beginning of Example 2 and 5 g of beef fat are then added to the medium. Preparation is then continued in the same way as described at the end of Example 2.

A flavouring product comparable with that of Example 2 is thus obtained.

EXAMPLE 10.

The procedure is as in Example 9, except that a cabbage powder is used instead of onion powder. The flavouring product obtained is similar to that of Example 9.

EXAMPLE 11.

An instant soup base is prepared by mixing the following ingredients:

salt	8.6 g
sodium glutamate	4.7 g
sugar	0.4 g
spices	0.03 g
inosine monophosphate	0.03 g
caramel colouring powder	0.01 g
beef fat	0.97 g
hydrogenated vegetable fat (Biscuitine C) (Biscuitine is a registered Trade Mark)	0.97 g
dehydrated tomato flakes	0.06 g
onion powder	0.16 g
dried parsley	0.06 g

This mixture is then dissolved in 1 litre of boiling water, followed by the addition of 2 g of the flavouring product of Example 1. The soup thus prepared has a pronounced taste and odour of meat.

EXAMPLE 12.

A sauce is prepared as follows:

80 g of hydrogenated vegetable fat (Biscuitine C) and 80 g of flour are mixed and the resulting mixture lightly browned in a frying pan. 1 litre of water is then added, followed by boiling for 2 minutes. Finally 2 g of the flavouring product of Example 2 are added. The sauce thus prepared has a meat taste.

WHAT WE CLAIM IS:—

1. A process for the production of a flavouring agent having a taste similar to that of cooked meat, which comprises subjecting a polysaccharide containing acid groups or vegetable material rich in polysaccharide containing acid groups to hydrolysis with a strong acid or to an equivalent enzymatic hydrolysis reaction, and subsequently reacting the hydrolysate obtained with at least one substance containing sulphur in sulphide form and at least one substance containing nitrogen in amino form at elevated temperature and at a pH-value in the range from pH 5 to pH 7.

2. A process as claimed in Claim 1, wherein, before the hydrolysate is reacted, the solids present in it are removed.

3. A process as claimed in Claim 1, wherein the solids are removed from the reaction product of the hydrolysate with the substance containing sulphur in sulphide form and the substance containing nitrogen in amino form.

4. A process as claimed in any of Claims 1 to 3, wherein, before the hydrolysate is reacted, it is treated with active carbon.

5. A process as claimed in any of Claims 1 to 4, wherein the polysaccharide containing acid groups is a pectin, algin or alginate, gum, cellulose or oxidised starch.

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6. A process as claimed in any of Claims 1 to 4, wherein the vegetable material rich in polysaccharide containing acid groups is pomace, lees of a citrus fruit, a beet pulp or a cossette.

7. A process as claimed in any of Claims 1 to 6, wherein the substance containing sulphur in sulphide form is cysteine or an alkaline hydrolysate of vegetable materials rich in sulphur-containing derivatives.

8. A process as claimed in Claim 7, wherein the alkaline hydrolysate is a hydrolysate of cabbage, onion or garlic, or of a juice or extract of a plant such as these.

9. A process as claimed in any of Claims 1 to 8, wherein the substance containing nitrogen in amino form is a wheat gluten hydrolysate.

10. A process for the production of a flavouring agent having a taste similar to that of cooked meat substantially as described with particular reference to any of the Examples 1 to 12, excluding the comparison tests.

11. A flavouring agent having a taste similar to that of cooked meat when obtained by a process as claimed in any of the preceding Claims.

12. An edible material containing a flavouring agent as claimed in any of Claims 1 to 11.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 515 962

1 515 962

(21) Application No. 25708/76 (22) Filed 21 June 1976
(31) Convention Application No. 9745/75
(32) Filed 25 July 1975 in
(33) Switzerland (CH)
(44) Complete Specification published 28 June 1978
(51) INT CL² A23L 1/231, 1/227, 1/228
(52) Index at acceptance A2B 1B 1C 1JY 1L 1X 6A
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(19)



(54) FLAVOURING

(71) We, SOCIETE DES PRODUITS NESTLE S.A., of Vevey, Switzerland, a Swiss body corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing a flavouring agent, more especially a flavouring agent with a taste similar to that of cooked meat.

Various synthetic flavouring agents with a flavour reminiscent of cooked meant have been produced by carrying out a Maillard reaction in the presence of a substance containing sulphur in sulphide form, more especially in the form of —SH. The Maillard reaction is a non-enzymatic browning reaction which occurs when substances such as amino acids, peptides or proteins are heated with saccharides and leads to the formation of substances with an aromatic character.

Most of the efforts made in this field are directed either towards a better choice of the amino acids, peptides or proteins, which explains why for example protein hydrolysates or yeast autolysates are frequently used, or towards a better choice of the saccharides, which explains why it is generally preferred to use pentoses, such as ribose or arabinose.

German Offenlegungsschrift No. 2,220,530 describes a process for the production of flavouring agents of the "meat aroma" type by a Maillard reaction, in which the substance containing sulphur in the form of —SH consists of egg or egg fractions. According to this German Offenlegungsschrift, it is proposed optionally to "dope" the reaction mixture subjected to said reaction by the addition of secondary ingredients, such as cabbage or onion juice. However, it is pointed out that these secondary ingredients would not be able on their own to impart a meat aroma. In the absence of egg or an egg fraction, the product obtained by the Maillard reaction does not have the taste of cooked meat (*cf.* also the end of Example 5 of the present specification).

The present invention emanates precisely from observation that, in the manufacture of flavouring agents having a taste similar to that of cooked meat by a Maillard reaction, vegetables such as cabbage, and onion, may be used as principal ingredients provided that they are treated beforehand with an alkaline agent.

Accordingly, a principal object of the present invention is to provide flavouring agents of the type commonly known as "meat flavours" of high quality and low price, because they are produced from readily available vegetable materials.

The present invention provides a process for the production of a flavouring agent having a taste similar to that of cooked meat which comprises subjecting a vegetable material rich in sulphur-containing compounds to hydrolysis with an alkaline agent, and subsequently reacting the hydrolysate obtained with at least one saccharide and at least one substance containing nitrogen in amino form at elevated temperature and at a pH-value in the range from 5 to 7.

The hydrolysate is preferably freed from the solids present in it either before it is reacted with the substances defined above or afterwards so as to obtain a homogeneous flavouring agent.

Vegetables or plants rich in sulphur-containing compounds are not rare in nature. They are encountered in particular among vegetables belonging to the family of crucifers or *Cruciferae*, for example cabbages, turnips, and to the family of *Liliaceae*, for example onions, garlic, leeks, asparagus. The vegetable materials rich in sulphur-containing compounds may thus be either the whole plant, preferably in divided form, or a part of or an extract of the plant, a juice or an oleoresin for example.

The hydrolysis reaction with an alkaline agent, for example sodium hydroxide, potassium hydroxide or the corresponding carbonates, converts the sulphur-containing compounds present in the vegetable material, for example disulphides, thiosulphinates, thiosulphonates, into substances containing sulphur primarily in the form of —SH. As a general rule, the hydrolysate obtained contains impurities in which sulphur is present in a form other than —SH, for example in the form of $—SO_2H$ or $—SO_3H$. It has been found that

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these substances do not have to be eliminated. Accordingly, the crude hydrolysate is preferably used directly, if convenient or desired after removal of the solids present in it.

As already known, the saccharide and the substance containing nitrogen in amino form may be selected for example from the following substances:

—pentoses, such as ribose and arabinose
—hexoses, such as glucose, mannose, fructose, sorbose
—disaccharides, such as lactose and maltose
—acid or enzymatic hydrolysates of polysaccharides (celluoses, starches) or of vegetable materials rich in polysaccharides
—uronic acids
—acid or enzymatic hydrolysates of polysaccharides containing acid groups (pectins, algins, alginates, gums, celluloses and oxidised starches) or of vegetable materials rich in polysaccharides containing acid groups (pomace, lees of citrus fruits, beet pulps and cossettes)
—ammonia and ammonium chloride
—amino acids, peptides, i.e. protein hydrolysates and yeast autolysates
—proteins.

Our co-pending Application No. 25707/76 (Serial No. 1,515,961) describes and claims a process for the production of a flavouring agent having a taste similar to that of cooked meat, which comprises subjecting a polysaccharide containing acid groups or a vegetable material rich in polysaccharide containing acid groups to hydrolysis with a strong acid or to an equivalent enzymatic hydrolysis reaction. The hydrolysate obtained is then reacted with at least one substance containing sulphur in sulphide form and at least one substance containing nitrogen in amino form at elevated temperature and at a pH-value in the range from pH 5 to pH 7. In the process of the present invention, polysaccharides not containing acid groups can be used as well, although this is less desirable.

Hydrolysis of the vegetable material rich in sulphur-containing compounds with the alkaline agent is preferably carried out at a pH value of at least pH 8, during the hydrolysis reaction. The type of alkaline agent used is of minor significance, and it is preferred to use conventional alkaline agents such as sodium hydroxide, potassium hydroxide, the corresponding carbonates and bicarbonates. In addition, it is of advantage to carry out the hydrolysis reaction under heat. At reflux temperature for example, hydrolysis times of from 1 to 24 hours may be considered to be satisfactory.

Finally, the conditions under which the reaction between the hydrolysate obtained, the saccharide(s) and the substance(s) containing nitrogen in amino form is carried out are the usual conditions for the Maillard reaction. Reference may be made to the preferred embodiment described hereinafter for indicative values of the reaction times and reaction temperatures.

In one preferred embodiment of the process according to the invention, a vegetable starting material consisting of cabbage, cauliflower, onion, garlic in divided form or even of powders, juices or oleoresins of cabbage, cauliflower onion and garlic, is subjected to alkaline hydrolysis with NaOH, KOH, Na_2CO_3 or $NaHCO_3$ (0.01 to 10 M) by heating under reflux for approximately 18 hours.

In a variant, the starting material is subjected before alkaline hydrolysis to an enzymatic treatment, for example to a treatment with alliinase, as described by G. G. Freeman and R. J. Whenham in J. Sci. Fd Agric. *25*, 499 (1974).

If desired, the solids present are eliminated after hydrolysis by filtration of the reaction medium to obtain a homogeneous medium. Thereafter, at least one saccharide selected from the following:

—ribose
—arabinose
—uronic acid
—acid or enzymatic hydrolysate of polysaccharides containing acid groups
—acid or enzymatic hydrolysate of vegetable materials rich in polysaccharides containing acid groups

is added in a quantity of from 5 to 100 g/l based on dry weight (the hydrolysates having optionally been treated with active carbon), as well as a vegetable protein hydrolysate, especially wheat gluten (200 to 800 g/l) and beef fat (5 to 30 g/l), and the pH-value is adjusted in the range from pH 5 to pH 7, advantageously around pH 5.8, by the addition of 37% hydrochloric acid. The mixture is heated under reflux for 1 to 4 hours, preferably for 2 hours, during which time the pH value may with advantage be kept at its initial value by adding sodium hydroxide.

In another variant of this preferred embodiment, the solids are only separated after the Maillard reaction.

The flavouring agent obtained is in the form of a dark-coloured liquid having a strong odour and a pronounced taste of cooked meat. It may be concentrated or dried, for example by freeze-drying, to form a paste or a powder which may be redissolved without difficulty. This product is stable and mak be stored in air for at least 6 months.

It may be directly used for providing a food product with a meat taste in quantities governed both by its concentration and by the type of food product in question. It may also be used for modifying the taste of a food product or for enhancing its meat taste. This

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product may be used either on its own or in conjunction with other agents which improve taste, such as monosodium glutamate or inosine-5'-phosphate.

Finally, the flavouring agent may be used for enhancing or modifying the taste of food-grade flavourings which will subsequently be used as flavouring agents.

The process according to the invention is illustrated by the following Examples, in which the ratios and percentages quoted represent values by weight unless otherwise stated.

EXAMPLES 1 to 4.

5 g of a vegetable according to the following Table, comminuted into particles with an average diameter of 1 mm, are suspended in 30 ml of a 2 N sodium hydroxide solution, followed by heating under reflux for 2 hours (104°C).

Examples	Vegetables
1	onion
2	garlic
3	cabbage
4	cauliflower

After cooling, the reaction medium is filtered and the filtrate collected. 25 g of a dry wheat gluten hydrolysate, 37% hydrochloric acid to adjust the pH to 5.8, 1 g of ribose and 2.5 g of beef are added to the filtrate.

The mixture is then heated under reflux for 2 hours (104°C), the pH-value being kept at pH 5.8 by the addition of sodium hydroxide.

The liquid obtained after cooling represents the flavouring agent having a taste similar to that of cooked meat. It is in the form of a brown to dark brown liquid with the odour of cooked meat.

The flavouring agents of Examples 1 to 4 are presented to a taste-testing panel who express their preferences as follows:

Rating	Hydrolysed vegetables	Examples
1	garlic	2
2	cabbage, cauliflower	3, 4
4	onion	1

The product of Example 2 (garlic) is judged to be excellent. The product of Example 1 (onion) is still acceptable although having a slight vegetable aftertaste which cannot be characterised as onion.

Similar results are obtained by using, instead of fresh vegetables, dehydrated vegetables in powder form, namely 2 g of onion powder (Asa Foetide, a product of Dixa, Saint-Gall, Switzerland), 2 g of garlic powder (Fridlin, Zoug, Switzerland), 2 g of cabbage powder, 2 g of cauliflower powder, respectively, the last two powders being laboratory samples obtained by dehydrating and drying fresh vegetables.

The flavouring agents thus obtained are satisfactory. However, they are not as good as the corresponding flavouring agents obtained from fresh vegetables.

Comparable corresponding results are obtained by hydrolysing the fresh vegetables or the vegetable powders with sodium carbonate or bicarbonate, again for 2 hours at reflux temperature.

EXAMPLES 5 and 6.

The procedure described in the preceding Examples is repeated using 4 g of vegetable juices obtained by cold pressing instead of whole vegetables. After these juices (onion juice: Example 5, garlic juice: Example 6) have been hydrolysed and subjected to a Maillard reaction, dark brown liquids are obtained with odours of boiled and roasted meat, respectively.

By way of comparison, Example 5 is repeated without hydrolysing the garlic juice beforehand. Accordingly, the garlic juice is directly reacted at pH 5.8 with the wheat gluten hydrolysate, ribose and beef fat.

It is found that the product obtained does not have the taste or odour of meat, but instead an intense taste of garlic.

EXAMPLES 7 and 8.

The procedure described in Examples 1 to 4 is repeated using an oleoresin of onion (Example 7) and garlic (Example 8), both products of Messrs. Raboud Metroz, Colodno-Monzese, France, instead of whole onion and garlic, respectively. After hydrolysis of the oleoresins and a Maillard reaction, brown to dark brown liquids are obtained with a taste of meat.

EXAMPLE 9.

The procedure is as in Example 2 (garlic powder), except that arabinose is used instead of ribose for the Maillard reaction. The product obtained has the same aroma as the product of Example 2.

EXAMPLE 10.

The procedure is as in Example 2 (fresh garlic), except that galacturonic acid is used instead of ribose for the Maillard reaction. The product obtained has a taste of cooked meat, although not as strong as that of the product of Example 2.

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EXAMPLE 11.

5 g of gum arabic are suspended in 100 ml of 2 N HCl, followed by heating under reflux (104°C) for 1 hour. After cooling, the reaction medium is filtered to eliminate the solids, followed by the addition to the filtrate of 100 g of a dry wheat gluten hydrolysate, 30 g based on dry weight of fresh garlic hydrolysate obtained in the same way as described in Example 2, sodium hydroxide to adjust the pH to 5.8 to 2 g of beef fat. The mixture is then heated under reflux for 2 hours (104°C), the pH-value being kept at pH 5.8 by the addition of sodium hydroxide. The product obtained is in the form of a brown liquid having a taste of cooked meat.

EXAMPLE 12.

The procedure of Example 11 is repeated with 15 g of beet pulp containing approximately 5 g of pectin.

After hydrolysis under reflux for 30 minutes, followed by a Maillard reaction with the hydrolysate obtained, mixed with wheat gluten hydrolysate, the fresh garlic hydrolysate of Example 2 and with beef fat, a flavouring agent similar to that of Example 11 is obtained.

EXAMPLE 13.

An instant soup base is prepared by mixing the following ingredients:

salt	8.6	g
sodium glutamate	4.7	g
sugar	0.4	g
spices	0.03	g
inosine monophosphate	0.03	g
caramel colouring powder	0.001	g
beef fat	0.97	g
hydrogenated vegetable fat (Biscuitine C) (Biscuitine is a registered Trade Mark)	0.97	g
dehydrated tomato flakes	0.06	g
onion powder	0.16	g
dried parsley	0.06	g

The mixture is then dissolved in 1 litre of boiling water, followed by the addition of 2 g of the flavouring agent of Example 12. The soup thus prepared has a pronounced taste and odour of meat.

WHAT WE CLAIM IS:—

1. A process for the production of a flavouring agent having a taste similar to that of cooked meat, which comprises subjecting a vegetable material rich in sulphur-containing compounds to hydrolysis with an alkaline agent, and subsequently reacting the hydrolysate obtained with at least one saccharide and at least one substance containing nitrogen in amino form at elevated temperature and at a pH in the range from pH 5 to pH 7.

2. A process as claimed in Claim 1, wherein, before it is reacted, the hydrolysate is freed from the solids present in it.

3. A process as claimed in Claim 1, wherein solids are removed from the reaction product of the hydrolysate with the saccharide and the substance containing nitrogen in amino form.

4. A process as claimed in any of Claims 1 to 3, wherein the vegetable material rich in sulphur-containing compounds is a fresh vegetable selected from garlic, cabbage, cauliflower and onion.

5. A process as claimed in any of Claims 1 to 3, wherein the vegetable material rich in sulphur-containing compounds is a powder-form vegetable selected from garlic, cabbage, cauliflower and onion.

6. A process as claimed in any of Claims 1 to 3, wherein the vegetable material rich in sulphur-containing compounds is an extract of a vegetable selected from garlic, cabbage, cauliflower and onion.

7. A process as claimed in Claim 6, wherein the extract is a juice or an oleoresin.

8. A process as claimed in any of Claims 1 to 7, wherein, before hydrolysis with the alkaline agent, the vegetable material rich in sulphur-containing derivatives is subjected to an enzymatic treatment with alliinase or with an enzyme equivalent to alliinase.

9. A process as claimed in any of Claims 1 to 8, wherein the saccharide is ribose, arabinose, a uronic acid, an acid or enzymatic hydrolysate of a polysaccharide containing acid groups or a vegetable material rich in polysaccharide containing acid groups.

10. A process as claimed in Claim 9, wherein the polysaccharide containing acid groups is a pectin, algin, alginate, gum or cellulose or an oxidised starch.

11. A process as claimed in Claim 9, wherein the vegetable material rich in polysaccharide containing acid groups is a pomace, lees of a citrus fruit, a beet pulp or a cossette.

12. A process as claimed in any of Claims 1 to 11, wherein the substance containing nitrogen in amino form is a wheat gluten hydrolysate.

13. A process as claimed in any of Claims 1 to 12, wherein hydrolysis of the vegetable material rich in sulphur-containing compounds with an alkaline agent is carried out by heating under reflux.

14. A process for the production of a flavouring agent having a taste similar to that of cooked meat substantially as described with particular reference to any of the Examples, excluding the comparison test at the end of Example 5.

15. A flavouring agent having a taste similar to that of cooked meat when obtained by a process as claimed in any of the preceding claims.

16. An edible material containing a flavouring agent as claimed in Claim 15.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

PATENT SPECIFICATION (11) 1 525 541

1 525 541

(21) Application No 35530/76 (22) Filed 26 Aug 1976 (19)
(31) Convention Application No 11033/75 (32) Filed 26 Aug 1975 in
(33) Switzerland (CH)
(44) Complete Specification Published 20 Sep 1978
(51) INT.CL.[2] A23L 1/231 1/227 1/229
(52) Index at Acceptance
A2B 6A 6G

(72) Inventors: Hermann Poiger
Lienhard Bodo Huster

(54) A PROCESS FOR PREPARING A FLAVOURING PRODUCT

(71) We SOCIÉTÉ DES PRODUITS NESTLÉ SA. of Vevey, Switzerland, a Swiss body corporate do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process for the production of a flavouring product reminiscent of meat in its taste, in which a mixture containing at least one yeast protein degradation product, a monosaccharide and a substance containing sulphur in sulphide form is reacted by heating.

There are already various processes for producing substances which are capable of imparting to a food, to which they are added, a reminiscent of that of meat. The production of substances such as these is virtually always based on the Maillard reaction in which at least one monosaccharide, a substance containing sulphur in sulphide form and an amino acid are used as reactants. Among the monosaccharides wh'ch have been used for this purpose, there may be mentioned pentoses, such as xylose, arabinose and ribose, and hexoses, such as galactose, mannose and glucose for example.

The sulphur compounds commonly used for this type of reaction include sulphur-containing amino acids, cystine, cysteine and methionine, or thiamine for example. So far as the amino acid sources are concerned, they are generally selected from the acid hydrolysates of vegetable proteins of all kinds, soya cake or peanut cake, wheat gluten for example, or from the autolysates of yeasts, such as brewer's yeast or baker's yeast.

It is thus known that these thoroughly mixed reactants can be heated to a temperature of 100°C or above for a certain period until the mixture browns and gives off an aroma reminiscent of that of meat. It is known that, depending upon the exact choice of the reactants and their proportions, it is possible to obtain nuances which are reminiscent more precisely of the aroma of beef or of e aroma of chicken or pork for example. It is also known that nucleotides, such as inosine or guanosine monophosphate, or sodium glutamate for example can also be added to these mixtures in order to enhance the flavour of the end product. Some conventional processes even make use of aromatic additives, such as extracts or powders of onion, celery or garlic for example. Some known products are highly aqueous other less aqueous, whilst some are fatty and others are non-fatty, and the production processes used are obviously governed to a large extent by these considerations of dry matter content and percentage of fats. At all events, it is remarkable to find that it is very difficult, in the production of aromatic substances intended to recall the flavour meat, to avoid certain after-tastes characteristic of the starting material used, such as the tast of yeast or the taste of protein hydrolysate, which in most cases tend to supplant or conceal the aroma given off or revealed during Maillard reaction.

An object of the present invention is to obviate this disadvantage.

The present invention produced a process for the production of a flavouring product reminiscent of meat in taste which comprises diluting a yeast autolysate with at least the same quantity by weight of water, precipitating substantially insoluble salts, especially alkaline-earth metal phosphates, by heating the diluted autolysate at a pH-value of from 7 to 8.5, separating solid fractions from the autolysate treated by heating so that only a solution is left, treating the residual solution by steam distillation, concentrating the treated solution by steam distillation, concentrating the treated soution by evaporation to a dry matter content of from 75% to 85% by

weight, mixing the concentrate obtained with at least one vegetable protein hydrolysate, a monosaccharide and a substance containing sulphur in sulphide form, and heating the mixture for 0.5 to 5 minutes to a temperature of from 100°C to 200°C to obtain a reaction product.

Our co-pending application No. 35531/76 (Serial No. 1525542) describes and claims a process for the production of a starting material for the preparation of bouillons for a yeast protein degradation product. This process comprises diluting a yeast autolysate with at least the same quantity by weight of water, precipitating substantially insoluble salts, especially alkaline-earth metal phosphates, by heating the diluted autolysate at a pH-value of from 7 to 8.5, separating solid fractions from the autolysate treated by heating so that only a solution is left, treating the residual solution thus obtained by steam distillation, concentrating the treated solution by evaporation to a dry matter content of from 50% to 80%by weight, mixing 0 to 8%by weight of fats, 0 to 5% by weight of monosaccharide, and 0 to 2% by weight of a nucleotide with the concentrated solution obtained, reacting the mixture obtained by heating at a pH-value of from 5.8 to 6.8 and drying the mixture.

The product obtained by the process according to the present invention is clearly distinguished from known products by its roasted meat flavour and by the complete absence of any after-taste indicative of the origin of the starting material used for its production.

A standard commercial-grade yeast autolysate, for example an autolysate of baker's yeast or of brewer's yeast, may be used as starting material for carrying out the process according to the invention. In the context of the invention, an autolysate is understood to be a hydrolysate obtained by the action of natural yeast enzymes present in the yeasts and not by the addition of an enzyme or any ezymatic preparation. Autolysates such as these are commercially available under the name of yeast extract in the form of brown paste with a high dry matter content. This paste is diluted in water in a ratio of one part by weight of paste to preferably one to four parts, more preferably about 1-5 to 2 parts by weight of water. The pH of the solution is heated to a temperature of for example from about 92°C to 98°C and may be left at that temperature for about 8 to 15 minutes. After cooling to ambient temperature, the solids which had precipitated (mainly alkaline-earth metal phosphates) are separated, for example, by sedimentation, filtration or centrifuging. The residual solution thus obtained may be heated to a temperature of from about 92°C to 98°C before being treated by steam distillation. This treatment may be carried out in countercurrent in a column filled with glass elements, such as fragments of tubes, or in a plate column, for example. The solution may be introduced at the head of the column in a ratio of about one part by weight of steam to approximately one to two parts by weight of solution. The solution thus treated may be concentrated in any type of conventional apparatus with one or several effects for example, although it is perferred to use a vacuum evaporator which harms the material being treated as little as possible. After the material being treated has reached a dry matter content of from 75% to 85% by weight, it is mixed with the vegetable protein hydrolysate, the monosaccharide and the substance containing sulphur in sulphide form in a ratio of for example 60 - 80 : 15 : 30 1 - 3 : 1 - 3 parts by weight. The vegetable protein hydrolysate may emanate from the treatment with hydrochloric acid of caked of oilseeds or from the protein residue left after the extraction of starch from cereals for example. The choice of the monosaccharide does not have any particular bearing upon the final result, and it is possible for example to use any pentose or hexose from the D or L series. The same applies to substance containing sulphur in sulphide form which may be selected as required for example from cystine, cysteine, methionine and other thiamines, either individually or in comination, more especially cf hydrochloride form. It is also possible to add to the mixture other standard ingredients, flavours or flavour strengtheners, such as a flavour or an extract of onion or inosie monosphate or other nucleotide for example. Mixing is preferably carried out under heat, for example at a temperature of from about 40°C to 50°C. The reaction should take place at a temperature in the range from 100°C to 200°C, preferably in the range from 110 to 150°C, over a period of from 30 seconds to 5 minutes, preferably from 1 to 3 minutes. The mixture dries to a certain extent during the reaction and its dry matter content may increase by about 5% for example. This reaction may be carried out in the mixer itself, for example in cases where a kneader equipped with a heating jacket is used, or in a suitable heat exchanger, such as a scraped-surface exchanger for example, or even in a conventional dryer. In the latter case, the reaction may be directly coupled with a possible drying operation to reach a dry matter content well in excess of 80 to 90%, namely of the order of 96 to 99.5%. However, it is preferred to distinguish between reaction and drying, and the reaction of the mixture and its optional drying to a residual moisture content of approximately 0.5 to 4% are preferably carried out separately. After this latter operation, the mass obtained may be ground, for example in a hammer mill, to reduce it into a powder.

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The process according to the invention is illustrated by the following Examples, in which the percentages quoted represented percent by weight.

EXAMPLE 1

33% of yeast extract are diluted in 66% of water in a double-jacketed stirrer-equipped boiler. The dry mater content of the solution is adjusted to 26%. The pH-value of the solution is adjusted to pH 7. The temperature of the solution is increased to 95°C and kept at that level for 10 minutes. The solution is then cooled to ambient temperature and the solids which have precipitated are separated from it be centrifuging. The temperature of the residual solution is then increased to 97°C. The solution thus preheated is passed downwards through a vertical column filled with glass elements in counter current to steam ascending through the column at the same throughput by weight. The purified solution obtained is concentrated in a circulation evaporator to a dry matter content of 80%. 1300 g of the paste obtained, 400 g of wheat gluten hydrolysate with a dry matter content of 80% (obatined by acid hydrolysis, followed by filtration, decolouration with active carbon and evaporation), 10g of natural aroma of fresh onions, 15 g of cysteine hydrochloride, 15 g of thiamine hydrochloride, 100 g of inosine monophosphate and 30 g of glucose are then mixed under heat at 45°C. The mixture obtained is introduced into a kneader formed by a cylindrical body with a double jacket in which rotates a hollow, i.e. heatable, screw to which longitudinal reciprocating movements are imparted. The mixture takes 3 minutes to pass through the kneader in which a temperature of 125°C is maintained. The reaction product obatined has a pleasant flavour with a distinct note of cooked meat.

EXAMPLE 2

40% of yeast extract and 60% of water are mixed in a double-jacketed boiler. The dry matter content of the solution obtained is adjusted to 32%. The pH-value of the solution is adjusted to pH 7.5 by the addition of sodium hyrdoxide. The solution is then heated to 95°C and kept at that temperature for 10 mintues. The solution is then cooled to ambient temperature and the solids is then cooled to ambient temperature and the solids have precipitated are separated from it by filtration. The pH-value of the solution is then adjusted to pH 7.2. The solution is steam distilled in a plate column in countercurrent in a ratio of one part by weight of solution of 0.8 part by weight of steam. The purified solution obtained is concentrated in a circulation evaporator to a dry matter content of 80%. 62.25% of the paste obtained, 25% of powder-form vegetable protein hydrolysate, 0.75% of extract of fresh onions, 0.75% of cysteine hydrochloride, 0.75% of thiamine hydrochloride, 5% of inosine monophosphate and 2.5% of glucose are mixed under heat at 45°C. The mixture is then introduced into a scraped-surface heat exchanger where it remains for 3 minutes at a temperature of from 120°C to 130°C. The reaction product obtained is dried *in vacuo* in a drying cabinet where it remains for 7 hours at a temperature of 65°C. The dry mass obtained is then ground in a hammer mill. The product obtained has a pleasant flavour with a distinct note of cooked meat.

EXAMPLE 3

An autolysate paste, treated with steam and concentrated by evaporation, is prepared in the same way as described in Example 1. 65.5% of this paste, 25% of powder-form vegetable protein hydrolysate, 0.5% of extract of fresh onions, 0.75% of cysteine hydrochloride, 0.75% of thiamine hydrochloride, 0.5% of methionine, 5% of inosine monophosphate and 2% of glucose are mixed under heat. The mixture is reacted for 3 minutes at a temperature of from 120 to 130°C in a scraped-surface heat exchanger. The reaction product obtained has a pleasant flavour with a distinct note of cooked meat.

EXAMPLE 4

A autolysate paste, treated with steam and concentrated by evaporation, is prepared in the same way as described in Example 2. 70% of this paste, 22% of powder-form vegetable protein hydrolysate, 0.5% of extract of fresh onions. 0.8% of cysteine hydrochloride, 0.8% of thiamine hydrochloride 4.3% of inosine monophosphate and 1.6% of glucose are mixed under heat. The mixture is introduced into a scraped-surface heat exchanger where it remains for 3 minutes at a temperature of from 115 to 120°C. The reaction product is dired *in vacuo* in a drying cabinet where it remains for 8 hours at 65%. A dry mass is obtained and is ground in a hammer mill. The finely granular product obtained has a pleasant flavour note of cooked meat.

WHAT WE CLAIM IS:

1. A process for the production of a flavouring product reminiscent of meat in taste, which comprises diluting a yeast autolysate with at least the same quantity by weight of water, precipitating substantially insoluble salts, especially alkaline-earth metal phosphate by heating the diluted autolysate at pH-value in the range from 7 to 8.5, separating solid fractions from the autoylsate treated by heating so that only a solution is left, treating the residual solution obtained by steam distillation, concentrating the treated solution by evaporation to a dry matter content of from 75% to 85% by weight, mixing the concentrate obtained with at least one vegetable protein hydrolysate, a monsaccharide and a substance containing sulphur in sulphide form, and heating the mixture for

0.5 to 5 minutes to a temperature in the range from 100°C to 200°C to obtain a reaction product.

2. A process as claimed in Claim 1, wherein the reaction product is dried to a dry matter content of from 96 to 99.5% by weight, and the dry product obtained is ground.

3. A process as claimed in Claim 1 or 2, wherein the mixture is heated to a temperature of from 110 to 150°C over a period of 1 to 3 minutes.

4. A process as claimed in any of Claims 1 to 3, wherein the yeast autolysate is diluted with 1.5 to 2 times its weight of water.

5. A process as claimed in any of Claims 1 to 4, wherein the diluted autolysate is heated for 8 to 15 minutes to a temperature in the range from 92 to 98°C.

6. A process as claimed in any of Claims 1 to 5, wherein the residual solution is treated in countercurrent in a ratio of 1 part by weight of steam to 1 to 2 parts by weight of solution.

7. A process as claimed in any of Claims 1 to 6, wherein the residual solution is heated to a temperature of from 92°C to 98°C before being treated by steam distillation.

8. A process as claimed in any of Claims 1 to 7, wherein the treated and concentrated yeast autolysate, the vegetable protein hydrolysate, the monosaccharide and the substance containing sulphur in sulphide form are mixed in a ratio of 60 - 80 : 15 - 30 : 1 - 3 : 1 - 3 parts by weight.

9. A process for the production of a flavouring product reminiscent of meat in tast substantially as described with particular reference to any of the Examples.

10. A flavouring product when prepared by a process as claimed in any of Claims 1 to 9.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1978.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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Case No.: IPR2023-00207
U.S. Patent No. 11,224,241

PATENT SPECIFICATION

836,694

NO DRAWINGS.

Inventors:—IAN DOUGLAS MORTON, PHILIP AKROYD and CHARLES GERARD MAY.

Date of filing Complete Specification : April 4, 1956.

Application Date : April 7, 1955. No. 10328/55.

Complete Specification Published : June 9, 1960.

Index at Acceptance :—Class 49, B(1L : 6A).

International Classification :—A23l.

COMPLETE SPECIFICATION.

Flavouring Substances and their Preparation.

ERRATA

SPECIFICATION NO. 836,694

Page 1, line 59, *after* "α" *insert* "and"

Page 1, line 74, *for* "Cured" *read* "Crude"

Page 3, line 43, *for* "L-Cysteine" *read* "L-cysteine"

Page 3, line 65, *for* "6.6" *read* "6.6-6.8"

Page 2, lines 63 and 67 and
Page 3, lines 19, 53, 65 and 82 and
Page 4, line 27 and
Page 5, lines 52, 53 and 56 *for* "*p*H" *read* "pH"

Page 4, line 1, *for* "a" *read* "ă"

Page 5, line 116, *for* "0.17" *read* "0.170"

Page 6, line 37, *for* "gram" *read* "grams"

THE PATENT OFFICE,
4th July, 1960

DS 77536/(8)/3992 200 7/60 DL

alkaline at the end of the reaction.

The monosaccharide is preferably a pentose, such as ribose, arabinose, or xylose. Pentoses are generally preferred to hexoses from the standpoint that pentoses give rise to flavours and aromas resembling closely those of cooked meats whereas if a hexose, such as glucose, is used in the absence of pentoses, a substance having a pleasant savoury smell and taste, rather than that of meat, is produced unless heating is continued for a longer time. It may be advantageous to use a mixture of monosaccharides which may contain either pentoses or hexoses or

also be used. Both racemic and naturally occurring forms of the amino acids can be used.

It has been found that fish protein is a suitable starting material for obtaining a mixture of amino acids for the reaction, provided that cysteine is added. Cured fish protein, such as cod flesh, may be used, but preferably, the fish should first be deflavoured, for instance, by the process described in Specification No. 784,905. The fish protein is then hydrolysed, for instance, by means of hydrochloric acid or caustic soda, and substantially neutralised. The sub-

Motif Exhibit 1150, Page 919 of 1599

PATENT SPECIFICATION 836,694

NO DRAWINGS.

Inventors:—IAN DOUGLAS MORTON, PHILIP AKROYD and CHARLES GERARD MAY.

Date of filing Complete Specification : April 4, 1956.

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Index at Acceptance:—Class 49, B(1L:6A).

International Classification:—A23l.

COMPLETE SPECIFICATION.

Flavouring Substances and their Preparation.

We, UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to artificial flavouring substances and to their preparation.

It has been found that flavouring substances capable of imparting to foodstuffs a savoury smell and taste, particularly resembling that of cooked meat, may be obtained by the reaction of a monosaccharide with an amino reagent comprising cysteine in the presence of water and at an elevated temperature, the reaction mixture being not alkaline at the end of the reaction.

The present invention provides, therefore, a process for making a flavouring substance which comprises reacting a pentose or hexose monosaccharide with cysteine in the presence of a large excess of water at an elevated temperature, the reaction mixture being not alkaline at the end of the reaction.

The monosaccharide is preferably a pentose, such as ribose, arabinose, or xylose. Pentoses are generally preferred to hexoses from the standpoint that pentoses give rise to flavours and aromas resembling closely those of cooked meats whereas if a hexose, such as glucose, is used in the absence of pentoses, a substance having a pleasant savoury smell and taste, rather than that of meat, is produced unless heating is continued for a longer time. It may be advantageous to use a mixture of monosaccharides which may contain either pentoses or hexoses or both. Best results are generally obtained if the monosaccharide, used alone or in admixture with other pentose or hexose monosaccharides, is ribose.

Di- tri-, or polysaccharides or simple derivatives of mono-, di- or polysaccharides which yield the required monosaccharide under the conditions of the reaction may also be used. As suitable monosaccharide derivatives there may be mentioned monoacetone glucose and methyl riboside.

Flavouring substances according to the invention may be obtained by using cysteine as the amino reagent. More fullbodied flavours are generally obtained by using cysteine in admixture with one or more, preferably three or more, other amino acids, such as glutamic acid, glycine, α β-alanine, threonine, histidine, lysine, leucine, *iso*-leucine, serine, valine or cystine. It is not essential to use the individual amino acids. Simple derivatives, such as salts, esters or hydroxy compounds, or di- tri-, or higher peptides, such as glutathione, or proteins, which give rise to the requisite amino acids under the conditions of the reaction, may also be used. Both racemic and naturally occurring forms of the amino acids can be used.

It has been found that fish protein is a suitable starting material for obtaining a mixture of amino acids for the reaction, provided that cysteine is added. Cured fish protein, such as cod flesh, may be used, but preferably, the fish should first be deflavoured, for instance, by the process described in Specification No. 784,905. The fish protein is then hydrolysed, for instance, by means of hydrochloric acid or caustic soda, and substantially neutralised. The sub-

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stantially neutralised hydrolysate may be used, as such, as the amino reagent, provided cysteine is added. The hydrolysate must be treated, for instance with charcoal, in order to remove phenylalanine and methionine, whilst cysteine or a source thereof must be added before using the mixture. The presence of substantial amounts of phenylalanine or of methionine in mixtures tend to give rise to undesirable floral or potato-like aromas and non meat-like flavours. Small amounts of other aromatic amino acids such as tyrosine and tryptophan may not be objectionable but large amounts should preferably be avoided. Other protein hydrolysates which have been suitably treated to remove phenylalanine and methionine such as groundnut hydrolysate or casein hydrolysate or mixtures of these or hydrolysed keratin may also be used as the amino reagent, provided cysteine is added.

Factors which may affect the nature and quality of the flavour produced include the nature and relative amounts of the monosaccharide and amino reagents used, the amount of water present and the time and temperature of heating. Thus, to obtain a product having a flavour resembling that of beef the total amino reagent should preferably contain about 1 to 3 times, by weight, of the total weight of cysteine, of amino acids or derivatives which will give rise to amino acids additional to cysteine or of derivatives which will give rise to such amino acids during the reaction. The use of ribose and cysteine in the absence of other amino acids tends to give a flavour akin to that of pork.

As little as 0.04 mole of monosaccharide per 1 mole of amino reagent may give a satisfactory flavouring substance. By "amino reagent" is meant the total of amino acids and derivatives thereof present, inclusive of cysteine. Amounts of monosaccharide up to 0.8 mole per 1 mole of amino reagent may be used but a greater amount of monosaccharide may be objectionable as it tends to give rise to excessive sweetness of flavour. Generally, it is preferred to use from 0.1 to 0.5 mole of monosaccharide per 1 mole of amino reagent.

Preferred flavouring substances having an aroma and taste akin to cooked meat are obtained when the ratio of cysteine to monosaccharide is between 0.4:1 and 2:1 by weight.

The amount of water present should, in practice, be at least 5, generally 15 to 25, times the amount, by weight of the total monosaccharide reagent. Amounts of up to 1500 times may, however, be used.

The *p*H at which the reaction is carried out is not critical although the mixture at the end of the reaction must not be alkaline. It is preferred to carry out the reaction at a *p*H of between 3 and 6.

The reaction mixture may be in the form of a solution or in the form of a slurry or sludgy mass, depending on the concentration of reagents and on the conditions of heating. The saccharide may be brought into solution before heating is begun in order to reduce any danger of charring. Stirring of the mixed reagents may be advisable during heating to reduce the danger of local overheating. Vigorous stirring during heating may reduce the time required for completion of the reaction.

The reaction may be carried out by heating the mixture under reflux. In many cases the mixture is maintained at its boiling point for from ½ to 4 hours, generally at least for 1 hour. Similar results may be achieved by heating for a longer period at a lower temperature, for instance 70° C., when 24 to 30 hours heating may be required. When using hexoses, it is preferred to heat the mixture under reflux for about 24 hours.

The process may also be carried out under reduced pressure or under increased pressure when lower or higher temperatures will be necessary to maintain the mixture at or near its boiling point. A reflux condenser is normally fitted to the reaction vessel whilst the reaction is in progress. Conditions of heating should be such as to avoid substantial caramelisation of the mixture.

The reaction may also be carried out by adding the reagents to a food product in which it is desired to incorporate a savoury or meat-like flavour, such as a protein, and heating the product to effect reaction, for instance by autoclaving in a sealed can. When carrying out the reaction by adding the reagents to a food product it may be necessary to add a small amount of water, but generally such products will already contain sufficient water to enable the reaction to proceed.

The reaction products may be used as such, or they may be converted to freeze dried powders. Such powders may tend to be hygroscopic.

Flavouring substances according to the invention may be incorporated in a wide range of meat or meat-like products. They may, for example, be incorporated either as solutions or powders, as is convenient, in protein gels, in luncheon meats, in dry soup mixes and in meat spreads.

It is preferred to let the flavouring substance age for about a week after its preparation, when optimum flavour is generally developed. The flavouring substance may tend to lose quality after about a month from its preparation. In the absence of air and light the substance or products in which it has been incorporated tend to retain their quality of flavour longer. Freeze-dried

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U.S. Patent No. 11,224,241

powders generally retain quality of flavour for a longer period than solutions.

The following examples illustrate the invention:—

EXAMPLE 1.

The following substances were mixed by stirring in a reaction vessel:—

Water	360 grams
D-Ribose	15 „
D-Glucose	18 „
β-Alanine	7 „
L-Cysteine	10 „
L-Glutamic acid	15 „
Glycine	5 „

The vessel was then heated under reflux for 2 hours by means of an oil bath at 130° C. After cooling the product to room temperature and keeping in a closed vessel for 2 days, it was then brought to a *p*H of 6.6—6.8 by addition of alkali. This brown-coloured solution had a taste and aroma resembling cooked beef; a portion was dried by freeze-drying and the flavouring solution obtained later by reconstituting the powder with water.

EXAMPLE 2.

The following substances were mixed and then treated in exactly the same manner as detailed in Example 1:—

Water	100 grams
D-Ribose	5 „
Glutathione (γ-glutamylcysteinylglycine)	10 „

The product, an orange-coloured, clear solution, had a taste and aroma resembling that of cooked beef.

EXAMPLE 3.

The following substances were mixed and then treated in exactly the same manner as detailed in Example 1:—

Water	300 grams
D-Ribose	3 „
L-Cysteine	9 „

The product, a pale yellow coloured solution, had a taste and aroma resembling that of cooked pork.

EXAMPLE 4.

Crude cod fish flesh (30 grams) was hydrolysed by refluxing with 6N-hydrochloric acid (200 grams) for 8 hours, then the acid was substantially distilled off at reduced pressure and the residual hydrolysate filtered and brought to *p*H = 6.7 with caustic soda. The dark coloured solution of low molecular weight amino compounds was then passed through a short column (3" × 2") of activated charcoal, giving a water-white solution. This solution (300 ml., containing 4.2 mg. of Kjeldahl nitrogen/ml.) was then heated to boiling for 3 hours after adding D-ribose (5 g.) and L-cysteine (3 g.), a reflux condenser being fitted to the vessel. After cooling the product to room temperature and keeping it for several days to "age" and mellow the flavour, it was adjusted to *p*H = 6.6 by addition of alkali. The deep-orange coloured solution had a strong taste and aroma resembling cooked beef.

Further experiments were carried out using deflavoured soya bean protein (30 g.) in place of the crude cod fish flesh, and deflavoured cod fish flesh (30 g.) in place of the crude cod flesh.

EXAMPLE 5.

Commercially available charcoal-treated hydrolysed (casein plus groundnut protein) powder (4 g.) and L-cysteine (2 g.) and D-glucose (1 g.) and D-xylose (1 g.) and water (100 g.) in a vessel fitted with a reflux condenser were heated to boiling for 3 hours. After cooling the product to room temperature, it was brought to *p*H = 6.7 by addition of alkali. The brown-coloured solution had an aroma and taste resembling cooked meat.

EXAMPLE 6.

Cod flesh solution prepared by hydrolysis followed by charcoal treatment, as described in Example 4, (50 ml.) and D-ribose (0.8 g.) and L-cysteine (0.6 g.) were added to a bland protein paste prepared from deflavoured groundnut protein (140 g.) and water (370 g.) in a can. The can was then sealed and autoclaved for 1½ hours at 10 pounds per square inch steam pressure. The can was opened after 6 weeks storing and the contents had a beef-like flavour.

This example was repeated using a deflavoured soya bean protein paste in place of groundnut protein paste and a similar tasting product was obtained.

WHAT WE CLAIM IS:—

1. A process for making a flavouring substance which comprises reacting a pentose or hexose monosaccharide with cysteine in the presence of a large excess of water at an elevated temperature, the reaction mixture being not alkaline at the end of the reaction.

2. A process according to Claim 1 in which at least one additional amino acid, other than phenylalanine and methionine, is present.

3. A process according to Claim 2 in which at least three additional amino acids, other than phenylalanine and methionine, are present.

4. A process according to Claim 2 or Claim 3 in which the additional amino acid or acids is or are chosen from glutamic acid,

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glycine, α and β-alanine, threonine, histidine, lysine, leucine, *iso*-leucine, serine and valine.

5. A process according to any preceding claim in which heating is carried out for from ¼ to 4 hours under reflux.

6. A process according to any preceding claim in which the amount of water is at least 5 times, by weight, the amount of monosaccharide present.

7. A process according to Claim 6 in which the amount of water present is from 15 to 25 times, by weight, the amount of monosaccharide present.

8. A process according to any preceding claim in which the molar ratio of monosaccharide to amino reagent is between 0.04:1 and 0.8:1 by weight.

9. A process according to Claim 8 in which the molar ratio of monosaccharide to amino reagent is between 0.1:1 and 0.5:1 by weight.

10. A process according to any preceding claim in which the ratio of cysteine to monosaccharide is between 0.4:1 and 2:1 by weight.

11. A process according to any preceding claim which is carried out at a *p*H between 3 and 6.

12. A process according to any preceding claim in which the amino reagent comprises hydrolysed protein.

13. A process according to Claim 12 in which the hydrolysed protein is keratin.

14. A process according to any preceding claim in which the amino reagent comprises a peptide.

15. A process according to Claim 14 in which the peptide is glutathione.

16. A process according to any preceding claim in which the monosaccharide is ribose.

17. A process of incorporating a meat-like flavour in a food product which comprises adding a pentose or hexose monosaccharide and cysteine to the food product in the presence of water and heating the mixture.

18. A process of incorporating a meat-like flavour in a protein which comprises adding a pentose or hexose monosaccharide and cysteine to the protein and heating the mixture in the presence of water.

19. A process according to Claim 16 or Claim 17 in which the monosaccharide is ribose.

20. A process according to any of Claims 1—13 in which the product is converted to a powder by freeze-drying.

21. Flavouring substances whenever made by a process substantially as described herein.

22. Food products which contain a flavouring substance whenever made by a process substantially as described herein.

UNILEVER LIMITED,
R. JONAS,
Agent for the Applicants.

PROVISIONAL SPECIFICATION.

Flavouring Substances and their Preparation.

We, UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare this invention to be described in the following statement:—

The present invention relates to artificial flavouring substances and to their preparation.

It has been found that flavouring substances capable of imparting to foodstuffs a savoury smell and taste, particularly resembling that of cooked meat, may be obtained by the reaction of a monosaccharide or a simple derivative thereof with an amino acid or a simple derivative thereof, such as a salt, in the presence of water and at an elevated temperature.

The monosaccharide is preferably a pentose, such as ribose, arabinose, or xylose but may be a hexose, such as glucose, fructose or glucosamine. As a simple monosaccharide derivative there may be mentioned monoacetone glucose. It may be advantageous to use a mixture of monosaccharides which may contain either pentoses or hexoses or both. Best results are generally obtained if the monosaccharide used alone or in admixture with other pentose or hexose monosaccharides is ribose. If a hexose, such as glucose, is used in the absence of pentoses, a substance having a pleasant savoury smell and taste, rather than that of meat, is produced. Di- or polysaccharides which yield the required monosaccharide under the conditions of the reaction may also be used.

Flavouring substances according to the invention may be obtained by using cysteine or cystine or a peptide containing a cysteine or cystine residue as the sole amino reagent. Better results are generally obtained by using cysteine or cystine in admixture with one or more, preferably three or more, other amino acids, such as glutamic acid, glycine, tryptophan, tyrosine, β-alanine, threonine, histidine, lysine, leucine, *iso*-leucine or valine. Di-, tri- or higher peptides, such as glutathione, which comprise the requisite amino acids may also be used in the reaction, although peptides of molecular weight greater than about 600 may be unsuitable.

It has been found that fish protein is a

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suitable starting material for obtaining a mixture of amino acids for the reaction, provided that cysteine or cystine is added. Preferably, the fish should first be deflavoured, for instance, by the process described in Specification No. 784,905. The fish protein is then hydrolysed, for instance by means of hydrochloric acid, and substantially neutralised. The substantially neutralised hydrolysate may be used, as such, as the amino reagent, provided cysteine or cystine is added. The product is improved by treating the substantially neutralised hydrolysate with charcoal in order to remove certain constituents, such as phenylalanine, and then adding cysteine or cystine or a peptide containing these before using the mixture. The presence of substantial amounts of phenylalanine or of methionine in mixtures may give rise to non meat-like flavours. Other suitably treated protein hydrolysates such as groundnut hydrolysate or casein hydrolysate or mixtures of these may also be used as the amino reagent.

The nature of the meat flavour may be varied by selection of the reagents. Thus, a product having a flavour resembling that of beef may be produced by the use of certain reagents in the reaction, whilst the use of other reagents will give rise to a product having a flavour akin to that of pork. Incorporation of lactic acid or other acids in the reaction mixture in many cases modifies the flavour of the resulting substance to some extent.

As little as 0.04 mol. of monosaccharide per 1 mol. of amino reagent may give a satisfactory flavouring substance. Amounts of monosaccharide up to 0.8 mol. per 1 mol. of amino reagent may be used but a greater amount of monosaccharide is generally objectionable as it tends to give rise to excessive sweetness of flavour. Generally, it is preferred to use from 0.1 to 0.5 mol., especially 0.3 mol., of monosaccharide per 1 mol. of amino reagent.

The amount of water present is usually at least 5, generally 15 to 25, times the amount of the total monosaccharide reagent. Amounts of up to 1500 times may, however, be used.

The *p*H at which the reaction is carried out is generally not critical although the *p*H of the mixture at the end of the reaction should not be alkaline. It is preferred to carry out the reaction at a *p*H between 3 and 6.

The reaction mixture may be in the form of a solution or in the form of a slurry or sludgy mass, depending on the concentration of reagents and on the conditions of heating. The saccharide may be brought into solution before heating is begun in order to reduce any danger of charring. Stirring of the mixed reagents may be advisable during heating to reduce the danger of local overheating. Vigorous stirring during heating may reduce the time required for completion of the reaction.

The reaction may be carried out by heating the mixture at or near the boiling point under reflux. In many cases the mixture is maintained at its boiling point for 1 to 4 hours. Similar results may be achieved by heating for a longer period at a lower temperature, for instance 70° C. The process may also be carried out under reduced pressure or under increased pressure when lower or higher temperatures will be necessary to maintain the mixture at or near its boiling point. A reflux condenser is normally fitted to the reaction vessel whilst the reaction is in progress. Conditions of heating should be such as to avoid substantial caramelisation of the mixture.

The reaction may also be carried out by adding the anhydrous reagents to a food product in which it is desired to incorporate a meat flavour and heating the product to effect reaction, for instance by autoclaving in a sealed can. When carrying out the reaction by adding the reagents to a food product it may be necessary to add a small amount of water, but generally such products will already contain sufficient water to enable the reaction to proceed.

It is preferred to let the flavouring substance age for about a week after its preparation, when optimum flavour is generally developed. The flavouring substance may tend to lose quality after about a month from its preparation. In the absence of air and light the substance or products in which it has been incorporated tend to retain their quality of flavour longer. Freeze-dried powders generally retain quality of flavour for a longer period than solutions.

The following examples illustrate the invention.

EXAMPLE 1.

The following substances were mixed by stirring in a reaction vessel:—

D-ribose	0.15	grams
β-alanine	0.11	„
L-cysteine or cystine	0.09	„
L-glutamic acid	0.17	„
DL-tryptophan	0.02	„
L-tyrosine	0.07	„
Water	3	ml.

Stirring was continued during the subsequent heating. A reflux condenser was fitted to the reaction vessel and this was then heated in an oil bath maintained at 140° for 4 hours. The reaction vessel was then allowed to cool and the flavouring substance was then decanted.

EXAMPLE 2.

A flavouring substance was obtained,

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using the same reaction as in Example 1, by mixing together and heating the following substances.

D-ribose	0.08 grams
D-glucose	0.09 „
Fructose	0.09 „
β-alanine	0.11 „
L-cysteine	0.10 „
L-glutamic acid	0.17 „
DL-trytophan	0.05 „
Water	3 ml.

EXAMPLE 3.

A flavouring substance was obtained, using the same reaction conditions as those described in Example 1 except that heating was discontinued after 2 hours, by mixing together and heating the following substances:—

D-ribose	0.15 grams
L-cysteine	0.10 „
Threonine	0.07 „
Glycine	0.045 „
L-tyrosine	0.07 „
DL-histidine	0.09 „
Water	3 ml.

EXAMPLE 4.

Cod flesh was deflavoured as described in our co-pending Application No. 24821/54 (Serial No. 784,905). The deflavoured flesh was hydrolysed with 6N hydrochloric acid and the hydrolysate solution so obtained was neutralised with sodium hydroxide solution, stirred with activated charcoal and then filtered.

2.5 ml. (containing 1.26% nitrogen) of the filtrate were added, with stirring, to 0.16 gram of L-cysteine and 0.10 gram of D-ribose in a reaction vessel. Stirring was continued during subsequent heating. A reflux condenser was fitted to the reaction vessel and this was then heated on an oil bath maintained at 140° C. for 45 minutes. The vessel was then taken off the oil bath, cooled to 70° C. and maintained at that temperature for 16 hours. The reaction mixture was then allowed to cool and the flavouring substance decanted.

EXAMPLE 5.

Glutathione	0.10 grams
D-ribose	0.05 „
Water	1 ml.

were mixed and heated under reflux for 2 hours at 100° C.

EXAMPLE 6.

Spray dried groundnut/ casein hydrolysate powder	0.4 grams
L-cysteine	0.2 „
D-glucose	0.1 „
D-xylose	0.1 „
Water	4 ml.

were mixed and heated under reflux for 2 hours at 100° C. and then 16 hours at about 70° C.

UNILEVER LIMITED,
R. JONAS,
Agent for the Applicants.

Abingdon: Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1960.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies may be obtained.

Case No.: IPR2023-00207
U.S. Patent No. 11,224,241

PATENT SPECIFICATION

NO DRAWINGS

Inventors: CHARLES GERARD MAY, and IAN DOUGLAS MORTON

858,660

Date of filing Complete Specification Oct. 4, 1957.

Application Date Oct. 5, 1956. No. 30504/56.

Complete Specification Published Jan. 11, 1961.

Index at acceptance:—Class 49, B6A.

International Classification:—A23l.

COMPLETE SPECIFICATION

Flavouring Substances and Their Preparation

[illegible] desired as exemplified by those

ERRATUM

SPECIFICATION NO. 858,660

Page 2. line 116. for "luncheam" read "luncheon"

THE PATENT OFFICE,
27th March, 1962

DS 88425/1(9)/R.158 200 3/61 PL

[illegible] which comprises reacting an amino reagent comprising cysteine in the presence of water and at an elevated temperature with an aldehyde containing at least 2 carbon atoms, which aldehyde is capable of existing only in the acyclic form and has at least one hydrogen atom attached to the same carbon atom as that to which an aldehyde (—CHO) group is attached.

Aldehydes containing from 2—8 carbon atoms have been found useful in processes according to the invention. Such aldehydes are for instance mono-aldehydes containing from 2—4 carbon atoms, di-aldehydes containing from 2—5 carbon atoms, alpha and beta hydroxy aldehydes containing from 2—8 carbon atoms, particularly C_3, C_6 and C_8 beta-hydroxy aldehydes which may be derived from C_2—C_4 acyclic unsubstituted mono-aldehydes by aldol condensation.

There may be mentioned as examples of unsubstituted mono-aldehydes: acetaldehyde, propionaldehyde and *n*- and isobutyraldehyde, as examples of di-aldehydes, glyoxal and glutaraldehyde and as examples of alpha-hydroxy aldehydes, glycollic aldehyde and glyceraldehyde. Mixtures of aldehydes may be

[*Price* [illegible]

Both naturally occurring (optically active) forms of the amino acids and optically inactive mixtures of dextro-rotary and levo-rotary isomers may be used.

It is not essential to use individual amino acids: salts, simple compounds such as esters or hydroxy compounds, peptides or proteins which will give rise to the desired amino acids under the conditions of reaction can be used.

In particular, it has been found that fish protein is a suitable starting material for obtaining a mixture of amino acids for the reaction, provided that cysteine or a source thereof is added. Crude fish protein, such as cod flesh, may be used but preferably the fish protein should first be deflavoured. The fish protein is hydrolysed, for instance by means of hydrochloric acid or caustic soda, and neutralised. The neutralised hydrolysate may be used, as such, as the amino reagent provided that cysteine or a source thereof is added. To obtain a flavouring substance capable of imparting a meat-like flavour to foodstuffs the hydrolysate must be treated, for instance with charcoal, in order to remove penylalanine and methionine, whilst cysteine

Motif Exhibit 1150, Page 926 of 1599

Case No.: IPR2023-00207
U.S. Patent No. 11,224,241

PATENT SPECIFICATION

NO DRAWINGS

Inventors: CHARLES GERARD MAY, and IAN DOUGLAS MORTON

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COMPLETE SPECIFICATION

Flavouring Substances and Their Preparation

We, UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to processes for the preparation of flavouring substances, flavouring substances so prepared and to food products containing such flavouring substances.

The present invention provides a process for the preparation of a flavouring substance which comprises reacting an amino reagent comprising cysteine in the presence of water and at an elevated temperature with an aldehyde containing at least 2 carbon atoms, which aldehyde is capable of existing only in the acyclic form and has at least one hydrogen atom attached to the same carbon atom as that to which an aldehyde (—CHO) group is attached.

Aldehydes containing from 2—8 carbon atoms have been found useful in processes according to the invention. Such aldehydes are for instance mono-aldehydes containing from 2—4 carbon atoms, di-aldehydes containing from 2—5 carbon atoms, alpha and beta hydroxy aldehydes containing from 2—8 carbon atoms, particularly C_4, C_6 and C_8 beta-hydroxy aldehydes which may be derived from C_2—C_4 acyclic unsubstituted mono-aldehydes by aldol condensation.

There may be mentioned as examples of unsubstituted mono-aldehydes: acetaldehyde, propionaldehyde and *n*- and isobutyraldehyde, as examples of di-aldehydes, glyoxal and glutaraldehyde and as examples of alpha-hydroxy aldehydes, glycollic aldehyde and glyceraldehyde. Mixtures of aldehydes may be used if desired, as exemplified by those obtained by the periodate oxidation of starch as is described, for instance, in the Journal of the American Chemical Society, 74. 5522, (1952).

Flavouring substances according to the invention may be obtained with advantage by using, in adition to cysteine, at least one of the amino acids arginine, glutamic acid, proline and histidine. Preferred flavours are obtained by using cysteine and at least one of said acids in admixture with one or more, preferably three or more, other amino acids such as glycine, alpha and beta-alanine, threonine, lysine, leucine, *iso*-leucine, serine, valine and cystine.

Both naturally occurring (optically active) forms of the amino acids and optically inactive mixtures of dextro-rotary and levo-rotary isomers may be used.

It is not essential to use individual amino acids: salts, simple compounds such as esters or hydroxy compounds, peptides or proteins which will give rise to the desired amino acids under the conditions of reaction can be used.

In particular, it has been found that fish protein is a suitable starting material for obtaining a mixture of amino acids for the reaction, provided that crysteine or a source thereof is added. Crude fish protein, such as cod flesh, may be used but preferably the fish protein should first be deflavoured. The fish protein is hydrolysed, for instance by means of hydrochloric acid or caustic soda, and neutralised. The neutralised hydrolysate may be used, as such, as the amino reagent provided that cysteine or a source thereof is added. To obtain a flavouring substance capable of imparting a meat-like flavour to foodstuffs the hydrolysate must be treated, for instance with charcoal, in order to remove penylalanine and methionine, whilst cysteine

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or a source thereof must be added before using the mixture. The presence of substantial amounts of phenylalanine or of methionine in mixtures tends to give rise to floral or potato-like aromas and non meat-like flavours. Small amounts of other aromatic amino acids such as tyrosine and tryptophan may not be objectionable but large amounts should preferably be avoided. Other protein hydrolysates which have been suitably treated to remove phenylalanine and methionine such as groundnut hydrolysate, casein hydrolysate, or mixtures of these may also be used as the amino reagent, provided that cysteine or a source thereof is added.

Factors which may affect the nature and quality of the flavour produced include the nature and relative amounts of the aldehyde and amino reagent used, the amount of water present and the time and temperature of heating. Thus, to obtain a product having a flavour particularly resembling that of meat the amino reagent should preferably contain about 1—4 times, by weight of the weight of cysteine present, of amino acids additional to cysteine, or sources thereof in amounts such as will give rise to an equivalent weight of such acids.

If desired, a proportion of pentose sugars, in particular ribose, may be included in reaction mixtures employed in processes according to the invention. Inclusion of such pentoses generally results in reaction products which impart flavours having a greater resemblance to that of beef. Excessive amounts of pentose sugars, however, may impart excessive sweetness to the flavouring substance.

As little as 0.1 mole of aldehyde per 1 mole of amino reagent may give a satisfactory flavouring substance. By "amino reagent" is meant the total of amino acids and derivatives thereof present inclusive of cysteine. Amounts of aldehyde of up to 1 mole per 1 mole of amino reagent may be used but greater amounts may be objectionable. 0.25 mole to 0.75 mole of aldehyde per 1 mole of amino reagent is preferred, the most preferred ratio being about 0.5 mole of aldehyde per 1 mole of amino reagent.

The reaction is carried out in the presence of water. The amount of water present should be at least 5, generally 15 to 25, times the amount, by weight of the aldehyde. Amounts of water of up to 1500 times may, however, be used.

Preferred flavouring substances can be obtained if the pH of the reaction mixture at the end of the reaction is not alkaline; it is preferred to carry out the reaction at pH of from 2 to 7.

The reaction mixture may be in the form of a solution or in the form of a slurry or sludgy mass, depending on the concentration of reagents and on the conditions of heating. In order to reduce any danger of charring, any solid reagent should be brought into solution to as great an extent as possible. Stirring of the mixed reagents may be advisable during heating to reduce the danger of local overheating. Vigorous stirring during heating may reduce the time required for completion of the reaction.

The reaction may be carried out by heating the mixture under reflux. In many cases the mixture is maintained at its boiling point for from ½ to 4 hours, generally at least for 1 hour. It is desirable that refluxing should not be continued for more than about 12 hours. Similar results may be achieved by heating for a longer period at a lower temperature, for instance 90° C., when about 18 hours is sufficient, or 70° C., when 24 to 30 hours heating may be required, or a lower temperature for a longer time. This process may also be carried out under reduced pressure or under increased pressure when lower or higher temperatures will be necessary to maintain the mixture at or near its boiling point. A reflux condenser is normally fitted to the reaction vessel whilst the reaction is in progress. Conditions of heating should be such as to avoid substantial caramelisation of the mixture. Any unreacted volatile aldehyde may be removed at the end of the reaction.

The reaction may also be carried out by adding the reagents to a food product in which it is desired to incorporate a savoury or meat-like flavour and heating the product to effect reaction, for instance by autoclaving in a sealed can. When carrying out the reaction by adding the reagents to a food product it may be necessary to add a small amount of water, but generally such products will already contain sufficient water to enable the reaction to proceed.

The reaction products may be used as such, or they may be converted to freeze-dried powders. Such powders may tend to be hygroscopic.

Flavouring substances according to the invention may be incorporated in a wide range of meat or meat-like products. They may, for example, be incorporated either as solutions or powders, as is convenient. Food products such as protein gels, luncheon meats, dry soup mixes, meat spreads, and similar products may, with advantage, have flavouring substances prepared according to the processes of the invention incorporated in them.

The flavouring substances prepared according to the processes of the invention may be used in food products where savoury flavours are required, or they may be used to enhance the flavour of meat-containing products.

It is preferred to let the flavouring substance age for about 3—5 days after its preparation, when optimum flavour is generally developed. The flavouring substances may tend to lose quality after about 3 weeks from its preparation. In the absence of air and

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light the substance or products in which it has been incorporated tend to retain their quality of flavour longer. Freeze-dried powders generally retain quality of flavour for a longer period than solutions.

The following examples illustrate the processes of the invention.

EXAMPLE 1

Deflavoured cod flesh (30 g.) was hydrolysed by refluxing with 6N-hydrochloric acid (200 g) for 8 hours. The acid was distilled off at reduced pressure and the residual hydrolysate after addition of water was filtered and brought to pH=6.7 with caustic soda. The dark coloured solution was then passed through a short column (3"×2") of activated charcoal giving a water-white solution. This solution (300 ml., containing 4.2 mg. of Kjeldahl nitrogen/ml.) was then heated to boiling, under reflux, for 3 hours after adding glyceraldehyde (5 g.) and L-cysteine (6 g.). Excess of glyceraldehyde was removed by steam distillation and the reaction mixture was then cooled to room temperature and stored for several days in a closed vessel. A meat-like flavour developed during this time.

EXAMPLE 2

The following ingredients were mixed and heated, under reflux, for 3 hours in an oil bath at 130° C.

L-cysteine - - - - - -	6 g.
Deflavoured cod flesh hydrolysate (prepared as in Example 1)	300 ml.
Iso-butyraldehyde - - - - -	3 g.

After 3 hours the reflux condenser was removed and heating continued for a short while in order to remove unreacted iso-butyraldehyde. The resulting solution had a taste and aroma resembling that of meat.

The example was repeated using (a) acetaldehyde (5 g.) and (b) propionaldehyde (5 g.) in place of iso-butyraldehyde and in both cases the resulting solution had a taste and aroma resembling that of meat.

WHAT WE CLAIM IS:—

1. A process for the preparation of a flavouring substance which comprises reacting an amino reagent comprising cysteine in the presence of water and at an elevated temperature with an aldehyde containing at least two carbon atoms, which aldehyde is capable of existing only in the acyclic form and has at least one hydrogen atom attached to the same carbon atom as that to which an aldehyde group is attached.

2. A process according to Claim 1, in which the aldehyde is a C_4, C_6 or C_8 beta hydroxy aldehyde.

3. A process according to Claim 1, in which the aldehyde is a di-aldehyde containing from 2 to 5 carbon atoms.

4. A process according to Claim 1, in which the aldehyde is a mono-aldehyde of from 2 to 4 carbon atoms.

5. A process according to Claim 4, in which the aldehyde is acetaldehyde.

6. A process according to Claim 4, in which the aldehyde is propionaldehyde.

7. A process according to Claim 1, in which the aldehyde compound is an alpha hydroxy aldehyde.

8. A process according to Claim 7, in which the aldehyde is glyceraldehyde.

9. A process according to any preceding claim, in which the amino reagent also contains at least one of the amino acids arginine, glutamic acid, proline and histidine.

10. A process according to Claim 9, in which the amino reagent contains at least three additional amino acids other than phenylalanine and methionine.

11. A process according to Claim 10, in which the additional amino acids are any of the amino acids: glycine, alpha and beta-alanine, threonine, lysine, leucine, iso-leucine, serine, valine and cystine.

12. A process according to any preceding claim, in which from 0.1 to 1 mole of aldehyde per 1 mole of amino reagent is used.

13. A process according to Claim 12, in which from 0.25 to 0.75 mole of aldehyde per 1 mole of amino reagent is used.

14. A process according to any preceding claim, in which the amount of water present is at least 5 times by weight of the weight of aldehyde.

15. A process according to any preceding claim, in which the amino reagent contains about 1 to 4 times by weight of the weight of cysteine present of amino acids additional to cysteine.

16. A process according to any preceding claim, which is carried out at a pH of from 2 to 7.

17. A process according to any preceding claim, in which the reaction is carried out by heating the amino reagent and the aldehyde under reflux.

18. A process of incorporating a savoury or meat-like flavour in a food product in which an amino reagent comprising cysteine and an aldehyde containing at least 2 carbon atoms, which aldehyde is capable of existing only in the acyclic form and has at least one hydrogen atom atached to the same carbon atom as that to which an aldehyde group is attached, are added to the food product and the food product is heated in the presence of water.

19. A process for making a flavouring substance substantially as hereinbefore described in Example 1 or 2.

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20. A flavouring substance prepared by a process according to any of Claims 1 to 17 inclusive.

21. A food product in which there is incorporated a flavouring substance prepared by the process of any of Claims 1 to 19 inclusive.

UNILEVER LIMITED,
R. Jonas,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Flavouring Substances and Their Preparation

We, UNILEVER LIMITED, a Company registered under the Laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare this invention to be described in the following statement:—

The present invention relates to artificial flavouring substances and to their preparation.

It has been found that flavouring substances capable of imparting to foodstuffs a savoury smell and taste, particularly resembling that of cooked meat, may be obtained by reacting an amino reagent comprising cysteine with an aliphatic aldehyde in the presence of water and at an elevated temperature.

Aliphatic aldehydes which may be used according to the invention include short chain, preferably C_2—C_4, aliphatic aldehydes, notably acetaldehyde, propionaldehyde and n- and *iso*-butyraldehyde. Short chain aliphatic dialdehydes, preferably containing 2—5 C atoms, including glyoxal and glutaraldehyde, short chain hydroxyaldehydes, such as glycollic aldehyde and glyceraldehyde, and short chain β-hydroxyaldehydes ("aldols"), particularly the C_4, C_5 and C_6 β-hydroxyaldehydes which may be derived from the C_2—C_4 simple aliphatic aldehydes described above by aldol condensation, may also be used.

Preferred mixtures of aldehydes for use according to the invention are those obtained by the periodate oxidation of starch, such as is described, for instance, in the Journal of the American Chemical Society, *74*, 5522, (1952).

Flavouring substances according to the invention may be obtained by using an amino reagent comprising (a) cysteine and (b) arginine or glutamic acid or proline or histidine. With reference to component (b), the acids may be used singly, or in combination. Preferred flavours are obtained by using components (a) and (b) in admixture with one or more, preferably three or more, other amino acids such as glycine, α and β-alanine, threonine, lysine, leucine, *iso*-leucine, serine, cystine and valine.

It is not essential to use individual amino acids: salts, simple compounds such as esters or hydroxy compounds, peptides or proteins which will give rise to the desired amino acids under the conditions of reaction can be used.

In particular, it has been found that fish protein is a suitable starting material for obtaining a mixture of amino acids for the reaction, provided that cysteine is added. Crude fish proteins, such as cod flesh, may be used, but preferably the fish should first be deflavoured, for instance, by the process described in Specification No. 784,905. The fish protein is then hydrolysed, for instance, by means of hydrochloric acid or caustic soda, and substantially neutralised. The substantially neutralised hydrolysate may be used, as such, as the amino reagent, provided cysteine is added. The hydrolysate must be treated, for instance, with charcoal, in order to remove phenylalanine and methionine, whilst cysteine or a source thereof must be added before using the mixture. The presence of substantial amounts of phenylalanine or of methionine is mixtures tends to give rise to undesirable floral or potato-like aromas and non meat-like flavours. Small amounts of other aromatic amino acids such as tyrosine and tryptophan may be objectionable but large amounts should preferably be avoided. Other protein hydrolysates which have been suitably treated to remove phenylalanine and methionine such as groundnut hydrolysate or casein hydrolysate or mixtures of these may be used as the amino reagent, provided cystein or a source thereof is added.

Factors which may affect the nature and quality of the flavour produced include the nature and relative amounts of the aldehyde and amino reagent used, the amount of water present and the time and temperature of heating. Thus to obtain a product having a flavour resembling that of meat the amino reagent should preferably contain about 1—4 times, by weight of the weight of cysteine present, of amino acids additional to cysteine, or amounts of derivatives such as will give rise to an equivalent weight of such acids.

If desired, a proportion of pentose sugars, in particular ribose, may be included in reaction mixtures according to the invention. Inclusion of such pentoses generally results in reaction products which impart flavours having a greater resemblance to that of beef. Excessive amounts of pentose sugars, however, may impart excessive sweetness to the flavouring substance.

As little as 0.1 mole of aldehyde per 1 mole

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of amino reagent may give a satisfactory flavouring substance. By "amino reagent" is meant the total of amino acids and derivatives thereof present, inclusive or cysteine. Amounts of aldehyde up to 1 mole per 1 mole of amino reagent may be used but greater amounts may be objectionable. 0.25 mole to 0.75 mole of aldehyde per 1 mole of amino reagent is preferred, the most preferred ratio being about 0.5 mole of aldehyde per 1 mole of amino reagent.

The amount of water present should be at least 5, generally 15 to 25, times the amount, by weight, of the aldehyde. Amounts of up to 1500 times may, however, be used.

The pH at which the reaction is carried out is not critical although the pH of the mixture at the end of the reaction should preferably not be alkaline. It is preferred to carry out the reaction at a pH of between 2 and 7.

The reaction mixture may be in the form of a solution or in the form of a slurry or sludgy mass, depending on the concentration of reagents and on the conditions of heating. In order to reduce any danger of charring, any solid reagent should be brought into solution to as great an extent as possible. Stirring of the mixed reagents may be advisable during heating to reduce the danger of local overheating. Vigorous stirring during heating may reduce the time required for completion of the reaction.

The reaction may be carried out by heating the mixture under reflux. In many cases the mixture is maintained at its boiling point for from ½ to 4 hours, generally at least for 1 hour. It is desirable that refluxing should not be continued for more than about 12 hours. Similar results may be achieved by heating for a longer period at a lower temperature, for instance 70° C., when 24 to 30 hours heating may be required. The process may also be carried out under reduced pressure or under increased pressure when lower or higher temperatures will be necessary to maintain the mixture at or near its boiling point. A reflux condenser is normally fitted to the reaction vessel whilst the reaction is in progress. Conditions of heating should be such as to avoid substantial caramelisation of the mixture. Any unreacted volatile aldehyde should be removed at the end of the reaction.

The reaction may also be carried out by adding the reagents to a food product in which it is desired to incorporate a savoury or meat-like flavour and heating the product to effect reaction, for instance by autoclaving in a sealed can. When carrying out the reaction by adding the reagents to a food product it may be necessary to add a small amount of water, but generally such products will already contain sufficient water to enable the reaction to proceed.

The reaction products may be used as such, or they may be converted to freeze-dried powders. Such powders may tend to be hygroscopic.

Flavouring substances according to the invention may be incorporated in a wide range of meat or meat-like products. They may, for example, be incorporated either as solutions or powders, as is convenient, in protein gels, in luncheon meats, in dry soup mixes and in meat spreads and similar products.

The flavouring substances may be used in artificial meat products, or they may be used to enhance the flavour of meat-containing products.

It is preferred to let the flavouring substance age for about 3—5 days after its preparation, when optimum flavour is generally developed. The flavouring substance may tend to lose quality after about 3 weeks from its preparation. In the absence of air and light the substance or products in which it has been incorporated tend to retain their quality of flavour longer. Freeze-dried powders generally retain quality of flavour for a longer period than solutions.

The following examples illustrate the invention.

Example 1

Deflavoured cod flesh (30 grams) was hydrolysed by refluxing with 6N-hydrochloric acid (200 grams) for 8 hours. The acid was substantially distilled off at reduced pressure and the residual hydrolysate after addition of water was filtered and brought to pH=6.7 with caustic soda. The dark coloured solution was then passed through a short column (3"×2") of activated charcoal giving a water-white solution. This solution (300 ml., containing 4.2 mg. of Kjeldahl nitrogen/ml.) was then heated to boiling, under reflux, for 3 hours after adding glyceraldehyde (5 g.) and L-cysteine (6 g.). The excess glyceraldehyde was removed by heating the flask without reflux condenser for a short time and the contents cooled to room temperature and stored for several days in a closed vessel. A meat-like flavour developed during this time.

Example 2

The following ingredients were mixed and heated, under reflux, for 3 hours in an oil bath at 130° C.

L-cysteine - - - - - -	6 g.
Deflavoured cod flesh hydrolysate (prepared as in Example 1)	300 ml.
Iso-butyraldehyde - - - -	3 g.

After 3 hours the reflux condenser was

removed and heating continued for a short while in order to remove unreacted isobutyraldehyde. The resulting solution had a taste and aroma resembling that of meat.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained

PATENT SPECIFICATION

NO DRAWINGS

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858,333

Date of filing Complete Specification: Oct. 4, 1957.

Application Date: Oct. 5, 1956. No. 30505/56.

Complete Specification Published: Jan. 11, 1961.

Index at acceptance:—Class 49, B6A.

International Classification:—A23l.

COMPLETE SPECIFICATION

Flavouring Substances and their preparation

We, UNILEVER LIMITED, a Company registered under the laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to processes for the preparation of flavouring substances, flavouring substances prepared by such processes and also to food products containing such flavouring substances.

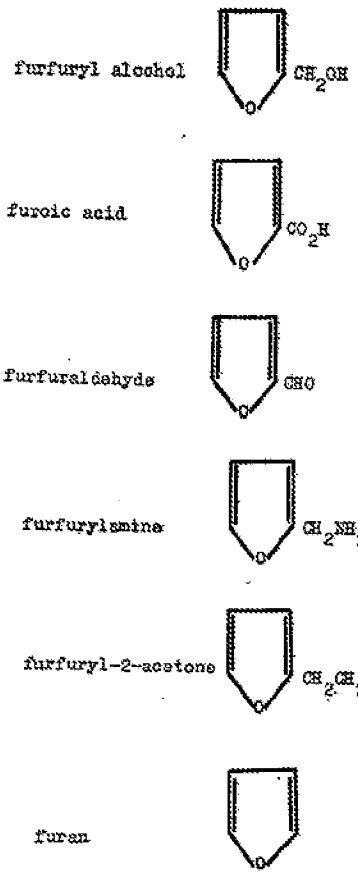
The present invention provides a process for the preparation of a flavouring substance which comprises reacting an amino reagent comprising cysteine with a furan compound as hereinafter defined in the presence of water and at an elevated temperature.

Flavouring substances capable of imparting a savoury odour or taste to foodstuffs, especially a meat-like taste, can be prepared by processes in accordance with the invention.

The term "furan compound" is used in this specification to denote a compound of the class consisting of furan and 2-substituted furans which have the 5-position unsubstituted.

Suitable substituent groups for the 2-position of the furan ring are carbon-containing groups linked to the furan ring through a carbon atom of the group. Such substituent groups include hydrocarbon groups, for instance alkyl groups. The substituent group may also be a substituted hydrocarbon group, for instance an alkyl group having attached thereto any one of the groups amino, hydroxy and acetyl: thus, examples of 2-substituted furan compounds which may be used in processes according to the invention will include furfurylamine, furfuryl alcohol and furfuryl-2-acetone [which may also be designated: 2-(2¹-acetylethyl)furan]. Other suitable substituent groups are those containing a carbonyl function, for instance aldehyde and carboxylic groups: thus examples of 2-substituted furans which may be used in processes according to the invention and which have such groups are furfuraldehyde and furoic acid.

Examples of furan compounds which may be used according to the invention are:



Furfuraldehyde is the preferred compound and should be freshly distilled before use. Other furan compounds which may be derived from pentoses and pentosans are also preferred.

In addition to cysteine the amino reagent

[*Price 3s. 6d.*]

Price 3s 6d. Price 75p.

Price 25p

Price 33p

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should preferably also contain at least one of the amino acids arginine, glutamic acid and proline. Preferred flavours can be obtained by using at least one, preferably three or more, other amino acids such as glycine, alpha and beta alanine, threonine, lysine, leucine, *iso*-leucine, serine, valine, histidine and cystine.

It is not essential to use individual amino acids. Salts, such as monosodium glutamate, simple compounds, such as esters or hydroxy compounds, peptides, such as glutathione, or proteins which will give rise to the desired amino acids under the conditions of reaction may be used. Both racemic and naturally occurring forms of the amino acids may be used.

In particular it has been found that fish protein is a suitable starting material for obtaining a mixture of amino acids for the reaction, provided that cysteine or a source thereof is added. Crude fish protein, such as cod flesh, may be used, but preferably the fish should first be deflavoured. The fish protein is then hydrolysed, for instance by means of hydrochloric acid or caustic soda, and substantially neutralised. The substantially neutralised hydrolysate may be used, as such, as the amino reagent, provided cysteine or a source thereof is added. To obtain a flavouring substance capable of imparting a meat-like taste to foodstuffs the hydrolysate must be treated, for instance with charcoal, in order to remove phenylalanine and methionine, whilst cysteine or a source thereof must be added before using the mixture. The presence of substantial amounts of phenylalanine or of methionine in mixtures tend to give rise to floral or potato-like aromas and non meat-like flavours. Small amounts of other aromatic amino acids such as tyrosine and tryptophan may not be objectionable but large amounts should preferably be avoided. Other protein hydrolysates which have been suitably treated to remove phenylalanine and methionine such as groundnut hydrolysate or casein hydrolysate or mixtures of these may also be used as the amino reagent, provided cysteine or a source thereof is added.

Factors which may affect the nature and quality of the flavour produced include the nature and relative amounts of the furan compound and amino reagent used, the amount of water present and the time and temperature of heating. Thus, to obtain a product having a savoury flavour particularly resembling that of meat the amino reagent should preferably contain about 1—4 times, by weight of the weight of cysteine present, of amino acids additional to cysteine, or amounts of derivatives such as will give rise to an equivalent weight of such acids.

If desired, a proportion of pentose sugars, in particular ribose, may be included in reaction mixtures employed in processes according to the invention. Inclusion of such pentoses generally results in reaction products which impart flavours having a greater resemblance to that of beef. Excessive amounts of pentose sugars, however, may impart excessive sweetness to the flavouring substance.

As little as 0.05 moles of furan compound per 1 mole of amino reagent may give a satisfactory flavouring substance. By "amino reagent" is meant the total amino acids and derivatives thereof present, inclusive of cysteine. Amounts of furan compound of up to 0.75 moles per 1 mole of amino reagent may be used but greater amounts may be objectionable. About 0.5 moles of furan compound per 1 mole of amino reagent is preferred.

The amount of water present should preferably be at least 5, generally 15 to 25, times the amount, by weight of the furan compound. Amounts of up to 1500 times may, however, be used.

Preferred flavouring substances can be obtained if the pH of the mixture at the end of the reaction is not alkaline; it is preferred to carry out the reaction at a pH of from 2 to 7.

The reaction mixture may be in the form of a solution or in the form of a slurry or sludgy mass, depending on the concentration of reagents and on the conditions of heating. In order to reduce any danger of charring, any solid reagent should be brought into solution to as great an extent as possible. Stirring of the mixed reagents may be advisable during heating to reduce the danger of local overheating. Vigorous stirring during heating may reduce the time required for completion of the reaction.

The reaction may be carried out by heating the mixture under reflux. In many cases the mixture is maintained at its boiling point for from $\frac{1}{2}$ to 4 hours, generally at least for 1 hour. It is desirable that refluxing should not be continued for more than about 12 hours. Similar results may be achieved by heating for a longer period at a lower temperature, for instance 90° C. when about 18 hours heating is necessary, 70° C. when 24 to 30 hours heating may be required, or at a lower temperature for an even longer time. The process may also be carried out under reduced pressure or under increased pressure when lower or higher temperatures will be necessary to maintain the mixture at or near its boiling point. A reflux condenser is normally fitted to the reaction vessel whilst the reaction is in progress. Conditions of heating should be such as to avoid substantial caramelisation of the mixture. Any unreacted furan compound should preferably be removed at the end of the reaction.

The reaction may also be carried out by adding the reagents to a food product in which it is desired to incorporate a savoury flavour and heating the product to effect reaction, for instance by autoclaving in a sealed can. When carrying out the reaction by adding the reagents

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to a food product it may be necessary to add a small amount of water, but generally such products will already contain sufficient water to enable the reaction to proceed. Care should be taken to avoid the presence of excess furan compound in the food product.

The reaction products may be used as such, or they may be converted to powders, for instance by freeze drying. Such powders may tend to be hygroscopic.

Flavouring substances prepared according to the processes of the invention may be incorporated in a wide range of meat or meat-like food products. They may, for example, be incorporated either as solutions or powders, as is convenient. Food products such as protein gels, luncheon meats, dry soup mixes, meat spreads, and similar products may, with advantage, have flavouring substances prepared according to the processes of the invention incorporated in them.

The flavouring substances prepared according to the processes of the invention may be used in food products where a savoury flavour is required and they may be used to enhance the flavour of meat-containing products.

It is preferred to let the flavouring substance age for about 3—5 days after its preparation, when optimum flavour is generally developed. The flavouring substance may tend to lose quality after about 3 weeks from its preparation. In the absence of air and light the substance or products in which it has been incorporated tend to retain their quality of flavour longer. Freeze-dried powders generally retain quality of flavour for a longer period than solutions.

The following examples illustrate the invention.

EXAMPLE 1.

Water	200	g.
DL-Cysteine	6	g.
Furfuraldehyde	5	g.
Arginine	1.6	g.

The above mixture was heated for 3 hours in a round-bottomed flask fitted with reflux condenser in an oil bath at 130° C. At the end of this time the reflux condenser was removed and heating carried out for a short time in order to remove unreacted furfuraldehyde. After cooling, and storage of the product in a closed vessel for two days it had a savoury meat-like flavour.

EXAMPLE 2.

Deflavoured cod flesh (30 grams) was hydrolysed by refluxing with 6N-hydrochloric acid (200 grams) for 8 hours. The acid was substantially distilled off at reduced pressure and the residual hydrolysate after addition of water was filtered and brought to pH 6.7 with caustic soda. The dark coloured solution was then passed through a short column (3"×2") of activated charcoal giving a water-white solution. This solution (300 c.c. containing 4.2 mg. of Kjeldahl nitrogen/mL) was then heated to boiling, under reflux, for 3 hours after adding furfuraldehyde (5 g.) and L-cysteine (6 g.). The excess furfuraldehyde was removed by heating the flask without reflux condenser for a short time and the contents cooled to room temperature and stored for several days in a closed vessel. A savoury meat-like flavour developed during this time.

EXAMPLE 3.

The following ingredients were mixed and heated, under reflux, for 3 hours in an oil bath at 130° C.

L-cysteine	6	g.
Deflavoured cod fish hydrolysate (prepared as in Example 2).	300	mls.
D-ribose	1	g.
Furfuraldehyde	4	g.

After 3 hours the reflux condenser was removed and heating continued for a short while in order to remove unreacted furfuraldehyde. The resulting solution had a taste and aroma resembling that of meat.

EXAMPLE 4.

The following ingredients were mixed and heated, under reflux, for 3 hours in an oil bath at 130° C.

L-cysteine	6	g.
Deflavoured cod fish hydrolysate	300	mls.
Furoic acid	5	g.

After storage for a few days in a closed vessel the resulting solution had a taste and aroma resembling that of meat.

EXAMPLE 5.

The following ingredients were mixed and heated under reflux, for 3 hours in an oil bath maintained at 130° C.

2-furfuryl acetone	5	g.
Deflavoured cod fish hydrolysate (prepared as in Example 2)	300	mls.
L-cysteine hydrochloride	6	g.

The solution obtained had a savoury taste and aroma.

EXAMPLE 6.

The following ingredients were heated under reflux in an oil bath which was maintained for 30 hours at 80° C.

Furfurylamine	5	g.
Deflavoured cod fish hydrolysate (prepared as in Example 2)	500	mls.
L-cysteine hydrochloride	6	g.

The resulting solution had a savoury aroma and taste.

WHAT WE CLAIM IS:—

1. A process for the preparation of a flavouring substance which comprises reacting an amino reagent comprising cysteine with a furan compound as hereinbefore defined in the

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presence of water and at an elevated temperature.

2. A process according to Claim 1 in which the furan compound is furan itself.

3. A process according to Claim 1 in which the furan compound is furfuraldehyde.

4. A process according to Claim 1 in which the furan compound is furfuryl alcohol.

5. A process according to Claim 1 in which the furan compound is furoic acid.

6. A process according to Claim 1 in which the furan compound is furfurylamine.

7. A process according to any one of the preceding claims in which the amino reagent also contains at least one of the amino acids arginine, glutamic acid and proline.

8. A process according to Claim 7 in which the amino reagent also contains at least three of the amino acids glycine, alpha and beta alanine, threonine, lysine, leucine, *iso*-lucine, serine, valine, histidine and cystine.

9. A process according to any one of the preceding claims in which from 0.05 to 0.75 moles of furan compound per 1 mole of amino reagent is used.

10. A process according to Claim 9 in which about 0.5 moles of furan compound per 1 mole of amino reagent is used.

11. A process according to any preceding claim in which the amount of water present is at least five times by weight of the weight of furan compound.

12. A process according to any one of the preceding claims in which the amino reagent contains about 1 to 4 times by weight of the weight of cysteine present of amino acids additional to cysteine.

13. A process according to any one of the preceding claims which is carried out at a pH of from 2 to 7.

14. A process according to any one of the preceding claims in which the reaction is carried out by heating the mixture under reflux.

15. A process of incorporating a meat-like flavour in a food product in which an amino reagent comprising cysteine and a furan compound are added to the food product in the presence of water and the food product is heated.

16. A process for the preparation of a flavouring substance substantially as hereinbefore described in any of Examples 1 to 4 inclusive.

17. A process for making a flavouring substance substantially as hereinbefore described in Example 5 or 6.

18. A flavouring substance whenever prepared by a process according to any of Claims 1 to 17 inclusive.

19. A food product containing a flavouring substance prepared by the process of any of Claims 1 to 17 inclusive.

UNILEVER LIMITED,
R. Jonas,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Flavouring Substances and their preparation

We, UNILEVER LIMITED, a Company registered under the laws of Great Britain, of Port Sunlight, in the County of Chester, England, do hereby declare this invention to be described in the following statement:—

The present invention relates to artificial flavouring substances and to their preparation.

It has been found that flavouring substances capable of imparting to foodstuffs a savoury smell and taste, particularly resembling that of cooked meat, may be obtained by reacting an amino reagent comprising cysteine with furan, tetrahydrofuran or a 2-substituted furan or a 2-substituted tetrahydrofuran in the presence of water and at an elevated temperature.

Preferably the substituent in the 2-position is a carbon-containing group linked to the furan ring through a carbon atom, although the substituent may be nitrogenous, such as an amino group. Suitable substituent groupings are aldehyde, alcohol and carboxyl groups.

The furan ring may bear simple substituents, such as hydrocarbon groups, additional to the 2-substituent, but preferably the 5-position of the furan ring should not be substituted.

As examples of suitable compounds there may be mentioned furfuryl alcohol, furoic acid and furfuraldehyde.

Furfuraldehyde is the preferred compound and should be freshly distilled before use. Furan compounds which can be derived from pentoses and pentosans are also preferred.

Flavouring substances according to the invention may be obtained by using an amino reagent comprising (a) cysteine and (b) arginine or glutamic acid or proline. With reference to component (b), the acids may be used singly, or in combination. Preferred flavours are obtained by using components (a) and (b) in admixture with one or more, preferably three or more, other amino acids such as glycine, α and β-alanine, threonine, lysine, leucine, *iso*-leucine, serine, cystine and valine.

It is not essential to use individual amino acids: salts, simple compounds such as esters or hydroxy compounds, peptides or proteins which will give rise to the desired amino acids under the conditions of reaction can be used.

In particular, it has been found that fish protein is a suitable starting material for obtaining a mixture of amino acids for the reaction, provided that cysteine is added. Crude

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fish protein, such as cod flesh, may be used, but preferably, the fish should first be deflavoured, for instance, by the process described in Specification No. 748,905. The fish protein is then hydrolysed, for instance, by means of hydrochloric acid or caustic soda, and substantially neutralised. The substantially neutralised hydrolysate may be used, as such, as the amino reagent, provided cysteine or is added. The hydrolysate must be treated, for instance, with charcoal, in order to remove phenylalanine and methionine, whilst cysteine or a source thereof must be added before using the mixture. The presence of substantial amounts of phenylalanine or of methionine in mixtures tend to give rise to undesirable floral or potato-like aromas and non meat-like flavours. Small amounts of other aromatic amino acids such as tyrosine and tryptophan may not be objectionable but large amounts should preferably be avoided. Other protein hydrolysates which have been suitably treated to remove phenylalanine and methionine such as groundnut hydrolysate or casein hydrolysate or mixtures of these may also be used as the amino reagent, provided cysteine or a source thereof is added.

Factors which may affect the nature and quality of the flavour produced include the nature and relative amounts of the furan and amino reagents used, the amount of water present and the time and temperature of heating. Thus, to obtain a product having a flavour resembling that of meat the amino reagent should preferably contain about 1—4 times, by weight of the weight of cysteine present, of amino acids additional to cysteine, or amounts of derivatives such as will give rise to an equivalent weight of such acids.

If desired, a proportion of pentose sugars, in particular ribose, may be included in reaction mixtures according to the invention. Inclusion of such pentoses generally results in reaction products which impart flavours having a greater resemblance to that of beef. Excessive amounts of pentose sugars, however, may impart excessive sweetness to the flavouring substance.

As little as 0.05 moles of furan compound per 1 mole of amino reagent may give a satisfactory flavouring substance. By "amino reagent" is meant the total of amino acids and derivatives thereof present, inclusive of cysteine. Amounts of furan up to 0.75 moles per 1 mole of amino reagent may be used but greater amounts may be objectionable. About 0.5 mole of furan per 1 mole of amino reagent is preferred.

The amount of water present should be at least 5, generally 15 to 25, times the amount, by weight, of the furan reagent. Amounts of up to 1500 times may, however, be used.

The pH at which the reaction is carried out is not critical although the pH of the mixture at the end of the reaction should preferably not be alkaline. It is preferred to carry out the reaction at a pH of between 2 and 7.

The reaction mixture may be in the form of a solution or in the form of a slurry or sludgy mass, depending on the concentration of reagents and on the conditions of heating. In order to reduce any danger of charring, any solid reagent should be brought into solution to as great an extent as possible. Stirring of the mixed reagents may be advisable during heating to reduce the danger of local overheating. Vigorous stirring during heating may reduce the time required for completion of the reaction.

The reaction may be carried out by heating the mixture under reflux. In many cases the mixture is maintained at its boiling point for from ½ to 4 hours, generally at least for 1 hour. It is desirable that refluxing should not be continued for more than about 12 hours. Similar results may be achieved by heating for a longer period at a lower temperature, for instance 70° C., when 24 to 30 hours heating may be required. The process may also be carried out under reduced pressure or under increased pressure when lower or higher temperatures will be necessary to maintain the mixture at or near its boiling point. A reflux condenser is normally fitted to the reaction vessel whilst the reaction is in progress. Conditions of heating should be such as to avoid substantial caramelisation of the mixture. Any unreacted furan compound should be removed at the end of the reaction.

The reaction may also be carried out by adding the reagents to a food product in which it is desired to incorporate a savoury or meat-like flavour and heating the product to effect reaction, for instance by autoclaving in a sealed can. When carrying out the reaction by adding the reagents to a food product it may be necessary to add a small amount of water, but generally such products will already contain sufficient water to enable the reaction to proceed.

The reaction products may be used as such, or they may be converted to freeze-dried powders. Such powders may tend to be hygroscopic.

Flavouring substances according to the invention may be incorporated in a wide range of meat or meat-like products. They may, for example, be incorporated either as solutions or powders, as is convenient, in protein gels, in luncheon meats, in dry soup mixes and in meat spreads and similar products.

The flavouring substances may be used in artificial meat products, or they may be used to enhance the flavour of meat-containing products.

It is preferred to let the flavouring substance age for about 3—5 days after its preparation, when optimum flavour is generally developed. The flavouring substance may tend to lose quality after about 3 weeks from its prepara-

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tion. In the absence of air and light the substance or products in which it has been incorporated tend to retain their quality of flavour longer. Freeze-dried powders generally retain quality of flavour for a longer period than solutions.

The following examples illustrate the invention.

EXAMPLE 1.

Water	200	gm.
Cysteine	6	gm.
Furfuraldehyde	5	gm.
Arginine	1.6	gm.

The above mixture was heated for 3 hours in a roundbottomed flask fitted with a reflux condenser in an oil bath at 130° C. At the end of this time the reflux condenser was removed and heating carried out for a short time in order to remove unreacted fufuraldehyde. After cooling, and storage of the product in a closed vessel for two days it had a savoury meat-like flavour.

EXAMPLE 2.

Deflavoured cod flesh (30 grams) was hydrolysed by refluxing with 6N-hydrochloric acid (200 grams) for 8 hr. The acid was substantially distilled off at reduced pressure and the residual hydrolysate after addition of water was filtered and brought to pH=6.7 with caustic soda. The dark coloured solution was then passed through a short column (3″×2″) of activated charcoal giving a water-white solution. This solution (300 c.c., containing 4.2 mg. of Kjeldahl nitrogen/cc.) was then heated to boiling, under reflux, for 3 hours after adding furfuraldehyde (5 g.) and L-cysteine (6 g.). The excess furfuraldehyde was removed by heating the flask without reflux condenser for a short time and the contents cooled to room temperature and stored for several days in a closed vessel. A savoury meat-like flavour developed during this time.

EXAMPLE 3.

The following ingredients were mixed and heated, under reflux, for 3 hours in an oil bath at 130° C.

L-cysteine	6	gm.
Deflavoured cod fish hydrolysate (prepared as in Example 2)	300	ml.
D-ribose	1	gm.
Furfuraldehyde	4	gm.

After 3 hours the reflux condenser was removed and heating continued for a short while in order to remove unreacted furfuraldehyde. The resulting solution had a taste and aroma resembling that of meat.

EXAMPLE 4.

The following ingredients were mixed and heated, under reflux, for 3 hours in an oil bath at 130° C.

L-cysteine	6	gm.
Deflavoured cod fish hydrolysate (prepared as in Example 2)	300	ml.
Furoic acid	5	gm.

After storage for a few days in a closed vessel the resulting solution had a taste and aroma resembling that of meat.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

Espacenet

Bibliographic data: JP2009516522 (A) — 2009-04-23

METHOD OF MODIFYING THE TEXTURE OF A PREPARATION

Inventor(s):

Applicant(s):

Classification:	**- international:** ***A23C9/12; A23C9/127; A23C9/13; A23C***
	- cooperative: **A23C9/1216**; **A23C9/1275**
Application number:	JP20080541774 20061121 Global Dossier
Priority number (s):	WO2006FI50506 20061121 ; FI20050005616 20051122
Also published as:	EP1951061 (A1) EP1951061 (A4) FI121525 (B) FI20055616 (A) WO2007060288 (A1)

Abstract not available for JP2009516522 (A)
Abstract of corresponding document: WO2007060288 (A1)

The invention relates to a method of manufacturing soured fresh dairy products by the use of a transglutaminase enzyme, an enzyme-activating compound and an acidifying agent and by the addition thereof to a protein source under such circumstances that the enzyme is active during acidifying.

Espacenet

Bibliographic data: JPH11508448 (A) — 1999-07-27

A PROCESS FOR MAKING CHEESE

Inventor(s):

Applicant(s):

Classification: **- international:** ***A23C19/032; A23C19/04;*** (IPC1-7): A23C19/032
- cooperative: **A23C19/0328**; **A23C19/043**; **C12Y203/02013**

Application number: JP19970504726 19960625

Priority number (s): WO1996DK00279 19960625 ; DK19950000764 19950630

Also published as: AU6188796 (A) AU695309 (B2) BR9609507 (A) CN1075354 (C) CN1189764 (A) more

Abstract not available for JPH11508448 (A)
Abstract of corresponding document: WO9701961 (A1)

The present invention relates to a process for making cheese comprising: a) adding to cheesemilk a transglutaminase, incubating for a suitable period, b) incubating with a rennet so as to cause clotting, and c) separating whey from the coagulate, and d) processing the coagulate into cheese. Also the cheese products produced by said process are contemplated. The invention is also directed towards the use of transglutaminase for maintaining proteins in the cheese material during a conventional cheese-making process.

Electronic Acknowledgement Receipt

EFS ID:	34907425
Application Number:	15913090
International Application Number:	
Confirmation Number:	9878
Title of Invention:	METHODS AND COMPOSITIONS FOR AFFECTING THE FLAVOR AND AROMA PROFILE OF CONSUMABLES
First Named Inventor/Applicant Name:	Rachel Fraser
Customer Number:	26191
Filer:	Kimberly M. Maize/Kirsten Neuman
Filer Authorized By:	Kimberly M. Maize
Attorney Docket Number:	38767-0015008
Receipt Date:	18-JAN-2019
Filing Date:	06-MAR-2018
Time Stamp:	22:08:59
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

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New International Application Filed with the USPTO as a Receiving Office

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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 November 2007 (29.11.2007)

PCT

(10) International Publication Number
WO 2007/137128 A1

(51) International Patent Classification:
A61K 8/37 (2006.01) *A61Q 17/04* (2006.01)

(21) International Application Number:
PCT/US2007/069160

(22) International Filing Date: 17 May 2007 (17.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/747,760 19 May 2006 (19.05.2006) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
---- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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WO 2007/137128 A1

(54) Title: GLYCERYL AND GLYCOL ACID COMPOUNDS

(57) Abstract: A composition comprising a glyceryl salicylate compound and/or a glycol salicylate compound. The compositions can be used to reduce the amount of moisture evaporated from skin, protect the skin from UV light, and treat aged or damaged skin.

DESCRIPTION

GLYCERYL AND GLYCOL ACID COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 60/747,760, filed May 19, 2006, the contents of which are incorporated by reference.

BACKGROUND OF THE INVENTION

A. Field of the Invention

[0002] The present invention relates generally to a compound that can be used in compositions such as cosmetic skin care compositions. The compound can include an acid molecule attached to a glycerol or glycol molecule *via* an ester linkage.

B. Description of Related Art

[0003] With ageing, chronic exposure to adverse environmental factors, or malnutrition, the visual appearance, physical properties, and physiological functions of skin can change in ways that are considered visually undesirable. The most notable and obvious changes include the development of fine lines and wrinkles, loss of elasticity, increased sagging, loss of firmness, loss of color evenness or tone, coarse surface texture, and mottled pigmentation. Less obvious, but measurable changes which occur as skin ages or endures chronic environmental insult include a general reduction in cellular and tissue vitality, reduction in cell replication rates, reduced cutaneous blood flow, reduced moisture content, accumulated errors in structure and function, alterations in the normal regulation of common biochemical pathways, and a reduction in the skin's ability to remodel and repair itself. Many of the alterations in appearance and function of the skin are caused by changes in the outer epidermal layer of the skin, while others are caused by changes in the lower dermis.

[0004] Several different approaches have been used to treat damaged skin caused by aging, environmental factors, chemicals, or malnutrition. These approaches can oftentimes have various drawbacks, such as significant irritation to the skin or skin toxicity.

SUMMARY OF THE INVENTION

[0005] The present invention overcomes deficiencies in the art. In a non-limiting aspect, the invention relates generally to compounds that can be used in compositions such as cosmetic and pharmaceutical compositions. In certain embodiments, the compound can include an acid molecule attached to a glyceryl or glycol molecule *via* an ester linkage. Generic and specific structures of these compounds are disclosed throughout this specification and incorporated into this section by reference.

[0006] In certain embodiments, the compounds can be incorporated into a composition. The composition can be cosmetic composition or a pharmaceutical composition. The composition can be topically applied to skin. The compositions can be included in a cosmetic vehicle. Non-limiting examples of cosmetic vehicles are disclosed in other sections of this specification and are known to those of skill in the art. Examples of cosmetic vehicles include emulsions (*e.g.*, oil-in-water and water-in-oil emulsions), creams, lotions, solutions (*e.g.*, aqueous or hydro-alcoholic solutions), anhydrous bases (*e.g.*, lipstick or a powder), gels, and ointments. In other non-limiting embodiments, the compositions of the present invention can be included in anti-aging, cleansing, or moisturizing products. The compositions can also be formulated for topical skin application at least 1, 2, 3, 4, 5, 6, 7, or more times a day during use. In other aspects of the present invention, compositions can be storage stable or color stable, or both.

[0007] In certain embodiments, the compositions of the present invention can include from about 0.001% to about 20%, by weight or volume, of glyceryl/acid or glycol/acid compounds, or a combination of both. It should be recognized, however, that the amount of the compounds in a composition can be modified below, within, or above this range based on the desired results (*e.g.*, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99%, or more, by weight or volume of the composition). Therefore, the amount of a glyceryl/acid or glycol/acid compound can include less than 0.001% or more than 5%, by weight or volume. In other aspects, the compositions can include 0.002, 0.003, 0.004...1, 2, 3, 4, 5, 6, ,7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 95, 96, 97, 98, 99%, or more or, or any range derivable therein, by weight or volume of glyceryl or glycol salicylate or a combination of both. In other embodiments, the compositions of the present invention

can further include a carnitine molecule. The carnitine molecule can be acylated (*e.g.*, acetyl-l-carnitine). In certain aspects, the ratio of any ingredient within the composition when compared to another ingredient can be from about 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 11:1, 12:1, 13:1, 14:1, 15:1, 16:1, 17:1, 18:1, 19:1, 20:1, 21:1, 22:1, 23:1, 24:1, 25:1, 26:1, 27:1, 28:1, 29:1, 30:1, 31:1, 32:1, 33:1, 34:1, 35:1, 36:1, 37:1, 38:1, 39:1, 40:1, 50:1, 60:1, 70:1, 80:1, 90:1, 100:1, or more or any number derivable therein, by weight or volume of the total composition. In other aspects, the ratio of any ingredient within the composition when compared to another ingredient can be from about 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, 1:10, 1:11, 1:12, 1:13, 1:14, 1:15, 1:16, 1:17, 1:18, 1:19, 1:20, 1:21 , 1:22, 1:23, 1:24, 1:25, 1:26, 1:27, 1:28, 1:29, 1:30, 1:31, 1:32, 1:33, 1:34, 1:35, 1:36, 1:37, 1:38, 1:39, 1:40, 1:50, 1:60, 1:70, 1:80, 1:90, 1:100, or more or any number derivable therein, by weight or volume of the total composition.

[0008] The compositions of the present invention can also be modified to have a desired oxygen radical absorbance capacity (ORAC) value. In certain non-limiting aspects, the compositions of the present invention can be modified to have an ORAC value per mg of at least about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90, 95, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10000, 15000, 20000, 30000, 50000, 100000 or more or any range derivable therein.

[0009] In other non-limiting aspects of the present invention, the compositions can further include a vitamin, a mineral, an essential fatty acid, an amino acid (including essential and non-essential amino acids), a flavinoid, and/or a protein, or a combination thereof. Non-limiting examples of vitamins include the B vitamins (*e.g.*, B1, B2, B6, B12, niacin, folic acid, biotin, and pantothenic acid), vitamin C, vitamin D, vitamin E (*e.g.*., tocopherol or tocopheryl acetate), vitamin A (*e.g.*, palmitate, retinyl palmitate, or retinoic acid), and vitamin K. Non-limiting examples of minerals include iron, potassium, phosphorus, magnesium, manganese, selenium, and calcium. Non-limiting examples of essential fatty acids include Omega 3 (linolenic acid), Omega 6 (linoleic acid) and Omega 9 (oleic acid) essential fatty acid, or a combination thereof. Non-limiting examples of amino acids include essential amino acids (*e.g.*., lysine, leucine, isoleucine, methionine, phenylalanine, threonine, tryptophan, valine, histidine, or arginine) and non-essential amino acids (*e.g.*., serine, asparagine, glutamine, aspartic acid, glutamic acid, alanine, tyrosine, cysteine, glycine, or

proline). Non-limiting examples of flavinoids include anthocyanin compounds (*e.g.*, cyanidin-3-glucoside and cyanidin-3-rutinoside).

[0010] The compositions in non-limiting aspects can have a pH of about 6 to about 9. In other aspects, the pH can be 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, or 14. The compositions can include a triglyceride. Non-limiting examples include small, medium, and large chain triglycerides. In certain aspects, the triglyceride is a medium chain triglyceride (*e.g.*, caprylic capric triglyceride). The compositions can also include preservatives. Non-limiting examples of preservatives include methylparaben, propylparaben, or a mixture of methylparaben and propylparaben.

[0011] Also disclosed is a method of treating or preventing a skin condition comprising topical application of a composition comprising a glyceryl/acid compound and/or a glycol/acid compound, wherein the topical application of the composition treats the skin condition. Non-limiting examples of skin conditions include pruritus, spider veins, lentigo, age spots, senile purpura, keratosis, melasma, blotches, fine lines or wrinkles, nodules, sun damaged skin, dermatitis (including, but not limited to seborrheic dermatitis, nummular dermatitis, contact dermatitis, atopic dermatitis, exfoliative dermatitis, perioral dermatitis, and stasis dermatitis), psoriasis, folliculitis, rosacea, acne, impetigo, erysipelas, erythrasma, eczema, and other inflammatory skin conditions. In certain non-limiting aspects, the skin condition can be caused by exposure to UV light, age, irradiation, chronic sun exposure, environmental pollutants, air pollution, wind, cold, heat, chemicals, disease pathologies, smoking, or lack of nutrition. The skin can be facial skin or non-facial skin (*e.g.*, arms, legs, hands, chest, back, feet, etc.). The method can further comprise identify a person in need of skin treatment. The person can be a male or female. The age of the person can be at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or more years old, or any range derivable therein.

[0012] The compositions of the present invention can also be used in methods for exfoliate the skin. This allows the user to shed dead skin cells and also encourages the skin's natural sloughing process. An advantage of this process is that it reveals and exposes "younger," fresher skin. The shedding process unclogs pores, keeps skin clean and helps reduce acne breakouts.

[0013] The methods of the present invention can also include topically applying an amount effective to: increase the stratum corneum turnover rate of the skin; decrease skin roughness; increase collagen synthesis in fibroblasts; increase cellular anti-oxidant defense mechanisms (*e.g.*., exogenous additions of anti-oxidants can bolster, replenish, or prevent the loss of cellular antioxidants such as catalase and glutathione in skin cells (*e.g.*, keratinocytes, melanocytes, langerhans cells, etc.) which will reduce or prevent oxidative damage to the skin, cellular, proteins, and lipids); inhibit melanin production in melanocytes; reduce or prevent oxidative damage to skin (including reducing the amount lipid peroxides and/or protein oxidation in the skin); enhance desmosomal degradation, leading to an increase in corneocyte desquamation; increase cytokines, hyaluronic acid, cell proliferation, collagen production and epidermal proliferation; normalize corneocyte cohesion; enhance lipid synthesis in the intercellular areas; target the sebum in the sebaceous glands; and activate fibroblasts.

[0014] The compositions of the present invention can also be used in a regimen alone or with other compositions (*e.g.*, skin care compositions). For instance, the composition of the present invention can be applied in the morning and/or evening at predetermined intervals and/or amounts. Alternatively, the compositions of the present invention can be applied in the morning and a second skin care composition can be applied in the evening and vice versa.

[0015] Also disclosed are methods for using the glyceryl/acid compounds and glycol/acid compounds as moisturizing agents, film-forming agents, UV absorption agents, and/or skin treatment agents. For instance, the compounds can maintain and/or increase the hydration (such as water content) of skin. The compounds can also lubricate the skin. The compounds can form a film or barrier on the outer surface of the skin which can reduce or prevent the evaporation of water from the skin. In certain aspects, the film can have tactile properties which make the skin feel soft or smooth. The compounds can also be used as UV absorption agents and can be used in methods for increasing the UV absorption characteristics of a composition such as, for example, a sunscreen composition. The compounds can be used in methods for increasing the SPF of a sunscreen composition. In certain aspects, the compounds can be used to increase the efficiency of existing sunscreen products and/or sunscreen agents that are used in such products. Alternatively, the compounds can be used as a stand alone sunscreen agent. In certain embodiments, the compounds can be used in methods for reducing or preventing cosmetic compositions from

chemical or physical deterioration that is induced by ultraviolet light. The compounds and/or compositions of the present invention can diffract or absorb a broad spectrum of UV radiation. For example, the compounds and/or compositions can absorb or diffract UVA (approximately 315 to 400nm), UVB (approximately 280 to 315) and/or UVC (approximately 10 to 280nm) light. In certain aspects, the compounds and/or compositions can absorb or diffract UV light ranging from about 1 to about 400nm, or any integer or range therein (*e.g.*, 2, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 399).

[0016] Also contemplated are kits that include the compositions of the present invention. In certain embodiments, the composition is comprised in a container. The container can be a bottle, dispenser, or package. The container can dispense a pre-determined amount of the composition. In certain aspects, the compositions is dispensed in a spray or mist, dollop, or liquid. The container can include indicia on its surface. The indicia can be a word, an abbreviation, a picture, or a symbol.

[0017] Also contemplated is a product comprising a composition of the present invention. In non-limiting aspects, the product can be a cosmetic product. The cosmetic product can be those described in other sections of this specification or those known to a person of skill in the art. Non-limiting examples of products include a moisturizer, a cream, a lotion, a skin softener, a foundation, a night cream, a lipstick, a cleanser, a toner, a sunscreen, a mask, or an anti-aging product.

[0018] It is contemplated that any embodiment discussed in this specification can be implemented with respect to any method or composition of the invention, and *vice versa*. Furthermore, compositions of the invention can be used to achieve methods of the invention.

[0019] The term "alkyl" includes straight-chain alkyl groups, branched-chain alkyl groups, cycloalkyl (alicyclic) groups, alkyl heteroatom-substituted cycloalkyl groups, and cycloalkyl heteroatom-substituted alkyl groups.

[0020] The term "alkoxy" includes a group having the structure —OR, where R is an alkyl group. Non-limiting examples of alkoxy groups include $-OCH_3$, $-OCH_2CH_3$, $-OCH_2CH_2CH_3$, $-OCH(CH_3)_2$, $-OCH(CH_2)_2$, *etc.*

[0021] The term "hydroxyalkyl" includes an alkyl group having at least one hydroxy group.

[0022] The term "about" or "approximately" are defined as being close to as understood by one of ordinary skill in the art, and in one non-limiting embodiment the terms are defined to be within 10%, within 5%, within 1%, and/or within 0.5%.

[0023] The terms "inhibiting" or "reducing" or any variation of these terms, when used in the claims and/or the specification includes any measurable decrease or complete inhibition to achieve a desired result.

[0024] The term "effective," as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

[0025] The use of the word "a" or "an" when used in conjunction with the term "comprising" in the claims and/or the specification may mean "one," but it is also consistent with the meaning of "one or more," "at least one," and "one or more than one."

[0026] The use of the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or."

[0027] As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0028] Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the examples, while indicating specific embodiments of the invention, are given by way of illustration only. Additionally, it is contemplated that changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0029] In today's image conscious society, people are continually looking for a product that can protect or improve the visual appearance of their skin. Often times, aged skin, uneven skin tone, or skin damaged by environmental factors such as UV light, chronic sun exposure, environmental pollutants, chemicals, disease pathologies, or smoking, is associated with unattractive skin. Compounds of the present invention can be used in all types of cosmetic compositions/formulations for treating, preserving, or preventing the appearance of aged or damaged skin.

[0030] For instance, the compounds of the present invention can have a wide variety of uses in compositions that are applied to skin. Non-limiting examples include using the compounds as a moisturizing agent, a film-forming agent, a UV absorption agent, and a skin treatment agent. As a moisturizing agent, the compounds can help maintain and/or increase the hydration of skin, thereby making the skin softer and more pliable. The compounds can also act as lubricants for the skin to treat, reduce, or prevent skin flaking and dry skin.

[0031] As a film-forming agent, the compounds can be used to form a film or barrier on the outer surface of the skin. This can be beneficial to the skin by reducing or preventing the evaporation of water from the skin. Additionally, the film can have tactile properties that make the skin feel soft and smooth.

[0032] As a UV absorption agent, the compounds can be used to protect the cosmetic composition from chemical or physical deterioration induced by ultraviolet light. The compounds can also be used as a sunscreen agent in sunscreen compositions. The compounds can also increase the sun protection factor (SPF) of a sunscreen composition that already includes a sunscreen agent.

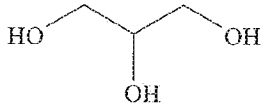
[0033] As a skin treatment agent, the compounds can be used as active ingredients in topical skin care compositions. Non-limiting examples of skin conditions that can be treated with the compounds of the present invention are disclosed throughout this specification.

[0034] These and other aspect of the invention are described in further non-limiting detail below.

A. Glyceryl/Acid and Glycol/Acid Compounds

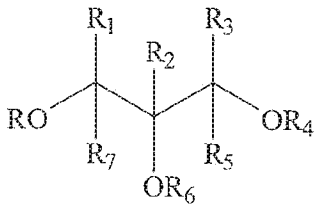
1. Glyceryl/Acid Compounds

[0035] A glyceryl/acid compound of the present invention can be derived from glycerol molecule which has the following structure:

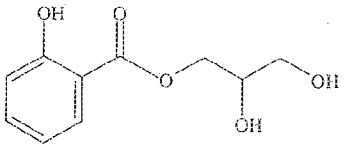


Glycerol

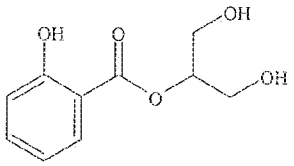
The acid portion of the glyceryl/acid compounds can be attached *via* an ester linkage of the OH group of the glycerol molecule and the COOH group of the acid molecule. In non-limiting aspects, a glyceryl/acid compound can have the following generic chemical structure:



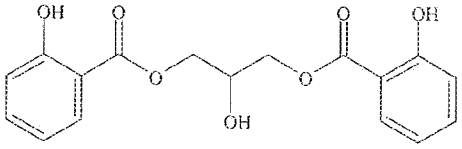
where R, R_1, R_2, R_3, R_4, R_5, and R_6 can each independently be an H, an acid molecule, a hydroxy, a halogen, an oxo (*e.g.*, ether), an alkoxy, a silyloxy, an acyl, an aryl, an acetyl, a carbonyl, a cyano, a heterocyclyl, an amido, an aminocarbonyl, an amino, -NH-alkyl, -$N(alkyl)_2$, -NH-(substituted alkyl), -N-(substituted $alkyl)_2$, -NH-aryl, -$N(aryl)_2$, an azido, a trialkylsilyloxy, an acyloxy, a acylamino, a bis-acylamino, an ester, a NO, a NO_2, or a sulfo (*e.g.*, thioether, thioester, thiocarbonyl, sulfonamido, sulfonyl, *etc.*). In certain aspects, the acid molecule is selected from the group consisting of salicylic acid, cinnamic acid, and benzoic acid, and derivatives and substituted acids thereof. Other non-limiting examples of acids that can be used in the context of the present invention are described in International Cosmetic Ingredient Dictionary and Handbook, 10^{th} Ed., 2004, which is incorporated by reference. In certain aspects, at least one of R, R_4, and R_6 is an acid, R and R_4 are acids, R and R_6 are acids, R_4 and R_6 are acids, or R, R_4, and R_6 are all acids. Non-limiting examples of certain glyceryl/acid compounds of the present invention are illustrated below:



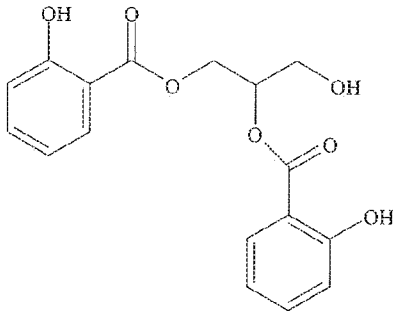
Glyceryl Mono-Salicylate



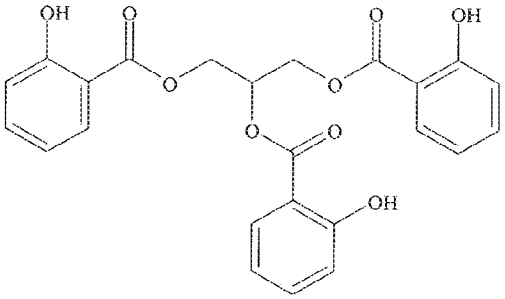
Glyceryl Mono-Salicylate



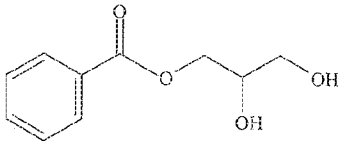
Glyceryl Di-Salicylate



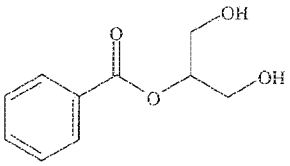
Glyceryl Di-Salicylate



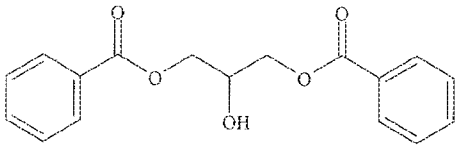
Glyceryl Tri-Salicylate



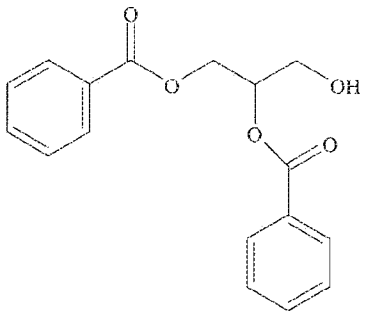
Glyceryl Mono-Benzoate



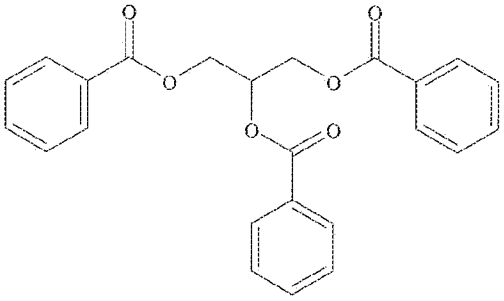
Glyceryl Mono-Benzoate



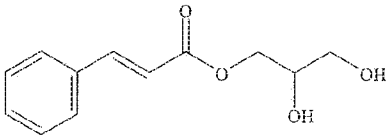
Glyceryl Di-Benzoate



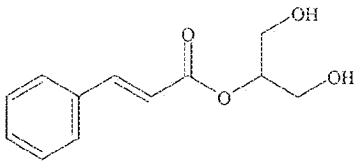
Glyceryl Di-Benzoate



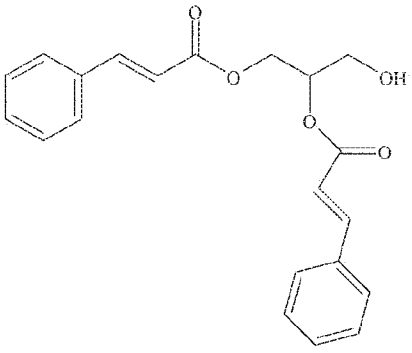
Glyceryl Tri-Benzoate



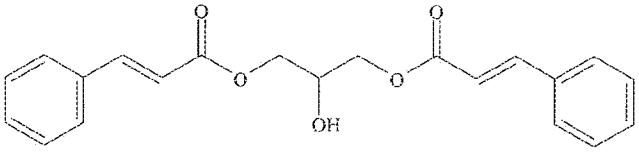
Glyceryl Mono-Cinnamate



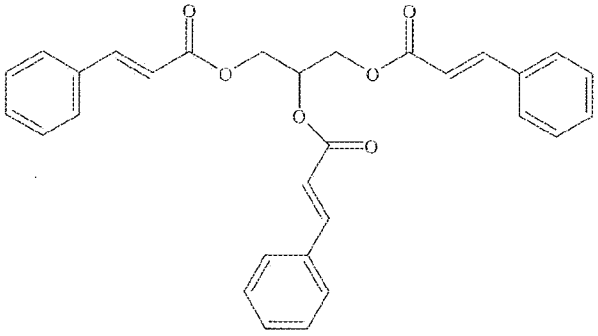
Glyceryl Mono-Cinnamate



Glyceryl Di-Cinnamate



Glyceryl Di-Cinnamate



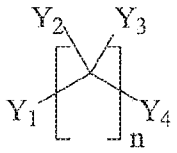
Glyceryl Tri-Cinnamate

[0036] The glyceryl/acid compounds and derivatives and modifications of the same can be prepared by using convention chemical synthesis techniques (*see, e.g.*., Organic Chemistry, 5th Ed.).

2. Glycol/Acid Compounds

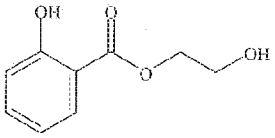
[0037] A glycol/acid compound of the present invention can be derived from a glycol molecule. Glycols are a generic class of dihydric alcohols. Non-limiting examples of glycols that can be used in the context of the present invention include: ethylene glycols (*e.g.*, 1, 2 ethane diol (monoethylene glycol), 2-hydroxyethoxy)ethan-2-ol (diethylene glycol); polyethylene glycols (PEGs); propylene glycols (*e.g.*, 1, 2 propane diol, 1, 3 propane diol, *etc.*); and butylene glycols (*e.g.*, 1, 2 butane diol, 1,3 butane diol, 1, 4 butane diol, *etc.*). Other non-limiting examples of glycols that can be used in the context of the present invention are described in International Cosmetic Ingredient Dictionary and Handbook, 10th Ed., 2004, which is incorporated by reference. It certain aspects, the glycol that is used can have similar physical and chemical characteristics to glycerol.

[0038] The acid portion of the glycol/acid compounds can be attached *via* an ester linkage of the OH group of the glycol molecule and the COOH group of the acid molecule. In non-limiting aspects, a glycol/acid compound can have the following generic chemical structure:

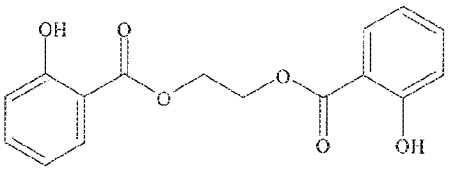


where n can be 2, 3, 4, 5, 6, 7, 8, 9, 10, or more, or any range therein. In certain aspects, n is an integer from 2 to 4. Y_1, Y_2, Y_3, and Y_4, can each independently be OY_5, an H, an acid molecule attached *via* an ester linkage, a hydroxy, a halogen, an oxo (*e.g.*, ether), an alkoxy, a silyloxy, an acyl, an aryl, an acetyl, a carbonyl, a cyano, a heterocyclyl, an amido, an aminocarbonyl, an amino, -NH-alkyl, -N(alkyl)$_2$, -NH-(substituted alkyl), -N-(substituted alkyl)$_2$, -NH-aryl, -N(aryl)$_2$, an azido, a trialkylsilyloxy, an acyloxy, a acylamino, a bis-acylamino, an ester, a NO, a NO_2, or a sulfo (*e.g.*, thioether, thiocster, thiocarbonyl, sulfonamido, sulfonyl, *etc.*). In certain aspects, the acid molecule is selected from the group consisting of salicylic acid, cinnamic acid, and benzoic acid, and derivatives and substituted acids thereof. Other non-limiting examples of acids that can be used in the context of the present invention are described in International Cosmetic Ingredient Dictionary and Handbook, 10th Ed., 2004, which is incorporated by reference. Y_5 can be anyone of the groups identified for Y_1, Y_2, Y_3, and Y_4. In certain aspects Y_5 is an acid group. In other

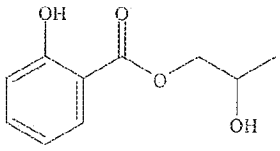
embodiments, at least two of Y_1, Y_2, Y_3, and Y_4 is a hydroxyl group. Non-limiting examples of certain particular glycol/acid compounds of the present invention are illustrated below:



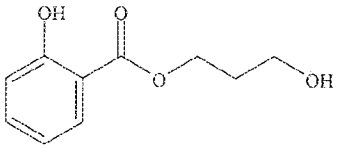
Ethylene Glycol Mono-Salicylate



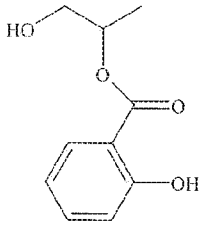
Ethylene Glycol Di-Salicylate



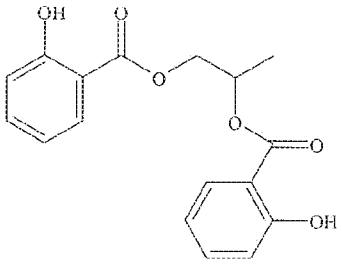
Propylene Glycol Mono-Salicylate



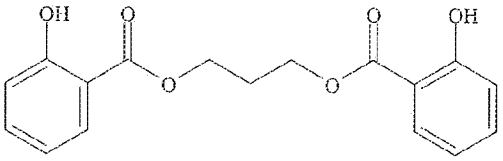
Propylene Glycol Mono-Salicylate



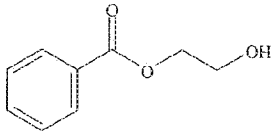
Propylene Glycol Mono-Salicylate



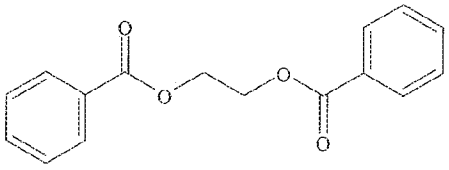
Propylene Glycol Di-Salicylate



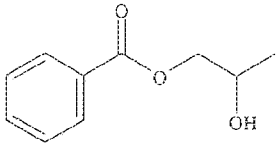
Propylene Glycol Di-Salicylate



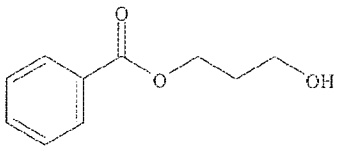
Ethylene Glycol Mono-Benzoate



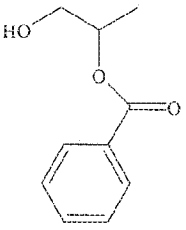
Ethylene Glycol Di-Benzoate



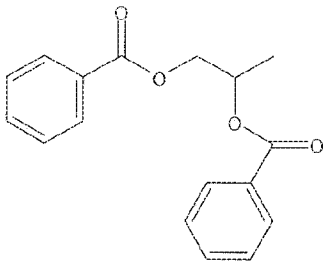
Propylene Glycol Mono-Benzoate



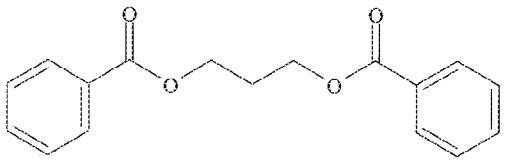
Propylene Glycol Mono-Benzoate



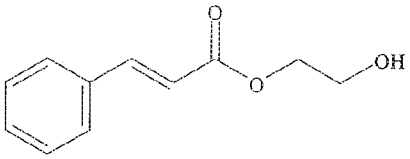
Propylene Glycol Mono-Benzoate



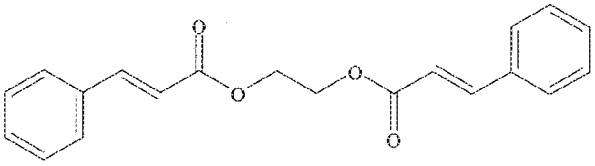
Propylene Glycol Di-Benzoate



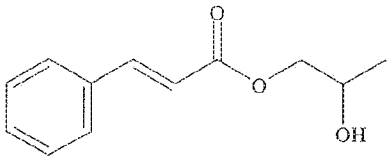
Propylene Glycol Di-Benzoate



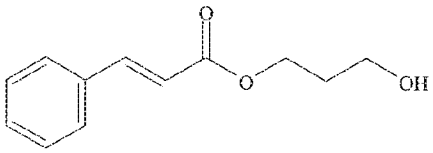
Ethylene Glycol Mono-Cinnamate



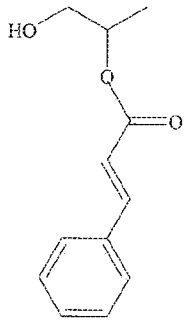
Ethylene Glycol Di-Cinnamate



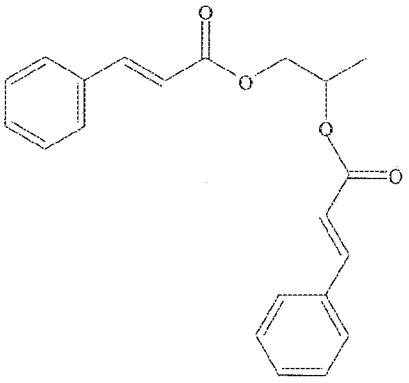
Propylene Glycol Mono-Cinnamate



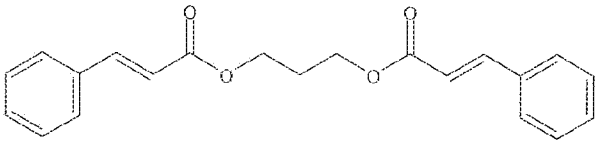
Propylene Glycol Mono-Cinnamate



Propylene Glycol Mono-Cinnamate



Propylene Glycol Di-Cinnamate



Propylene Glycol Di-Cinnamate

[0039] The glycol/acid compounds and derivatives and modifications of the same can be prepared by using convention chemical synthesis techniques (*see, e.g.*., Organic Chemistry, 5th Ed.).

3. Modifications and Derivatives of Glyceryl/Glycol/Acid Compounds

[0040] Modifications or derivatives of the glyceryl/acid and glycol/acid compounds disclosed throughout this specification are contemplated as being useful with the methods and compositions of the present invention. Derivatives and modifications may be prepared and the properties of such derivatives and modified compounds may be assayed for their desired properties by any method known to those of skill in the art.

[0041] In certain aspects, "derivative" refers to a chemically modified glyceryl/acid or glycol/acid compound that still retains the desired effects of the compound prior to the chemical modification. Such derivatives may have the addition, removal, or substitution of one or more chemical moieties on the glyceryl, glycol, and/or acid portion of the compounds. Non-limiting examples of the modifications that can be made to these portions of the compounds include the addition or removal of alkyl groups, carboxyl groups, carbonyl groups, hydroxyl groups, nitro groups, amino groups, amide groups, azo groups, sulfate groups, sulfonate groups, sulfono groups, sulfhydryl groups, sulfonyl groups, sulfoxido groups, phosphate groups, phosphono groups, phosphoryl groups, and/or halide groups. Additional modifications can include an addition or a deletion of one or more atoms of the atomic framework, for example, substitution of an ethyl by a propyl or substitution of a phenyl by a larger or smaller aromatic group. In a cyclic or bicyclic structure, hetero atoms such as N, S, or O can be substituted into the structure instead of a carbon atom.

B Compositions

[0042] The compounds of the present invention can be incorporated into all types of compositions (*e.g.*, cosmetic and pharmaceutical compositions). A person of ordinary skill would recognize that the compositions can include any number of combinations of glyceryl/acid compounds, glycol/acid compounds, and/or additional ingredients, or derivatives thereof. The concentrations of the glyceryl/acid compounds, glycol/acid compounds, and/or additional ingredients, or derivatives thereof, can vary for a given composition. This variation can oftentimes depend on the desired characteristics of the final composition. In non-limiting embodiments, for example, the compositions may include in

their final form, for example, at least about 0.0001%, 0.0002%, 0.0003%, 0.0004%, 0.0005%, 0.0006%, 0.0007%, 0.0008%, 0.0009%, 0.0010%, 0.0011%, 0.0012%, 0.0013%, 0.0014%, 0.0015%, 0.0016%, 0.0017%, 0.0018%, 0.0019%, 0.0020%, 0.0021%, 0.0022%, 0.0023%, 0.0024%, 0.0025%, 0.0026%, 0.0027%, 0.0028%, 0.0029%, 0.0030%, 0.0031%, 0.0032%, 0.0033%, 0.0034%, 0.0035%, 0.0036%, 0.0037%, 0.0038%, 0.0039%, 0.0040%, 0.0041%, 0.0042%, 0.0043%, 0.0044%, 0.0045%, 0.0046%, 0.0047%, 0.0048%, 0.0049%, 0.0050%, 0.0051%, 0.0052%, 0.0053%, 0.0054%, 0.0055%, 0.0056%, 0.0057%, 0.0058%, 0.0059%, 0.0060%, 0.0061%, 0.0062%, 0.0063%, 0.0064%, 0.0065%, 0.0066%, 0.0067%, 0.0068%, 0.0069%, 0.0070%, 0.0071%, 0.0072%, 0.0073%, 0.0074%, 0.0075%, 0.0076%, 0.0077%, 0.0078%, 0.0079%, 0.0080%, 0.0081%, 0.0082%, 0.0083%, 0.0084%, 0.0085%, 0.0086%, 0.0087%, 0.0088%, 0.0089%, 0.0090%, 0.0091%, 0.0092%, 0.0093%, 0.0094%, 0.0095%, 0.0096%, 0.0097%, 0.0098%, 0.0099%, 0.0100%, 0.0200%, 0.0250%, 0.0275%, 0.0300%, 0.0325%, 0.0350%, 0.0375%, 0.0400%, 0.0425%, 0.0450%, 0.0475%, 0.0500%, 0.0525%, 0.0550%, 0.0575%, 0.0600%, 0.0625%, 0.0650%, 0.0675%, 0.0700%, 0.0725%, 0.0750%, 0.0775%, 0.0800%, 0.0825%, 0.0850%, 0.0875%, 0.0900%, 0.0925%, 0.0950%, 0.0975%, 0.1000%, 0.1250%, 0.1500%, 0.1750%, 0.2000%, 0.2250%, 0.2500%, 0.2750%, 0.3000%, 0.3250%, 0.3500%, 0.3750%, 0.4000%, 0.4250%, 0.4500%, 0.4750%, 0.5000%, 0.5250%, 0.0550%, 0.5750%, 0.6000%, 0.6250%, 0.6500%, 0.6750%, 0.7000%, 0.7250%, 0.7500%, 0.7750%, 0.8000%, 0.8250%, 0.8500%, 0.8750%, 0.9000%, 0.9250%, 0.9500%, 0.9750%, 1.0%, 1.1%, 1.2%, 1.3%, 1.4%, 1.5%, 1.6%, 1.7%, 1.8%, 1.9%, 2.0%, 2.1%, 2.2%, 2.3%, 2.4%, 2.5%, 2.6%, 2.7%, 2.8%, 2.9%, 3.0%, 3.1%, 3.2%, 3.3%, 3.4%, 3.5%, 3.6%, 3.7%, 3.8%, 3.9%, 4.0%, 4.1%, 4.2%, 4.3%, 4.4%, 4.5%, 4.6%, 4.7%, 4.8%, 4.9%, 5.0%, 5.1%, 5.2%, 5.3%, 5.4%, 5.5%, 5.6%, 5.7%, 5.8%, 5.9%, 6.0%, 6.1%, 6.2%, 6.3%, 6.4%, 6.5%, 6.6%, 6.7%, 6.8%, 6.9%, 7.0%, 7.1%, 7.2%, 7.3%, 7.4%, 7.5%, 7.6%, 7.7%, 7.8%, 7.9%, 8.0%, 8.1%, 8.2%, 8.3%, 8.4%, 8.5%, 8.6%, 8.7%, 8.8%, 8.9%, 9.0%, 9.1%, 9.2%, 9.3%, 9.4%, 9.5%, 9.6%, 9.7%, 9.8%, 9.9%, 10%, 11%, 12%, 13%, 14%, 15%, 16%, 17%, 18%, 19%, 20%, 21%, 22%, 23%, 24%, 25%, 26%, 27%, 28%, 29%, 30%, 35%, 40%, 45%, 50%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, or 99% or any range derivable therein, of at least one of the glyceryl/acid compounds, glycol/acid compounds, and/or additional ingredients, or derivatives thereof. In certain non-limiting aspects, the percentages can be calculated by weight or volume of the total composition. A person of ordinary skill in the art would understand that the concentrations can vary depending on the addition, substitution, and/or subtraction of the glyceryl/acid compounds, glycol/acid compounds, and additional ingredients, or derivatives thereof.

C Additional Ingredients

[0043] In addition to the glyceryl/acid compounds and/or glycol/acid compounds disclosed throughout this specification, compositions of the present invention can include additional ingredients such as cosmetic ingredients and pharmaceutical active ingredients. Non-limiting examples of these additional ingredients are described in the following subsections.

1. Cosmetic Ingredients

[0044] The CTFA International Cosmetic Ingredient Dictionary and Handbook (2004) describes a wide variety of non-limiting cosmetic ingredients that can be used in the context of the present invention. Examples of these ingredient classes include: fragrances (artificial and natural), dyes and color ingredients (*e.g.*, Blue 1, Blue 1 Lake, Red 40, titanium dioxide, D&C blue no. 4, D&C green no. 5, D&C orange no. 4, D&C red no. 17, D&C red no. 33, D&C violet no. 2, D&C yellow no. 10, and D&C yellow no. 11), adsorbents, lubricants, solvents, moisturizers (including, *e.g.*, emollients, humectants, film formers, occlusive agents, and agents that affect the natural moisturization mechanisms of the skin), water-repellants, UV absorbers (physical and chemical absorbers such as paraaminobenzoic acid ("PABA") and corresponding PABA derivatives, titanium dioxide, zinc oxide, *etc.*), essential oils, vitamins (*e.g.* A, B, C, D, E, and K), trace metals (*e.g.* zinc, calcium and selenium), anti-irritants (*e.g.* steroids and non-steroidal anti-inflammatories), botanical extracts (*e.g.* aloe vera, chamomile, cucumber extract, ginkgo biloba, ginseng, and rosemary), anti-microbial agents, antioxidants (*e.g.*, BHT and tocopherol), chelating agents (*e.g.*, disodium EDTA and tetrasodium EDTA), preservatives (*e.g.*, methylparaben and propylparaben), pH adjusters (*e.g.*, sodium hydroxide and citric acid), absorbents (*e.g.*, aluminum starch octenylsuccinate, kaolin, corn starch, oat starch, cyclodextrin, talc, and zeolite), skin bleaching and lightening agents (*e.g.*, hydroquinone and niacinamide lactate), humectants (*e.g.*, sorbitol, urea, and manitol), exfoliants, waterproofing agents (*e.g.*, magnesium/aluminum hydroxide stearate), skin conditioning agents (*e.g.*, aloe extracts, allantoin, bisabolol, ceramides, dimethicone, hyaluronic acid, and dipotassium glycyrrhizate). Non-limiting examples of some of these ingredients are provided in the following subsections.

a. Preservatives

[0045] Non-limiting examples of preservatives that can be used in the context of the present invention include quaternary ammonium preservatives such as polyquaternium-1 and benzalkonium halides (*e.g.*, benzalkonium chloride ("BAC") and benzalkonium bromide), parabens (*e.g.*, methylparabens and propylparabens), phenoxyethanol, benzyl alcohol, chlorobutanol, phenol, sorbic acid, thimerosal or combinations thereof.

b. Moisturizers

[0046] Non-limiting examples of moisturizing agents that can be used with the compositions of the present invention can be found in the International Cosmetic Ingredient Dictionary, 10th Ed., 2004. Examples include amino acids, chondroitin sulfate, diglycerin, erythritol, fructose, glucose, 1,2,6-hexanetriol, honey, hyaluronic acid, hydrogenated honey, hydrogenated starch hydrolysate, inositol, lactitol, maltitol, maltose, mannitol, natural moisturizing factor, salts of pyrollidone carboxylic acid, potassium PCA, sodium glucuronate, sodium PCA, sorbitol, sucrose, trehalose, urea, and xylitol.

c. Emollients

[0047] Non-limiting examples of emollients include, but are not limited to, vegetable oils, mineral oils, silicone oils, synthetic and natural waxes, petrolatum, lanolin, aluminum magnesium hydroxide stearate (which can also function as a water repellent), and fatty acid esters. Non-limiting examples of vegetable oils include safflower oil, corn oil, sunflower seed oil, and olive oil.

d. Antioxidants

[0048] Non-limiting examples of antioxidants include, but are not limited to, acetyl cysteine, ascorbic acid, ascorbic acid polypeptide, ascorbyl dipalmitate, ascorbyl methylsilanol pectinate, ascorbyl palmitate, ascorbyl stearate, BHA, BHT, t-butyl hydroquinone, cysteine, cysteine HCl, diamylhydroquinone, di-t-butylhydroquinone, dicetyl thiodipropionate, dioleyl tocopheryl methylsilanol, disodium ascorbyl sulfate, distearyl thiodipropionate, ditridecyl thiodipropionate, dodecyl gallate, erythorbic acid, esters of ascorbic acid, ethyl ferulate, ferulic acid, gallic acid esters, hydroquinone, isooctyl thioglycolate, kojic acid, magnesium ascorbate, magnesium ascorbyl phosphate, methylsilanol ascorbate, natural botanical anti-oxidants such as green tea or grape seed extracts, nordihydroguaiaretic acid, octyl gallate, phenylthioglycolic acid, potassium ascorbyl tocopheryl phosphate, potassium sulfite, propyl gallate, quinones, rosmarinic acid, sodium