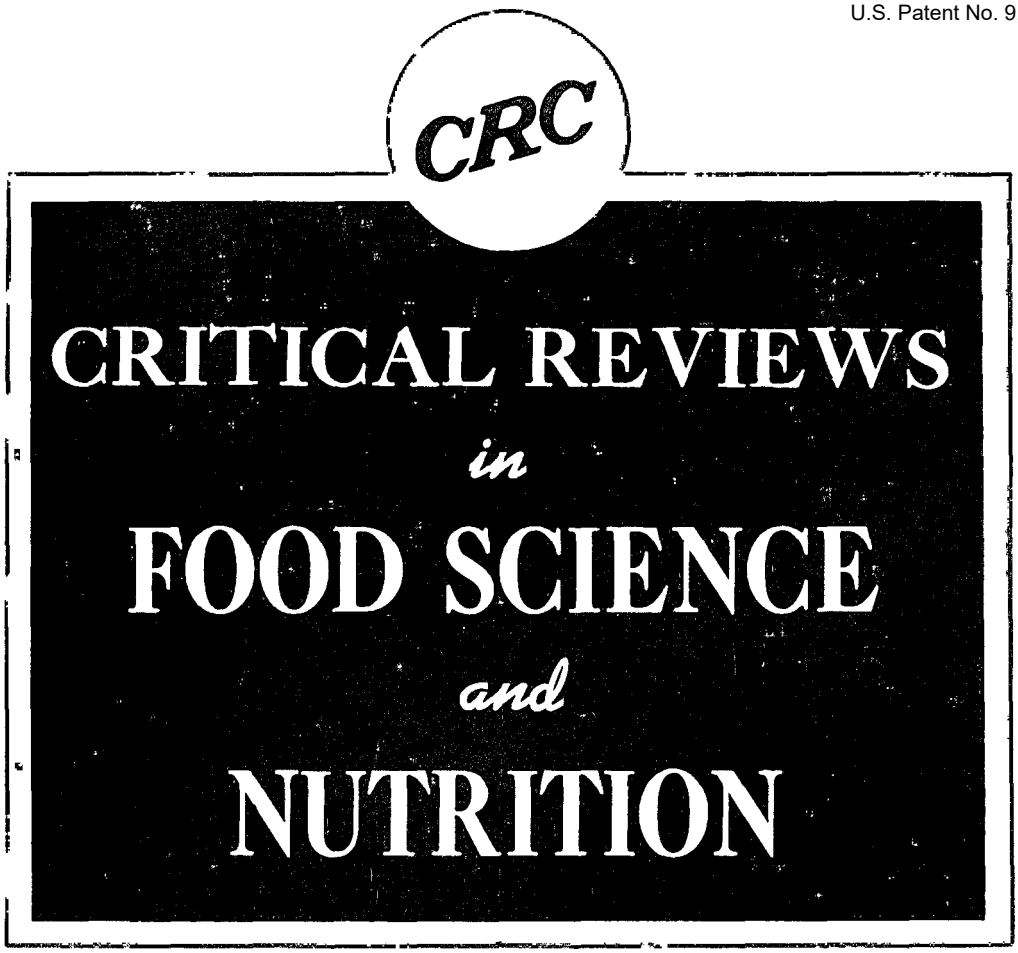


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Current information relating to the chemical composition of both natural and simulated meat flavors is presented, with particular reference to beef flavor. The origin of natural meat flavor is described in terms of the nature of the precursors and the formation pathways of volatile components contributing to meat flavor. A table listing the aroma components of natural beef is included and their relative contributions to the overall flavor is considered. The historical development of commercial meat flavorings is traced from the early spice blends and meat extracts to the thermally produced imitation meat flavors (processed meat flavorings) including "reaction products" and flavorings derived from natural meat. Some G.B. and U.S. "reaction products" patents and meat flavor contributing compounds patented since 1960 are summarized in tabular form.

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U.S. Patent No. 9,943,096



# NATURAL AND SIMULATED MEAT FLAVORS (WITH PARTICULAR REFERENCE TO BEEF)

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## I. INTRODUCTION

Meat has constituted an important part of our diet for many years — not only as a good source of protein, but also for its sensory properties, flavor being one of the most important.[1] The flavor of cooked meat has been extensively studied over the last two decades. Beef flavor has received the greatest attention — probably because it is the most popular meat in the Western world, and therefore the identification of desirable beef flavor has great commercial significance, hence the particular reference to beef in this review.

Meat flavorings are needed for use in convenience and processed foods, accepted by many as a major part of their diet.[2] They are also increasingly required for flavoring meat analogues to counter malnutrition and as complete or partial meat substitutes to achieve lower retail prices and diets with lower levels of cholesterol and saturated fats.[3,4] Consumers expect these products to taste like meat and therefore the development of improved meat flavors will undoubtedly increase consumer acceptance of meat analogues and in turn increase their sales to a significant level.[5]

This demand has resulted in numerous patents issued on the production of imitation meat flavors, e.g., by heating together a wide range of compounds.[6] Chang, in 1976, stated that "such flavors have odors reminiscent of meat — *even though their final chemical constitution and the reactions taking place are unknown* — but they do not possess the unique, characteristic flavor of meat, e.g., beef."[6] The chemistry involved in flavor production may well parallel that which occurs in natural meat, and a better understanding of this will permit the production of superior flavors for use in meat analogues.[7]

No chemical or sensory comparisons of natural and simulated meat flavors have yet been reported. The lack of chemical data has already been substantiated by the earlier reference to Chang's statement,[6] and a recent quotation by Wasserman supports the nonexistence of sensory data: "There has been a plethora of patents in recent years and more products and processes are being patented. Unfortunately, there has been no published critical sensory evaluation of the flavors produced with respect to similarity to meat flavors, flavor intensity, or consumer acceptability."[8]

It was this literature background which, in our continuing studies on meat flavor, precipitated this review and recently initiated in our laboratory a project designed to compare the aroma components and sensory properties of some available commercial beef flavors with those of genuine beef; the initial results of this study have recently been published.[9,10]

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The scope of the background literatures in the fields of natural and simulated meat flavors is vast. Several reviews have dealt primarily with natural meat flavor, e.g.,[1,6,8,11-23] while others have concentrated primarily on simulated meat flavors.[2-4,24-26] Worthy of particular note are those by Herz and Chang[13] and Dwivedi.[19] These are extremely comprehensive, dealing mainly with natural meat flavor and factors which affect it. The present review is not intended in any way as a sequel to these. The aim on this occasion is to summarize current published information relating to chemical compositions and formation of both natural and simulated meat flavor compounds so that comparisons of the two are facilitated. Consequently, aspects such as the role of enzymes in muscle biochemistry and the effect on flavor of various preslaughter factors and postslaughter conditions will not be considered. These aspects were well covered in the review by Dwivedi,[19] and the latter topic also takes priority in recent reviews by Sink[27] and Ford and Park.[28] Also, since most of the relevant background literature has concentrated on beef, few interspecies comparisons will be made.

A better knowledge of meat aroma chemicals and the role of precursors in meat flavor formation is critical. At present it is still very difficult to compound meat flavors without some of the natural product or an extract of it present as a foundation.[29] Thus, a complete appreciation of all meat aroma components and the appropriate use of precursors is the only way to ensure a wide range of processed and novel foods which will be attractive to the consumer.[29]

## II. NATURAL MEAT FLAVOR (WITH PARTICULAR REFERENCE TO BEEF)

Two important aspects of flavor contribute to our appreciation of any food — meat being no exception — i.e., taste and aroma. The flavor of cooked meat is due to a complex mixture of compounds many of which are produced during heating. They include

1. Volatile compounds with odor properties
2. Nonvolatiles, water soluble compounds with taste and tactile properties
3. Potentiators and synergists[19]

Of these, the volatile compounds are by far the most important.

### A. Taste Compounds

In general, these are present in relatively large concentrations and are frequently essential intermediates in the biochemistry of the animal. They contribute few taste sensations — one or a combination of more than one of the four basic tastes — sweet, sour, salty, and bitter. The most important taste compounds in meat are inorganic salts (salty), hypoxanthine (bitter), sugars (sweet), organic acids (sour), nucleotides, amino acids, and peptides, e.g., anserine and carnosine, often present in relatively high concentrations.[30]

Most amino acids contribute sweet and/or bitter tastes; a few contribute sour quality while it is only the sodium salts of glutamic acid and aspartic acid which provide saltiness.[31] Amino acids giving predominantly sweet taste sensations include hydroxyproline, alanine, glycine, serine, and threonine;[31,32] predominantly bitter tastes are given by histidine, arginine, methionine, valine, isoleucine, leucine, phenylalanine, and tryptophan; and sour tastes are characteristic of aspartic acid, glutamic acid, histidine, and asparagine.[31] Many peptides are associated with bitterness caused by the hydrophobic action of amino acid side-chains.[33]

Other components of meat which have genuine taste properties include inosinic acid, succinic acid, lactic acid, orthophosphoric acid, and pyrrolidone carboxylic acid.[1,29]

The term "umami" taste has been coined by the Japanese for the characteristic taste of monosodium glutamate (MSG) and 5′-ribonucleotides; some peptides also have a similar taste quality. Umami substances increase overall taste intensity, enhance mouthfulness, mildness, and increase palatability.[34]

By far the most abundant extractive compounds of muscles are creatine and creatine phosphate since they constitute approximately 0.5% of fresh muscle.[35] While creatine has little taste, creatinine has a markedly bitter taste but this is only noticeable at twice the concentration present in meat. The recommended usage of creatine in meat extracts and carnosine in soup preparations is due to their contribution to mouthfeel. Anserine is desired because its flavor lingers in the mouth. Arginine, lysine, and histidine exert the same effect.[35]

Some of the volatile compounds in cooked meat may also possess taste properties, but this aspect has received little attention. Certainly some heterocyclic compounds are taste-active neurophysiologically in the cat and dog.[30]

## B. Flavor Potentiators and Synergists

Flavor potentiators (or enhancers) are compounds which have by themselves no sensory effect, but even in small quantities enhance the flavor of other agents.[36] Two main groups exist. The first includes certain L-amino acids containing five carbon atoms, e.g., L-glutamic acid. The second group consists of certain 5′-nucleotides containing 6-hydroxypurine, e.g., guanosine-5′-monophosphate (5′-GMP), inosine-5′-monophosphate (5′-IMP) and xanthosine-5′-monophosphate (5′-XMP). The isomeric 2′- and 3′-nucleotides are not flavor enhancers and so it is only the 5′-nucleotides that are important.[36] These are also more significant biochemically, e.g., 5′-IMP is formed during aging from adenosine-5′-triphosphate (ATP) in meat and is by far the major 5′-nucleotide in dead muscle.[13] 5′-GMP is approximately four times as efficient as 5′-IMP as a flavor enhancer, but its concentration in meat is probably so small that it has little effect.[35] In meat, the most important potentiators are glutamic acid, MSG, and 5′-IMP. A recently proposed structural requirement of potentiator molecules is two negative charges separated by one to seven carbon atoms.[33]

The 5′-ribonucleotides have strong flavor potentiating effects individually, but more importantly, they exhibit a potent synergistic effect (binary synergism) when present, as in meat, in conjunction with glutamic acid or MSG.[37] Additionally, mixtures of glycine, glutamic acid and 5′-IMP exhibit strong ternary synergism.[35] The 5′-nucleotides enhance flavor notes described as meaty, brothy, MSG-like, mouthfilling, dry, astringent; they suppress sulfurous, cabbage-like and hydrolyzed vegetable protein flavor notes while qualities such as buttery, sour, sweet, oily, fatty, starchy, and burned are not affected.[38]

Autolysis cleaves 5′-IMP, albeit slowly to insosine. Such decrease in 5′-IMP concentrations occurs on chilled storage and yet no flavor diminution has been recorded.[39]

## C. Aroma Compounds

These are volatile compounds, some being more soluble in water and others more soluble in lipid-like or organic media. They are present in low concentrations, and give rise to a variety of different odor sensations. In contrast to the nonvolatiles, few are essential intermediates in the biochemistry of the animal.[29] They derive mainly from carbohydrates, fats, and proteins.[29] With minor variations, the composition of all meat is similar and this is reflected in the lists of volatile flavor compounds from different meats.[19,40]

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There is no doubt that volatile compounds contribute most to meat flavor, and they have been studied extensively since about 1960. The number of new identifications increased considerably between 1965 and 1975, since when there has been a distinct reduction in the number of publications on this subject, despite the higher resolving capacity of glass capillary columns in gas chromatography and the use of glass capillary gas chromatography/mass spectrometry for identification purposes.[41]

Table 1 lists the aroma compounds so far identified from cooked beef. The list is extremely long — more than 450 compounds — which include several members of a host of different chemical classes. However, no single compound uniquely responsible for cooked beef aroma has been identified, although some have been described as meat-like.[8] Therefore, despite the great progress recently made, the search for a specific character impact compound has not been fully successful. According to Flament et al.,[41] numerous characteristic and powerful odorants remain to be identified, these being present in trace amounts. It is essential, however, in any eager search for characteristic trace volatiles, to keep isolation methods as simple as possible and fully representative of normally cooked beef so that artefacts do not cloud the issue.

It would appear, therefore, that current identities as summarized in Table 1 are incomplete. However, in theory all volatiles present in a food contribute to its overall odor, although some compounds are more important than others. Even if key compounds exist for beef aroma, it is an oversimplification to believe that a flavor can be reconstituted by proper combination of these few compounds.[29] This has been possible only in a very few exceptional cases. The relative contribution of the compounds presented in Table 1 to the overall aroma of cooked beef is therefore important.

### *1. Relative Contributions of Aroma Compounds to Cooked Beef Aroma*

Direct evidence of the relative contribution to cooked beef aroma of the compounds listed in Table 1 is difficult to glean from the literature for several reasons; e.g., no true character impact compounds exist, very few studies have been quantitative, threshold values for all compounds are not available, and additive, antagonistic, and synergistic effects will occur.[8] However, certain propositions regarding the likely contributions of various classes of compounds have been made, and these often relate to the cooking method.

Despite different cooking methods quoted in publications, e.g., boiling, stewing, simmering, frying, roasting, grilling, and broiling, two main types of heated beef flavors can be conveniently considered as "boiled" and "roasted" flavors. Differences in flavor due to cooking are probably a direct function of temperature and degree of moisture in the meat.[19] Characteristically, boiled beef flavor is produced in the presence of water whereby the temperature during boiling does not exceed 100°C; roasted aromas are liberated under relatively dryer heating conditions where the temperature rises above 100° C.[15] Roasted qualities are not peculiar to conventional oven-roasted beef, however, since they are also characteristically present in the aromas of canned, pressure-cooked, and fried beef.

The references quoted in Table 1 were therefore divided into two groups, i.e., those involving isolation of flavor volatiles from beef heated at 100° C (i.e., boiled beef aroma) and above 100° C (i.e., roasted aromas of heated beef), respectively. Some conclusions are as follows.

Some of the earliest attempts at analyzing *boiled* beef aroma during the early 1960s reported the presence of simple carbonyl compounds, alcohols, acids, hydrocarbons, esters, thiols, sulfides, and ammonia.[51,52,54,58,64,86,89] Chang et al.[62] proposed that these did not represent the complete spectrum of volatile components, nor were they the important ones. In their search for the crucial constituents, they isolated in 1968 2,4,5-trimethyl-3-oxazoline and 3,5-dimethyl-1,2,4-trithiolane from two fractions possessing boiled beef

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## Table 1
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Aliphatic Hydrocarbons

| | | Ref. |
|---|---|---|
| Butane | $CH_3(CH_2)nCH_3$, n = 2 | 42 |
| Pentane | n = 3 | 42, 43 |
| Hexane | n = 4 | 6, 42—46 |
| Heptane | n = 5 | 6, 42, 43, 45—47 |
| Octane | n = 6 | 6, 42, 43, 45—49 |
| Nonane | n = 7 | 45, 47—50 |
| Decane | n = 8 | 47—50 |
| Undecane | n = 9 | 45, 48—50 |
| Dodecane | n = 10 | 6, 44—46, 48, 49 |
| Tridecane | n = 11 | 6, 45, 46, 48—50 |
| Tetradecane | n = 12 | 6, 45—50 |
| Pentadecane | n = 13 | 6, 44—50 |
| Hexadecane | n = 14 | 6, 44—50 |
| Heptadecane | n = 15 | 6, 44—50 |
| Octadecane | n = 16 | 6, 44, 46, 48—50 |
| Nonadecane | n = 17 | 48, 49 |
| Eicosane | n = 18 | 48, 49 |
| Heneicosane | n = 19 | 48, 49 |
| Docosane | n = 20 | 48, 49 |
| Tricosane | n = 21 | 48, 49 |
| Tetracosane | n = 22 | 48, 49 |
| Pentacosane | n = 23 | 48, 49 |
| 2-Methylbutane | $(CH_3)_2CHCH_2CH_3$ | 51 |
| 2-Methylpentane | $(CH_3)_2CH(CH_2)_2CH_3$ | 6, 46 |
| 3-Methylpentane | $CH_3CH_2CH(CH_3)CH_2CH_3$ | 6, 46 |
| 2-Methylheptane | $(CH_3)_2CH(CH_2)_4CH_3$ | 47 |
| 2-Methyloctane | $(CH_3)_2CH(CH_2)_5CH_3$ | 6, 46 |
| 3-Methyloctane | $CH_3CH_2CH(CH_3)(CH_2)_4CH_3$ | 6, 46 |
| 3-Methylnonane | $CH_3CH_2CH(CH_3)(CH_2)_5CH_3$ | 6, 46 |
| 3-Methylundecane | $CH_3CH_2CH(CH_3)(CH_2)_7CH_3$ | 6, 46 |
| 2-Methyldodecane | $(CH_3)_2CH(CH_2)_9CH_3$ | 6, 46 |
| 2-Methyltridecane | $(CH_3)_2CH(CH_2)_{10}CH_3$ | 6, 46 |
| 3-Methyltridecane | $CH_3CH_2CH(CH_3)(CH_2)_9CH_3$ | 6, 46 |
| 4-Methyltridecane | $CH_3(CH_2)_2CH(CH_3)(CH_2)_8CH_3$ | 6, 46 |
| 4-Methyltetradecane | $CH_3(CH_2)_2CH(CH_3)(CH_2)_9CH_3$ | 6 |
| 4-Ethyltetradecane | $CH_3(CH_2)_2CH(CH_2CH_3)(CH_2)_9CH_3$ | 46 |
| 6(?)-Methyltetradecane | $CH_3(CH_2)_4CH(CH_3)(CH_2)_7CH_3$ | 50 |
| 2-Methylpentadecane | $(CH_3)_2CH(CH_2)_{12}CH_3$ | 6, 46 |
| Hex-1-ene | $CH_2{=}CH(CH_2)_3CH_3$ | 47 |
| Hex-2-ene | $CH_3CH{=}CH(CH_2)_2CH_3$ | 45 |
| Hept-1-ene | $CH_2{=}CH(CH_2)_4CH_3$ | 45, 47 |
| Hept-2-ene | $CH_3CH{=}CH(CH_2)_3CH_3$ | 45 |
| Oct-1-ene | $CH_2{=}CH(CH_2)_5CH_3$ | 45, 47 |
| Oct-3-ene | $CH_3CH_2CH{=}CH(CH_2)_3CH_3$ | 45 |
| Non-1-ene | $CH_2{=}CH(CH_2)_6CH_3$ | 47 |
| Dec-1-ene | $CH_2{=}CH(CH_2)_7CH_3$ | 47 |
| Dec-2-ene | $CH_3CH{=}CH(CH_2)_6CH_3$ | 45 |
| Undec-1-ene | $CH_2{=}CH(CH_2)_8CH_3$ | 6, 44, 46, 47 |
| Undec-4-ene[a] | $CH_3(CH_2)_2CH{=}CH(CH_2)_5CH_3$ | 47 |
| Dodec-1-ene | $CH_2{=}CH(CH_2)_9CH_3$ | 45, 47 |
| Tridec-1-ene | $CH_2{=}CH(CH_2)_{10}CH_3$ | 6, 46, 47 |
| Tetradec-1-ene | $CH_2{=}CH(CH_2)_{11}CH_3$ | 47, 49 |
| Pentadec-1-ene | $CH_2{=}CH(CH_2)_{12}CH_3$ | 6, 44, 46 |
| Hexadec-1-ene | $CH_2{=}CH(CH_2)_{13}CH_3$ | 47, 49 |

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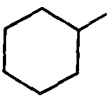
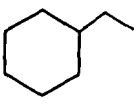
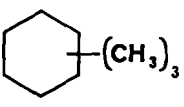
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

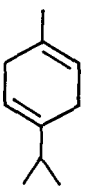
### Aliphatic Hydrocarbons

| | | Ref. |
|---|---|---|
| Heptadec-1-ene | $CH_2{=}CH(CH_2)_{14}CH_3$ | 6, 46, 47 |
| Octadec-1-ene | $CH_2{=}CH(CH_2)_{15}CH_3$ | 49 |
| a Dimethylbutene | | 47 |
| 2-Methylpent-1-ene | $CH_2{=}C(CH_3)(CH_2)_2CH_3$ | 45 |
| a 2-Methylpentadecene | | 6 |
| a $C_{20}$ Branched alkene (MW 280; br @ $C_{13}$) | | 47 |
| a $C_{20}$ Branched alkene (MW 280; br @ $C_{13}$) | | 47 |
| Hexa-2,4-diene | $CH_3CH{=}CHCH{=}CHCH_3$ | 45 |
| a $C_{20}$ Branched alkadiene (MW 278; br @ $C_{13}$) | | 47 |

### Alicyclic Hydrocarbons

| | | |
|---|---|---|
| Cyclohexane | | 6, 46 |
| Methylcyclohexane |  | 6, 46 |
| Ethylcyclohexane |  | 6, 46 |
| a Trimethylcyclohexane |   | 6, 46 |

### Terpenoids

| | | |
|---|---|---|
| a Terpene (not necessarily hydrocarbon) | | 43 |
| $\gamma$-Terpinene |  | 6, 46 |

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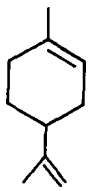
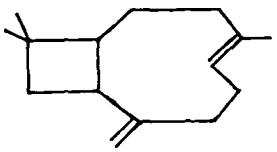
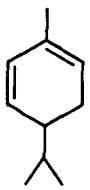
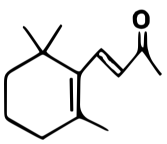
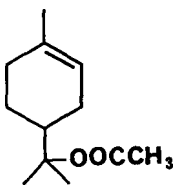
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Terpenoids

| | | Ref. |
|---|---|---|
| Limonene |  | 45 |
| Caryophyllene |  | 6, 46 |
| α-Phellandrene |  | 6, 46 |
| β-Ionone |  | 6, 46 |
| Terpinylacetate (α-shown) |  | 6, 46 |

### Aliphatic Alcohols

| | | |
|---|---|---|
| Methanol | $CH_3OH$ | 43, 52 |
| Ethanol | $CH_3CH_2OH$ | 6, 44, 46, 48, 49, 53, 54 |
| Propan-1-ol | $CH_3CH_2CH_2OH$ | 6, 46, 53, 54 |
| Propan-2-ol | $(CH_3)_2CHOH$ | 53 |

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## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Aliphatic Alcohols

| | | Ref. |
|---|---|---|
| Butan-1-ol | $CH_3(CH_2)_3OH$ | 6, 43, 44, 46, 48—50, 53 |
| Butan-2-ol | $CH_3CH_2CH(OH)CH_3$ | 48, 49, 53 |
| Pentan-1-ol | $CH_3(CH_2)_4OH$ | 6, 43, 44, 46, 48—50, 53 |
| Hexan-1-ol | $CH_3(CH_2)_5OH$ | 6, 43, 46, 48—50, 53 |
| Heptan-1-ol | $CH_3(CH_2)_6OH$ | 45, 48, 49, 53 |
| Heptan-2-ol | $CH_3(CH_2)_4CH(OH)CH_3$ | 50, 55 |
| Heptan-3-ol | $CH_3(CH_2)_3CH(OH)CH_2CH_3$ | 50, 55 |
| Heptan-4-ol | $CH_3(CH_2)_2CH(OH)(CH_2)_2CH_3$ | 50 |
| Octan-1-ol | $CH_3(CH_2)_7OH$ | 6, 44, 46, 50, 53 |
| Octan-3-ol | $CH_3(CH_2)_4CH(OH)CH_2CH_3$ | 50, 55 |
| Octan-4-ol | $CH_3(CH_2)_3CH(OH)(CH_2)_2CH_3$ | 50, 55 |
| Nonan-1-ol | $CH_3(CH_2)_8OH$ | 47, 55 |
| Decan-1-ol | $CH_3(CH_2)_9OH$ | 55 |
| Undecan-1-ol | $CH_3(CH_2)_{10}OH$ | 55 |
| Dodecan-1-ol | $CH_3(CH_2)_{11}OH$ | 56 |
| 2-Methylpropan-1-ol | $(CH_3)_2CHCH_2OH$ | 6, 44, 46 |
| a Methylbutanol | | 47 |
| 3-Methylbutan-1-ol | $(CH_3)_2CH(CH_2)_2OH$ | 6, 44—46, 48, 49, 53 |
| 4-Methylhexan-2-ol | $CH_3CH_2CH(CH_3)CH_2CH(OH)CH_3$ | 6, 46 |
| 6-Methylheptan-1-ol | $(CH_3)_2CH(CH_2)_5OH$ | 6, 46 |
| 2-Ethoxyethanol | $CH_3CH_2OCH_2CH_2OH$ | 6, 46 |
| 2-Butoxyethanol | $CH_3(CH_2)_3OCH_2CH_2OH$ | 6, 46, 50 |
| 2,3-Butanediol | $CH_3CH(OH)CH(OH)CH_3$ | 50 |
| Pent-1-en-3-ol | $CH_2{=}CHCH(OH)CH_2CH_3$ | 6, 43, 46 |
| a Hexenol | | 45 |
| Hex-2-en-1-ol | $CH_3(CH_2)_2CH{=}CHCH_2OH$ | 6, 44, 46 |
| Hex-3-en-1-ol | $CH_3CH_2CH{=}CH(CH_2)_2OH$ | 45 |
| Oct-1-en-3-ol | $CH_3(CH_2)_4CH(OH)CH{=}CH_2$ | 6, 43, 44, 46, 48, 49 |
| Oct-2-en-1-ol | $CH_3(CH_2)_4CH{=}CHCH_2OH$ | 50 |
| 3-Methylhex-2-en-1-ol | $CH_3(CH_2)_2C(CH_3){=}CHCH_2OH$ | 45 |

### Aliphatic Aldehydes

| | | |
|---|---|---|
| Formaldehyde | HCHO | 51 |
| Acetaldehyde | $CH_3CHO$ | 43, 51, 52, 54, 57, 58 |
| Propanal | $CH_3(CH_2)_nCHO$, n = 1 | 43, 53, 54 |
| Butanal | n = 2 | 6, 43, 46 |
| Pentanal | n = 3 | 6, 43, 44, 46, 48—50, 53 |
| Hexanal | n = 4 | 6, 43—50, 56, 58 |
| Heptanal | n = 5 | 6, 44—46, 48—50, 53 |
| Octanal | n = 6 | 6, 44, 46, 48—50, 53 |
| Nonanal | n = 7 | 6, 44, 46, 48—50, 53, 58 |
| Decanal | n = 8 | 43, 49, 50 |
| Undecanal | n = 9 | 50, 53 |
| Dodecanal | n = 10 | 50 |
| Tridecanal | n = 11 | 49 |
| Tetradecanal | n = 12 | 50 |
| Pentadecanal | n = 13 | 6, 46, 50 |
| Hexadecanal | n = 14 | 6, 46, 50 |

## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Aliphatic Aldehydes

| | | Ref. |
|---|---|---|
| Heptadecanal | n = 15 | 50 |
| 2-Methylpropanal | $(CH_3)_2CHCHO$ | 43, 51, 59 |
| 2-Methylbutanal | $CH_3CH_2CH(CH_3)CHO$ | 43, 45, 46, 59, 60 |
| 3-Methylbutanal | $(CH_3)_2CHCH_2CHO$ | 6, 44, 46—48, 50, 53, 61 |
| 2-Ethylbutanal | $(CH_3CH_2)_2CHCHO$ | 6, 46 |
| Propenal (acrolein) | $CH_2{=}CHCHO$ | 59 |
| But-2-enal (crotonal) | $CH_3CH{=}CHCHO$ | 59 |
| Pent-4-enal | $CH_2{=}CH(CH_2)_2CHO$ | 45 |
| Hex-2-enal | $CH_3(CH_2)_nCH{=}CHCHO$, n = 2 | 45, 50 |
| Hept-2-enal | n = 3 | 45, 50 |
| Oct-2-enal | n = 4 | 6, 44, 46, 48, 49 |
| Non-2-enal | n = 5 | 48—50 |
| Dec-2-enal | n = 6 | 48—50 |
| Undec-2-enal | n = 7 | 49, 50 |
| Dodec-2-enal | n = 8 | 50 |
| Tridec-2-enal | n = 9 | 50 |
| Hexa-2,4-dienal | $CH_3CH{=}CHCH{=}CHCHO$ | 45 |
| Hepta-2,4-dienal | $CH_3(CH_2)_nCH{=}CHCH{=}CHCHO$, n = 1 | 62 |
| Octa-2,4-dienal[a] | n = 2 | 50 |
| Nona-2,4-dienal | n = 3 | 50 |
| Deca-2,4-dienal | n = 4 | 48—50, 52 |
| Undeca-2,4-dienal | n = 5 | 50 |
| Dodeca-2,4-dienal | n = 6 | 44 |
| 6-Methylhept-2-enal | $(CH_3)_2CH(CH_2)_2CH{=}CHCHO$ | 6, 46, 59 |
| Glyoxal | CHO<br>\|<br>CHO | 59 |
| Pyruvaldehyde (2-oxopropanal) | $CH_3COCHO$ | 59 |
| 3-Methyl-4-oxopentanal | $CH_3COCH(CH_3)CH_2CHO$ | 6, 46 |

### Aliphatic Ketones

| | | |
|---|---|---|
| Acetone (propanone) | $CH_3COCH_3$ | 6, 43, 46, 47, 54, 57, 58, 63—65 |
| Butanone | $CH_3CH_2COCH_3$ | 43, 47, 51, 53, 60 |
| Pentan-2-one | $CH_3(CH_2)_2COCH_3$ | 43, 45, 47 |
| Pentan-3-one | $CH_3CH_2COCH_2CH_3$ | 43 |
| Hexan-2-one | $CH_3(CH_2)_3COCH_3$ | 43, 45 |
| Heptan-2-one | $CH_3(CH_2)_4COCH_3$ | 43 |
| Heptan-3-one | $CH_3(CH_2)_3COCH_2CH_3$ | 54 |
| Octan-2-one | $CH_3(CH_2)_5COCH_3$ | 6, 43, 46 |
| Octan-3-one | $CH_3(CH_2)_4COCH_2CH_3$ | 43 |
| Octan-4-one | $CH_3(CH_2)_3CO(CH_2)_2CH_3$ | 6, 44, 46 |
| Nonan-2-one | $CH_3(CH_2)_6COCH_3$ | 43, 45 |
| Nonan-3-one | $CH_3(CH_2)_5CO\ CH_2CH_3$ | 6, 44, 46 |
| Nonan-4-one | $CH_3(CH_2)_4CO(CH_2)_2CH_3$ | 43 |
| Decan-2-one | $CH_3(CH_2)_7COCH_3$ | 6, 43, 46 |
| Undecan-2-one | $CH_3(CH_2)_8COCH_3$ | 49, 50 |
| Undecan-4-one | $CH_3(CH_2)_6CO(CH_2)_2CH_3$ | 45 |
| Dodecan-2-one | $CH_3(CH_2)_9COCH_3$ | 49, 50 |
| Dodecan-3-one | $CH_3(CH_2)_8COCH_2CH_3$ | 6, 44, 46 |

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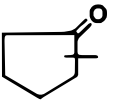
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Aliphatic Ketones

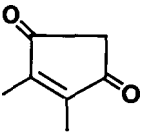
| | | Ref. |
|---|---|---|
| Tridecan-2-one | $CH_3(CH_2)_{10}COCH_3$ | 45, 48—50 |
| Pentadecan-2-one | $CH_3(CH_2)_{12}COCH_3$ | 6, 46, 48—50 |
| Hexadecan-2-one | $CH_3(CH_2)_{13}COCH_3$ | 49 |
| Heptadecan-2-one | $CH_3(CH_2)_{14}COCH_3$ | 48—50 |
| 3-Methylbutanone | $(CH_3)_2CHCOCH_3$ | 66 |
| 4-Methylpentan-2-one | $(CH_3)_2CHCH_2COCH_3$ | 59 |
| 3-Methylhexan-2-one | $CH_3(CH_2)_2CH(CH_3)COCH_3$ | 6, 46 |
| 5-Methylhexan-2-one | $(CH_3)_2CH(CH_2)_2COCH_3$ | 6, 46 |
| 6-Methylheptan-2-one | $(CH_3)_2CH(CH_2)_3COCH_3$ | 6, 46 |
| 3-Hydroxybutanone (acetoin) | $CH_3CH(OH)COCH_3$ | 6, 44—46, 48—50, 53, 56 |
| An octenone | | 45 |
| 6-Methylhept-5-en-2-one | $CH_3C(CH_3)=CH(CH_2)_2COCH_3$ | 43 |
| Butan-2,3-dione (diacetyl) | $CH_3COCOCH_3$ | 6, 42—46, 50, 64 |
| Pentan-2,3,-dione | $CH_3CH_2COCOCH_3$ | 50, 60 |
| Octan-2,3-dione | $CH_3(CH_2)_4COCOCH_3$ | 50 |

### Alicyclic Ketones

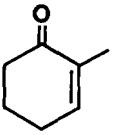
a Methylcyclopentanone — 66



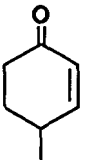
4,5-Dimethylcyclopent-4-ene-1,3-dione — 41



2-Methylcyclohex-2-enone — 41



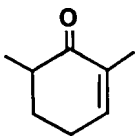
4-Methylcyclohex-2-enone — 41



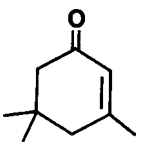
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Alicyclic Ketones

| | | Ref. |
|---|---|---|
| 2,6-Dimethylcyclohex-2-enone | | 41 |



| | | |
|---|---|---|
| 3,5,5-Trimethylcyclohex-2-enone | | 41 |

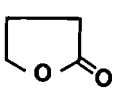


### Aliphatic Carboxylic Acids

| | | |
|---|---|---|
| Formic acid | HCOOH | 64 |
| Acetic acid | $CH_3COOH$ | 6, 46, 50, 56, 64 |
| Propanoic acid | $CH_3(CH_2)_nCOOH$, n = 1 | 6, 44, 46, 56, 54 |
| Butanoic acid | n = 2 | 6, 36, 44, 46, 50, 56 |
| Pentanoic acid | n = 3 | 56 |
| Hexanoic acid | n = 4 | 6, 44, 46, 56 |
| Heptanoic acid | n = 5 | 67 |
| Octanoic acid | n = 6 | 67 |
| Nonanoic acid | n = 7 | 67 |
| Decanoic acid | n = 8 | 67 |
| Dodecanoic acid | n = 10 | 58 |
| Tetradecanoic acid | n = 12 | 58 |
| Pentadecanoic acid | n = 13 | 58 |
| Hexadecanoic acid | n = 14 | 58 |
| Heptadecanoic acid | n = 15 | 58 |
| 2-Methylpropanoic acid | $(CH_3)_2CHCOOH$ | 54, 56, 64 |
| 2-Methylpentanoic acid | $CH_3(CH_2)_2CH(CH_3)COOH$ | 56 |
| 4-Methylpentanoic acid | $(CH_3)_2CH(CH_2)_2COOH$ | 56 |
| 9,12-Octadecadienoic (linoleic) acid | $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH{-}(CH_2)_7COOH$ | 58 |
| Lactic acid | $CH_3CH(OH)COOH$ | 56, 64 |

### Lactones

| | | |
|---|---|---|
| 4-Hydroxybutanoic acid, lactone (γ-butyrolactone)<br>4-Butanolide | | 50 |



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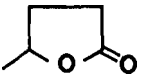
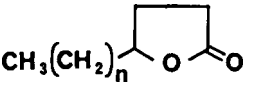
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Lactones

| | | Ref. |
|---|---|---|
| 4-Hydroxypentanoic acid, lactone | | 44, 46, 50, 68 |

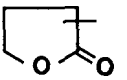


| | | |
|---|---|---|
| 4-Hydroxyhexanoic acid, lactone | | 45, 46, 49, 50 |

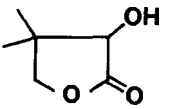



n = 1

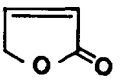
| | | |
|---|---|---|
| 4-Hydroxyheptanoic acid, lactone | n = 2 | 45, 49, 50, 69, 70 |
| 4-Hydroxyoctanoic acid, lactone | n = 3 | 45, 49, 50, 69, 70 |
| 4-Hydroxynonanoic acid, lactone | n = 4 | 49, 50, 70 |
| 4-Hydroxydecanoic acid, lactone | n = 5 | 44, 49, 50, 66, 69, 70 |
| 4-Hydroxyundecanoic acid, lactone | n = 6 | 70 |
| 4-Hydroxydodecanoic acid, lactone | n = 7 | 45, 48, 49, 69, 70 |
| 4-Hydroxytridecanoic acid, lactone | n = 8 | 69, 70 |
| 4-Hydroxytetradecanoic acid, lactone | n = 9 | 49, 69, 70 |
| 4-Hydroxypentadecanoic acid, lactone | n = 10 | 69 |
| 4-Hydroxyhexadecanoic acid, lactone (γ-hexadecalactone) | n = 11 | 69, 70 |
| a 4-Hydroxymethylbutanoic acid, lactone | | 50 |



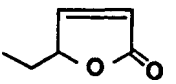
| | |
|---|---|
| 3,3-Dimethyl-2,4-dihydroxybutanoic acid, γ-lactone<br>pantolactone | 41 |




| | |
|---|---|
| 4-Hydroxybut-2-enoic acid, lactone<br>2-Butenolide | 23 |



| | |
|---|---|
| 4-Hydroxyhex-2-enoic acid, lactone | 23 |



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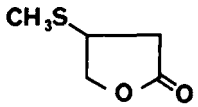
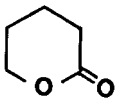
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Lactones

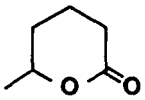
| | | Ref. |
|---|---|---|
| 3-Methylthio-4-hydroxybutanoic acid, γ-lactone<br>β-methylthio-γ-butyrolactone<br>4,5-Dihydro-4-methylthio-2(3H) furanone | | 41 |



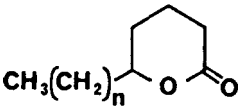

| | | |
|---|---|---|
| 5-Hydroxypentanoic acid, lactone (δ-pentalactone) | | 50 |




| | | |
|---|---|---|
| 5-Hydroxyhexanoic acid, lactone | | 69, 70 |

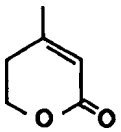



| | | |
|---|---|---|
| 5-Hydroxyheptanoic acid, lactone | | 50 |




n = 1

| | | |
|---|---|---|
| 5-Hydroxyoctanoic acid, lactone | n = 2 | 50 |
| 5-Hydroxynonanoic acid, lactone | n = 3 | 50 |
| 5-Hydroxydecanoic acid, lactone | n = 4 | 49, 50, 69, 70 |
| 5-Hydroxyundecanoic acid, lactone | n = 5 | 70 |
| 5-Hydroxydodecanoic acid, lactone | n = 6 | 49, 50, 69, 70 |
| 5-Hydroxytridecanoic acid, lactone | n = 7 | 69, 70 |
| 5-Hydroxytetradecanoic acid, lactone | n = 8 | 49, 50, 69, 70 |
| 5-Hydroxypentadecanoic acid, lactone | n = 9 | 69, 70 |
| 5-Hydroxyhexadecanoic acid, lactone | n = 10 | 69, 70 |
| 5-Hydroxyoctadecanoic acid, lactone | n = 12 | 69 |
| 3-Methyl-5-hydroxypent-2-enoic acid, lactone<br>Anhydromevalolactone | | 23, 41 |




### Aliphatic Esters

| | | |
|---|---|---|
| Methyl formate | $HCOOCH_3$ | 65 |

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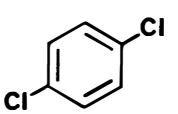
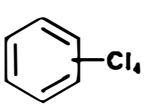
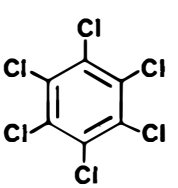
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

| | | Ref. |
|---|---|---|
| **Aliphatic Esters** | | |
| Ethyl formate | $HCOOCH_2CH_3$ | 6, 46, 48, 49 |
| Methyl acetate | $CH_3COOCH_3$ | 43, 46 |
| Ethyl acetate | $CH_3COOCH_2CH_3$ | 6, 43—46, 48, 49 |
| Pentyl acetate | $CH_3COO(CH_2)_4CH_3$ | 45 |
| Acetol acetate (2-ketopropan-1-yl acetate) | $CH_3COOCH_2COCH_3$ | 60 |
| Ethyl butyrate | $CH_3(CH_2)_2COOCH_2CH_3$ | 43 |
| Methyl palmitate | $C_{15}H_{31}COOCH_3$ | 45 |
| Ethyl lactyl lactate | $CH_3CH(OH)COOCH(CH_3)COOC_2H_5$ | 41 |
| Butyl lactyl lactate | $CH_3CH(OH)COOCH(CH_3)COOC_4H_9$ | 41 |
| **Aliphatic Ethers** | | |
| Dipentyl ether | $CH_3(CH_2)_4O(CH_2)_4CH_3$ | 44 |
| Dihexyl ether | $CH_3(CH_2)_5O(CH_2)_5CH_3$ | 71 |
| 1,1-Diethoxyethane | $(CH_3CH_2O)_2CH-CH_3$ | 6, 46 |
| **Aliphatic Amines** | | |
| Ammonia | $NH_3$ | 57, 58, 64 |
| Methylamine | $CH_3NH_2$ | 57, 58 |
| **Chlorine Containing Compounds**[b] | | |
| Chloroform | $CHCl_3$ | 6, 46, 49 |
| a Tetrachloroethane | | 47 |
| 1-Chloropropan-2-ol | $CH_3CH(OH)CH_2Cl$ | 6, 46 |
| 1,4-Dichlorobenzene |  | 6, 46 |
| a Tetrachlorobenzene |  | 49 |
| Hexachlorobenzene |  | 49 |

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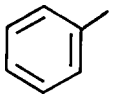
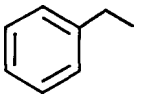
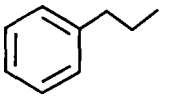
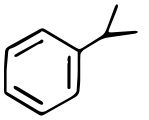
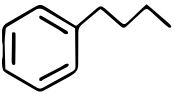
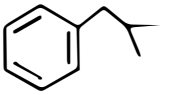
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Benzenoid Compounds

| | | Ref. |
|---|---|---|
| Benzene | | 6, 43—50, 73 |
| Toluene |  | 6, 43—47, 50, 73 |
| Ethylbenzene |  | 6, 45, 46, 73 |
| *n*-Propylbenzene |  | 6, 43, 45—47, 73 |
| Isopropylbenzene (cumene) |  | 49 |
| a $C_3$ benzene | | 47 |
| *n*-Butylbenzene |  | 45, 50, 73 |
| Isobutylbenzene |  | 43 |

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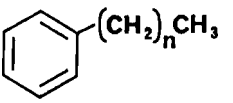
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

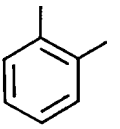
### Benzenoid Compounds

| | | Ref. |
|---|---|---|
| *n*-Pentylbenzene | | 45, 73 |

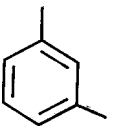



n = 4

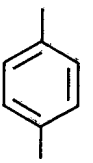
| | | |
|---|---|---|
| *n*-Hexylbenzene | n = 5 | 45, 73 |
| *n*-Heptylbenzene | n = 6 | 45, 73 |
| *n*-Octylbenzene | n = 7 | 45, 73 |
| *n*-Nonylbenzene | n = 8 | 45, 73 |
| *n*-Decylbenzene | n = 9 | 45, 73 |
| *o* − Xylene | | 43, 45, 47—50, 73 |



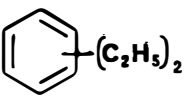
| | | |
|---|---|---|
| *m*-Xylene | | 43, 45, 46, 48, 49, 73 |



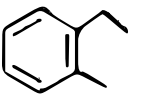
| | | |
|---|---|---|
| *p*-Xylene | | 43, 45, 47, 50, 73 |



| | | |
|---|---|---|
| a Diethylbenzene | | 50 |




| | | |
|---|---|---|
| 1-Ethyl-2-methylbenzene | | 43, 45, 73 |



## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Benzenoid Compounds

| | Ref. |
|---|---|
| 1-Ethyl-3-methylbenzene | 43, 46 |
| 1-Ethyl-4-Methylbenzene | 6, 43 |
| 1-Methyl-2-propylbenzene | 43 |
| 1-Methyl-3-propylbenzene | 43 |
| 4-Isopropyl-1-methylbenzene (*p*-cymene) | 6, 46 |
| 1-Ethyl-2-propylbenzene | 43 |
| 1-Ethyl-3-propylbenzene | 43 |

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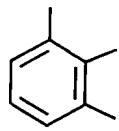
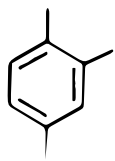
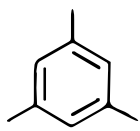
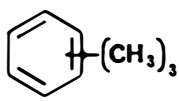
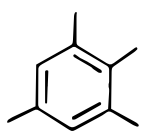
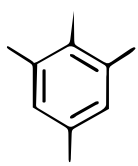
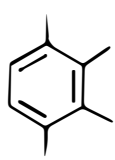
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

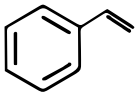
### Benzenoid Compounds

| | | Ref. |
|---|---|---|
| 1,2,3-Trimethylbenzene |  | 43, 50 |
| 1,2,4-Trimethylbenzene |  | 43, 45, 73 |
| 1,3,5-Trimethylbenzene |  | 42, 43, 45, 50 |
| a Trimethylbenzene |   | 46 |
| 1,2,3,5-Tetramethylbenzene |  | 73 |
| 1,2,4,5-Tetramethylbenzene |  | 73 |
| 1,2,3,4-Tetramethylbenzene |  | 45 |

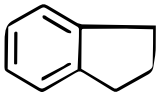
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Benzenoid Compounds

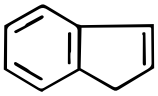
| | Ref. |
|---|---|
| $C_4$ alkylbenzene | 46 |
| $C_5$ alkylbenzene | 46 |
| $C_6$ alkylbenzene | 46 |
| Styrene (vinylbenzene) | 43, 45, 47, 73 |



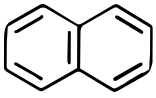
| | |
|---|---|
| a Dimethylstyrene | 6, 46 |
| Indan | 47 |



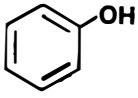
| | |
|---|---|
| Indene | 43 |



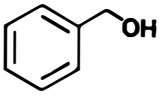
| | |
|---|---|
| Napthalene | 6, 45, 46 |



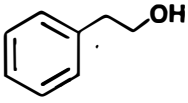
| | |
|---|---|
| Phenol | 6, 45—47, 49, 50 |




| | |
|---|---|
| Benzylalcohol | 6, 43, 45, 46, 50 |




| | |
|---|---|
| 2-Phenylethanol | 48, 49 |



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## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Benzenoid Compounds

| | Ref. |
|---|---|
| *p*-Cresol | 48 |
| a Cresol | 45 |
| a Vinylguaiacol | 50 |
| 2,6-Di-*t*-butyl-*p*-hydroxytoluene (BHT)[c] | 6, 44—46 |
| Anisole | 45 |
| a Methoxytoluene | 45 |
| 2-*t*-Butyl-*p*-hydroxyanisole (BHA)[c] | 45 |

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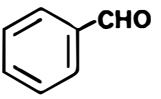
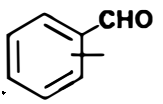
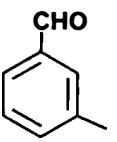
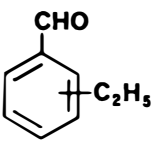
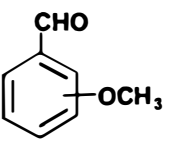
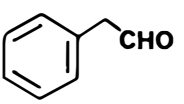
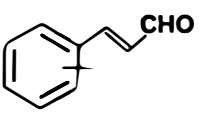
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Benzenoid Compounds

| | | Ref. |
|---|---|---|
| Benzaldehyde |  | 6, 44—47, 50 |
| a Methylbenzaldehyde |  | 45 |
| 3-Methylbenzaldehyde (poss. 2-methyl) |  | 6, 44, 46 |
| an-Ethylbenzaldehyde |  | 6, 45—47 |
| a Methoxybenzaldehyde |  | 45 |
| Phenylacetaldehyde |  | 49, 50, 74 |
| a-Methylcinnamaldehyde |  | 50 |

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## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

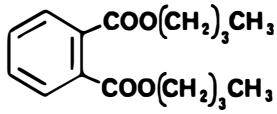
### Benzenoid Compounds

| | Ref. |
|---|---|
| Acetophenone | 45, 55 |
| *o*-Hydroxyacetophenone | 77 |
| a Methylacetophetone<br>a Tolylmethylketone | 6, 45, 46 |
| Benzylmethylketone | 45 |
| a 4-Phenylbutanone | 45 |
| Benzoic acid | 50 |
| *m*-Tolunitrile | 47 |
| Diethyl phthalate | 6, 46 |

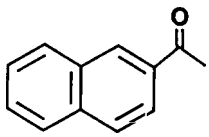
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Benzenoid Compounds

| | | Ref. |
|---|---|---|
| Dibutylphthalate | | 6, 46 |

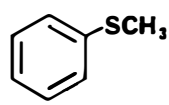



| | | |
|---|---|---|
| Acetylnaphthalene | | 45 |

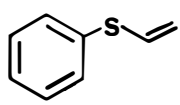



### Sulfur Compounds (Not Heterocyclics)

| | | |
|---|---|---|
| Hydrogen sulfide | $H_2S$ | 43, 52, 54, 57, 64, 65 |
| Carbonyl sulfide | COS | 43 |
| Dimethyl sulfide | $CH_3SCH_3$ | 43, 45, 50, 75 |
| Diethyl sulfide | $CH_3CH_2SCH_2CH_3$ | 76 |
| Dibutyl sulfide | $CH_3(CH_2)_3S(CH_2)_3CH_3$ | 76 |
| Dipentyl sulfide | $CH_3(CH_2)_4S(CH_2)_4CH_3$ | 76 |
| Di-isopentyl sulfide | $(CH_3)_2CH(CH_2)_2S(CH_2)_2CH(CH_3)_2$ | 76 |
| Diallyl sulfide / Prop-2-enylthioprop-2-ene | $CH_2{=}CHCH_2SCH_2CH{=}CH_2$ | 6, 44, 46, 71 |
| Ethyl methyl sulfide | $CH_3CH_2SCH_3$ | 47, 75 |
| Methyl propyl sulfide | $CH_3(CH_2)_2SCH_3$ | 6, 44, 46 |
| Methyl butyl sulfide[a] | $CH_3(CH_2)_3SCH_3$ | 76 |
| Methyl pentyl sulfide | $CH_3(CH_2)_4SCH_3$ | 45 |
| Ethyl butyl sulfide | $CH_3(CH_2)_3SCH_2CH_3$ | 76 |
| Ethyl isobutyl sulfide[a] | $(CH_3)_2CHCH_2SCH_2CH_3$ | 76 |
| Propyl-isopropyl sulfide | $(CH_3)_2CHS(CH_2)_2CH_3$ | 45 |
| Allyl methyl sulfide / Prop-2-enylthiomethane | $CH_2{=}CHCH_2SCH_3$ | 6, 44, 46, 71 |
| Methyl phenyl sulfide[a] / Thioanisole | | 76 |




| | | |
|---|---|---|
| Vinyl phenyl sulfide | | 76 |




| | | |
|---|---|---|
| Carbon disulfide | $CS_2$ | 43 |
| Dimethyl disulfide | $CH_3S_2CH_3$ | 6, 43, 45—47, 50, 64, 75, 76 |

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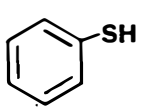
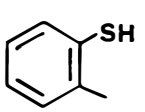
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Sulfur Compounds (Not Heterocyclics)

| | | Ref. |
|---|---|---|
| Diethyl disulfide | $CH_3CH_2S_2CH_2CH_3$ | 45, 75 |
| Dipropyl disulfide | $CH_3(CH_2)_2S_2(CH_2)_2CH_3$ | 45 |
| Di-isopropyl disulfide | $(CH_3)_2CHS_2CH(CH_3)_2$ | 76 |
| Dibutyl disulfide[a] | $CH_3(CH_2)_3S_2(CH_2)_3CH_3$ | 76 |
| Di-isobutyl disulfide | $(CH_3)_2CHCH_2S_2CH_2CH(CH_3)_2$ | 76 |
| Di-*t*-butyl disulfide | $(CH_3)_3CS_2C(CH_3)_3$ | 76 |
| Dipentyl disulfide | $CH_3(CH_2)_4S_2(CH_2)_4CH_3$ | 76 |
| Ethyl methyl disulfide | $CH_3CH_2S_2CH_3$ | 75 |
| Methyl vinyl disulfide | $CH_2{=}CHS_2CH_3$ | 75 |
| Dimethyl trisulfide | $CH_3S_3CH_3$ | 43 |
| 3-(Methylthio) propanal (methional) | $CH_3SCH_2CH_2CHO$ | 61, 77 |
| 1,1-Bis-(methylthio) methane | $CH_3SCH_2SCH_3$ | 43 |
| 1,1-Bis-(methylthio) ethane | $(CH_3S)_2CHCH_3$ | 75 |
| Methylthioacetate | $CH_3COSCH_3$ | 75 |
| Ethylthiopropionate | $CH_3CH_2COSCH_2CH_3$ | 45 |
| Dimethyl sulfone | $CH_3SO_2CH_3$ | 50 |
| Methanethiol | $CH_3SH$ | 52, 54, 57, 63, 75 |
| Ethanethiol | $CH_3CH_2SH$ | 52, 54, 63, 65 |
| Propan-1-thiol | $CH_3(CH_2)_2SH$ | 56 |
| Butan-1-thiol | $CH_3(CH_2)_3SH$ | 56, 76 |
| Hexan-1-thiol | $CH_3(CH_2)_5SH$ | 76 |
| Heptan-1-thiol | $CH_3(CH_2)_6SH$ | 76 |
| 2-Methylpropan-1-thiol | $(CH_3)_2CHCH_2SH$ | 75 |
| *t*-Butylthiol[a] | $(CH_3)_3CSH$ | 76 |
| 2-Methylbutan-1-thiol | $CH_3CH_2CH(CH_3)CH_2SH$ | 75 |
| { 1,1-Dimethylpropan-1-thiol | | 76 |
| { *t*-Pentylthiol | $CH_3CH_2C(CH_3)_2SH$ | |
| 2,2-Dimethylpropan-1-thiol | $(CH_3)_3CCH_2SH$ | 76 |
| 3-Methylbutan-2-thiol | $CH_3CH(SH)CH(CH_3)_2$ | 75 |
| { 1-Methylheptan-1-thiol | | 76 |
| { Sec. octylthiol | $CH_3(CH_2)_5CH(CH_3)SH$ | |
| 1-(Methylthio) ethanethiol | $CH_3SCH(CH_3)SH$ | 61 |
| 1,2-Ethanedithiol | $HS(CH_2)_nSH$, n = 2 | 76 |
| 1,3-Propanedithiol | n = 3 | 76 |
| 1,4-Butanedithiol | n = 4 | 76 |
| 1,5-Pentanedithiol | n = 5 | 76 |
| 1,6-Hexanedithiol | n = 6 | 76 |
| Thiophenol[a] | | 76 |




| | | |
|---|---|---|
| 2-Methylthiophenol[a] | | 76 |

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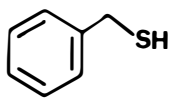
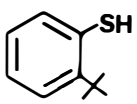
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Sulfur Compounds (Not Heterocyclics)

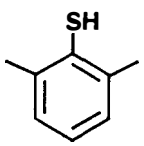
| | Ref. |
|---|---|
| Benzylthiol[a] | 76 |



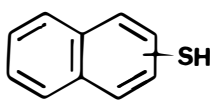

| | |
|---|---|
| 2-*t*-Butylthiophenol[a] | 76 |




| | |
|---|---|
| 2,6-Dimethylthiophenol | 76 |



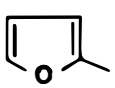

| | |
|---|---|
| Naphthalene thiol | 75 |



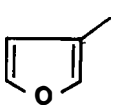

### Furans and Derivatives

| | |
|---|---|
| Furan | 43, 60 |

| | |
|---|---|
| 2-Methylfuran | 43, 47 |




| | |
|---|---|
| 3-Methylfuran | 43, 67 |



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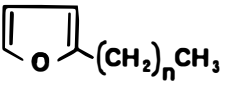
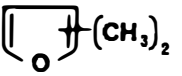
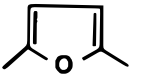
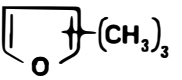
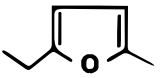
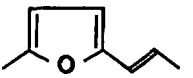
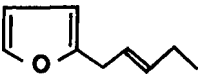
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Furans and Derivatives

| | | Ref. |
|---|---|---|
| 2-Ethylfuran | | 45, 47, 67 |
| |  | |
| | n = 1 | |
| 2-Propylfuran | n = 2 | 43, 45 |
| 2-Butylfuran | n = 3 | 43, 45 |
| 2-Pentylfuran | n = 4 | 6, 43—46, 50, 68, 71 |
| 2-Hexylfuran | n = 5 | 43, 50 |
| 2-Heptylfuran | n = 6 | 45, 50 |
| 2-Octylfuran | n = 7 | 50 |
| a Dimethylfuran | | 45 |
| |  | |
| 2,5-Dimethylfuran | | 43, 60 |
| |  | |
| a Trimethylfuran | | 45 |
| |  | |
| 2-Methyl-5-ethylfuran | | 43, 45 |
| |  | |
| 2-(Prop-1-enyl)-5-methylfuran | | 43 |
| |  | |
| 2-(Hex-2-enyl) furan | | 43 |
| |  | |

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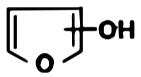
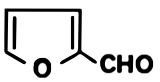
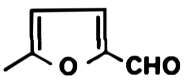
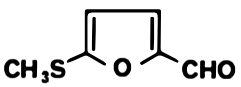
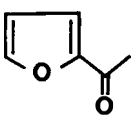
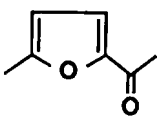
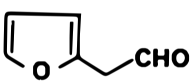
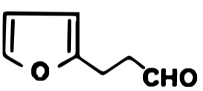
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Furans and Derivatives

| | Ref. |
|---|---|
| a Furfuryl alcohol | 6, 46, 49 |
|  | |
| 2-Furaldehyde (furfural) | 6, 45, 46, 49, 61 |
|  | |
| 5-Methyl-2-furaldehyde | 6, 46 |
|  | |
| 5-Methylthio-2-furaldehyde[d] | 6, 44—46 |
|  | |
| 2-Acetylfuran (2-Furfurylmethylketone) | 6, 45, 46, 55 |
|  | |
| 5-Methyl-2-acetylfuran | 6, 46 |
|  | |
| (2-Furyl)acetaldehyde | 45 |
|  | |
| 3-(2-Furyl)-propanal | 45 |
|  | |

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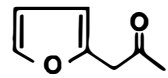
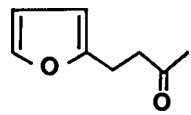
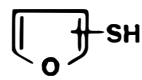
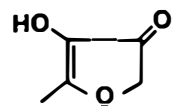
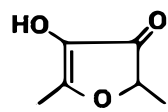
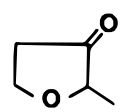
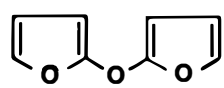
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Furans and Derivatives

| | Ref. |
|---|---|
| 1-(2-Furyl)propan-2-one | 55 |
|  | |
| 4-(2-Furyl)-butan-2-one | 45 |
|  | |
| Furfurylthiol | 76 |
|  | |
| Dihydrofuran | 45 |
| | |
| 4-Hydroxy-5-methyl-3(2H)-furanone<br>4-Hydroxy-5-methyl-2-dihydrofuran-3-one | 56 |
|  | |
| 4-Hydroxy-2,5-dimethyl-3(2H)-furanone<br>4-Hydroxy-2,5-dimethyl-2-dihydrofuran-3-one | 56 |
|  | |
| 2-Methyltetrahydrofuran-3-one | 44 |
|  | |
| 2,2′-Difurfuryl ether | 45 |
|  | |

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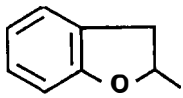
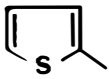
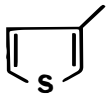
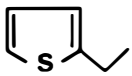
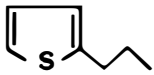
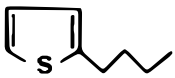
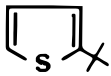
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Furans and Derivatives

| | | Ref. |
|---|---|---|
| 2-Methyldihydrobenzofuran |  | 45 |

### Thiophens and Derivatives

| | | |
|---|---|---|
| Thiophen | | 43, 75, 76, 78 |
| 2-Methylthiophen |  | 43, 45, 47, 75, 76, 78 |
| 3-Methylthiophen |  | 43 |
| 2-Ethylthiophen |  | 45, 75 |
| 2-Propylthiophen |  | 45 |
| 2-Butylthiophen |  | 45, 75 |
| 2-*t*-Butylthiophen |  | 76 |

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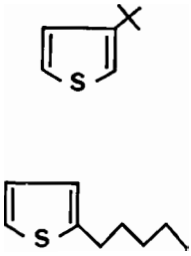
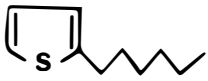
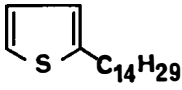
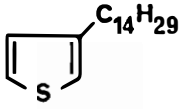
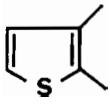
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Thiophens and Derivatives

| | | Ref. |
|---|---|---|
| 3-*t*-Butylthiophen |  | 76 |
| 2-Pentylthiophen |  | 43, 45, 75 |
| 2-Hexylthiophen |  | 45 |
| 2-Heptylthiophen | | 45 |
| 2-Octylthiophen | | 45, 75 |
| 3-Octylthiophen | | 75 |
| 2-Tetradecanylthiophen |  | 75 |
| 3-Tetradecanylthiophen |  | 75 |
| 2,3-Dimethylthiophen[a] |  | 43 |

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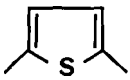
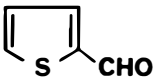
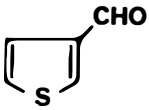
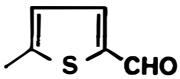
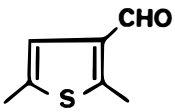
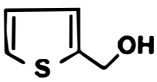
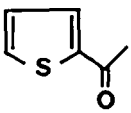
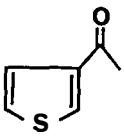
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Thiophens and Derivatives

| | | Ref. |
|---|---|---|
| 2,5-Dimethylthiophen |  | 43, 45 |
| Thiophen-2-carboxaldehyde |  | 6, 44, 46, 68, 75 |
| Thiophen-3-carboxaldehyde |  | 75 |
| 5-Methylthiophen-2-carboxaldehyde |  | 75, 79 |
| 2,5-Dimethylthiophen-3-carboxaldehyde |  | 68, 75, 79 |
| 2-(Hydroxymethyl)thiophen |  | 75 |
| 2-Acetylthiophen |  | 45, 75, 78 |
| 3-Acetylthiophen |  | 75 |

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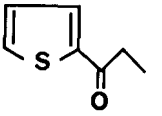
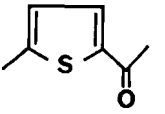
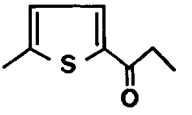
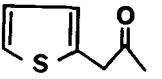
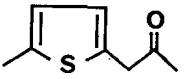
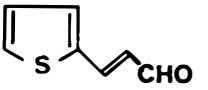
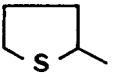
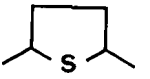
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Thiophens and Derivatives

| | Ref. |
|---|---|
| 2-Propionylthiophen | 75, 79 |
|  | |
| 2-Acetyl-5-Methylthiophen | 75 |
|  | |
| 5-Methyl-2-propionylthiophen | 75, 79 |
|  | |
| 2-Thienylpropanone | 75 |
|  | |
| (2-Methyl-5-thienyl) propanone | 75 |
|  | |
| 3-(2-Thienyl) propenal (2-thienylacrolein) | 75 |
|  | |
| 2-Methyltetrahydrothiophen | 76 |
|  | |
| 2,5-Dimethyltetrahydrothiophen[a] | 76 |
|  | |

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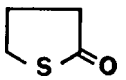
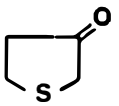
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Thiophens and Derivatives

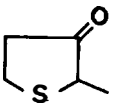
| | Ref. |
|---|---|
| Tetrahydrothiophen-2-one<br>γ-Thiobutyrolactone | 23 |



| | |
|---|---|
| Tetrahydrothiophen-3-one | 75 |



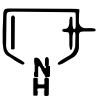
| | |
|---|---|
| 2-Methyltetrahydrothiophen-3-one | 75, 78 |



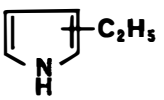
### Pyrroles and Derivatives

| | |
|---|---|
| Pyrrole | 23, 47, 81 |

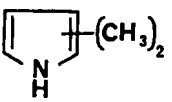
| | |
|---|---|
| a Methylpyrrole (prob. 2-methyl-) | 23, 47, 81 |



| | |
|---|---|
| An ethylpyrrole | 47, 81 |



| | |
|---|---|
| a Dimethylpyrrole (2,4,-or 2,5-) | 47 |



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## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyrroles and Derivatives

| | Ref. |
|---|---|
| a Trimethylpyrrole | 47, 81 |
| a Dimethylethylpyrrole | 47, 81 |
| a $C_5$ saturated substituted pyrrole (prob. N-pentyl-) | 47, 81 |
| 2-Formylpyrrole | 6, 46, 78 |
| 2-Acetylpyrrole | 6, 46, 49, 50 |
| 2-Acetyl-N-methylpyrrole | 55 |
| Ethylmethylmaleinimide | 41 |
| Dimethylmaleinimide | 41 |

### Pyridines and Derivatives

| | |
|---|---|
| Pyridine | 6, 46 |

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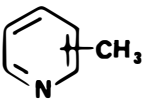
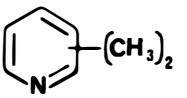
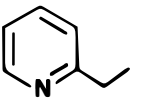
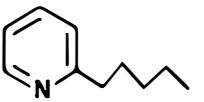
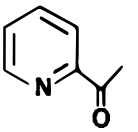
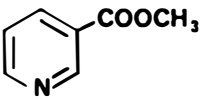
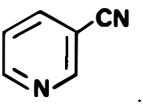
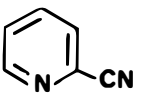
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyridines and Derivatives

| | Ref. |
|---|---|
| a Methylpyridine (prob. 2-methyl-)  | 47, 81 |
| a-Dimethylpyridine (prob. 3,4-dimethyl-)  | 47, 81 |
| 2-Ethylpyridine  | 77 |
| a $C_3$ pyridine (prob. *n*-propyl-) | 47, 81 |
| 2-n-Pentylpyridine  | 77 |
| 2-Acetylpyridine  | 23 |
| Methylnicotinate  | 23 |
| Nicotinonitrile  | 23 |
| Pyridine-2-carbonitrile  | 23 |

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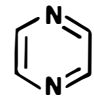
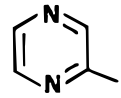
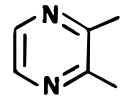
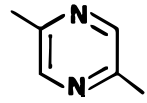
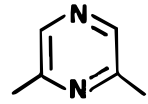
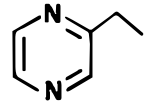
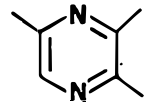
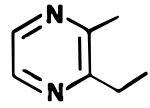
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyrazines and Derivatives

| | Ref. |
|---|---|
| Pyrazine | 41, 78 |
|  | |
| Methylpyrazine | 6, 41, 46, 47, 77, 78 |
|  | |
| 2,3-Dimethylpyrazine | 41, 77, 78 |
|  | |
| 2,5-Dimethylpyrazine | 6, 41, 46, 77, 78, 82 |
|  | |
| 2,6-Dimethylpyrazine | 41, 47, 78, 79, 82 |
|  | |
| Ethylpyrazine | 23, 41, 47, 48, 78 |
|  | |
| Trimethylpyrazine | 41, 47, 48, 78 |
|  | |
| 2-Ethyl-3-methylpyrazine | 41, 48, 82 |
|  | |

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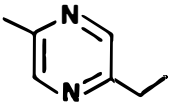
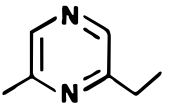
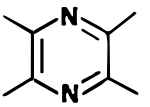
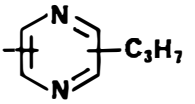
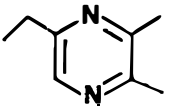
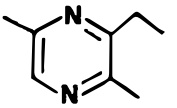
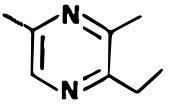
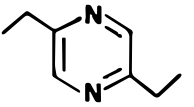
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyrazines and Derivatives

| | | Ref. |
|---|---|---|
| 2-Ethyl-5-methylpyrazine |  | 41, 47, 77, 78, 82 |
| 2-Ethyl-6-methylpyrazine |  | 41, 47, 78, 82 |
| Tetramethylpyrazine |  | 41, 77, 78, 82 |
| a Methylpropylpyrazine[a] |  | 78, 82 |
| 2,3-Dimethyl-5-ethylpyrazine |  | 41, 47, 78, 82 |
| 2,5-Dimethyl-3-ethylpyrazine |  | 6, 41, 46, 47, 77, 78, 82 |
| 3,5-Dimethyl-2-ethylpyrazine |  | 41, 78, 82 |
| 2,5-Diethylpyrazine |  | 41 |

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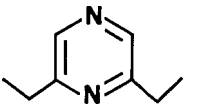
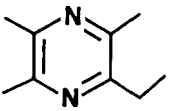
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyrazines and Derivatives

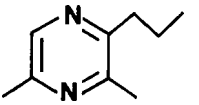
| | Ref. |
|---|---|
| 2,6-Diethylpyrazine | 41, 48, 49, 78, 82 |



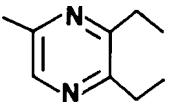
| | |
|---|---|
| a $C_5$ saturated substituted pyrazine (poss. isobutylmethyl-)[a] | 47 |
| 2-Ethyl-3,5,6-trimethylpyrazine | 41, 82 |



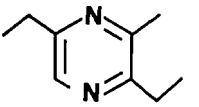
| | |
|---|---|
| 2,6-Dimethyl-3-propylpyrazine | 41, 82 |



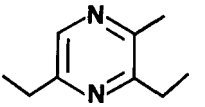
| | |
|---|---|
| 2,3-Diethyl-5-methylpyrazine | 41, 78, 82 |



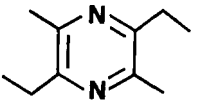
| | |
|---|---|
| 2,5-Diethyl-3-methylpyrazine | 41, 77, 78 |



| | |
|---|---|
| 2,6-Diethyl-3-methylpyrazine | 41, 78, 82 |



| | |
|---|---|
| 3,6-Diethyl-2,5-dimethylpyrazine | 78 |



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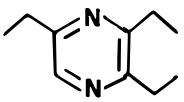
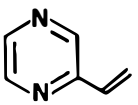
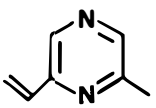
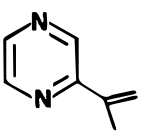
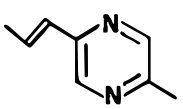
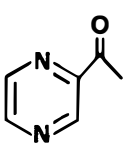
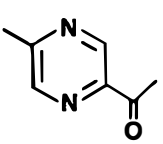
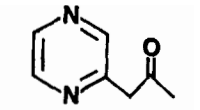
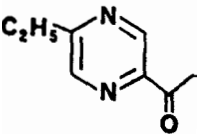
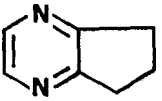
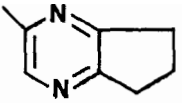
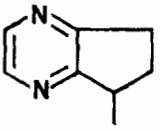
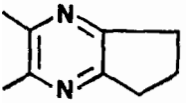
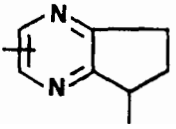
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyrazines and Derivatives

| | | Ref. |
|---|---|---|
| Triethylpyrazine |  | 41, 77, 78 |
| Vinylpyrazine[a] |  | 78 |
| 2-Methyl-6-vinylpyrazine[a] |  | 78 |
| Isopropenylpyrazine |  | 41, 77, 78 |
| 2-Methyl-5-propenylpyrazine |  | 12, 78 |
| Acetylpyrazine |  | 78 |
| 2-Acetyl-5-methylpyrazine |  | 78 |

## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

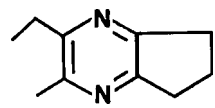
### Pyrazines and Derivatives

| | Ref. |
|---|---|
| 1-(2-Pyrazinyl)-propan-2-one (2-acetonylpyrazine) | 78 |
|  | |
| 2-Acetyl-5-ethylpyrazine | 78 |
|  | |
| 5H-6,7-Dihydrocyclopenta [*b*] pyrazine "cyclopentapyrazine" | 78, 83, 84 |
|  | |
| 2-Methyl-5H-6,7-dihydro-cyclopenta [*b*] pyrazine | 78, 83, 84 |
|  | |
| 5-Methyl-5H-6,7-dihydro-cyclopenta [*b*] pyrazine | 78, 83, 84 |
|  | |
| 2,3-Dimethyl-5H-6,7-dihydro-cyclopenta [*b*] pyrazine | 84 |
|  | |
| 2,5(or3,5)-Dimethyl-5H-6,7-dihydrocyclopenta [*b*] pyrazine | 78, 83, 84 |
|  | |

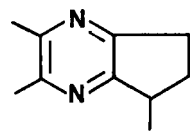
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyrazines and Derivatives

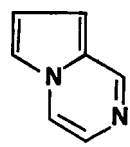
| | Ref. |
|---|---|
| 2-Ethyl-3-methyl-5H-6,7-dihydrocyclopenta [*b*]pyrazine | 84 |



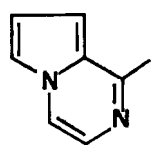
| | |
|---|---|
| 2,3,5-Trimethyl-5H-6,7-dihydrocyclopenta [*b*]pyrazine | 84 |



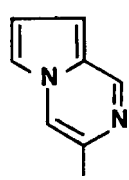
| | |
|---|---|
| Pyrrolo-[1,2-*a*]pyrazine | 41, 85 |



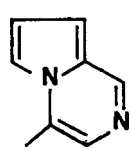
| | |
|---|---|
| 3-Methyl (pyrrolo [1,2-*a*]) pyrazine | 41, 85 |



| | |
|---|---|
| 5-Methyl (pyrrolo [1,2-*a*])pyrazine | 41, 85 |



| | |
|---|---|
| 6-Methyl(pyrrolo [1,2-*a*])pyrazine | 41, 85 |



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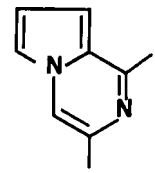
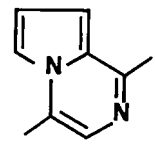
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Pyrazines and Derivatives

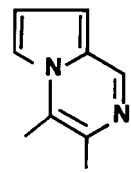
| | Ref. |
|---|---|
| 3,5-Dimethyl (pyrrolo [1,2-*a*]) pyrazine | 41, 85 |



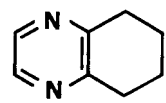
| | |
|---|---|
| 3,6-Dimethyl (pyrrolo [1,2-*a*]) pyrazine | 41, 85 |



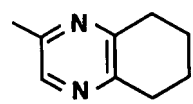
| | |
|---|---|
| 5,6-Dimethyl (pyrrolo [1,2-*a*]) pyrazine | 41, 85 |



| | |
|---|---|
| 5,6,7,8-Tetrahydroquinoxaline | 78 |

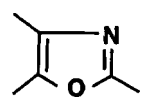


| | |
|---|---|
| 2-Methyl-5,6,7,8-tetrahydroquinoxaline | 78 |

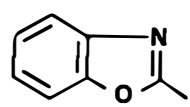


### Oxazoles, Oxazolines, Etc.

| | |
|---|---|
| 2,4,5-Trimethyloxazole | 6, 46, 50, 86 |



| | |
|---|---|
| 2-Methylbenzoxazole | 23 |



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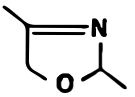
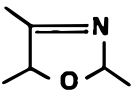
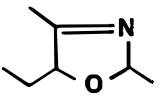
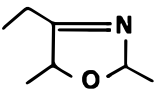
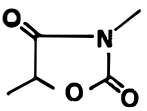
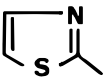
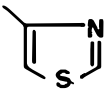
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Oxazoles, Oxazolines, Etc.

| | Ref. |
|---|---|
| 2,4-Dimethyl-3-oxazoline  | 86 |
| 2,4,5-Trimethyl-3-oxazoline  | 6, 44, 46, 62, 86 |
| 2,4-Dimethyl-5-ethyl-3-oxazoline  | 86 |
| 2,5-Dimethyl-4-ethyl-3-oxazoline  | 86 |
| 3,5-Dimethyl-1,3-oxazolidin-2,4-dione  | 41 |

### Thiazoles and Thiazolines

| | |
|---|---|
| Thiazole | 75 |
| 2-Methylthiazole  | 75 |
| 4-Methylthiazole  | 75 |

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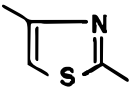
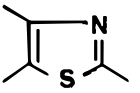
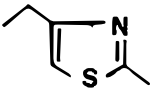
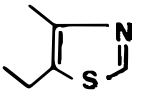
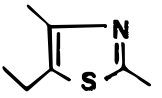
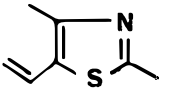
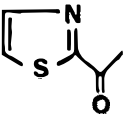
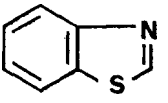
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Thiazoles and Thiazolines

| | Ref. |
|---|---|
| 2,4-Dimethylthiazole  | 74, 75, 86 |
| 2,4,5-Trimethylthiazole  | 75, 86 |
| 4-Ethyl-2-methylthiazole  | 75 |
| 5-Ethyl-4-methylthiazole  | 75 |
| 2,4-Dimethyl-5-ethylthiazole  | 86 |
| 2,4-Dimethyl-5-vinylthiazole  | 75 |
| 2-Acetylthiazole  | 6, 46, 74, 75, 78, 86, 87 |
| Benzothiazole  | 6, 46, 50, 55 75 |

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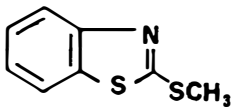
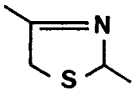
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Thiazoles and Thiazolines

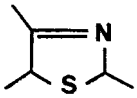
| | Ref. |
|---|---|
| 2-Methylthiobenzothiazole | 23, 41, 88 |



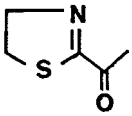

| | |
|---|---|
| 2,4-Dimethyl-3-thiazoline | 86 |




| | |
|---|---|
| 2,4,5-Trimethyl-3-thiazoline | 86 |




| | |
|---|---|
| 2-acetyl-2-thiazoline | 50, 74, 75 |




### Other Sulfur Heterocyclics

| | |
|---|---|
| Ethylene sulfide (thiran) | 43 |

| | |
|---|---|
| Propylene sulfide (thetin) | 43, 76 |

| | |
|---|---|
| 1,3-Dithiane | 76 |

| | |
|---|---|
| 1,4-Dithiane | 76 |

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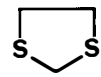
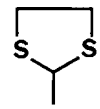
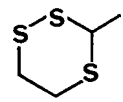
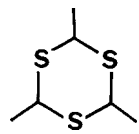
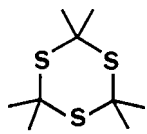
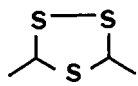
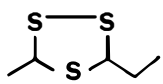
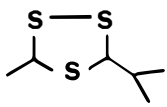
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Other Sulfur Heterocyclics

| | Ref. |
|---|---|
| 1,3-Dithiolane | 62, 76 |
|  | |
| 2-Methyl-1,3-dithiolane | 62, 76 |
|  | |
| 3-Methyl-1,2,4-trithiane | 41 |
|  | |
| 2,4,6-Trimethyl-1,3,5-trithiane trithioacetaldehyde | 75, 86 |
|  | |
| Hexamethyl-1,3,5-trithiane trithioacetone | 75, 86 |
|  | |
| 3,5-Dimethyl-1,2,4-trithiolane (*cis and trans*) | 6, 41, 43, 44, 46, 61, 62, 68, 75, 76, 78 |
|  | |
| 3-Ethyl-5-methyl-1,2,4-trithiolane (*cis and trans*) | 41 |
|  | |
| 3-Isopropyl-5-methyl-1,2,4-trithiolane (*cis and trans*) | 41 |
|  | |

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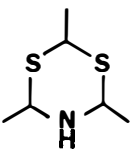
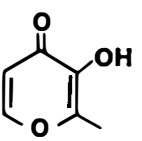
## Table 1 (continued)
## VOLATILE COMPONENTS OF NATURAL BEEF AROMA

### Miscellaneous

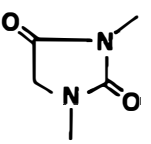
| | Ref. |
|---|---|
| 5,6-Dihydro-2,4,6-trimethyl-1,3,5-dithiazine thialdine | 61, 75, 86 |



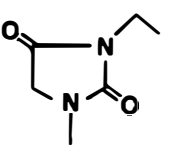
| | |
|---|---|
| Maltol | 23, 68 |



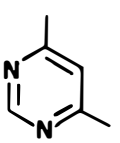
| | |
|---|---|
| 1,3-Dimethylhydantoin | 41 |



| | |
|---|---|
| 3-Ethyl-1-methylhydantoin | 41 |



| | |
|---|---|
| 4,6-Dimethylpyrimidine | 41 |



| | |
|---|---|
| 4-Acetyl-2-methylpyrimidine | 41 |

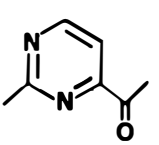


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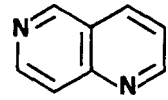
**Table 1 (continued)**
**VOLATILE COMPONENTS OF NATURAL BEEF AROMA**

**Miscellaneous**

| | Ref. |
|---|---|
| 1,6-Naphthyridine  | 41 |

*Note:* As far as possible, systematic nomenclature has been used. This means that nonsystematic names in the literature have been corrected or rationalized.

[a] Tentative identification.
[b] Chlorine-containing compounds are almost certainly contaminants, possibly from pesticide residues in the meat or derived from refrigerants; they are not normally considered natural components of any food flavor
[c] 2,6-di-*t*-Butyl-*p*-hydroxytoluene (BHT) and 2-*t*-Butyl-*p*-hydroxyanisole (BHA): it is unlikely that these are a part of the natural beef aroma complex; they almost certainly derive from animal feed, being well-known antioxidants
[d] 5-Methylthio-2-furaldehyde — incorrect identification (according to Ohloff and Flament[23]

aroma.[62] It was at first thought that these were character impact compounds, but later work at the same laboratories showed that, when synthesized neither possessed the odor of boiled beef.[44] Persson and von Sydow[43] reaffirmed that the trithiolane was probably not important, while Brinkman et al.[61] provided evidence that it may have been formed during the isolation procedure. The latter also identified 5,6-dihydro-2,4,6-trimethyl-1,3,5-dithiazine (thialdine) in a beef broth flavor isolate. This also may have been an artefact but due to the great ease of its formation, it was proposed as a genuine component.

Further attempts at searching for the key compounds of boiled beef aroma resulted in the identification of several other unusual compounds. For example, two furanones were reported by Tonsbeek et al.[56] in 1968, i.e., 4-hydroxy-5-methyl-3(2H)-furanone which had a roast chicory odor and its 2,5-dimethyl homolog possessing a caramel odor. Later Tonsbeek et al. isolated 2-acetyl-2-thiazoline.[74] This had a strong aroma of fresh baked bread crusts, and 225 kg of beef were required for its identification. In 1972 Brinkman et al.[61] identified a new dithiohemiacetal, 1-(methylthio)ethanethiol in the headspace volatiles of beef broth. This had a strong odor of fresh onions. In 1973 Hirai et al.[44] identified thiophen-2-carboxaldehyde in a boiled beef isolate. None of these compounds was proved to be chiefly responsible for the aroma however.

Volatile compounds isolated from beef heated to temperatures exceeding 100° C (e.g., canned beef, pressure-cooked beef, shallow fried beef, and conventionally roasted beef) have shown considerable similarities and *roasted* notes are characteristically present in the aromas; these have frequently been attributed to the alkylpyrazines identified,[48,49,55,82] although few, if any, of these compounds have meaty aromas.[8] They frequently have roasted, nutty, green, or earthy qualities.[88,90] Acetylpyrazines have a surprisingly intense and characteristic roasted note reminiscent of popcorn.[90,91] When used in conjunction with thiazolidines and/or cyclohexenones, 1-(2-pyrazinyl)propan-2-one (identified in beef flavor[78]) imparts a toasted and burned note to foods.[92] The bicyclic pyrazines have roasted, grilled, burned, and animal notes.[84,88]

However, there is evidence to suggest that pyrazines are not the sole contributors or

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even the main contributors to the spectrum of more desirable odor qualities associated with the roasted aromas of heated beef compared with that of boiled beef. Several other chemical classes would also seem to be important. For example, Liebich et al.[50] found that carbonyl compounds, including 3-methylbutanal, contributed to roasted beef flavor. Self et al.[52] and Hodge et al.[93] have reported that many (Strecker) aldehydes contribute to "browned", roasted and toasted aromas. Persson and von Sydow demonstrated that certain carbonyl and sulfur compounds are responsible for the high heat off-flavor (retort flavor) of canned beef;[43] several sulfides and thiophens were identified by Mussinan and Katz[94] in the strong roast aroma emanating on heating a model meat system; Wilson et al.[75] identified many sulfur compounds (sulfides, thiophens, thiazole, trithioacetaldehyde, and trithioacetone) in the aroma of pressure-cooked beef particularly at high temperature; sulfides and 3-methylbutanal were also among the compounds implicated in burnt aroma of canned beef by Persson and von Sydow;[67] MacLeod and Coppock[81] provided evidence that carbonyl compounds (particularly 3-methylbutanal), sulfides and also pyrroles and pyridines are probably important in roasted aromas of heated beef and tentatively suggested that benzenoids and furans may contribute to the desirable qualities associated with well-cooked boiled beef. Pyrroles have been reported in several roasted foods, e.g., coffee, peanuts, cocoa, and also in tobacco — the most abundant being 2-formylpyrrole and 2-acetylpyrrole.[88] Chang and Peterson[46] suggested that these two pyrroles, together with benzothiazole (which has a quinoline, heated-rubber-like odor) may contribute to the retort flavor of canned beef stew.

Chang and Peterson have listed carbonyl compounds, together with aliphatic hydrocarbons, aromatic hydrocarbons (including alkylbenzenes), saturated alcohols, esters, and ethers as classes which in their opinion are not primary contributors to meat flavor.[6,46] Their evidence for the carbonyls is that in their studies of the oxidative decomposition products of refined animal fats and oils, no odor reminiscent of meat was detected. Also, lean beef, trimmed of fat, produced on boiling a delicious boiled beef flavor and although a limited number of carbonyl compounds was identified, none of them individually possessed meaty notes.[44] Diacetyl and acetoin occur frequently in food aromas and are considered to provide a buttery note to cooked meat.[44,87] It is likely that many carbonyls arising from lipid oxidation are not important contributors whereas certain aldehydes (e.g., Strecker aldehydes) and certain ketones — possibly arising during Maillard reaction — contribute to desirable roasted qualities of beef. Based on gas chromatographic odor port assessments of the alkylbenzenes (many of which were like mothballs, fatty, green), Min et al.[73] suggested that these compounds play little if any role in the odor of lean roast beef, although they could play a more important role in the odor of cooked beef fat.

Classes of compounds believed by Chang and Peterson to be important contributors to meat aroma are lactones, furanoid or hydrofuranoid compounds, acyclic sulfur-containing compounds, and heterocyclic compounds containing sulfur, nitrogen, and oxygen.[6,46] Direct evidence for this belief is not presented. Lactones have been identified both in roast beef drippings and in boiled beef aroma (see Table 1) and many have a strong coconut-like flavor.[6] Unsaturated lactones have been patented for enhancing deep fat fried flavor of snack foods[46,95] and so their role is probably not primary but indeed similar to that suggested already for certain carbonyl compounds in imparting roasted qualities, as opposed to beef qualities. Schutte[29] has suggested that carbonyl compounds, heterocyclic compounds, sulfur compounds, nitrogen-containing compounds, and some phenols are the most important in meat flavor. Recently in their analysis of roast beef aroma, Min et al.[45] reported that the acidic fraction possessed a weak, objectionable, sour odor; the basic fraction had an earthy, nutty, and roasted odor while the neutral fraction was the only one to present a pleasant beef-like aroma. In this fraction, hydrocarbons,

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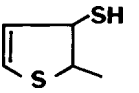
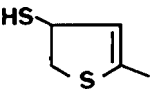
alkylbenzenes and carbonyl compounds were thought to be of lesser importance than the lactones, furanoids, and sulfur containing compounds.[45] The basic fraction may contribute to roasted beef aroma and normally contains pyrazines, oxazoles, and thiazoles.[86,96]

Several thiols have been reported to possess a variety of meaty notes.[8,97] These are

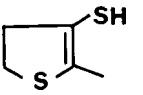
3-Mercapto-2-methyl-2,3-dihydrothiophen* — sweet, roast meat



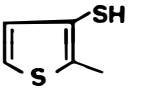

4-Mercapto-2-methyl-4,5-dihydrothiophen* — roast meat



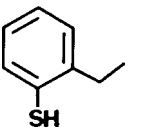

3-Mercapto-2-methyl-4,5-dihydrothiophen* — meaty



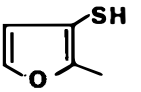

3-Mercapto-2-methylthiophen* — roast meat




2-Ethylbenzenethiol — burnt, meat-like



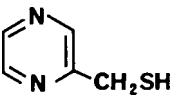

2-Methylfuran-3-thiol† — roasted meat



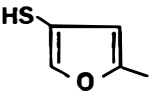

* These compounds were identified in reaction mixtures of furanone derivatives and hydrogen sulfide (see Section II.C.3.e).[98]

† These are thiamin degradation products.[99]

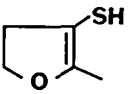
Pyrazine methanethiol — roasted meat



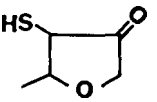

4-Mercapto-2-methylfuran* — green, meaty



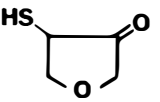

3-Mercapto-2-methyl-4,5-dihydrofuran*† — roasted meat




4-Mercapto-5-methyl-3-oxotetrahydrofuran* — meaty




4-Mercapto-3-oxotetrahydrofuran* — green, meaty




None of these have yet been identified in cooked beef aroma.

Although dimethylsulfide and methional can produce unpleasant odors in foods,[88] they also possess remarkable sensory properties resulting in odor addition or synergism.[100] They are also known to be extraordinarily effective modifiers of flavor quality.[88] Aliphatic disulfides and trisulfides are probably important due to their low odor thresholds. Dimethyl trisulfide in concentration as low as 10 ppb significantly contributes to the overall flavor of roasted chicken leg meat.[101]

Table 1 shows clearly that most of the very recent publications have reported the presence of various heterocyclic compounds in cooked beef aroma. These are important in roasted flavors generally and especially so in meat.[23] In general they possess an extraordinarily high odor strength and are often present in such minute traces that two decades ago their discovery was hindered because their concentration was below the analytical detection limit at that time.[88] Several heterocyclic compounds have been isolated from "browned" flavors, arising from nonenzymic browning reactions and are mainly associated with a caramel-like, sweet, fruity, nutty, burned odor impression at low concentration and an acrid burned character at higher concentrations.[88,102] An interesting correlation of molecular structure and odor properties is evident here in that a

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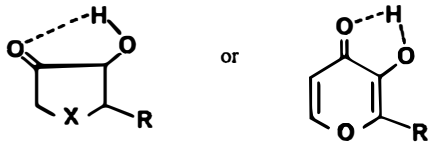
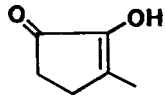
common structural feature of many of these heated food odorants is a planar enol-carbonyl configuration of alkyl substituted 5- or 6-membered cyclic $\alpha$-diketones stabilized by H-bonding,[88] e.g.,




(a) (b)

Examples from Table 1 are the 4-hydroxy-3(2H) furanones (≡ Structure a) and maltol (≡ Structure b), which have marked caramel-like odor properties. The 4-hydroxy-5-methyl-3(2H) furanone also has a roasted chicory root odor, while its 2,5-dimethyl homolog has a specific burned pineapple odor.[88] If the acidic hydrogen atom of these furanones is substituted by alkyl groups (i.e., alkoxy derivatives) or the hydroxyl group is missing, the caramel-like odor disappears. The five carbon analogs of these two furanones and of maltol are also associated with caramel odor due to the same structural features. One of these, cyclotene, is a known product of the Maillard reaction,[102] although not yet identified in cooked beef flavor.




Cyclotene
(2-hydroxy-3-methyl-2-cyclopenten-1-one)

It is thought that 4-hydroxy-5-methyl-3(2H) furanone may also contribute to beef flavor by acting as a precursor in reaction with hydrogen sulfide.[98] This reaction product mixture possessed a roasted meaty odor and contained some of the thiols previously mentioned but none of the compounds identified (see Section II.C.3.e) have yet been isolated from cooked beef.

Thiophens are also believed to contribute to roasted notes in several foods, e.g., meat, coffee, fried onions.[79] 4,5-Dihydro-3(2H)-thiophenone and its methyl homolog — both identified recently in cooked beef[75,78] have been described as having, respectively, an odor of onion/garlic and green, burned coffee-like.[103] 4-Hydroxy-2,5-dimethyl-2,3-dihydrothiophen-3-one has been described as a flavoring agent having a roasted and burned meat aroma.[104]

Several members of the oxazoles, oxazolines, thiazoles, and thiazolines have been described as nutty; other odor descriptions frequently associated with the oxazoles and oxazolines are sweet, green, woody, musty, and vegetable-like.[86] Some thiazoles and thiazolines, however, have meaty odors, e.g., 2,4-dimethylthiazole, 2,4-dimethyl-5-ethylthiazole, trimethylthiazoline, 4-acetyl-2,5-dimethylthiazole and 5-acetyl-2,4-dimethylthiazole.[86,90] The first three have been identified in cooked beef aroma.[74,75,86] Thiazoles and thiazolines also have lower odor threshold values than the oxazoles and oxazolines[86] and are therefore likely to be more important contributors to roasted meat aromas. A cereal-like, roasted popcorn odor is associated with 2-acetylthiazole while 2-acetylthiazoline has a bread-like odor.[86,90] Pittet and Hruza[90] showed that when the substituent is adjacent to the ring nitrogen, there is significant odor similarities between thiazoles and the corresponding pyrazines and pyridines. For example, lower 2-alkyl-

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**Table 2**
**SUMMARIZED COMPARISON OF VOLATILE COMPONENTS OF BOILED[a] (B) AND ROASTED[b] (R) AROMA OF HEATED BEEF**

| Chemical class | Comparison |
|---|---|
| Aliphatic hydrocarbons | R (high and low mol wt) > B (mostly high mol wt) |
| Alicyclic hydrocarbons | R only |
| Terpenoids | R only |
| Benzenoids | R > B |
| Aliphatic alcohols | R > B (mostly low mol wt) |
| Aliphatic aldehydes | |
| saturated | R (high and low mol wt) > B (mostly low mol wt) |
| unsaturated | R > B (mostly high mol wt) |
| Aliphatic ketones | R (high and low mol wt) > B (mostly low mol wt) |
| Alicyclic ketones | R > B |
| Aliphatic carboxylic acids | B > R |
| Lactones | R > B |
| Aliphatic esters | R > B |
| Aliphatic amines | B > R |
| Sulfides (not heterocyclic) | R > B |
| Thiols (not heterocyclic) | B > R |
| Furans and derivatives | R > B |
| Thiophens and derivatives | R > B |
| Pyrroles and derivatives | R > B |
| Pyridines and derivatives | R > B |
| Pyrazines and derivatives | R > B |
| Quinoxalines | R only |
| Thiazoles and thiazolines | R > B |
| Oxazoles and oxazolines | R > B |
| Dithianes, dithiolanes, Trithianes, Trithiolanes | B > R |
| Hydantoins | B only |

[a] Boiled aroma used in this context for procedures where in general the temperature during isolation did not exceed 100° C — with two exceptions.[44,61] (References 6, 12, 23, 41, 44, 46, 47, 51, 52, 54, 56-58, 61-64, 68, 71, 74, 76, and 81).

[b] Roasted aroma used in this context for procedures wherein the temperature during isolation exceeds 100° C and includes shallow fried, canned, pressure-cooked, and roasted beef (References 6, 23, 41, 43, 45-50, 55, 59, 65, 67, 70, 73, 75, 77, 78, and 81-87).

thiazoles and pyridines are generally green and vegetable-like; the equivalent pyrazines are similar but more nutty. Increased substitution confers added nutty, roasted, and meaty notes in the thiazoles; corresponding pyrazines are similar but more roasted. In general 5-substituted thiazoles are more sulfury and roasted and some are meaty as described.

Table 2 compares the classes of volatile compounds identified in boiled vs. roasted aromas of heated beef (with no regard to concentrations or threshold values). It shows that aliphatic carboxylic acids, aliphatic amines, thiols (not heterocyclic), dithianes, dithiolanes, trithianes, and trithiolanes have been identified more frequently in boiled beef aroma than in roasted aromas of heated beef while the converse is true for all other chemical classes; some classes, i.e., alicyclic hydrocarbons, terpenoid compounds, and quinoxalines, have only been reported when temperatures during isolation have exceeded 100° C.

It is therefore clear that the aroma profile of cooked meat is due to the sum of all the

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sensory effects produced simultaneously at the olfactory epithelium by a large number of volatiles of different structures present in a particular quantitative proportion.[23,39,81] Differences in cooked beef flavor, e.g., boiled vs. roasted are similarly explained,[81] as also has the deterioration of flavor on storage and freeze-drying of beef stew.[6] Recent investigations suggest that heterocycles contribute significantly to the aroma impression of meat.[23] However, it is important to remember that many flavor compounds, which themselves are not at all reminiscent of meat flavor, can play a role, since synosmic effects do occur, i.e., two or more compounds together giving a combined flavor sensation which is very different from that of any one single component.[29]

### 2. *Meat Aroma Precursors*

In the late 1950s commercial lean beef extract was analyzed by Bender and co-workers[105,106] who reported that 2% of the extract, by weight, consisted of amino acids including methylhistidine, serine, methionine, alanine, leucine, isoleucine, histidine, taurine, and citrulline. Also present were peptides, proteins, inorganic salts, guanidines, purines, pyrimidines, carnitine, choline, urea, ammonia, organic acids, and inosinic acid. Reducing sugars were not detectable.

During the 1960s many workers reported that the flavor precursors of meat are extractable with cold water. Hornstein and Crowe[58,107] lyophilized a cold water extract of raw lean beef and pork. The dried extract produced an odor of roast meat on heating. They suggested that the lean of different meats possessed similar basic meaty aroma, but that species aroma originated in the fat and was probably due to carbonyl compounds.[57] This has since been questioned, however, and on present knowledge is an over-simplification.

Batzer and co-workers[108,109] also extracted lean raw beef with ice-cold water. By careful dialysis, they separated from the dialysate and diffusate two fractions which possessed beefy aroma on heating; their compositions are presented in Table 3. The principal components involved in beef flavor development were reported to be inosinic acid, inorganic phosphate, and glycoprotein of which the carbohydrate was glucose.[110] The principal amino acids in the protein moiety were $\beta$-alanine and serine with smaller quantities of glycine, glutamic acid, alanine, leucine, and isoleucine. When mixtures of some of these amino acids were added to a solution of glucose, inosine, and inorganic phosphate, meaty flavors developed on heating in water or fat.

Wasserman and Gray[111] attempted to verify these results. They similarly obtained two fractions which possessed beefy aroma on heating. Their compositions were slightly different from the fractions of Batzer et al.[108–110] and are also summarized in Table 3. Later Wasserman and co-workers[112] separated aqueous lean beef muscle extract on Bio-Gel P-2; two of the seven fractions obtained had meaty aromas (see Table 4). Tyrosine, phenylalanine, taurine, and glutamic acid could be removed from the fractions without seriously affecting the aroma.

Macy et al.[113,114] reported that the amino compounds of pork, lamb, and beef were quite similar qualitatively and quantitatively except that cysteic acid and ornithine were common only to pork and lamb, and that glutathione was present only in lamb. In all three cases, taurine, anserine, carnosine, and alanine were the major constituents of unheated samples, and losses during heating were relatively large. Other important constituents which degraded during heating were glutamic acid, glycine, lysine, serine, cystine, methionine, leucine, isoleucine, and methylhistidine. They also showed that the level of amino acids initially increases during roasting (probably due to protein hydrolysis) and possibly involves cathepsins or other proteolytic enzymes in the tissue.[115–117] This liberation of amino acids during cooking is probably important in the development of meat flavor, and, whenever cysteine was released, recognizable beef aromas resulted. Macy et al. also reported the presence of glucose, fructose, ribose, and some unidentified

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## Table 3
## COMPOSITION OF LEAN BEEF EXTRACTS EXHIBITING MEATY AROMA ON HEATING

| Batzer et al.[108-110] | | Wasserman and Gray[111] | |
|---|---|---|---|
| **$Aa_2$** | **$Ab_2$** | **$Aa_2$** | **$Ab_2$** |
| Inosinic acid | Amino acids | Inosine | No reducing sugar |
| Taurine | Peptides | Hypoxanthine | Hypoxanthine |
| Asparagine | No reducing sugar | Isoleucine | Inosine |
| Glutamine | | Glutamic acid | Alanine |
| Anserine | | Arginine | Arginine |
| Carnosine | | Glutamine | Glutamic acid |
| Quaternary ammonium compounds | | Glycine | Glutamine |
| | | Methionine | Glycine |
| | | Alanine | Isoleucine |
| | | Hydroxyproline | Methionine |
| Glycoprotein | | Glucose | |
| ↓ Hydrolysis | | Deoxyribose | Peptide |
| | | | ↓ Hydrolysis |
| Glucose | | | Ammonia |
| Serine | | | Aspartic acid |
| Glutamic acid | | | Threonine |
| Glycine | | | Serine |
| Alanine | | | Glutamic acid |
| Isoleucine | | | Proline |
| Leucine | | | Glycine |
| β-Alanine | | | Alanine |
| Proline | | | Methionine |
| Levulinic acid | | | Isoleucine |
| Inorganic phosphate | | | Tyrosine |
| | | | Phenylalanine |
| | | | Histidine |
| | | | Arginine |
| | | | Tryptophan |
| | | | Valine |

## Table 4
## COMPOSITION OF FRACTIONS OF AQUEOUS LEAN BEEF MUSCLE EXTRACT EXHIBITING MEATY AROMA ON HEATING[112]

| Fraction 1 | | Fraction 2 | |
|---|---|---|---|
| Asparagine | Organic phosphate | Asparagine | Glucose |
| Creatine | Glucose-6-phosphate | Creatine | Fructose |
| Glutamine | a Sugar phosphate | Glutamine | Ribose |
| Phosphate | Lactic acid | Phosphate | Aspartic acid |
| Serine | Anserine | Serine | Creatinine |
| Taurine | Carnitine | Taurine | Inosinic acid |
| Arginine | Choline | Alanine | Phenylalanine |
| Cysteic acid | Histidine | Carnosine | Urea |
| Alanine | Isoleucine | Glutamic acid | |
| Carnosine | Leucine | Glycine | |
| Glutamic acid | Lysine | Methionine | |
| Glycine | 1-Methylhistidine | Organic Phosphate | |
| Methionine | Valine | | |
| Proline | | | |

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carbohydrate material in beef, lamb, and pork extracts.[114] The concentrations of these carbohydrates in the three species were quite similar — glucose being present in the greatest quantities followed by fructose, ribose, and then the unknown fraction. Ribose appeared to be the most labile to heating and fructose the most stable. Pearson showed that the degree of browning and flavor development during cooking was related to the amount of reducing sugars in the tissues.[118]

It was therefore concluded that:

1. Only low molecular weight water-soluble materials are meat flavor precursors.[75,119]
2. High molecular weight proteins, e.g., muscle fibrils and sarcoplasmic proteins are not important.[41,75,119]
3. The amino acid and carbohydrate composition of lean pork, beef, and lamb are similar and this is reflected in the similarity of their lean meat odor.[75,119]
4. A specific glycoprotein and inosinic acid may be precursors for beef flavor or parts thereof.[75]
5. Polypeptides and hypoxanthine may play an important role in meat aroma.[119]
6. Browning type reactions between amino acids (and/or peptides) and reducing sugars probably occur, although they may not be the sole mechanisms involved in aroma production.[75,119]

The evidence that amino acids, peptides, and carbohydrates — particularly ribose — are important precursors of meat aroma was confirmed by May[2] and Heath,[120] who concluded that only those fractions (extractable from raw beef with cold water) containing compounds of molecular weight $<200$ produce any beef flavor on heating. These consisted of cysteine, $\beta$-alanine, glutamic acid, tryptophan, peptides, glucose, glucosamine, fructose, and ribose. May[2] showed that both cysteine and ribose disappeared completely on cooking, and therefore concluded that these are the two compounds mainly involved in meat flavor production.

At a symposium in 1976 Mabrouk[35] summarized 15 classes of organic compounds as meat flavor precursors: (1) glycopeptides, (2) nucleic acids, (3) free nucleotides, (4) peptide-bound nucleotides, (5) nucleotide sugar, (6) nucleotide sugaramine, (7) nucleotide acetylsugaramine, (8) nucleosides, (9) peptides, (10) free amino acids, (11) free sugars, (12) sugar phosphate, (13) sugaramine, (14) amines, and (15) organic acids. The glycopeptide fraction was analyzed from a beef ultrafiltrate subjected to preparative gel permeation chromatography and then preparative thin layer chromatography. Four of the seven fractions separated possessed meaty odor on heating. The amino acids present are shown in Table 5. Fraction 2 had the strongest beef aroma.[35,121] Mabrouk also stated that their earlier work analyzing the glycopeptide fraction showed that one fraction giving an intense meaty odor on heating contained, in addition, glucosamine, hydroxylysine, phosphoserine, and taurine.[35,122] They also identified and quantified 22 of the 27 free amino compounds detected in aqueous beef extract.[35,123] These were anserine (29.43), $\alpha$-alanine (18.17), glutamic acid (11.6), leucine (9.73), valine (6.9), methionine and sulfoxide (6.48), phenylalanine (6.04), tyrosine (5.44), isoleucine (5.07), serine (3.6), threonine (3.17), glycine (3.1), glucosamine (3.04), lysine (2.4), phosphoserine (1.84), arginine (1.53), $\beta$-alanine (0.96), aspartic acid (0.95), proline (0.94), cystine (0.6) hydroxylysine (0.59), and taurine (0.09). The figures in brackets indicate mg/100 g fresh weight of meat. Also present in beef were phosphoethanolamine, glycerophosphoethanolamine, urea, histidine, 1-methylhistidine, and carnosine.[35] The free amino compounds of beef, pork, and lamb were remarkably similar but differed quantitatively, the most obvious differences being the high content of acidic, basic and sulfur-containing amino acids, and the low content of the dipeptides anserine and carnosine in lamb compared with beef and pork. These variations and also pH variations

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**Table 5**
**AMINO ACIDS OF FOUR FRACTIONS EXHIBITING MEATY AROMA ON HEATING AND OBTAINED FROM A GLYCOPEPTIDE FRACTION OF RAW BEEF ULTRAFILTRATE[35,121]**

| Amino acid | Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 |
|---|---|---|---|---|
| Histidine | +[a] | + | + | – |
| Glutamic acid | +[a] | +[a] | + | + |
| β-Alanine | +[a] | + | + | – |
| Aspartic acid | +[a] | + | + | + |
| Glycine | +[a] | +[a] | + | + |
| α-Alanine | +[a] | +[a] | +[a] | +[a] |
| Arginine | +[a] | + | – | – |
| Serine | + | +[a] | + | + |
| Tyrosine | + | + | – | – |
| Leucine | + | + | + | + |
| 1-Methylhistidine | + | + | – | – |
| Tryptophan | + | + | +[a] | + |
| Threonine | + | + | +[a] | + |
| Lysine | + | + | – | – |
| Valine | + | + | + | + |
| Isoleucine | + | + | + | + |
| Ornithine | + | + | – | + |
| Phenylalanine | + | + | + | – |
| α-Aminobutyric acid | + | + | – | – |
| Proline | | | + | +[a] |
| Methionine | | | + | + |
| Methionine sulfoxide | | | + | + |

*Note:* Ammonia was also present in all four fractions.

[a] Indicates major components.

in the three species may well explain qualitative and/or quantitative variations in flavor volatiles accounting for species flavor differences.

Free creatine and creatine phosphate are the most abundant extractive compounds of muscle — mostly present as creatine phosphate.[35] These compounds (and also purine and its derivatives) are thought not to be involved in the development of meaty aroma. Mabrouk et al.[122] also identified ribose, deoxyribose, glucose, mannose, and galactose in diffusate fractions from beef semimembranous tissue. The fraction containing these sugars and methionine and cysteine produced meaty aromas on heating.

Inosinic acid (inosine-5′-monophosphate, 5′-IMP), has already been mentioned as a beef flavor precursor. It is produced from ATP post-mortem.[36,110] Resting muscle contains 5-7 micromoles per gram of ATP; this is the major nucleotide in live muscle.[124] Also present in smaller amounts are guanosine-, cytidine-, inosine-, and uridine-5′-phosphates. Mabrouk has also reported eight fractions of peptide-bound nucleotides in beef and one of these exhibited meaty aroma on heating.[35] Rigor is associated with a decrease in ATP content. At slaughter, the formation of adenosine-5′-monophosphate (AMP) and adenosine diphosphate (ADP) results from the removal of the two terminal phosphate groups from ATP by the combined catalytic action of ATPase and myokinase systems.[13,19] The AMP is rapidly deaminated autolytically to inosinic acid by the action of AMP-deaminase. Thus, 5′-IMP is by far the major 5′-nucleotide in dead muscle.[13] Some 5′-IMP may also derive from cleavage of nicotinamide adenine dinucleotide. However, it is itself cleaved slowly, but still autolytically, by 5′-nucleotidase or

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nonspecific phosphomonoesterase to form inosine which is converted by muscle phosphorylase or riboside hydrolase or else by microfloral activity to hypoxanthine and ribose or ribose-5-phosphate. Hypoxanthine can then form xanthine, uric acid, and ring cleavage products. Thus nucleotides are potential sources of reducing sugars, in particular free ribose and ribose phosphate[19] — well-known Maillard reaction participants.

Macy et al.[115] investigated the effect of cooking on nucleotides, nucleosides, and bases of beef, pork, and lamb and reported that AMP content increased on heating, probably due to hydrolysis of ADP and ATP; also inosinic acid (the prominent nucleotide in all three species) was degraded by heating.

Lipids also act as flavor precursors; however, some confusing reports have appeared in the literature regarding their role in meat flavor formation. Hornstein and Crowe[58,107] suggested that species aroma derived from the fat and that carbonyl compounds were probably responsible. In 1969 Pippen et al.[125,126] showed that fat isolated from cooked poultry has a characteristic poultry flavor but this is not so for fat isolated from raw poultry and then heated. They therefore suggested that flavor volatiles formed in the lean meat are absorbed or dissolve in the fat during cooking. Certainly, fat from cooked poultry, particularly roasted poultry, does contain sulfur compounds, e.g., methional and methanethiol.[1] Sanderson et al.[51] considered that lipid-soluble carbonyl compounds contributed more to meat flavor than water-soluble carbonyls. Pepper and Pearson[127] indicated that there were some differences between the protein present in lean muscle and that of adipose tissue (trimmable subcutaneous and intermuscular fatty tissues). It was suggested therefore that the water-soluble fraction from adipose tissue may make a distinct and characteristic contribution to meat flavor above and beyond that related to the lipid portion. Wasserman and Spinelli[128] showed that precursors of the characteristic species aromas of beef, lamb, and pork were present in the lipids extracted from adipose tissue with a chloroform-methanol mixture. However, water-washing of the extract removed components involved in the formation of these odors. Amino acids and glucose were identified in the wash, but this produced a nonspecies-specific roast meat aroma on heating to dryness. In 1974 Pepper and Pearson[129] demonstrated the presence of creatine, creatinine, cytosine, and uracil in a diffusate of beef adipose tissue.

As a generalization, the two main classes of lipids in meat, i.e., depot or subcutaneous fat on the one hand and intramuscular or tissue lipids on the other hand,[130,131] have been insufficiently differentiated and specified in meat flavor publications.

Hornstein et al.[57] extracted the intramuscular fat from lean beef; the muscle contained 4.6% total lipids of which 75% was triglyceride, consisting mainly of the fatty acids oleic, stearic and palmitic acids. The remainder was a phospholipid fraction containing cephalins (40 to 45%), lecithins (40 to 45%), and sphingomyelins (10 to 15%) and some protein. Therefore, compared with depot fats, tissue lipids contain proportionately larger amounts of phospholipids which occur largely, if not entirely, in association with proteins as lipoproteins and proteolipids.[131] The phospholipids contain a high content of unsaturated fatty acids, especially linoleic acid.[1] They are therefore very susceptible to oxidation and consequent production of volatile compounds. Harkes and Begemann[132] have showed that linolenic and arachidonic acids from the phospholipid fraction of chicken meat are oxidized to mono and polyunsaturated aldehydes, believed to be important in the species-specific flavor of cooked chicken.

The importance of the intramuscular fat and in particular the proteins associated with it has been understressed. Chang and Peterson[21] have recently stated (rightly so) that lipids per se cannot produce some of the sulfur and nitrogen containing heterocyclic compounds recently identified in meat. However, proteins chemically associated with lipids could act as their precursors but it should be emphasized that such heterocycles have not been proved to contribute species-specific aromas. Whatever the compounds

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which are responsible for interspecies flavor differences and whatever their source (lipid or nonlipid material), significant sensory differences ($p \leqslant 0.05$) do exist between the aromas of cooked lean beef, pork, and lamb *l. dorsi* muscles; the three species were also correctly identified from their cooked aromas a significant ($p \leqslant 0.05$) number of times.[133] Thus the volatile components responsible for species differences are produced from lean muscle and if lipid per se is an important contributor, the 4.6% intramuscular fat is sufficient.

Other meat aroma precursors include biotin, coenzyme A, and in particular, thiamin.[1,12,99,134-136]

During aging an increased supply of many meat aroma precursors occurs. At aging temperature, enzymes present in raw meat continue to act on meat components and this activity decreases with aging time.[137] Proteases produce an increase in N-terminal amino groups[138] and in free amino acids, principally alanine, glutamic acid, leucine and cystine,[13] — liberated from the sarcoplasmic proteins. Lipolytic enzymes also operate and an increase in free fatty acid concentration occurs.[139] As already described, ATP breakdown results in inosine, hypoxanthine, ribose (and ribose-5-phosphate) which when heated in the presence of various amino acids give rise to meat aroma. An increase in concentration of other soluble carbohydrate intermediates of glycolysis especially reducing sugars and lactic acid also occurs on aging and some glycogen is converted into glucose by $\alpha$-amylase.[140] This, together with the simultaneous production of free amino acids, provides a pool of Maillard reactants.

### 3. *Formation of Meat Flavor Volatiles*

Fresh raw meat has little or no odor and so the aroma components of Table 1 develop during heating, either directly or indirectly from the nonvolatile precursors already described. Unfortunately, there is insufficient knowledge regarding the reactions which occur.[1] They are governed by temperature and degree of moisture in the meat.[8]

Primary reactions occurring on heating include degradation of sugars, pyrolysis of proteins and amino acids, and lipid degradation. Additionally, interreaction of two or more precursors may occur, as in the Strecker degradation, Maillard reaction, and protein/lipid interactions. Subsequently, a host of secondary reactions occurs, involving the products of the above reactions (e.g., hydrogen sulfide, ammonia, thiols, and others), thus increasing still further the complexity of the mechanisms of meat flavor development and the variety of compounds which may be formed. Some interesting compounds (see Section II.C.3.e) are likely to arise in this way. Chemical reactions occurring during meat aroma formation include oxidation, fragmentation, recombination, rearrangements, hydrolysis, dehydration, decarboxylation, condensation, and cyclization.[35,76,141]

Because meat is such a complex system and so many interactions can occur, many workers have attempted to simplify the system by performing model reactions involving a reduced number of precursors (which either occur in meat or are likely to be present) under conditions intended to simulate cooking.[8] Many have offered reaction mechanisms to explain the formation of aroma compounds. Much interesting chemistry has been proposed but the formation of the same components in natural meat and their contribution, if formed, to meat aroma, is uncertain.[8,76] Nevertheless, with our current state of knowledge, they provide useful information regarding potential reactions which could occur in meat.

The main types of reactions leading to meat flavor may be summarized as follows:[1]

1. Pyrolysis of peptides and amino acids
2. Degradation of sugars (particularly reducing sugars)
3. Interactions involving sugars, peptides, amino acids, or their degradation products

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4. Degradation and reaction of ribonucleotides
5. Reaction of hydrogen sulfide, ammonia, thiols etc., with other components (volatile or nonvolatile)
6. Oxidation, hydrolysis, dehydration, and decarboxylation of lipids
7. Thiamin degradation

Although current information on these is incomplete, numerous reports have appeared in the recent literature. Some of the more salient of these are now reviewed.

### *a. Pyrolysis of Peptides and Amino Acids*

Temperatures higher than those normally attained when cooking meat have been used in thermal decomposition studies of amino acids. However, based on the energies of activation of these reactions, trace (significant) quantities of the products may arise during cooking.[3,19] Pyrolysis products of some amino acids present in meat are listed in Tables 6 through 10. They frequently include ammonia, carbon dioxide, amines, amino acids, hydrocarbons, nitriles, and carbonyl compounds. Pyridines have been reported from $\beta$-alanine,[146] cysteine,[151] and cystine.[151] Aromatic amino acids form several benzenoid compounds;[142,144,148,149] e.g., benzene, toluene, and ethylbenzene are obtained on pyrolyzing phenylalanine, and the corresponding hydroxy compounds derive from tyrosine.[143] Hydrogen sulfide is evolved from all sulfur amino acids,[150] methionine also producing several thiols and sulfides;[142,143,150] cysteine and cystine create several thiazole derivatives,[150,151] while cysteine specifically also produces a series of thiophens.[151] Pyrazines are characteristic pyrolysis products of $\beta$-hydroxyamino compounds,[147,152] such as serine and threonine and are not formed from other amino acids, the amino acid clearly serving as the source of both carbon and nitrogen of the pyrazine molecule.[147] However, different compositions of pyrazine mixtures are obtained when the same compound is heated under different conditions. Some pyrroles also arise from heating serine and threonine[152] and also form proline[142] and hydroxyproline.[143] Indole and some of its derivatives are included in the pyrolysis products of tryptophan.[144,149]

Merritt and Robertson[143] observed that the compounds formed on pyrolyzing a peptide depended on the sequence of amino acids. As suggested by Dwivedi, this could explain the formation in meat of volatile compounds not obtained on heating model systems of single amino acids.[19]

### *b. Sugar Degradations*

Caramelized sugar flavors are formed when sugars are heated alone or in the presence of acids, alkalis, or buffers. Bound water is lost between 100 and 130° C without altering molecular structure. With increasing temperature up to 180° C, a molecule of water splits off forming anhydrides; further heating to 220° C causes loss of a second water molecule and the formation of furfural from pentoses and hydroxymethylfurfural from hexoses. At temperatures of about 300° C, caramelization occurs resulting in the formation of many highly odorous and pungent substances, among which furans and their derivatives often dominate; also usually present are carbonyl compounds, alcohols, and both aliphatic and aromatic hydrocarbons.[153] Sugar degradation is an important source of di- and tricarbonyls which may react subsequently with amino acids in Strecker degradations.

Some thermal degradation products of glucose are shown in Table 11. Again temperatures used in sugar degradation studies have been higher than in meat cooking and especially so for the formation of benzenoid compounds,[154] but possible formation of trace quantities during roasting cannot be ruled out. Min et al.[73] have recently proposed this source for the alkylbenzenes they identified in roast beef. Some degradation products of sugars have more than six carbon atoms, probably arising from

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## Table 6
## SOME PYROLYSIS PRODUCTS OF VALINE, LEUCINE, AND ISOLEUCINE

| Valine | Leucine | Isoleucine |
|---|---|---|
| Hydrogen[142] | Hydrogen[142] | Hydrogen[142] |
| Nitrogen[143] | Nitrogen[143] | Nitrogen[143] |
| Carbon monoxide[145] | Carbon monoxide[145] | Carbon monoxide[145] |
| Carbon dioxide[142,143,145] | Carbon dioxide[142,143,145] | Carbon dioxide[142,143,145] |
| Ammonia[143,145] | Ammonia[143,145] | Ammonia[143,145] |
| Water[142] | Water[142] | Water[142] |
| Methane[142,143] | Methane[142,143] | Methane[142,143] |
| Propane[145] | Isobutane[145] | Butane[145] |
| Isobutane[145] | 2-Methylbutane[145] | 2-Methylbutane[145] |
| Propene[145] | Isobutylene[145] | Butene[145] |
| Isobutylene[145] | 3-Methylbut-1-ene[145] | 2-Methylbut-1-ene[145] |
| Methylpropanal[143] | Methylpropanal[145] | 2-Methylbutanal[143,145] |
| Acetone[145] | 3-Methylbutanal[143,145] | Butanone[145] |
| Butanone[142] | Acetonitrile[143] | Acetonitrile[143] |
| Acetonitrile[143] | 3-Methylbutanonitrile[142] | 2-Methylbutanonitrile[142] |
| Methylpropanonitrile[142] | Propenonitrile[143] | Propenonitrile[143] |
| Propenonitrile[143] | 2-Methylpropylamine[145] | 2-Methylbutylamine[145] |
| 2-Methylpropylamine[145] | 3-Methylbutylamine[145] | Bis-(2-methylbutyl) amine[145] |
| Bis-(2-methylpropyl) amine[145] | Bis-(3-methylbutyl) amine[145] | N-(2-methylbutylidene)-2-methylbutylamine[145] |
| N-(2-methylpropylidene)-2-methylpropylamine[145] | N-(2-methylpropylidene)-3-methylbutylamine[145] | |
| | N-(3-methylbutylidene)-3-methylbutylamine[145] | |

## Table 7
## SOME PYROLYSIS PRODUCTS OF α-ALANINE AND β-ALANINE

| α-Alanine | β-Alanine |
|---|---|
| Hydrogen[142] | Hydrogen[142] |
| Nitrogen[143] | Nitrogen[143] |
| Carbon monoxide[146] | Carbon monoxide[146] |
| Carbon dioxide[142,143,146] | Carbon dioxide[142,143,146] |
| Ammonia[143,146] | Ammonia[143,146] |
| Water[142] | Water[142] |
| Methane[142,143] | Methane[142,143] |
| Ethane[146] | Ethylene[146] |
| Ethylene[146] | Propene[146] |
| Propene[146] | Acetone[142,146] |
| But-2-ene[146] | Butanone[142] |
| Acetaldehyde[143,146] | Acetic acid[143] |
| Acetone[142] | Acetonitrile[143,146] |
| Butanone[142] | Propenonitrile[143] |
| Acetonitrile[143] | Pyridine[146] |
| Propanonitrile[142] | 3-Methylpyridine[146] |
| Propenonitrile[143] | 2,4-Dimethylpyridine[146] |
| Ethylamine[146] | 3,5-Dimethylpyridine[146] |
| N-ethylidene-ethylamine[146] | 2,3,5-Trimethylpyridine[146] |
| Propionamide[146] | Poly-β-alanine[146] |
| N-ethylpropionamide[146] | |
| 5-Ethyl-2-methylpyridine[146] | |

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**Table 8**
**SOME PYROLYSIS PRODUCTS OF PHENYLALANINE AND TYROSINE**

| Phenylalanine | Tyrosine |
|---|---|
| Hydrogen[142] | Hydrogen[142] |
| Nitrogen[143] | Nitrogen[143] |
| Carbon dioxide[142–144] | Carbon dioxide[142–144] |
| Ammonia[143] | Ammonia[143,149] |
| Water[142,144] | Water[142,144] |
| Methane[142,143] | Methane[142–144] |
| Acetaldehyde[149] | Toluene[143,144] |
| Benzene[142–144,148] | Phenol[144,149] |
| Toluene[142,143,148,149] | *p*-Cresol[144,149] |
| Ethylbenzene[144,148,149] | *m*-Cresol[144,149] |
| Propylbenzene[144] | Xylenol(dimethylphenol)[144] |
| Styrene[142,143,148] | *p*-Ethylphenol[144] |
| Propenylbenzene[144] | *o* or *m*-Ethylphenol[144] |
| Indene[144] | Acetonitrile[143,144] |
| Stilbene[149] | Propenonitrile[143] |
| Phenylacetylene[144] | Methylamine[149] |
| 1,2-Diphenylethane[144,149] | Aniline[149] |
| Benzaldehyde[149] | 2-Phenylethylamine[149] |
| Phenylacetaldehyde[149] | Tyramine[149] |
| Acetonitrile[143,144] | |
| Propenonitrile[143] | |
| Phenylacetonitrile[142,143] | |
| 2-Phenylpropionitrile[149] | |
| Benzylamine[149] | |
| 2-Phenylethylamine[144,149] | |
| Indole[149] | |

fragmentation of polymers.[154] Apart from the two members listed in Table 7, furanones may readily form from sugars other than glucose present in meat. For example, thermal acid degradation of 2-deoxyribose gives 5-methyl-3(2H)furanone;[158] 2,5-dimethyl-3(2H) furanone can result from heating fructose (> 130°C), as also can 4-hydroxy-2,5-dimethyl-3(2H) furanone.[159] The latter is also formed during base-catalyzed fructose degradation in boiling aqueous solutions.[160] Its 5-methyl homolog similarly forms at 100°C in aqueous solution — this time from ribose-5-phosphate by base-catalyzed $\beta$-elimination of phosphoric acid followed by an acid-catalyzed dehydration of the resulting 5-deoxydehydropentose.[161] The optimum pH for this reaction is, appropriately, that of meat, i.e., approximately pH 5.5.[161]

### *c. Strecker Degradation of Amino Acids*

Strecker degradation is the oxidative deamination and decarboxylation of an $\alpha$-amino acid into an aldehyde containing one fewer carbon atom. A dicarbonyl, or potential dicarbonyl compound, participates in the reaction, which involves decarboxylation and transamination.

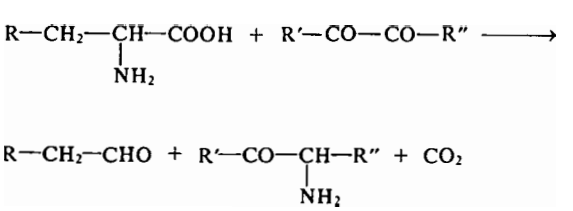


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**Table 9**
**SOME PYROLYSIS PRODUCTS OF CYSTEINE, CYSTINE, AND METHIONINE**

| Cysteine | Cystine | Methionine |
|---|---|---|
| Hydrogen[142] | Nitrogen[143] | Hydrogen[142] |
| Carbon dioxide[142] | Carbon dioxide[143] | Nitrogen[143] |
| Ammonia[143,150] | Ammonia[143,150] | Carbon dioxide[142,143] |
| Water[142] | Methane[143] | Ammonia[143] |
| Methane[142] | Acetaldehyde[150] | Water[142] |
| Acetaldehyde[150] | Acetonitrile[143] | Methane[142,143] |
| Acetone[142] | Propenonitrile[143] | Acetaldehyde[150] |
| Acetonitrile[142] | Ethylamine[150] | Propanal[150] |
| Ethylamine[150] | Mercaptoethylamine[150] | Methylpropanal[150] |
| Mercaptoethylamine[150] | Methanethiol[150] | Acetone[150] |
| Isoleucine[150] | α-Alanine[150] | Acetonitrile[142,143] |
| Cystine[150] | Isoleucine[150] | Propanonitrile[142] |
| Ammonium carbonate[150] | Methionine[150] | Propenonitrile[142,143] |
| Hydrogen sulfide[150] | Ammonium carbonate[150] | Ethylamine[150] |
| Carbon disulfide[143] | Sulfur[150] | Propylamine[150] |
| Carbonyl sulfide[143] | Hydrogen sulfide[150] | Prop-2-enylamine[150] |
| Sulfur dioxide[143] | Carbon disulfide[143] | But-2-enylamine[150] |
| 2-Methylpyridine[151] | Carbonyl sulfide[143] | 3-(Methylthio)propylamine[150] |
| 2-Ethyl-5-methylpyridine[151] | Sulfur dioxide[143] | Methanethiol[150] |
| Thiophen[151] | 2-Methylpyridine[151] | Methional[150] |
| 2-Methylthiophen[151] | 2-Ethyl-5-methyl-pyridine[151] | Hydrogen sulfide[150] |
| 3-Methyltetrahydrothiophen[151] | a Methylthiophen[143] | Carbon disulfide[143] |
| 2,5-Dimethylthiophen[151] | 2-Methylthiazole[151] | Carbonyl sulfide[143] |
| 2(or 3)-Ethylthiophen[151] | 5-Ethyl-2-methyl-thiazole[151] | Sulfur dioxide[143] |
| 2,3-Dihydro-4(or 5)-ethylthiophen[151] | 2-Methylthiazoline[151] | Dimethylsulfide[142] |
| 2,3,5-Trimethylthiophen[151] | 2-Methylthiazolidine[150] | Methylpropylsulfide[143] |
| 3(or 4)-Ethyl-2-methylthiophen[151] | | |
| 3-Methylpropylthiophen[151] | | |
| 2,4-Dimethyl-5-ethylthiophen[151] | | |
| 2-Ethylthiazole[151] | | |
| 2-Methylthiazoline[151] | | |
| 2-Methylthiazolidine[150,151] | | |

Thus, acetaldehyde is formed from alanine, propanal from α-aminobutyric acid, 3-methybutanal from leucine, 2-methylpropanal from valine, phenylacetaldehyde from phenylalanine, butanal from norvaline, benzaldehyde from phenylglycine, 2-methylbutanal from isoleucine, and methional (which further readily decomposes to methanethiol, dimethylsulfide, dimethyl disulfide, and acrolein) from methionine.[29,162] Diketones may be metabolic products within muscle tissue or may arise from carbohydrates on heating and include, e.g., butan-2,3-dione, pyruvaldehyde and pyruvic acid. Strecker aldehydes often undergo further reactions and the α-aminoketone formed may dimerise forming pyrazines,[93] thus, increasing the number of volatile products obtained.

Some highly reactive and odorous compounds result from the Strecker degradation of cysteine.[3] The initial products, which are capable of further reactions, are hydrogen sulfide, ammonia, acetaldehyde, and mercaptoacetaldehyde (see Figure 1). Furthermore, the original diketone is released for further Strecker (and Maillard) propagations. Kobayashi and Fujimaki[163] identified hydrogen sulfide, acetaldehyde, and mercaptoacetaldehyde in refluxed aqueous cysteine/ninhydrin. Palamand et al.[164] reported meaty aroma even at 100° C on heating 40% aqueous solution of cysteine with pyruvaldehyde (methylglyoxal) for 30 min.

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## Table 10
## SOME PYROLYSIS PRODUCTS OF SERINE AND THREONINE

| Serine | Threonine |
|---|---|
| Hydrogen[142] | Nitrogen[143] |
| Nitrogen[143] | Carbon dioxide[143] |
| Carbon dioxide[142,143] | Ammonia[143] |
| Ammonia[143,152] | Methane[143] |
| Water[142] | Propanal[152] |
| Methane[142,143] | Acetonitrile[143] |
| Acetaldehyde[152] | Propenonitrile[143] |
| Acetone[142] | Pyrrole[152] |
| Paraldehyde[152] | 2-Methylpyrrole[152] |
| Acetonitrile[142,143] | 4-Ethyl-3-methylpyrrole[152] |
| Propenonitrile[143] | Methylpyrazine[147] |
| Ethylamine[152] | 2,5-Dimethylpyrazine[147,152] |
| Ethanolamine[152] | Trimethylpyrazine[147,152] |
| Pyrrole[152] | 2,5-Dimethyl-3-ethylpyrazine[147,152] |
| 2-Methylpyrrole[152] | 4-Methylpropylpyrazine[152] |
| a Dimethylpyrrole[152] | Pyrazine, mol wt 136[147] |
| 4-Ethyl-3-methylpyrrole[152] | Pyrazine, mol wt 136[147] |
| Pyrazine[143,147,152] | Pyrazine, mol wt 150[147] |
| Methylpyrazine[147,152] | Pyrazine, mol wt 150[147,152] |
| 2,3-Dimethylpyrazine[147] | Pyrazine, mol wt 164[147,152] |
| Ethylpyrazine[147,152] | Pyrazine, mol wt 178[147] |
| 2-Ethyl-6-methylpyrazine[147,152] | |
| 2,5-Dimethyl-3-ethylpyrazine[147] | |
| 2,6-Diethylpyrazine[147,152] | |
| 2,6-Diethyl-3-methylpyrazine[152] | |
| Pyrazine, mol wt 150[147] | |
| Pyrazine, mol wt 150[147] | |
| Pyrazine, mol wt 164[147] | |
| 2,5-Diketo-3,6-dimethylpiperazine[152] | |

## Table 11
## SOME THERMAL DEGRADATION PRODUCTS OF GLUCOSE

- Alcohols
  - Methanol[155]
  - Ethanol[155]
- Aldehydes
  - Formaldehyde[156]
  - Acetaldehyde[154,155]
  - Propanal[154]
  - Butanal[154,155]
  - Pentanal[155]
  - 2-Methylpropanal[154,155]
  - 2-Methylbutanal[155]
  - Prop-2-enal[154,155]
  - But-2-enal[154]
  - Pent-2-enal[154]
  - 2-Methylpropenal[154]
  - Penta-1,3-dienal[154]
- Ketones
  - Propanone[154,155]
  - Butanone[154,155]
  - Pentan-2-one[154]
  - Pentan-3-one[154,155]
  - Hexan-2-one[154]
  - Hexan-3-one[154]
  - Buta-2, 3-dione[154,156]
  - Penta-2,3-dione[154]
  - But-3-en-2-one[154]
  - Pent-3-en-2-one[154]
  - 3-Methylbut-3-en-2-one[154]

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**Table 11 (continued)**
**SOME THERMAL DEGRADATION PRODUCTS OF GLUCOSE**

Cyclopentanone[154]
3-Methylcyclopenta-1,2-dione[156]
Cyclopent-2-en-1-one[154]

Acids
Formic acid[154,155]
Acetic acid[154-156]
Propanoic acid[154,155]
Butanoic acid[154,155]
Pentanoic acid[155]
2-Methylpropanoic acid[154,155]
2-Methylbutanoic acid[155]
Levulinic acid[154]
Succinic acid[155]
Tartaric acid[155]
Pyruvic acid[154]

Benzenoid compounds
Benzene[154]
Toluene[154]
*o*-Xylene[154]
*m*-Xylene[154]
*p*-Xylene[154]
Ethylbenzene[154]
1,3,5-Trimethylbenzene[154]
1,2,4-Trimethylbenzene[154]
1,2,3-Trimethylbenzene[154]
Phenol[156]
Resorcinol[154]
Pyrocatechol[154]

Furans and derivatives
Furan[154-156]
2-Methylfuran[154-156]
3-Methylfuran[154]
2-Ethylfuran[154]
2,5-Dimethylfuran[154]
2-Vinylfuran[154]
2-Propylfuran[154,156]
2-Isopropylfuran[154]
2-Ethyl-5-methylfuran[154]
2,3,5-Trimethylfuran[154]
2-Isopropyl-5-methylfuran[154]
5-Methyl-2-vinylfuran[154]
5-Methyl-2-propylfuran[154]
2,5-Diethylfuran[154]
2-(*cis*-Prop-1-enyl)furan[154]
2-(*trans*-Prop-1-enyl)furan[154]
2-Isopropenylfuran[154]
5-Methyl-2-(*cis*-prop-1-enyl)furan[154]
5-Methyl-2-(*trans*-prop-1-enyl)furan[154]
2,3-Benzofuran[156]
2-Furfural[154,156]
3-Furfural[154]
3-Methyl-2-furfural[154]
5-Methyl-2-furfural[156]
5-(Hydroxymethyl)-2-furfural[154,155]
2-Acetylfuran[154,156]
2-Acetyl-5-methylfuran[154,156]
2-Methyltetrahydrofuran-3-one[154]
4-Hydroxy-2,5-dimethyl-3(2H) furanone[154]
1-(2-Furyl)propan-1,2-dione[156]
2-Furoic acid[155]
Methylfuroate[156]
2-Methyl-3-(2-furyl)prop-2-en-furan[154]

Miscellaneous
4-Hydroxypent-2-enoic acid lactone[156]
Hydroquinone[154]
1,6-Anhydro-β-D-glucopyranose[154,155]
1,4:3,6-Dianhydro-β-D-glucopyranose[154]
Kojibiose[157]
Sophorose[157]
Nigerose[157]
Laminaribiose[157]
Maltose[157]
Cellobiose[157]
Isomaltose[157]
Gentiobiose[157]

### *d. Maillard Reaction*

This is induced by heating compounds containing a free amino group (e.g., amino acids, amines, peptides, proteins, ammonia) with carbonyl compounds (e.g., aldehydes, ketones, reducing sugars); it is probably the principal reaction occurring in meat flavor production.[8] Many of the compounds listed in Table 1, particularly some of the more recently identified heterocycles,[23] can be attributed to it. It is an open ended complex reaction consisting of a series of interreactions and decompositions and resulting in numerous volatile products frequently including aliphatic aldehydes, furans and derivatives, ketones (including α-dicarbonyls), alcohols, cyclic ethers, pyrroles, pyridines, pyrazines, oxazoles, and oxazolines; if sulfur-containing amino acids are involved, products may include thiols, sulfides, thiophens, thiazoles, and thiazolines. It may occur through the Amadori reaction pathway and may involve Strecker degradation of the amino acid. It can occur at 90° C, is inhibited by water, and increases with time and temperature.[147] Chuyen et al.[165] have reported that peptides are more reactive than amino acids in nonenzymic browning.

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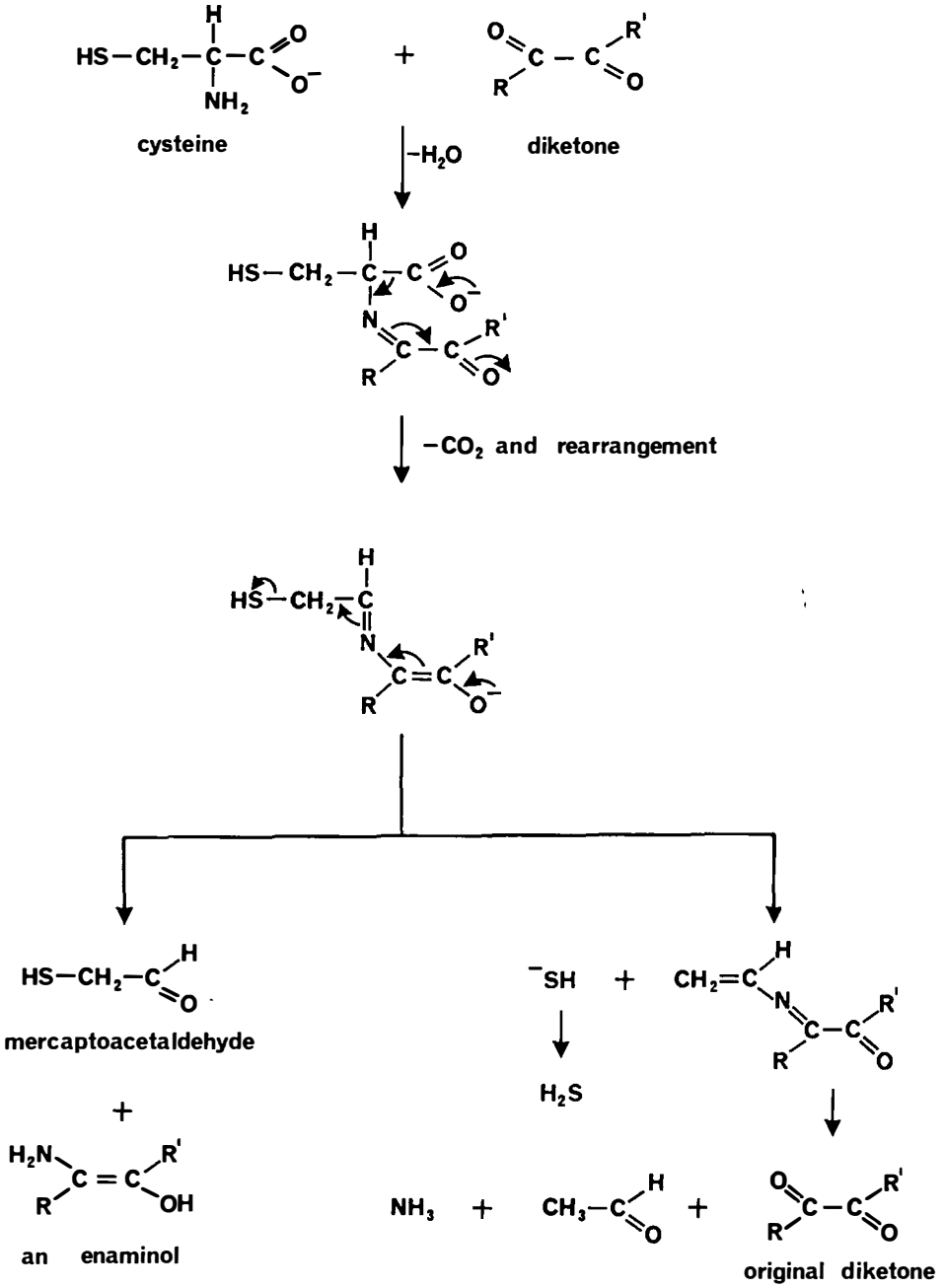


FIGURE 1. The Strecker degradation of cysteine.[1]

Because of its importance in flavor propagation, the Maillard reaction has been reviewed by several workers.[93,102,166–172] To give this complex reaction full credit would require an article far longer than this. In any case the mechanisms involved in the formation of many of the volatile compounds in Table 1 are unknown or little understood. In addition, many secondary reactions occur, some of which appear to be very important. Therefore, only those aspects of the reaction which are best understood and are likely to be important in their contribution to meat aroma will be discussed.

The first stage of the Maillard reaction is widely accepted. It involves an addition

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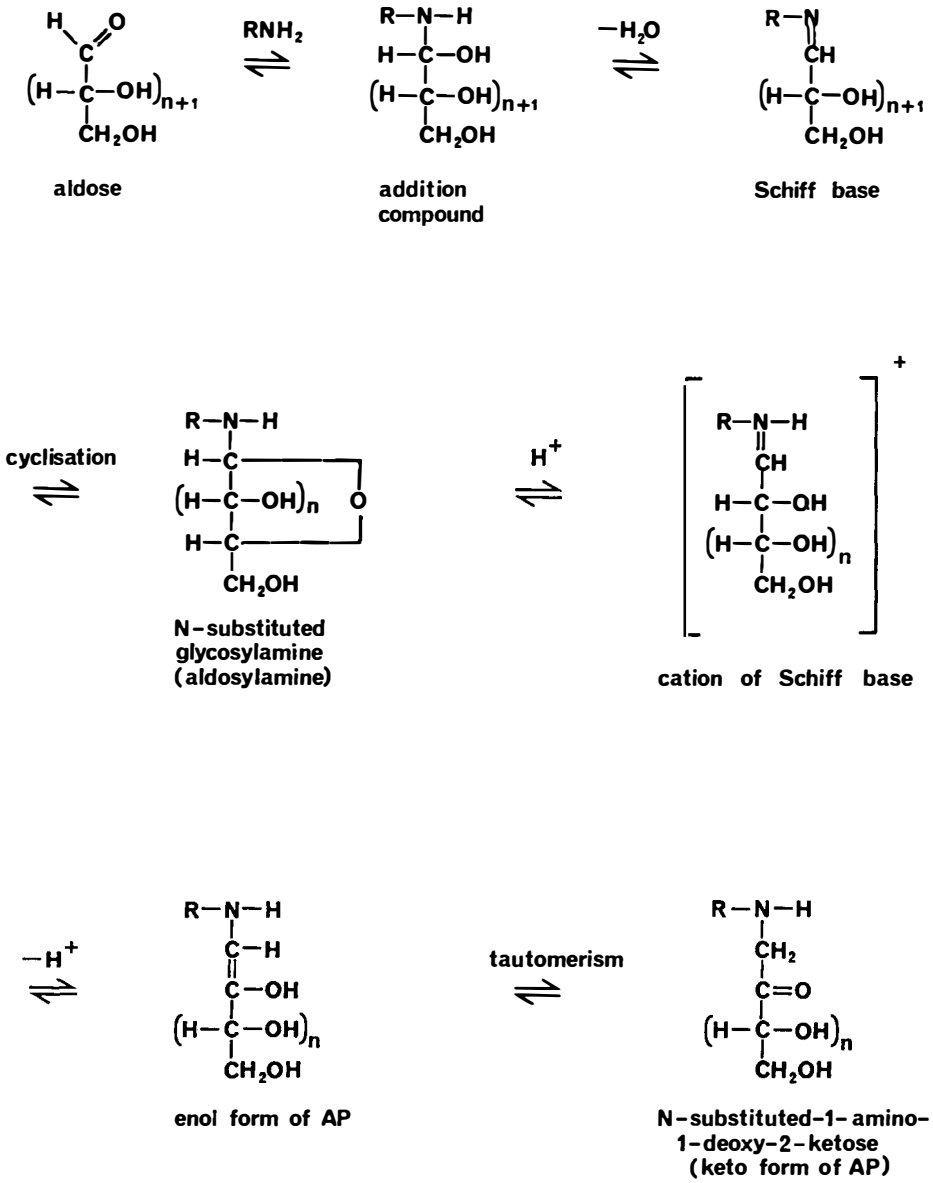


FIGURE 2. Formation of Amadori product (AP) from aldose + amine. (Adapted with permission from Hodge, J. E., *J. Agric. Food Chem.*, 1, 931, 1953. American Chemical Society:)

reaction of the amine to the carbonyl group, followed by elimination of water forming a Schiff base. This cyclizes producing an N-substituted glycosylamine which undergoes an acid-catalyzed Amadori rearrangement forming the Amadori product (AP), i.e., an N-substituted-1-amino-1-deoxy-2-ketose.[167,168,173] The scheme for an aldose plus amine is shown in Figure 2.

The importance of the APs in flavor production during heating has been recognized for some time, and the effect of water content of the food is important.[174] For example, optimal formation of glucose/amino acid APs occurs at a water content of 25 to 30% (model system 100°C/1 hr),[174] a region often encountered during cooking and processing. van den Ouweland et al.[174] reported that during frying of meat, approximately 60% of the initial water is lost. In the surface layers this loss is even higher,

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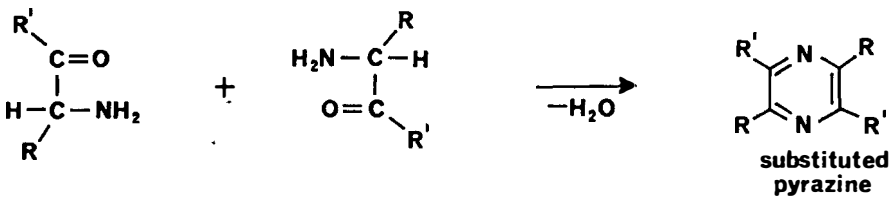
and conditions are created at which the Maillard reaction is favored.[174] A considerable decrease in amino nitrogen and in glucose, fructose, and ribose concentrations occurred when a beef diffusate was heated (125° C/1 hr),[175] and the glucose/glycine AP has been isolated from roasted meat.[174]

The nonvolatile APs are the key compounds in that they are heat-labile and, on low temperature thermolysis, decompose forming volatile flavor compounds via 1-deoxyosones and 3-deoxyosones, respectively.[162] The former may be transformed into $\alpha$-dicarbonyls with which amino acids can undergo Strecker degradation, and — as already discussed — some Strecker aldehydes are potent aroma components. The amino ketones simultaneously formed may be transformed into pyrazines. For example,




Some simple reactions of APs are presented in Figure 3.

Further reactions of the unstable AP's on heating have been reported.[102,173,176,177] The reaction conditions and the character of the amino compound determine the range of aroma components formed.[102] A scheme for the formation of several furan derivatives identified in beef aroma has been presented by Tressl et al.[102] and is summarized in Figure 4. While hexoses form 5-methylfurfural and 4-hydroxy-2,5-dimethyl-3(2H) furanone (Figure 4), pentoses give rise to furfural and 4-hydroxy-5-methyl-3(2H)-furanone, respectively. For example, this latter compound has been synthesized by heating amines with xylose, ribose, ribose-5-phosphate or, incidentally, glucuronic acid.[178,179] During these reactions the oxygen of the furan ring may be substituted by nitrogen or sulfur, forming the corresponding pyrroles and thiophen derivatives.[102] Shibamoto et al.[180] identified several pyrroles in the reaction mixture of furfural, ammonia, and hydrogen sulfide showing that exchange of nitrogen for the oxygen in the furan ring does occur on heating.

Maltol, a $\gamma$-pyrone identified in beef aroma, also may arise from decomposition of a hexose AP. Its immediate precursor is probably 5-hydroxy-5,6-dihydromaltol, an important precursor of caramel compounds,[102] and identified in sugar-amine model reactions by Mills et al.[181] This compound, together with smaller amounts of the compounds shown adjacent to it in Figure 5, were formed on decomposition at 140° C of 1-deoxy-1-L-prolino-D-fructose.[177] On heating with proline, 5-hydroxy-5,6-dihydromaltol gives rise to 5-hydroxymaltol, maltol and 4-hydroxy-2,5-dimethyl-3(2H) furanone;[177] the latter two appear in Table 1 and it is likely that the other compounds mentioned here may also be identified in cooked beef aroma in the future.

Proline and hydroxyproline have secondary amino groups and therefore do not undergo Strecker degradation. The formation of several pyrroles and pyridines which are present in Table 1, from the reaction of proline and glucose under roasting conditions has been reported.[102,182] The reaction products included pyrrole, 2-methyl-, 3-methyl-, 2-ethyl-, 2,5-dimethyl-, N-methyl-, N-propyl-pyrrole, pyridine, 2-methyl-, 3-methyl-, 2-ethyl-, 2,3-dimethyl- and 2-formyl-pyridine.[102] Several N-acylpyrrolidines and 2,3-dihydroindolines were also reported, but have not been identified in beef aroma. Bicyclic pyrrole compounds have also been isolated from a proline/glucose model reaction.[182] The similar reaction of hydroxyproline with glucose has produced over 50 nitrogen heterocycles and in contrast to the proline system, only N-substituted products were obtained, e.g., N-alkylpyrroles, N-acylpyrroles, and N-furfurylpyrroles. The 2,3-dihy-

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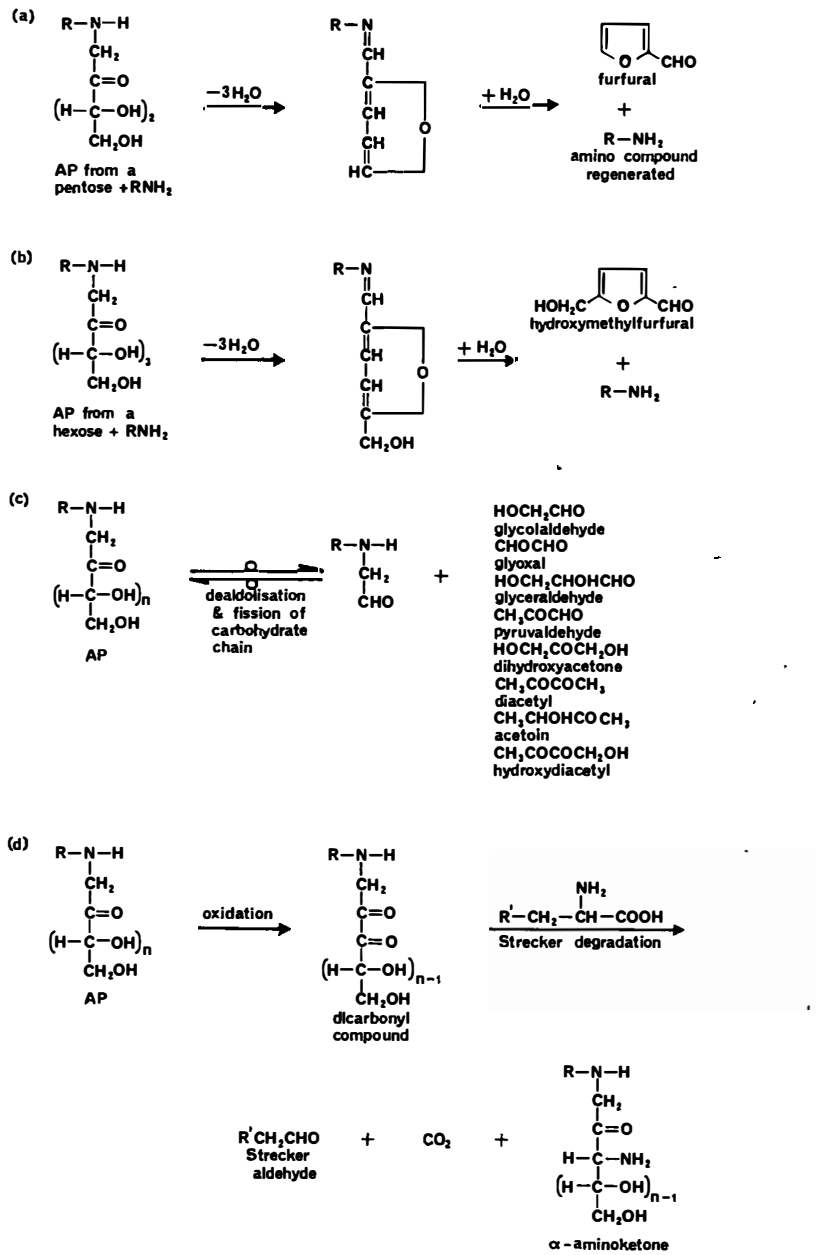


FIGURE 3. Some reactions of Amadori products (APs).[162,167]

droindolenes were again identified, but no pyridines. None of these products appears in Table 1, however.

The pyrazines most frequently produced thermally are the alkyl, alkenyl, and acyl pyrazines. Mechanisms of their formation have been reported;[183–186] they can be formed as already described by dimerization of α-aminoketone Strecker products. Newell et al.[187] using a model system of glucose/amino acid, and van Praag et al.[188] using glucose/ammonia, both concluded that the reaction required free ammonia and that the same pyrazines were produced regardless of the amino acids since it only served as a source of free ammonia.[8] Tetramethylpyrazine is formed by reaction of butan-2,3-dione and ammonia.[84] Conversely Koehler and coworkers[189,190] showed that the amino acid

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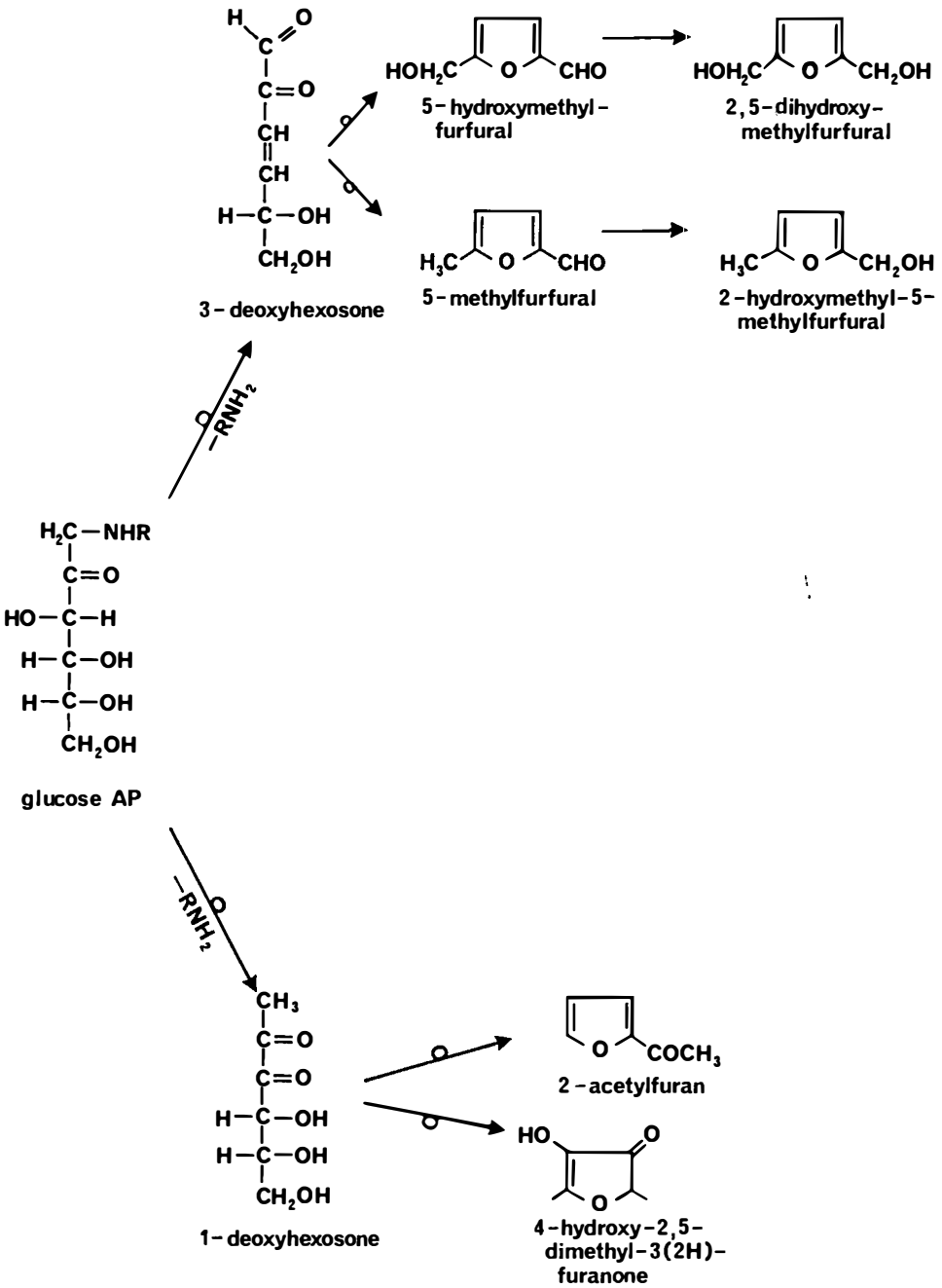


FIGURE 4. Formation of furanoid compounds from glucose Amadori compound.[102] (From Tressl, R., et al., *Progress in Flavor Research*, Applied Science, London, 1979, 198. With permission.)

nitrogen reacts directly with the sugar system producing different pyrazines. The type and concentration of pyrazines formed depended on the carbon source, e.g., the particular sugar or sugar degradation products such as glyoxal, acetaldehyde, glycerol, propanal, hydroxyacetone, butan-2,3-dione, and also glucosamine. Recently Shibamoto and Bernhard,[191,192] using sugar/ammonium hydroxide model systems, showed that glucose gave a series of alkylpyrazines, while rhamnose produced a series of dihydrocyclopentapyrazines and tetrahydroquinoxalines. Both of these classes of

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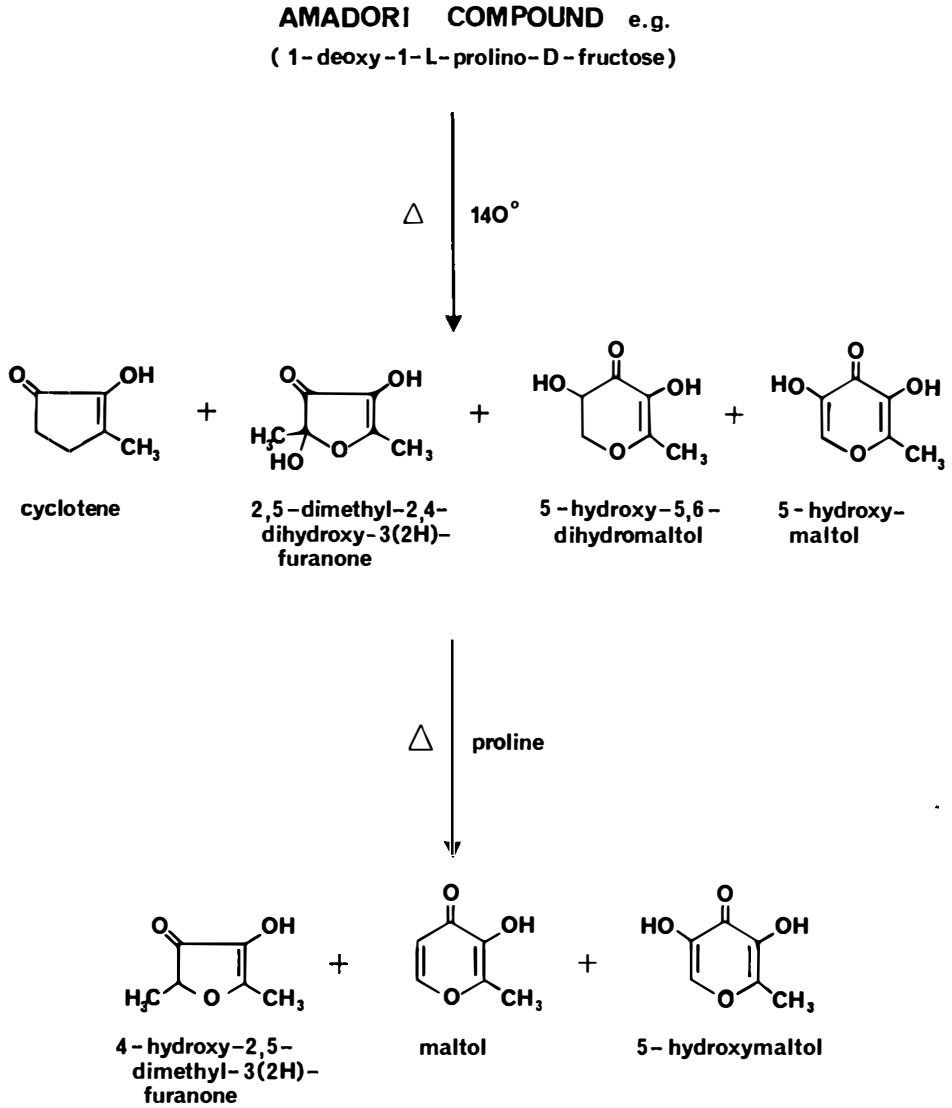


FIGURE 5. Compounds with caramel odors which arise by Maillard reaction.[102,177]

compounds have been identified in cooked beef aroma (see Table 1). Shibamoto and Russell[193,194] heated a solution of glucose, ammonia, and hydrogen sulfide. The volatiles produced resembled closely beef odor and included thiophens, furans, 2,4-dimethyl-3-thiazoline, methanethiol, dimethylsulfide, alkylthiazoles, and pyrazines; several of the compounds formed have been identified in cooked beef aroma. Increasing the concentration of ammonia increased the total yield of pyrazines and also changed the ratio of the individual pyrazines formed, due partly to a greater amount of ammonia available for reaction and partly to increased pH causing greater fragmentation of the sugar and the formation of more carbonyl compounds.[180,191,193,194] Wasserman explains that when meat is initially heated (normal pH 5.5 approximately) the mechanism for pyrazine formation, involving carbonyl/amino acid (or amine) reaction, is likely to be favored but as the concentration of ammonia increases on liberation from amino acids on continued heating, the pH increases and induces the reaction described by Shibamoto et al. Using the same model system, Shibamoto and Russell determined the effects of temperature on pyrazine formation. Although some pyrazines were formed at −5°C (after 30

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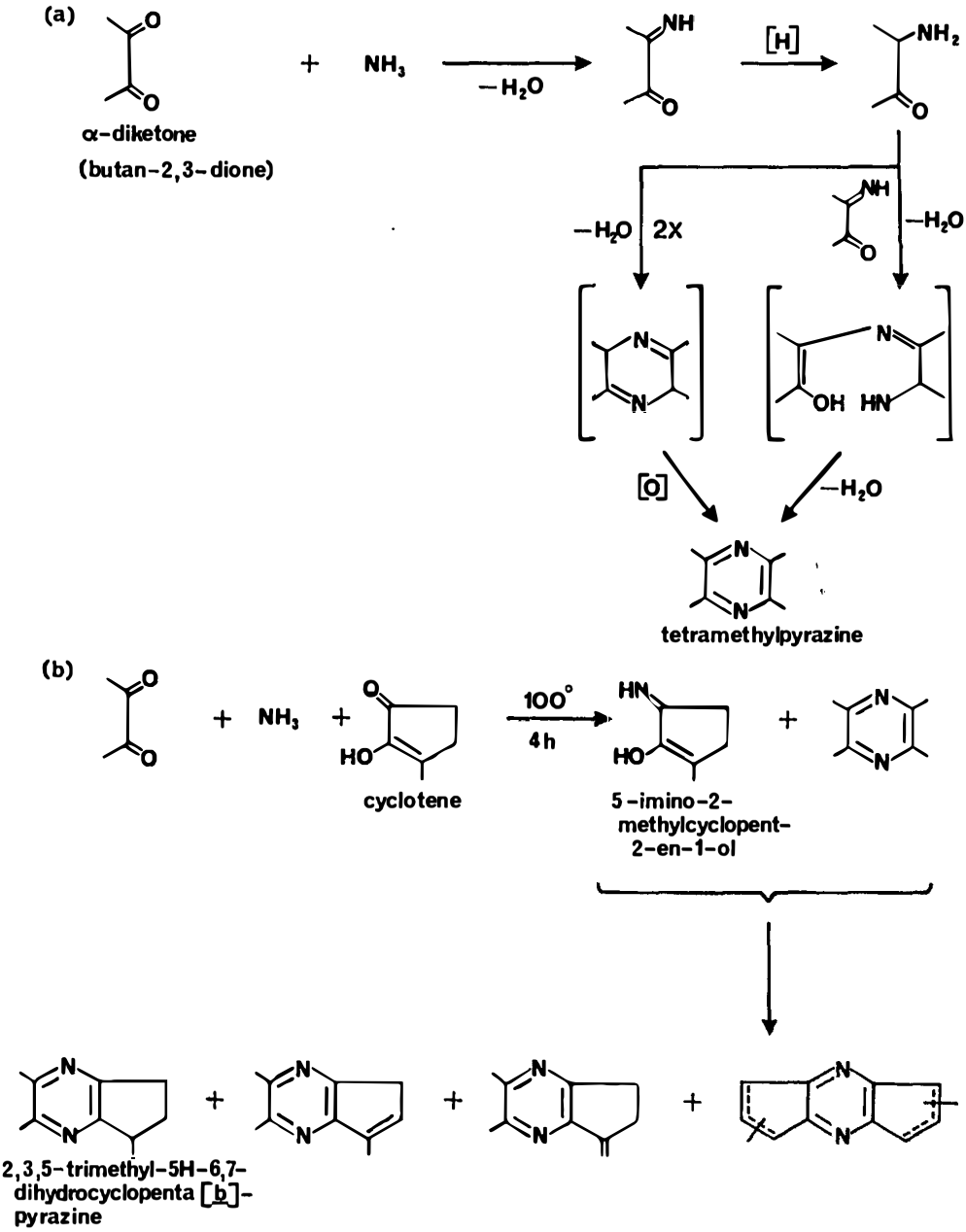


FIGURE 6. Formation of alkyl-5H-6,7 dihydroxycyclopenta [*b*] pyrazines from Maillard reaction products. (From Flament, I., et al., *Helv. Chim. Acta*, 59, 2310, 1976. With permission.)

days), significant pyrazine formation began at 70° C and increased to optimum at 120° C/2 hr.[193,194] Reineccius et al.[195] also showed that pyrazine formation occurred at time-temperature relationships as low as 30 min at 70° C. Other investigators have reported no pyrazine formation below 100° C.[8] They were formed in greater concentrations during cooking of beef by microwave radiation than by conventional means.[47]

Alkyl-5H-6,7-dihydrocyclopenta [*b*]pyrazines, present in both boiled and roasted aromas of heated beef, arise from condensation of hydroxycyclopentenones with α-dicarbonyls in the presence of ammonia.[84,196] All these reactants are available in heated meat. Alkyl hydroxycyclopentenones are Maillard reaction products; a typical

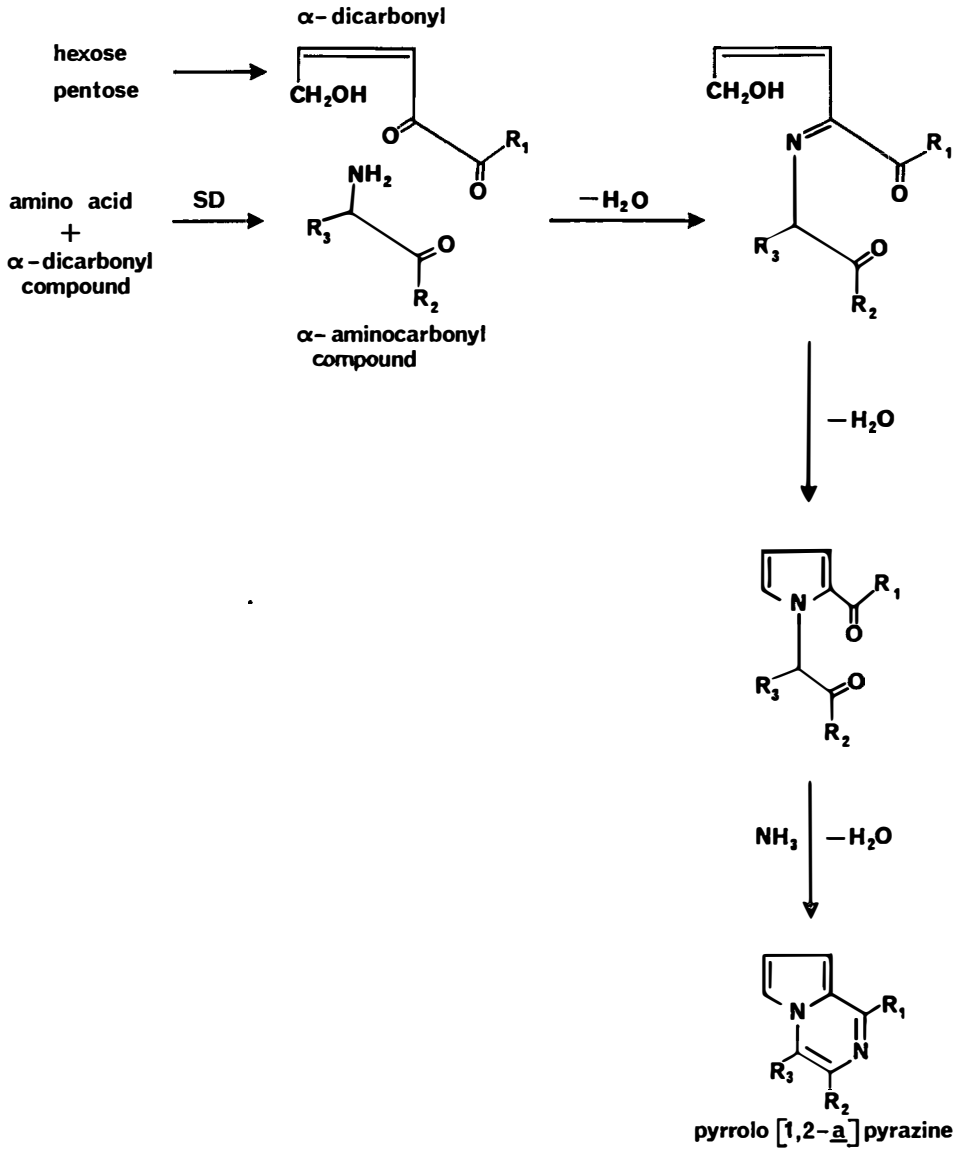


FIGURE 7. Formation of pyrrolo [1,2-*a*] pyrazines. (From Flament, I., et al., *Helv. Chim Acta*, 60, 1877, 1977. With permission.)

example is 2-hydroxy-3-methylcyclopent-2-enone, i.e., cyclotene (see Figure 5). The series of reactions leading to the formation of these pyrazines is shown in Figure 6.[84] Unsaturated bicyclic structures are also formed.

Pyrrolo[1,2-*a*]pyrazines probably arise by condensation of a sugar degradation product (α-dicarbonyl compound) with a Strecker degradation product (α-aminocarbonyl compound) in the presence of ammonia,[85] as shown in Figure 7.

van den Ouweland et al.[174] concluded that the majority of the volatile products evolved from heating the AP of glycine/glucose (this has been isolated from meat) and of glycine/fructose above their melting points were furan and pyrrole derivatives. The list of compounds identified is summarized in Table 12.

Maillard reactions involving cysteine and/or cystine have been extensively studied.[197-204] Possible reaction products are carbonyl compounds, amines, benzenoids, acids, lactones, thiols, furan derivatives, thiophen derivatives, thianes, thiolanes, pyrroles,

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**Table 12**
**VOLATILE DEGRADATION PRODUCTS FROM GLUCOSE/GLYCINE AND FRUCTOSE/GLYCINE AMADORI COMPOUNDS[174]**

| Glucose/glycine only | Fructose/glycine only[a] | Glucose/glycine and fructose/glycine |
|---|---|---|
| Methanol | Propanal | Acetaldehyde |
| Pyran-2-one | Ethanol | Pentanal |
| 2-Acetylpyridine | Tetrahydropyrrole | Hydroxyacetone |
| | 2,3-Dimethylpyrazine | Acetic acid |
| | 3-Hydroxybutan-2-one | Furfural |
| | Ethyl-2-methylpyrazine | 2-Acetylfuran |
| | Trimethylpyrazine | 5-Methylfurfural |
| | Propionamide | Propionic acid |
| | N-Methyl-2-formylpyrrole | 2-Acetyl-N-methylpyrrole |
| | 1-Aminopropane | 2-(Hydroxymethyl)furan |
| | Butyramide | 2-(Hydroxymethyl)-5-methylfuran |
| | 2-Furfurylpropylketone | 2-Hydroxycyclopent-2-enone |
| | 3-Hydroxypyran-2-one | 2-Butenolide |
| | 2-Pyrrolidone | 2,3-Dihydromaltol |
| | | 2-Acetylpyrrole |
| | | 2-Formyl-5-methylpyrrole |
| | | 2,3-Dihydro-5-hydroxymaltol |

[a] More carbohydrate chain scission products formed; also nitrogen plays an active role.

pyridines, pyrazines, thiazoles, thiazolines, and thiazolidines, including several members listed in Table 1. Some examples of the volatile products of the reactions of cysteine/cystine with pyruvaldehyde, glucose, and ribose, respectively, are summarized in Tables 13 to 15. Kato et al.[197] showed that far more thiophen derivatives arise from cysteine/pyruvaldehyde reaction than from the corresponding reaction involving cystine (see Table 13). They made similar comparisons of glucose/cysteine and glucose/cystine reaction products and showed that more thiophens and pyrazines were identified in the cysteine system while more thiazoles and furan derivatives arose from cystine (see Table 14). Thiophen derivatives have also been eminent in the reaction products of cysteine/xylose — a model system approximating cooked meat,[94] and in a cysteine/cystine-ribose system (see Table 15). Mulders[200] has proposed a scheme for the formation of 5-methylthiophen-2-carboxaldehyde (see Table 1) from reaction of mercaptoacetaldehyde (the highly reactive Strecker aldehyde of cysteine) and but-2-enal which can arise from aldol condensation of acetaldehyde followed by dehydration.[200] As far as foods are concerned, with the exception of American cranberries,[205] thiophens and their derivatives have been identified exclusively in cooked or roasted foods,[88] and so their formation from Maillard type reactions involving cysteine seems very likely. Interaction of glucose degradation products (carbonyl compounds) with hydrogen sulfide also produces thiophens, including thiophen aldehydes and ketones.[193,194] The three tetrahydrothiophenones shown in Table 1, i.e., tetrahydrothiophen-2-one, tetrahydrothiophen-3-one and its methyl homolog have been identified in model reactions of cysteine with xylose,[94] glucose,[198] or pyruvaldehyde.[197] Several mercaptothiophens result from the reaction of hydrogen sulfide with 4-hydroxy-5-methyl-3(2H) furanone or its 2,5-dimethyl homolog,[98] but none of these has been identified in cooked beef aroma. Neither have thienothiophens, known to arise from cysteine/cystine-ribose[200] and cysteine/glucose[98,198] reactions.

Alkylthiazoles and acylthiazoles have been isolated from model reactions of cysteine/cystine with xylose,[203] ribose,[200] pyruvaldehyde,[197] or glucose[197] (see Tables 13-15). Alkenyl thiazoles were also identified in the cysteine/xylose reaction.[203] The

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**Table 13**
**SOME VOLATILE STRECKER DEGRADATION PRODUCTS OF CYSTEINE/PYRUVALDEHYDE AND CYSTINE/PYRUVALDEHYDE[197]**

| Cysteine/pyruvaldehyde | Cystine/pyruvaldehyde |
|---|---|
| Benzene | Acetic acid |
| Benzoic acid | Benzoic acid |
| *p*-methylbenzoic acid | *p*-Methylbenzoic acid |
| Phenol | 5-Methylfurfural |
| 2-Furoic acid | 2,5-Dimethyl-3-ethylfuran |
| 2,5-Dimethylpyrazine | 2-Furoic acid |
| 2,5-Dimethyl-3-ethylpyrazine | 2,5-Dimethylpyrazine |
| Trimethylpyrazine | 2,5-Dimethyl-3-ethylpyrazine |
| Thiophen | 2-Thiophenoic acid |
| 3-Methylthiophen | 2-Methylthiazole |
| 2,5-Dimethylthiophen | 4(or 5)-Ethyl-2-methylthiazole |
| 2(or 3)-Ethylthiophen | 2-Acetyl-4-methylthiazole |
| 2-Methyltetrahydrothiophen-3-one | |
| Thiazole | |
| 5(or 4)-Methylthiazole | |
| 5(or 4)-Ethylthiazole | |
| 2-Ethylthiazole | |
| 2-Ethylthiazoline | |

2,4-dimethyl-5-vinylthiazole of Table 1 is easily formed by dehydration of the corresponding alcohol, i.e., 5-(2-hydroxymethyl)-2,4-dimethylthiazole.[206] The 2-acetylthiazole of Table 1 may arise from oxidation of 2-acetyl-2-thiazoline believed to arise from Strecker degradation of cysteine by pyruvaldehyde[200] or from the addition of pyruvaldehyde to cysteamine and subsequent oxidation.[88] Several 2-alkylthiazolines and 2-alkylthiazolidines have also been identified in cysteine/sugar reactions,[197,203] but have not been reported in beef aroma.

Oxazoles may arise by Strecker degradation of aminoketones resulting from the condensation of $\alpha$-dicarbonyl compounds with amino acids.[88] The model reaction of furfural, hydrogen sulfide, and ammonia produces 2,4-dimethyloxazole.[180] 2,4,5-Trimethyl-3-oxazoline is formed from reaction of alanine and butan-2,3-dione[183] and some of the other oxazolines in Table I may be formed in analogous ways. In fact 2,4,5-trimethyl-3-oxazoline also forms readily from the reaction of two carbonyl compounds identified in cooked beef aroma, i.e., acetaldehyde and acetoin in the presence of ammonia.[207]

Several of the sulfur compounds listed in Table 1 arise from Maillard reactions or Strecker degradations of cysteine and cystine. Hydrogen sulfide is a common heat-induced product, formed for example, from interaction of cysteine with xylose,[204] ribose,[200] or $\alpha$-diketones[163] and also on pyrolysis of sulfur-containing amino acids (see Table 9). Methanethiol is mainly formed by cleavage of methionine.[150,208] Short chain aliphatic thiols are formed in cysteine/cystine-ribose reactions.[200] Benzylmethylsulfide has been isolated in a model system (cysteine/xylose) approximating cooked meat,[94] though not in beef aroma. The diastereoisomeric 3,5-dimethyl-1,2,4-trithiolanes, thialdine, aliphatic disulfides and dimethyl trisulfide have also been identified in the cysteine/xylose model reaction.[94]

Apart from contributing itself to meat flavor, hydrogen sulfide also acts as a precursor for other flavor compounds.[1] A few examples have already been quoted. It is evolved continuously on simmering beef; its release increases with time and cooking temperature, probably as a result of protein denaturation and reduction of disulfide links to thiol

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## Table 14
## SOME VOLATILE REACTION PRODUCTS OF GLUCOSE/CYSTEINE AND OF GLUCOSE/CYSTINE

| Glucose/cysteine | Glucose/cystine |
|---|---|
| Ethanol[197] | Ethanol[197] |
| But-2-en-1-ol(crotyl alcohol)[198] | Propanone[199] |
| Acetic acid[197] | Acetic acid[197] |
| But-2-en-1-al(crotonaldehyde)[198] | Furfural[197] |
| Propanal[199] | Furfuryl alcohol[197] |
| Hexanal[198] | Furfural alcohol[197] |
| Butanone[198] | 5-Methylfurfural[197] |
| Methylvinylketone[198] | 5-Ethyl-2-methylfuran[197] |
| Buta-2,3-dione (diacetyl)[198] | Pyridine[197] |
| Penta-2,3-dione[198] | 3-Methylpyridine (β-picoline)[197] |
| Cyclopentanone[198] | 5-Ethyl-2-methylpyridine[197] |
| Cyclohexanone[198] | Methylpyrazine[197] |
| Benzene[198] | Methanethiol[199] |
| Toluene[198] | Ethanethiol[199] |
| *m*-Xylene[198] | Propanethiol[199] |
| *p*-Xylene[198] | 2-Methylthiazole[197] |
| Benzaldehyde[198] | 2,4(or 5)Dimethylthiazole[197] |
| Furfural[198] | 2-Methyl-4-(or5)ethylthiazole[197] |
| 5-Methyl-2-furfural[198] | Trimethylthiazole[197] |
| 2-Acetylfuran[197,198] | 2-Methylthiazoline[197] |
| 2-Acetyl-5-methylfuran[197,198] | |
| Pyridine[197] | |
| 2-Methylpyridine (α-picoline)[197] | |
| 3-Methylpyridine (β-picoline)[198] | |
| Methylpyrazine[197] | |
| 2,5-Dimethylpyrazine[197] | |
| 6-Ethyl-2-methylpyrazine[197] | |
| 3-Ethyl-2-methylpyrazine[197] | |
| 2,5-Dimethyl-3-ethylpyrazine[197] | |
| Methanethiol[199] | |
| Propanethiol[199] | |
| Pentanethiol[199] | |
| Thiophen[197,198] | |
| Hydroxythiophen[197] | |
| 2-Methylthiophen[198] | |
| 3-Methylthiophen[198] | |
| 2-Ethylthiophen[198] | |
| 2,3-Dimethylthiophen[198] | |
| 2,5-Dimethylthiophen[198] | |
| 2-Thiophenthiol[198] | |
| 3-(Methylthio)thiophen[198] | |
| 2-Formylthiophen[198] | |
| 2-Formyl-5-methylthiophen[198] | |
| 2-Acetylthiophen[198] | |
| 2-Propionylthiophen[198] | |
| Dihydro-3(2H)thiophenone[198] | |
| 2,3-Benzothiophen[198] | |
| Thieno [3,2,*b*] thiophen[198] | |
| 2-Methylthiazoline[197] | |

groups.[8] Persson and von Sydow[43] showed that as cooking time of canned beef increased from 15 to 75 min, hydrogen sulfide evolution increased threefold. Methanethiol and ethanethiol also increased in concentration in the aroma. On storage of the product, however, marked losses of both hydrogen sulfide and methanethiol occurred,[67] possibly due to interactions with other components in the beef.[8]

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**Table 15**
**SOME VOLATILE REACTION PRODUCTS OF CYSTEINE/CYSTINE-RIBOSE[200]**

| | |
|---|---|
| Carbon disulfide | 2,6-Diethyl-3-methylpyrazine |
| Hydrogen sulfide | 2-Acetylpyrazine |
| Methanethiol | 2-Acetyl-3-methylpyrazine |
| Ethanethiol | 6,7-Dihydro-5H-cyclopentapyrazine |
| Propan-1-thiol | 2-Methyl-6,7-dihydro-5H-cyclopentapyrazine |
| Acetaldehyde | 2-Formylthiophen |
| Methylamine | 3-Acetylthiophen |
| Propylamine | 2-Formyl-5-methylthiophen |
| Pentylamine/isopentylamine | 2-Formyl-3-methylthiophen |
| Furfural | 3-Acetyl-2-methylthiophen |
| Furfuryl alcohol | 2-Acetyl-5-methylthiophen |
| 2-Acetylfuran | 5-Acetyl-2-methylthiophen |
| 1(2-Furyl)-2-propanone | Thieno[3,2-*b*]thiophen |
| *trans*-1,2-(2,2′-Difuryl)ethene | Thieno[3,4-*b*]thiophen |
| Pyrrole | 3-Methyl-1,2,4-trithiane |
| 2-Formyl-1-methylpyrrole | 2-Methylthiazole |
| 2-Acetylpyrrole | 5-Ethylthiazole |
| 1-Furfurylpyrrole | 5-Ethyl-2-methylthiazole |
| 2-Methylpyridine | 2,4,5-Trimethylthiazole |
| 5-Ethyl-2-methylpyridine | 2,4-Dimethyl-5-ethylthiazole |
| Methylpyrazine | 2-Acetylthiazole |
| Propylpyrazine | 2-Propionylthiazole |
| Alkylpyrazine | 2-Butyrylthiazole |
| 2,5-Dimethylpyrazine | 2-(2-Furyl)thiazole |
| 2-Ethyl-6-methylpyrazine | |

### *e. Reactions of Hydrogen Sulfide and/or Ammonia and/or Thiols, etc. with other Meat Aroma Components*

van den Ouweland and co-workers[1,98] have reported the reaction of 4-hydroxy-5-methyl-3(2H) furanone with hydrogen sulfide forming a complex mixture of compounds possessing an overall odor of roasted meat. They identified the major components as mercapto-substituted furan and mercapto-substituted thiophen derivatives. The reaction is summarized in Figure 8. The first stage in the formation of the thiophen derivatives involves substitution of the ring oxygen by sulfur to give the thio-analog. The 2,5-dimethyl homolog of the furanone acts in a similar way and cysteine may act as a hydrogen sulfide donor.[98] van den Ouweland et al. remark that the important feature of this model system is the meaty odor associated with many of the individual products of the reaction (see Figure 8) — certainly contrasting with most of the components isolated from meat itself.[1] They also state that several of these products have gas chromatographic retention times and odor port assessments which are very similar to those of trace components detected from a natural beef broth aroma isolate, and which have so far defied identification.[1]

Model reactions using aldehydes and hydrogen sulfide have suggested that this may also be a source of interesting sulfur compounds. At atmospheric pressure, acetaldehyde and hydrogen sulfide give mainly cyclic trimers, e.g., dioxathianes, oxadithianes, and trithianes.[209] No examples of the first two classes have been identified in cooked beef aroma but 2,4,6-trimethyl-1,3,5-trithiane, i.e, trithioacetaldehyde has been reported;[75,86] (1,3,5-trithianes have also been identified in model reactions of fatty aldehydes, hydrogen sulfide, thiols, and ammonia,[80] and also from furfural, hydrogen sulfide, ammonia reaction mixtures[180]). However, reaction of acetaldehyde and excess hydrogen sulfide in a closed vessel gave rise via bis-(1-mercaptoethyl) sulfide as intermediate to some compounds listed in Table 1, namely 3,5-dimethyl-1,2,4-trithiolane and diethyldisulfide.

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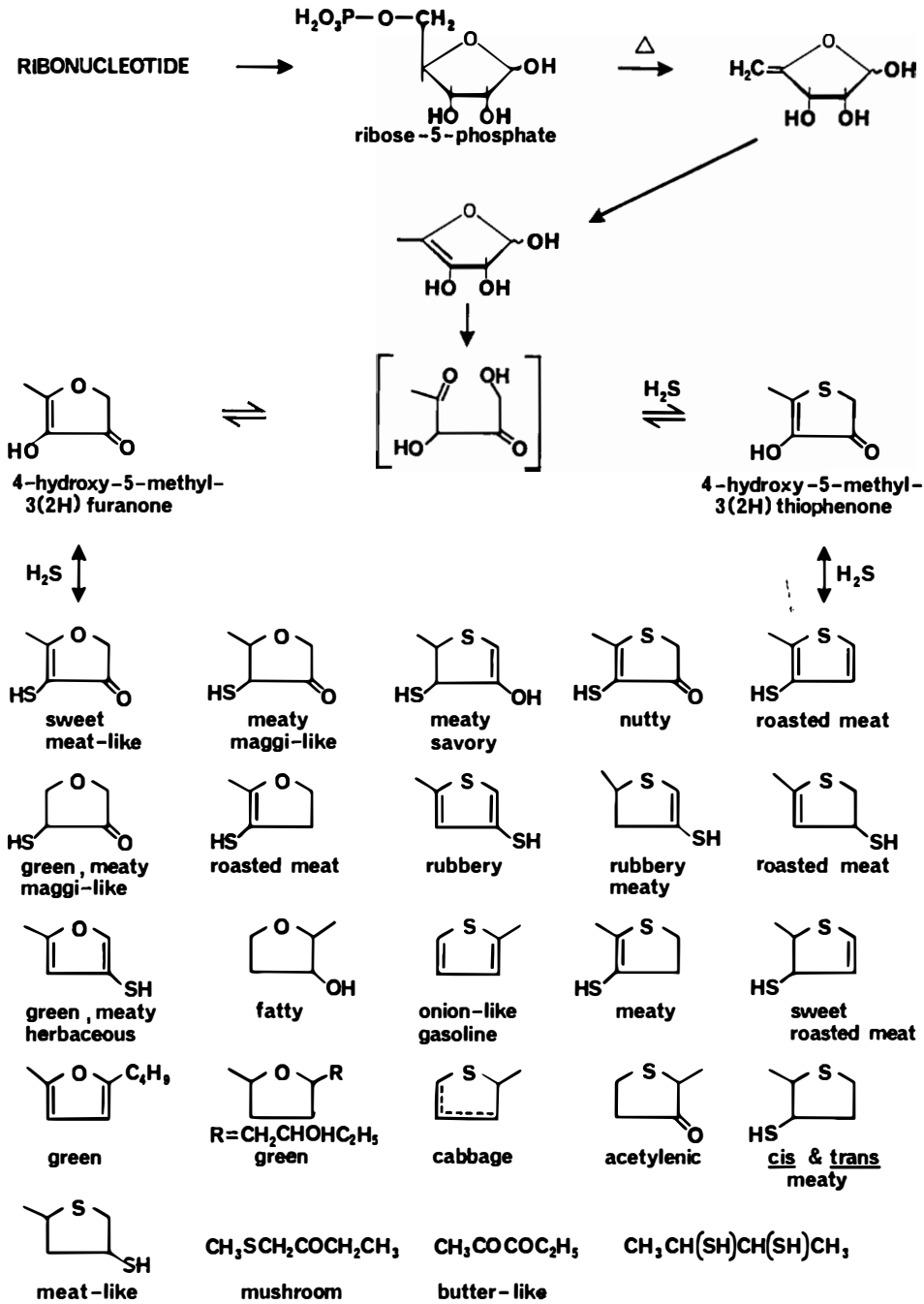


FIGURE 8. Formation from ribonucleotides of 4-hydroxy-5-methyl-3(2H) furanone and its reaction with hydrogen sulfide.[1,98]

In the presence of ammonia, dithiazines and thiadiazines are formed. One dithiazine, i.e., thialdine has been reported in heated beef aroma.[61,75,86] These reactions are summarized in Figure 9.

Takken et al.[209] have reported their extensive and systematic studies of similar reactions but using $\alpha$-dicarbonyls in addition to aldehydes, hydrogen sulfide, and ammonia. Various combinations were studied, the $\alpha$-dicarbonyls being either butan-2,3-

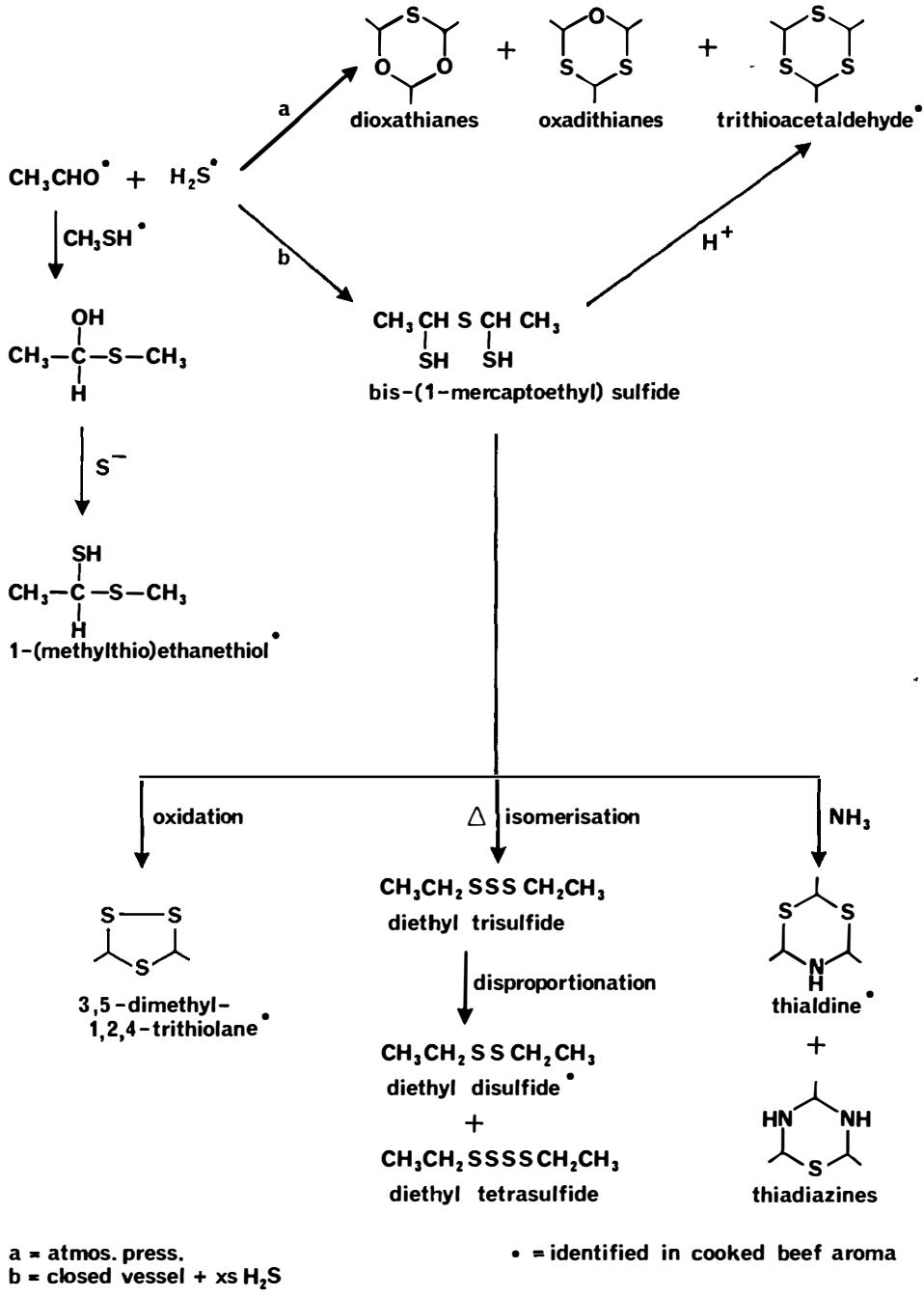


FIGURE 9. Some reactions of aldehydes and hydrogen sulfide. (Reprinted with permission from Takken, H. J., et al., in *Phenolic, Sulfur and Nitrogen Compounds in Food Flavors*, ACS Symp. Ser. 26, 1976, 116. American Chemical Society.)

dione, pentan-2,3-dione or pyruvaldehyde; the aldehydes used were acetaldehyde, propanal, or but-2-enal. All reaction mixtures gave relatively similar products (except for the reaction involving butan-2,3-dione and but-2-enal), e.g., thiazoles, thiazolines, oxazoles, oxazolines, isothiazoles, thialdine, dithiolenes, trithianes, and mercaptoalkenes.[209] The suggested formation pathways in the reaction of butan-2, 3-dione,

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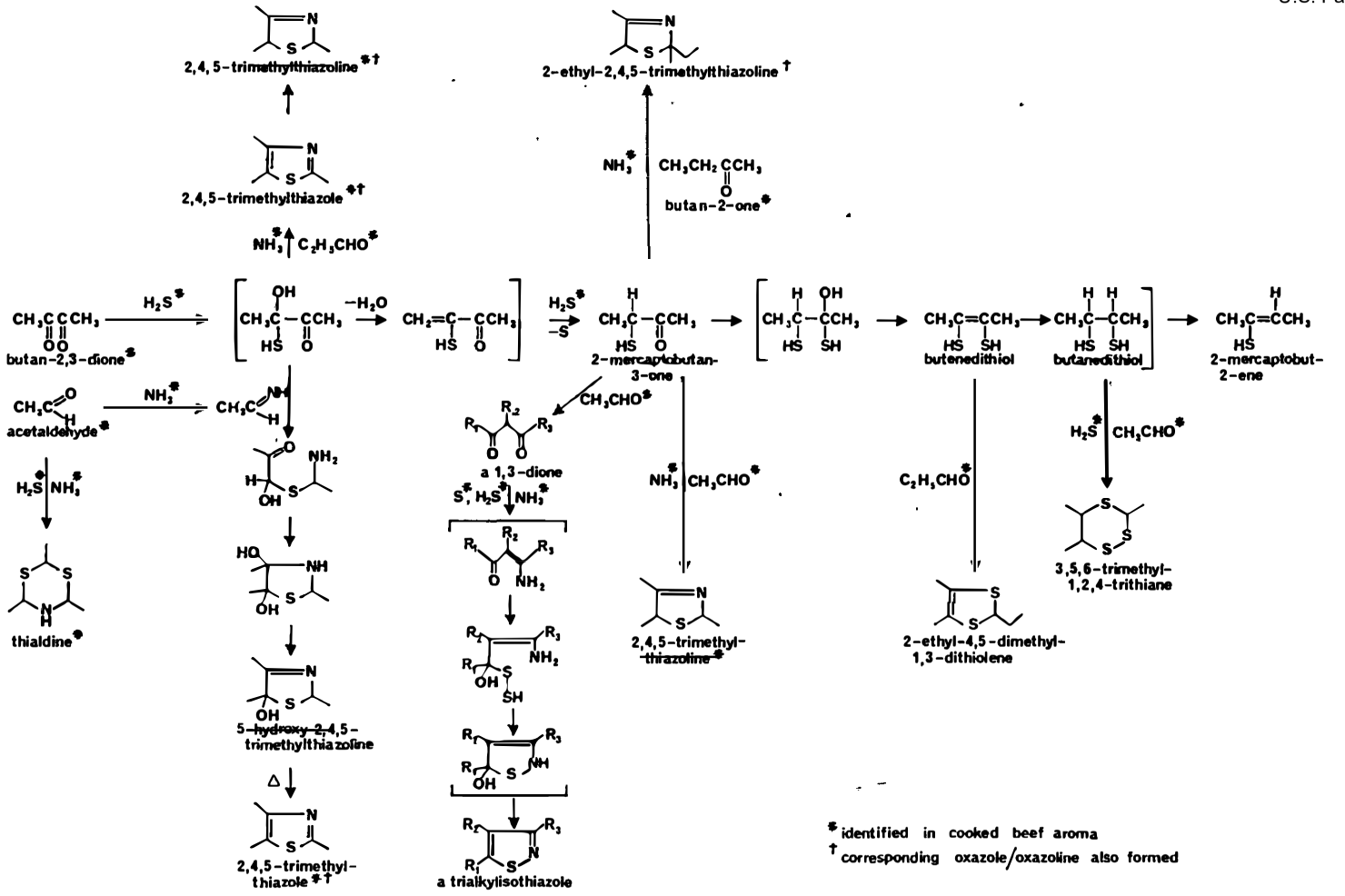


FIGURE 10. Possible formation pathways in the reaction of butan-2,3-dione with acetaldehyde/propanal, hydrogen sulfide and ammonia.[209]

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acetaldehyde/propanal, hydrogen sulfide, and ammonia are summarized in Figure 10. Compounds identified in cooked beef aroma are asterisked.

Thialdine is formed from a mixture of acetaldehyde, propanal, and ammonium sulfide,[210] in addition to the reaction of acetaldehyde, hydrogen sulfide, and ammonia.[80] In the latter reaction, the concentration of thialdine formed at 90° C was less than at 20° C; this is explained by its thermal lability,[80,209] a property which also applies to the thiazolines which are less stable to heat than the corresponding oxazolines.[86] For example, 3-thiazoline is thermally dehydrogenated in the presence of elemental sulfur to the corresponding thiazole.[211] Thus, corresponding thiazoles and thiazolines frequently coexist. In the same way as 2,4,5-trimethyl-3-thiazoline is formed from ammonia, acetaldehyde and 2-ketobutan-3-thiol (itself readily formed from diacetyl and hydrogen sulfide), 2,4,5-trimethyl-3-oxazoline is correspondingly formed from ammonia, acetaldehyde, and acetoin.[86]

Methanethiol, a decomposition product of methionine, also takes part in secondary reactions. It readily yields dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide.[29] Reaction of acetaldehyde with methanethiol and hydrogen sulfide gives rise to 1-(methylthio)ethanethiol[212] (see Figure 9) as also does a model reaction of other aliphatic aldehydes, hydrogen sulfide, and methanethiol.[80] It is also well established that thiols can undergo equilibrium reactions with disulfides.[213] It is possible therefore, that 1-(methylthio)ethanethiol might undergo such reactions with dimethyl disulfide; this would result in the formation of substituted 2,4,5-trithiahexanes and 2,4,5,7-tetrathiaoctanes (see Figure 11). Such compounds have not been identified in cooked beef aroma but are present in the headspace of roasted pork.[213]

### *f. Lipid Degradation*

Thermal degradation of lipids in the absence of oxygen involves dehydration, decarboxylation, hydrolysis, dehydrogenation and carbon-carbon cleavage reactions.[214] Free fatty acids are released, preferentially the shorter chain and unsaturated acids.[214] Products also include hydrocarbons (saturated and unsaturated), $\beta$-ketoacids which form alkan-2-ones (methylketones), lactones, and esters.[214,215] During cooking, however, thermal and oxidative degradation of lipids proceed simultaneously. Oxidation of depot triglycerides and of tissue phospholipids will occur. Although the phospholipids content of meat is relatively small in comparison with the triglyceride fraction, they are particularly important because of their susceptibility to oxidation due to their high unsaturated fatty acid content, especially linoleic and arachidonic acid, and also because they exist in closer contact with tissue catalysts or pro-oxidants such as trace metals or metalloporphyrins.[216] Some workers believe that the iron of heme pigments needs to be in the oxidized state,[217,218] while others claim that both ferrous and ferric iron are equally active.[219,220]

Oxidation of unsaturated lipids may be atmospherically induced, i.e., autoxidation, enzymically catalyzed, or thermally induced, especially during roasting. The formation of odor and flavor compounds by lipid oxidation has been reviewed.[221–223] The reaction is propagated by a free-radical mechanism, the production of free radicals being promoted by external energy sources, e.g., heat, $\gamma$-irradiation.[215] Initiation is by abstraction of hydrogen by a free radical from an $\alpha$-methylene group of the fatty acid or glyceride. The fatty free-radical formed is oxidized, forming a hydroperoxide radical which stabilizes itself by hydrogen abstraction from another $\alpha$-methylene group, thus setting up a chain reaction. The allylic hydroperoxides thus formed yield volatile compounds by a host of different decomposition routes.[222]

Well-known products of lipid oxidation include saturated acids, unsaturated acids, hydroxyacids, branched chain acids, keto acids, saturated alcohols, unsaturated alcohols, esters, alkanals, alk-2-enals, alk-2,4-dienals, alkyl branched aldehydes,

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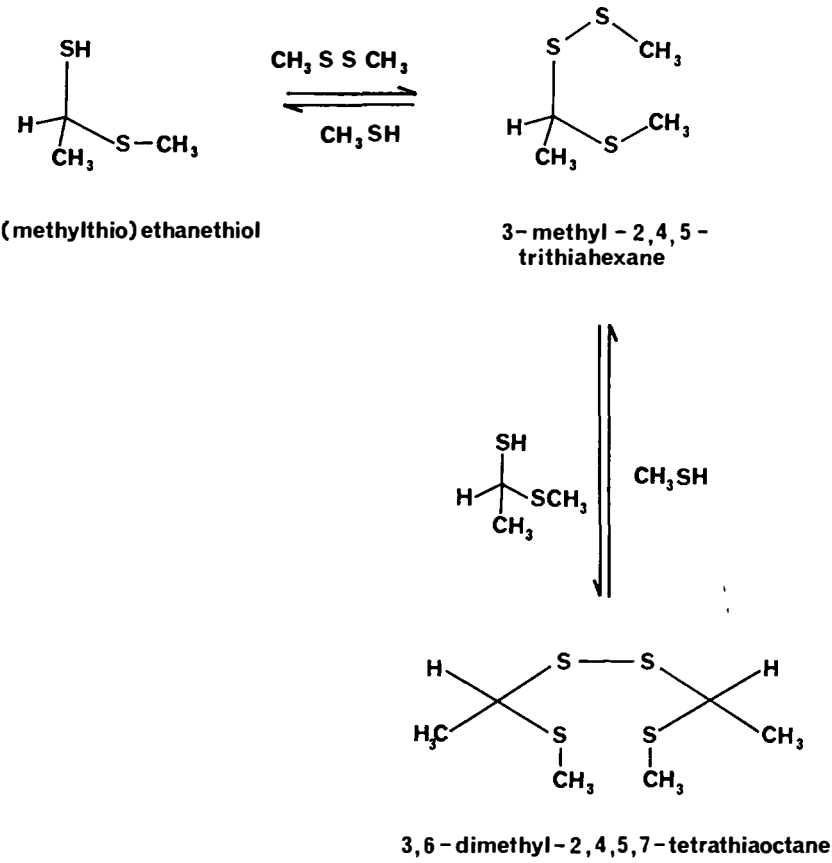


FIGURE 11. Proposed formation of trithiahexanes and tetrathiaoctanes from 1-(methylthio) ethanethiol. (From Dubs, P. and Stüssi, R., *Helv. Chim Acta*, 161, 2355, 1978. With permission.)

hydroxyaldehydes, saturated ketones, unsaturated ketones, ketoaldehydes, diketones, saturated lactones, unsaturated lactones, furans, benzenoids, alkanes, and alkenes.[222,224] Some terpenoid compounds, e.g., $\beta$-ionone may also arise from carotenoids. Several members of these classes have been isolated in cooked beef aromas from lean muscle and also from beef drippings, e.g.,[50] and beef fat[49,50,59] (see Table 1).

Free fatty acids, especially the $C_{18}$ unsaturated acids, released from triglycerides and phospholipids by lipolytic enzymes during aging,[139] are the main source, via oxidation, of carbonyl compounds implicated in meat flavor, particularly fat flavor[107] and roasted flavor.[50] Thus total carbonyl concentration increases in beef muscle during aging even before cooking begins.[225]

The predominant components of oxidative degradation of linoleic and linolenic acids are alkanals, alk-2-enals, alk-2,4-dienals, the corresponding alcohols and both saturated and unsaturated ketones.[162] Pentanol, hexanol and oct-3-en-l-ol derive from linoleic acid; alk-2-enols and alk-2,4-dienols may arise from the corresponding aldehydes by reduction or chemical disproportion respectively.[162] Deca-*trans*, 2-*trans*, 4-dienal and deca-*trans*, 2-*cis*, 4-dienal, isolated from heated beef fat[49,50] and also from a wide variety of foods, are believed to impart a desirable deep fat flavor.[141] Alk-2-enals may be further oxidized to the carboxylic acids which may cyclize during heating forming the corresponding lactones.[222]

Some years ago, $\delta$-lactones appeared more important in the flavor of animal products and $\gamma$-lactones in the flavor of plant materials.[222] However, several members of both

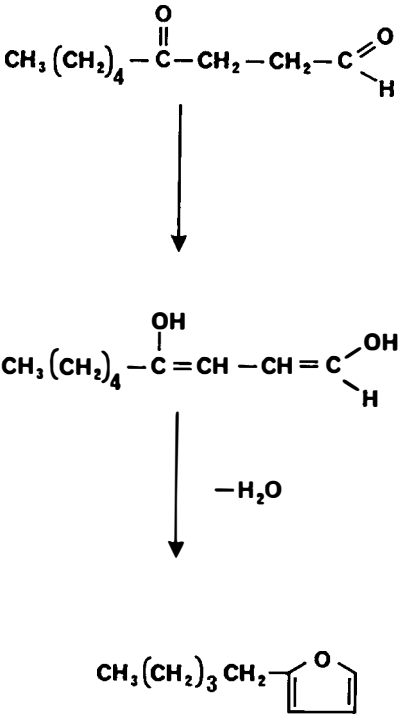


FIGURE 12. Proposed formation of 2-pentylfuran from 4-ketononanal. (From Chang, S. S., et al., *Chem. Ind.*, 1927, 1966. With permission.)

types are listed from beef aroma isolates in Table 1. They can arise from 4- and 5-hydroxyacids lactonised by heat. Watanabe and Sato[226] passed air through oleic, stearic, palmitic, and myristic acids at 180° C and isolated several $\gamma$- and $\delta$-lactones. They postulated that oxidation of oleic acid yields the 4- and 5-hydroperoxyoctanoic acid radicals which form $\gamma$- and $\delta$-octalactones, respectively, during further oxidation. Similar treatment of saturated aldehydes and alcohols yields lactones also.[227] Pantolactone derives from pantothenic acid.[23] Unsaturated $\gamma$-lactones may arise from pyrolysis of 4-keto-acids,[222] e.g., $\alpha$-ketobutyric acid, an oxidation product of threonine, may act as precursor.[228]

Chang et al.[229] have proposed the formation of 2-pentylfuran from 4-ketononanal, possibly derived from oxidised linoleic acid (see Figure 12). Alternatively it may form from $\gamma$-2-nonenolactone.[222] It has also been identified together with butylfuran (and *p*-xylene, propylbenzene, and butylbenzene) in oxidation products of deca-*trans*, 2-*trans*, 4-dienal,[222,230] itself a thermal oxidative decomposition product of fat.[230]

The above-mentioned benzenoid compounds and others listed in Table 1 may therefore derive from lipids. Several benzenoids have been reported in corn oil used for deep fat frying.[231] Kawada et al.[232] proposed the scheme shown in Figure 13 for the formation of benzoic acid and benzaldehyde from linoleic acid.[222] Min et al.[73] have suggested that long chain 2,4-dienals may form alkylbenzenes by a 6-membered ring cyclization reaction involving loss of water similar to the above. Alkylbenzenes may also be formed from long chain unsaturated hydrocarbons themselves formed by thermal oxidation of fatty acids (see Figure 14).[73] Naphthalenes may also derive from lipid oxidation.[222]

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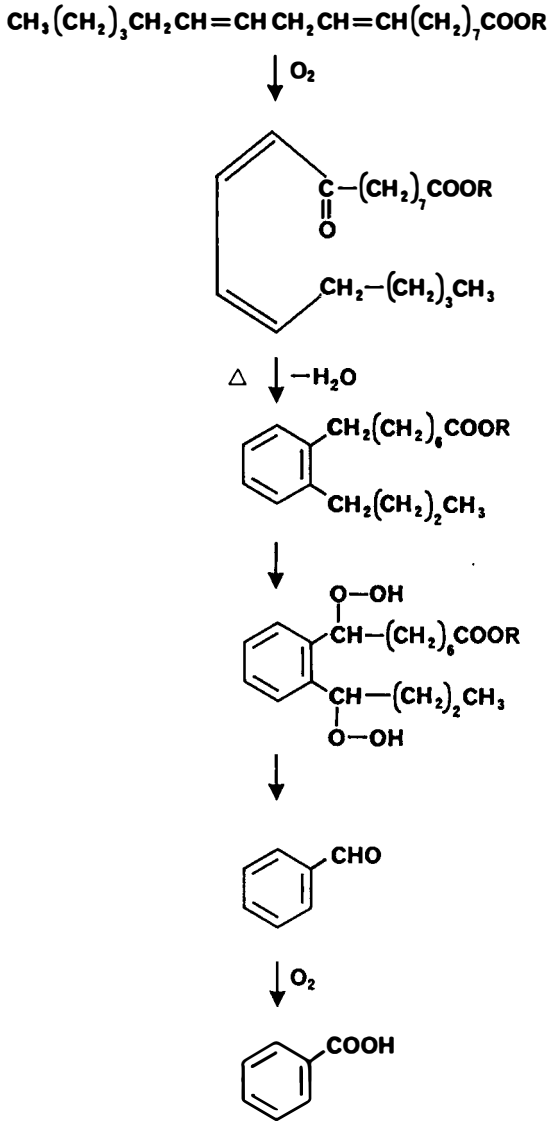


FIGURE 13. Proposed formation of benzoic acid and benzaldehyde from linoleate. (From Kawada, T., et al., *J. Am. Oil. Chem. Soc.*, 44, 134, 1967. With permission.)

The series of alkanes and alk-1-enes of Table 1 may be attributed to thermal degradation of fats.[231] Alkanes ($C_1$-$C_{15}$) and alk-1-enes ($C_2$-$C_{14}$) are also well-known products of $\gamma$-irradiation of lipids. They have been identified in $\gamma$-irradiated beef,[233–235] and are also formed in greater concentrations during cooking of beef by microwaves than by conventional means.[47,81] Reactions occurring during $\gamma$-irradiation and subsequently are probably not dissimilar from those induced thermally. Direct radiation-induced bond cleavage of fatty acid chains forming primary alkyl free radicals accounts for virtually all the hydrocarbons identified in $\gamma$-irradiated lipids.[222] Bond rupture in an irradiated triglyceride occurs preferentially adjacent to the ester link; thus C-1 alkanes and alkenes predominate in the products.[234,235] The next most preferred cleavage is at the carbon atom $\beta$ to the ester group, and so C − 2 alkanes and alkenes are abundant. Other

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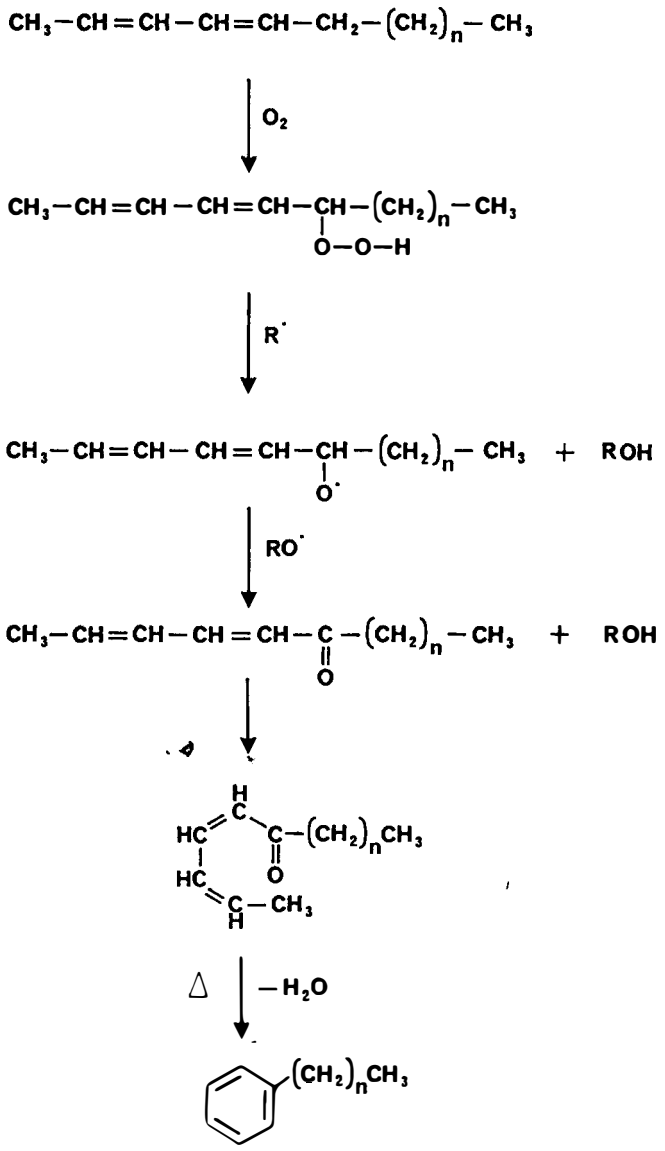


FIGURE 14. Formation of alkylbenzenes from long chain hydrocarbons derived by thermal oxidation of fatty acids. (Reprinted from Min, B. S. D., et al., *J. Food Sci.*, 42, 504, 1977. Copyright by Institute of Food Technologists.)

cleavages are random, leading to lower molecular weight hydrocarbons in lesser concentrations.[234–236] Since the reactions proceed rapidly, the presence of oxygen has little effect on the degradation products of $\gamma$-irradiated fats. Conversely thermal oxidation during conventional cooking is slower, allowing consumed oxygen to be replenished and giving rise to carbonyl and other compounds in addition to hydrocarbons.[222,236] Scission of hydroperoxides may also produce hydrocarbons.[222]

Warmed-over flavor (WOF) is a flavor defect attributed to lipid oxidation products;[237] it develops in cooked meat on short-term refrigerated storage. In all meats other than pork, unsaturated phospholipids appear to be the precursors, and nonheme iron may be an important prooxidant.[237]

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### g. Thiamin Degradation

In 1973 Dwivedi and Arnold[136] reviewed the degradation of thiamin in foods and in model systems; they concluded that heating of thiamin solutions at pH 6.0 or below resulted in cleavage at the methylene bridge producing 4-methyl-5-(2-hydroxyethyl) thiazole as the main sulfur-containing product. At pH 7.0 and above hydrogen sulfide was the major product along with minor amounts of numerous other sulfur containing compounds, i.e., cleavage of the thiazole ring having occurred. Thiamin degradation products identified up to 1973 were

- 2-Methyl-4-amino-5-hydroxymethylpyrimidine
- 4-Methyl-5-(2-hydroxyethyl thiazole)
- Thiothiazolone
- 2-Methylthiophen[a]
- 2-Methyl-4,5-dihydrothiophen
- 2-Methylfuran[a]
- Thiamin disulfide
- Hydrogen sulfide[a]
- Elemental sulfur
- Carbinol base of thiamin
- Thiochrome
- Formic acid[a]
- 5-Hydroxy-3-mercaptopentan-2-one
- 2-Methyl-4-amino-5-aminopyrimidine
- 3-Mercaptopropanol
- 2-Methylthio-5-methylfuran (tentative)
- 4,5-Dimethylthiazole (tentative)
- 2-Methyl-3-oxotetrahydrothiophen (tentative)[a]
- 2-Acetyltetrahydrothiophen (tentative)

[a] The compounds have been identified in cooked beef aroma (see Table 1) and could therefore arise from thiamin.

Recently, van der Linde et al.[99] reported five primary products of thermally degraded thiamin (see Table 16) identified also by other workers,[136] the thiazole being the main component of the volatile fraction.[99] Buffered (phosphate) solutions of thiamin heated at 130° C gave three classes of volatile components, namely sulfur compounds (including thiophens), furans, and thiazoles, (see Table 16).[99] Several thiophens and thiazoles had previously been identified in buffered thiamin solutions (120° C).[135,238,239] The 3-mercaptopentan-2-one has not been identified in cooked beef aroma nor is it a common food volatile; however, it is on the U.S. FEMA/GRAS list and has been claimed for use in meat flavors.[99] The thiazoles probably derive from the primary product, 4-methyl-5-(2-hydroxyethyl) thiazole. For example, 4-methyl-5-vinylthiazole would arise by dehydration;[240] reduction of this would account for 4-methyl-5-ethylthiazole while oxidation and reduction of the same compound could give rise to the 4,5-dimethylthiazole which could also form by loss of formaldehyde from the primary hydroxythiazole.[99]

van der Linde et al.[99] believe that the key intermediate compound is the primary 5-hydroxy-3-mercaptopentan-2-one and proposed the schemes summarized in Figure 15 for its decomposition. Two of the compounds shown here, i.e., 2-methyl furan-3-thiol and 3-mercapto-2-methyl-4,5-dihydrofuran, have been reported to possess roasted meat odors and were present in the reaction mixture of hydrogen sulfide and hydroxyfuranones.[98] Although only six of the volatile compounds listed in Table 16 have been identified in cooked beef aroma, it is likely that the others are present and several have been reported in a number of other foods.[99]

## III. SIMULATED MEAT FLAVORINGS (WITH PARTICULAR REFERENCE TO BEEF)

Over recent years the most common types of simulated meat flavorings have been

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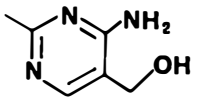
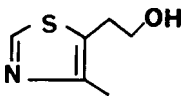
## Table 16
## THE VOLATILE COMPONENTS OF THERMALLY DEGRADED THIAMIN (130° C)[99]

### Primary Products

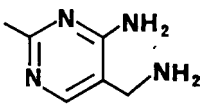
2-Methyl-4-amino-5-hydroxymethylpyrimidine




4-Methyl-5-(2-hydroxyethyl)thiazole (main component)



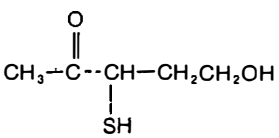

2-Methyl-4-amino-5-aminomethylpyrimidine




Formic acid[a]

HCOOH

5-Hydroxy-3-mercaptopentan-2-one




### Secondary Products

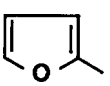
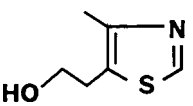
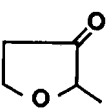
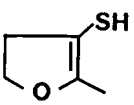
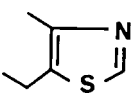
| Sulfur compounds | Furans | Thiazoles |
|---|---|---|
| Hydrogen sulfide[a] $H_2S$[a] | 2-Methylfuran[a]  | 4-Methyl-5-(2-hydroxyethyl)thiazole  |
| 3-Mercaptopropanol $HOCH_2CH_2CH_2SH$ | 2-Methyl-3-oxotetrahydrofuran  | |
| 3-Mercaptopentan-2-one $CH_3COCH(SH)CH_2CH_3$ | 2-Methyl-3-thio-4,5-dihydrofuran  | 5-Ethyl-4-methyl-thiazole[a]  |

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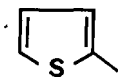
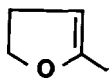
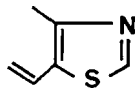
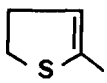
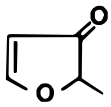
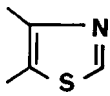
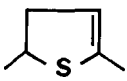
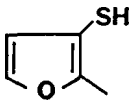
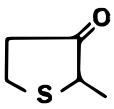
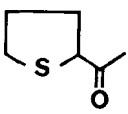
**Table 16 (continued)**
**THE VOLATILE COMPONENTS OF THERMALLY DEGRADED THIAMIN (130° C)[99]**

**Secondary Products**

| Sulfur compounds | Furans | Thiazoles |
|---|---|---|
| 2-Methylthiophen[a]  | 2-Methyl-4,5-dihydrofuran  | 4-Methyl-5-vinyl thiazole  |
| 2-Methyl-4,5-dihydrothiophen  | 2-Methyl-3-oxo-2,3-dihydrofuran  | 4,5-Dimethylthiazole  |
| 2,5-Dimethyl-4,5-dihydrothiophen  | 2-Methyl-3-thiofuran  | |
| 2-Methyl-3-oxotetrahydrothiophen[a]  | | |
| 2-Acetyltetrahydrothiophen  | | |

[a] Indicates compounds identified in cooked beef aroma.

processed meat flavors — so called because they are the result of thermal processing of a mixture of food components; they possess to varying degrees the sensory properties of cooked meat.[3] Generally, the flavor character is that of beef, sometimes chicken or pork, but more often just meaty.[2]

They can be prepared as liquids, concentrated to a paste, or dried to a free-flowing powder.[2] The latter may have wider applications, but loss of some of the lower-boiling volatile compounds may occur during drying. Pastes may be inconvenient in use, but are said to retain more flavor "body" and aroma and do not suffer the disadvantage of sedimentation during storage — a phenomenon which occurs in some liquids.[2]

Unfortunately, and despite recent advances, simulated meat flavorings have not yet achieved the degree of sophistication reached by, for example, fruit or chocolate flavors.[3] This is probably because of the relative complexity of meat flavor which is difficult to reconstruct. The long list of references at the end of this review indicates the effort applied

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to identify unique flavoring compounds so that artificial flavors may simulate more closely the natural product.[2-4,19] Of increasing importance in formulating meat flavorings are chemicals which have not yet been identified in natural meat aromas, e.g., the range of mercaptofurans and mercaptothiophens of van den Ouweland and Peer.[98]

More detailed information on the nature of simulated meat flavorings is presented in the following historical development of commercial meat flavors.

## A. Early Commercial Meat Flavorings

### *1. Spice Blends*

The first simulated meat flavorings were skillfully blended spices.[3,241] Spices have been known and used since 3000 BC and their application extended to food flavoring around 2000 BC.[242] An extensive and lucrative spice trade began to flourish during the 12th century and this has continued to expand.[242] The selection and proportion of spices used vary considerably according to the type of meat product and regional preferences.

### *2. Meat Extracts*

As long ago as 1865, Hieling established a factory in South America to make a preparation of meat designed to contain the so-called "extractives", i.e., creatine, xanthine, hypoxanthine, and carnosine.[243] Since then, meat extracts have been used for many years, as a byproduct from the corned beef industry.[244] There are two general types — essence of meat and meat extract.[245] The former is the product of prolonged water extraction of meat to produce a liquid which gels on cooling. Usually 13 or 14 parts of meat yield one part of extract with a moisture content of 34%.[245] Meat extract is obtained by immersing meat in boiling water for a limited time. The resultant extract is concentrated, usually in open pans, to yield a dark brown, pungent, acrid, paste-like, semisolid material. Usually 50 parts or more of trimmed meat yield, as a byproduct, one part of extract with a moisture content of 17%.[245] According to the patent literature, although each product possesses some meaty flavor when diluted to "use concentration", they also produce pungent, salty, unclean, unpleasant, animal flavors and odors.[245] They are prepared by a time-consuming procedure and are relatively expensive. Because of these limitations, food processors have for some years sought alternatives. While meat extract is still used in some countries as a flavor, in others it is now only used when necessary to form part or all of a legal meat requirement.[246]

### *3. Flavor Enhancers Used in Conjunction with Spices*

The first flavor enhancer identified was monosodium-L-glutamate (MSG), isolated in 1909 from a seaweed called seatangle prevalent in Japan.[36] Soon after this discovery MSG was produced commercially from plant protein hydrolysate. In fact it was the first chemical seasoning produced commercially and has been widely used to enhance the flavor of natural foods.[36] A nucleotide was also isolated as far back as 1913, from a Japanese fish called bonito, but the nucleotide potentiators did not come into full realization until about 1960 when a process for preparing them from ribonucleic acid was developed.[36]

Once the importance of MSG and the 5′-nucleotides as flavor potentiators were recognized and they became commercially available; they were combined with spices to supply some of the brothy character of meat and to enhance the flavor of natural meat.[3,4,241] It is preferable to use 5′-nucleotides in conjunction with MSG, because of the synergism which occurs.[247] This increase in flavor potency is more marked when the ratio of nucleotides to MSG in the mixture is lower.[248] It is claimed that if this synergistic activity had not been discovered, the 5′-nucleotides would not have been used commercially.[36,38] However, they do have several specific properties of their own, regardless of the foods to which they are added (see Section II.B).

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### 4. Protein Hydrolysates

The production of high quality hydrolyzed proteins and yeast autolysates made further contributions to the development of meat flavorings.[241] This was not surprising, since free amino acids are known meat flavor precursors (see Section II.C.2). Total free amino acids in aqueous extract of beef muscle constitute 27.7% by weight.[119] Post-mortem catheptic activity in muscle can be closely paralleled with the hydrolysis of vegetable and yeast protein. Hydrolyzed proteins were initially used in conjunction with spice blends and nucleotides and these were the first formulations which exhibited characteristic meaty notes.[3,4] During the early postwar years, protein hydrolysates began to play a significant role, not only because of their superior flavor qualities but also because economic conditions resulted in higher prices and inconsistent quality of meat extracts.[241,244] Nowadays a wide range of different hydrolysates are available, each with its own individual properties and flavor. Depending on the original protein, they may either possess a mild meaty flavor, acting largely as flavor enhancers, or else they have a strong meaty aroma and taste which develops even more during cooking. Commercial protein hydrolysates can be prepared from any reasonably rich protein source such as wheat gluten, maize gluten, soybean meal, casein, meat meal, fish meal, hoof, horn, and blood meal. In practice, however, many manufacturers prefer to use vegetable protein sources exclusively.[249]

#### a. Hydrolyzed Vegetable Protein (HVP)

Industrially, three hydrolysis methods are possible, i.e., enzymic, alkaline, or acid hydrolysis.[249] The latter method — using hydrochloric acid — is preferred; it is relatively low in cost, rapid, and produces good flavors.[249] Impurities present in the HVP play an essential part. Complete hydrolysis of the protein is desirable, and the higher the ratio of acid to protein the lower the extent of amino acid destruction and the better the flavor; equally large excesses of acid are avoided because of the high salt levels which would result on neutralization. During filtering, depending on the grade of charcoal used and treatment, some or all of the aromatic amino acids, especially tyrosine and phenylalanine, as well as the HVP impurities may be removed; strongly flavored (suitable for beef flavors) or more bland products (for chicken and pork) may be obtained. Finally, adequate stirring during neutralization is essential to prevent local pockets of alkalinity which decompose some amino acids.[2] The salt produced during neutralization contributes to the taste of the product; MSG formed from glutamic acid-rich proteins confers flavor potentiation, while hydrolysis of starch and other carbohydrate material present in conjunction with the protein, yields Maillard reactants.

#### b. Hydrolyzed Yeast

The hydrolysis is usually achieved by proteolytic enzymes occurring naturally within the yeast.[249] A liquid slurry of yeast cells is brought to a temperature of 50°C and maintained during complete autolysis.[246] This product may be sold as autolyzed yeast (AY). However, a further process of extraction may take place, thereby removing insoluble matter. The resultant product is known as "yeast extract" and although more expensive than AY, gives a fuller, meatier flavor.[246] The clear extract may be concentrated to a paste or spray-dried to a powder.[246]

The foregoing has showed that during the early development of meat flavorings, the main impact came from the use of spice blends, meat extracts, protein hydrolysates, and flavor enhancers.[2,244] However, they gave very little, if any, meat aroma.[2] Consequently, they were not very successful, since a major contribution to the sought-after flavor had to be in the aroma. The situation at this stage was well summarized by Kuramoto and Katz[241] who stated that "as good as HVP, yeast autolysates, MSG, ribonucleotides, and

spice blends are in flavoring soups, bouillon, and gravies, they are a long way from the type and quality needed for developing fabricated meat analogues."[241]

This need for improved meat flavors provided the impetus for the extensive research outlined in the next section of this review, and which led to the development of thermally produced simulated meat flavors (processed meat flavors).[244]

## B. Processed Meat Flavorings

The research which began in the late 1950s, in contrast with previous attempts, was based on reasonably sound chemical analysis.[3,4] Four different approaches were followed:[3]

1. Analysis of volatile flavor components produced on cooking meat
2. Isolation and characterization of flavor precursors
3. Analysis of the flavor components of heated model systems
4. Systematic evaluation and application of heated model systems resulting in processed meat flavors

The concept of thermal processing was not surprising (see Section II.C.3). Not only is heating important, but time and temperature are critical for producing different flavors[1] (see Section II.C.1.). Many groups were active but patent claims for synthetic meat flavorings were relatively few up to the early 1960s.

Starting with the basic pioneering work of Batzer et al.[108,110] (see Section II.C.2), and followed by several other researchers, the importance of reducing sugars and amino acids and the significance of the Maillard reaction was appreciated. This was an important discovery which revolutionized the meat flavor industry from then on. In an attempt to capitalize on this basic information, a large number of "reaction product" patents have been granted.

### *1. "Reaction Product" Meat Flavors*

A summary of some G.B. and U.S. patents based on "reaction products" (in which meat flavor precursors are allowed to react with each other) issued since 1960, is presented chronologically in Table 17. The first patent was issued to Morton et al.[250] Before dealing with the patent literature, it is interesting to note briefly the stages which led to this discovery. These were described in a review.[2] They began by analyzing the volatiles of cooked beef, but in common with other workers, found no character impact compounds and were unable to distinguish chemically between stewed and roast beef aroma.[2] They therefore studied the flavor precursors, and isolated from raw beef a fraction possessing roast beef flavor on heating. Paper chromatographic analysis of this *uncooked* extract showed 30 amino acids (in particular cysteine, $\beta$-alanine, glutamic acid and tryptophan) small peptides, glucose, fructose, ribose, and glucosamine.[2] Similar analysis of a *cooked* extract showed that ribose had disappeared completely and that the amounts of cysteine and possibly glutamic acid had decreased.[2] They stressed the relevance of amino acids (in particular cysteine) and ribose (per se or from autolyzed nucleotides), and the first of the new type of imitation beef flavors was prepared by heating aqueous mixtures of ribose, cysteine, $\beta$-alanine, glutamic acid, and tryptophan.[2]

Heating single amino acids with various sugars gave a variety of aromas, usually depending on temperature and time of heating. Whenever cysteine was used, recognizable beef aroma resulted and a large number of sulfur volatiles and carbonyl compounds, including furfurals were identified. Pentoses needed less reaction time than hexoses and because of availability and price, xylose was substituted for ribose, although the resulting flavor was not so good. It was also noted that, in the absence of amino acids,

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## Table 17
## SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| 1 | G.B. 836,694 (1960) | Morton et al.[250] | Meat | In general cysteine + additional amino acids (other than phenylalanine and methionine) or in a hydrolyzed protein form + a pentose or hexose |
| | | | Cooked pork | Cysteine + ribose |
| | | | Roasted beef | Cysteine + glutamic acid + β-alanine + glycine + ribose + glucose |
| | | | Roasted beef | A sulfur-containing polypeptide (e.g., glutathione) + ribose |
| | | | Cooked meat | Cysteine + casein hydrolysate or groundnut hydrolysate + glucose + xylose |
| | | | Roasted beef | Cysteine + defatted cod fish flesh or soybean protein hydrolysate + ribose |
| 2 | U.S. 2,934,435 (1960) | May and Neots[251] | Meat-like | An amino acid source (cysteine or cystine essential) + a pentose + a furan or 2-substituted furan, e.g., furfural |
| 3 | U.S. 2,934,436 (1960) | May et al.[252] | Meat-like | Cysteine or cystine + glyceraldehyde |
| 4 | U.S. 2,934,437 (1960) | Morton et al.[253] | Meat-like | Cysteine or cystine + a pentose or hexose or glyceraldehyde |
| 5 | U.S. 2,955,041 (1960) | Broderick et al.[254] | Meat-like | 2-Mercaptoethanol derivatives, e.g., mercaptoacetaldehyde, 2,5-dihydroxy-1,4-dithiane + a food (medium) |
| 6 | G.B. 858,333 (1961) | May[255] | Meat-like | Cysteine + a mixture of certain amino acids + furan or a 2-substituted furan |
| 7 | G.B. 858,660 (1961) | May and Morton[256] | Meat-like | Cysteine + additional amino acids other than methionine and phenylalanine + defatted fish protein (optional) + aldehydes (acyclic and at least $C_2$) |
| 8 | U.S. 3,157,516 (1964) | Huber et al.[257] | Chicken | Cysteine or cystine + ascorbic acid or isoascorbic acid |
| 9 | G.B. 1,032,334 (1965) | Nestlé Products, Ltd.[258] | Meat extract like | Cysteine or glutathione or protein in a hydrolysate form, e.g., yeast, blood, liver + a mixture of amino acids + a pentose or hexose + 5′-nucleotide (optional) + lactic acid |
| 10 | G.B. 1,082,504 (1965) | Pfizer Co.[259] | Beef | Cysteine + alanine + glycine + glutamic acid or its acceptable salt + HVP + a pentose or hexose + sucrose + 5′-nucleotides + edible fat |
| 11 | G.B. 1,099,711 (1965) | International Flavors and Fragrances, Inc. (I.F.F.)[260] | Beef | Cysteine + yeast hydrolysate + 5′-nucleotides (optional) + MSG (optional) + inorganic |

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## Table 17 (continued)
## SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| | | | | salts such as chlorides and phosphates (optional) |
| | | | Pork | Methionine + yeast hydrolysate + 5′-nucleotides (optional) + inorganic salts such as chlorides and phosphates (optional) |
| | | | Roasted meat | Cysteine + yeast hydrolysate + pyruvic acid, pyruvaldehyde or dihydroxyacetone + MSG, 5′-nucleotides (optional) + inorganic salt such as phosphates and chlorides (optional) |
| 12 | G.B. 1,069,104 (1966) | I.F.F., Inc.[261] | Chicken | A mixture of amino acids at least one of which contains sulfur or a sulfur-containing polypeptide + an alkyl aldehyde of 5 to 8 carbon atoms + an alkanone or hydroxy substituted alkanone having 4 to 8 non-quaternary carbon atoms + thiamin + triglyceride fat |
| 13 | G.B. 1,076,948 (1966) | Ajinomoto Co., Inc.[262] | Meat-like | A mixture of amino acids + 5′-nucleotides + lactic acid (final product in paste or damp state), calcium salt of lactic acid (final product in powder form) + succinic acid + phosphate (for adding to mouthfullness or mouth satisfaction) |
| 14 | G.B. 1,084,619 (1966) | I.F.F., Inc.[263] | Roasted | Hydrolysate of a proteinaceous material + thiamin + 3-acetyl-3-mercaptopropan-1-ol + organic carboxylic acid |
| 15 | G.B. 1,130,631 (1966) | May and Soeters[264] | Meat | A mixture of amino acids or plant or animal protein hydrolysate (cysteine/cystine present) + a pentose and/or hexose + a fatty material |
| 16 | G.B. 1,126,889 (1966) | Kyowa Hakko Kogyo Co., Ltd. (K.H.K.)[265] | Beef-like | Lysine, hydrolyzed protein, or casein hydrolysate or a mixture of arginine, methionine, cystine and cysteine + ribose-5-phosphate |
| 17 | G.B. 1,148,449 (1966) | Corn Products Co.[266] | Meat extract-like | Amino acids other than cysteine, e.g., MSG and protein hydrolysate + a pentose and/or hexose + taurine + lactic acid or succinic acid and phosphate (optional) |
| 18 | U.S. 3,271,167 (1966) | Perret and McMahan[267] | Beef, H.V.P. type | Glutamic acid + $\alpha$-ketobutyric acid (or its physiologically acceptable salts) + inosinic acid (or its salt) |

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## Table 17 (continued)
## SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| 19 | G.B. 1,115,610 (1967) | K.H.K. Co., Ltd.[268] | Cooked meat | A mixture of amino acids + a pentose or hexose + 5′-nucleotides + thiamin + a C16-C18 saturated or unsaturated fatty acid or ester |
| 20 | G.B. 1,135,123 (1967) | Pfizer and Co., Inc.[269] | Beef | Cysteine or cystine + HVP + glutamic acid, alanine, glycine + a pentose or hexose + 5′-nucleotides + sucrose + edible fat (optional) |
| 21 | G.B. 1,182,976 (1967) | Pfizer and Co., Inc.[270] | Chicken | Cysteine and/ or cystine + glycine + HVP + arabinose or glucose + sucrose + MSG + edible fat + coconut oil |
| 22 | U.S. 3,316,099 (1967) | Hoersch[271] | Meat-like | A mixture of certain amino acids preferably asparatic acid, glycine, histidine, glutamic acid, proline, and cysteine + an edible nitrite + reacting the mixture under a semipermeable layer of an oil of animal origin |
| 23 | G.B. 1,146,337 (1968) | Giacino[272] | Meat-like | Cysteine + glycine + glutamic acid + HVP + a pentose or a hexose + thiamin (or supplied in materials containing it, such as yeast) + taurine + a triglyceride fat |
| 24 | G.B. 1,198,398 (1968) | K.H.K. Co., Ltd.[273] | Meat extract-like | HVP or yeast autolysate or protein substance, e.g., groundnut + a mixture of pentose and hexose + 5′-nucleotides + an organic acid + inorganic salt |
| 25 | G.B. 1,205,882 (1968) | Tonsbeek[274] | Meat extract-like | Glutamic acid or its salt or HVP or meat extract + at least one additional amino acid selected from methionine, alanine, tryptophan and cysteine + 5′-nucleotides + lactic acid and succinic acid |
| 26 | G.B. 1,221,482 (1968) | van der Zijden[275] | Meat extract-like | Glutamic acid or its salt + 5′-nucleotides + succinic acid + pyrrolidone carboxylic acid (or its precursor such as glutamine) |
| 27 | G.B. 1,224,989 (1968) | Tonsbeek[276] | Meat-like | A mixture of amino acids + 5′-nucleotides + an organic acid + 4-hydroxy-2,3-dihydrofuran-3-one |
| 28 | U.S. 3,365,306 (1968) | Perret[277] | Meat-like | Cysteine or cystine + HVP + glutamate, alanine, glycine (optional) + a pentose or hexose + sucrose (optional) + 5′-nucleotides + fat (optional) |

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## Table 17 (continued)
## SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| 29 | U.S. 3,394,015 (1968) | Giacino[278] | Meat-like | Cysteine (or other sulfur-containing amino acid or $H_2S$ or thiols) + HVP (carbohydrate free) + thiamin |
| 30 | U.S. 3,394,016 (1968) | Bidmead[279] | Roasted meat | $H_2S$ releasing compound (including amino acids) + an aliphatic carboxylic acid (including protein hydrolysate) + 3-acetyl-3-mercaptopropan-1-ol + thiamin |
| 31 | U.S. 3,394,017 (1968) | Giacino[280] | Chicken | Sulfur-containing polypeptide + $C_5$-$C_8$ aldehydes, e.g., hexanal + ketones, e.g., diacetyl + thiamin |
| 32 | U.S. 3,578,465 (1968) | van der Zijden[281] | Meat-like | Glutamic acid or glutamine + 5'-nucleotides (optional) + succinic acid + pyrrolidone carboxylic acid |
| 33 | G.B. 1,206,265 (1969) | Kitada et al.[282] | Meat-like | Cysteine and/or cystine + a mixture of amino acids + a pentose or hexose |
| 34 | G.B. 1,232,719 (1969) | Shimazaki et al.[283] | Meat extract-like | Cysteine and/or cystine + a mixture of amino acids + a pentose or hexose + 5'nucleotides + an edible fat + inorganic salt |
| 35 | G.B. 1,234,927 (1969) | Ralston Purina Co.[284] | Beef extract-like | Defatted fish protein + MSG + pentose or hexose |
| 36 | G.B. 1,283,913 (1969) | van den Ouweland and Peer[285] | Cooked meat | $H_2S$ or other sulfur-containing compound capable of liberating $H_2S$ + furanones; 3 preferred ones: 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 |
| 37 | U.S. 3,480,447 (1969) | Hack and Konigsdorf[286] | Meat extract-like | A substantially cysteine-free amino acid component + a pentose or hexose + taurine |
| 38 | G.B. 1,256,462 (1970) | Evers[287] | Meat-like | HVP + furan derivatives + sucrose + beef fat + furyl monosulfides, disulfides, and thiols (for meat or cooked meat flavor), dihydrofuryl sulfides, disulfides, thiols (for a roasted flavor) + inorganic salt (NaCl) |
| 39 | G.B. 1,284,357 (1970) | Gasser[288] | Roasted beef | HVP + yeast hydrolysate + wheat gluten hydrolysate + enzymatically hydrolyzed meat extract + ribose or glucose + 5'-nucleotides + lactic acid |
| 40 | G.B. 1,302,525 (1970) | de Groot et al.[289] | Meat-like | A mixture of amino acids + 5'-nucleotides + precursors or |

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## Table 17 (continued)
## SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| | | | | reactants which are converted to 4-hydroxy-2,3-dihydrofuran-3-one during food preparation, e.g., heptane-3,4-dione-2,5-diacetate which will form 5-ethyl-2-methyl-4-hydroxy-2,3-dihydrofuran-3-one + pyrrolidone carboxylic acid or its precursors + aldehydes + ketones + inorganic salt |
| 41 | G.B. 1,311,638 (1970) | Givaudan Co., Ltd.[290] | Meat-like | Cysteine + a mixture of amino acids + methionine + proline + sulfur containing polypeptide (optional) + a pentose (preferably ribose) and a polyalcohol (preferably glycerin) |
| 42 | G.B. 1,318,460 (1970) | van Pottelsberghe de la Potterie[291] | Beef | Protein hydrolysate free from cysteine and cystine + methionine + a pentose or hexose + saccharine |
| 43 | G.B. 1,325,335 (1970) | Broderick and Marcus[292] | Meat-like | Cysteine or cystine + methionine + a ribonucleotide reactant for example a 50:50 (by weight) mixture of commercial disodium guanosine-5′-monophosphate + disodium inosine-5′-monophosphate |
| 44 | U.S. 3,493,395 (1970) | Soeters[293] | Savoury-meat | HVP (or amino acid mixtures) + reducing sugars + cysteine + fat/oil, e.g., tallow, lard, hydrogenated vegetable oil |
| 45 | U.S. 3,519,437 (1970) | Giacino[294] | Meat-like | A source of amino acids such as hydrolyzed protein (optional) + thiamin + taurine + water or triglyceride fat (as a vehicle) |
| 46 | U.S. 3,524,747 (1970) | O'Hara and Ota[295] | Beef | A mixture of amino acids (not cysteine) + 5′-nucleotide + lactac acid + phosphate |
| 47 | U.S. 3,532,514 (1970) | May[296] | Savoury-meat | Cysteine + reducing sugars + fatty material |
| 48 | U.S. 3,532,515 (1970) | Broderick and Marcus[297] | Meat-like | Cysteine or cystine + ribonucleotide |
| 49 | G.B. 1,313,830 (1971) | Mussinan et al.[298] | Meat-like | HVP + MSG + an alkanethiol, preferably 2-methyl-3-butanethiol + tetramethylpyrazine |
| 50 | U.S. 3,615,600 (1971) | Tonsbeek[299] | Meat | Amino acids or HVP (including glutamic acid) + 5′-nucleotides + succinic acid + a hydroxycarboxylic acid ($C_2$-$C_5$) including lactic acid (wt. ratio succinic: lactic acids preferably 1:40 → 1:80 |
| 51 | U.S. 3,620,772 (1971) | Kitada et al.[300] | Meat-like | Cysteine or cystine + a pentose or hexose (alk. pH, optimum 9.5) |

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## Table 17 (continued)
## SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| 52 | G.B. 1,357,091 (1972) | Mosher[301] | Roasted meat | HVP and/or autolyzed yeast + 5′-nucleotides + S-acetyl-mercaptosuccinic acid or its anhydride |
| 53 | G.B. 1,382,335 (1972) | Theron et al.[302] | Meat extract-like | Acid hydrolyzed protein + an egg component in enzyme hydrolyzed form + MSG + a mixture of pentose + hexose + a sulfide component, e.g., cabbage or onion juice |
| 54 | G.B. 1,384,332 (1972) | Gasser[303] | Meat-like | Cysteine + methionine + a hexose + yeast hydrolyzate + thiamin + beef and chicken fat + enzymes present in fresh meat + vegetable extract |
| 55 | U.S. 3,642,497 (1972) | Gunther[304] | Meat-like | $H_2S$ or inorganic sulfide + acid + a pentose |
| 56 | U.S. 3,645,753 (1972) | Gasser[305] | Meat-like | Yeast hydrolysate + hydrolyzed meat extract + HVP + lactic acid |
| 57 | U.S. 3,645,754 (1972) | Wiener[306] | Meat-like | Certain inorganic sulfides or hydrosulfide sulfur compounds ($H_2S$, $(NH_4)_2S$) + carbohydrate |
| 58 | U.S. 3,660,114 (1972) | Thomas[307] | Chicken | HVP + a mixture of amino acids + sugar, e.g., glucose + MSG + 5′-nucleotides + edible fat |
| 59 | U.S. 3,689,289 (1972) | Perret[308] | Chicken | Cysteine or cystine + a bland protein hydrolysate + a hexose + arachidonic acid and/or methyl or ethyl arachidonate |
| 60 | U.S. 3,697,295 (1972) | van den Ouweland, G.A.M. and Peer,[309] | Roasted meat | Sulfides or substances capable of liberating hydrogen sulfide + furanone (e.g., 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one |
| 61 | U.S. 3,716,379 (1973) | van Pottelsberghe, de la Potterie,[310] | Chicken and Beef | HVP (cysteine-free) + a pentose or hexose + thiamin |
| 62 | U.S. 3,716,380 (1973) | van Pottlesberghe, de la Potterie[311] | Beef | Protein hydrolysate + methionine + carbohydrate + an aliphatic carboxylic acid (optional) |
| 63 | U.S. 3,741,775 (1973) | Lee[312] | Roasted beef, cooked beef | Cysteine + a 6-desoxyhexose + thiamin |
| 64 | U.S. 3,761,287 (1973) | Jaeggi[313] | Meat-like | Amino acids, e.g., cysteine + proline + methionine + possibly other amino acids + a pentose + a polyalcohol like glycerin |
| 65 | U.S. 3,804,953 (1974) | Bentz and Scarpellino[314] | Meat-like | $H_2S$ + water soluble carbonyls ($C_1$-$C_6$) e.g., pyruvaldehyde, acetaldehyde in large excess $H_2O$ at room temperature |

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## Table 17 (continued)
## SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| 66 | U.S. 3,840,674 (1974) | Mosher[315] | Roasted meat | HVP + S-acetylmercaptosuccinic acid + flavor enhancers like nucleotides |
| 67 | U.S. 3,881,022 (1974) | Gasser[316] | Roasted beef | Yeast autolysate + a hexose + enzymes present in fresh meat (to hydrolyze proteins, nucleotides and to convert the hexose into its phosphate) |
| 68 | U.S. 3,879,561 (1975) | Smith and Stewart[317] | Meat | HVP + starch/dextrin + corn syrup solids + glucose + NaCl + caramel |
| 69 | U.S. 3,928,643 (1975) | Ishiguro and Ichikawa[318] | Beef | Plasma solids of beef cattle or pig's blood + ribose or ribose-5-phosphate |
| 70 | U.S. 3,930,046 (1975) | Baugher and Township[319] | Meat-like | Hydrolyzed whey protein + cysteine + xylose + thiamin |
| 71 | U.S. 3,966,985 (1976) | Pfizer Co., Inc.[320] | Meat-like | Cysteine + cystine + methionine + a pentose or hexose + plasteins |
| 72 | G.B. 1,447,730 (1976) | Chhuy and Day[321] | Meat | Enzyme digest of meat + sulfur compound, e.g., $H_2S$, inorganic sulfides, sulfur amino acids, alkylthiols, alkyl sulfides + thiazole or thiamin (optional); also see reference[322] |
| 73 | G.B. 1,471,907 (1977) | Ishiguro and Ichikawa[323] | Beef | Animal protein, e.g., blood plasma solids + ribose or ribose-5-phosphate + $H_2O$ (boiled beef aroma) or fat (fried beef aroma) |
| 74 | G.B. 1,515,961 (1978) | Heyland and Philippossian[324] | Meat | Hydrolysis product of polysaccharide containing acid groups, e.g., pectins, alginates, gum arabic + sulfide + amino compound |
| 75 | G.B. 1,515,962 (1978) | Heyland[325] | Meat | Alkaline hydrolysis product of vegetable rich in sulfur, e.g., garlic, onion, cabbage + sugar + amino compound, e.g., ammonia, ammonium chloride, amino acid, protein, autolyzed yeast |
| 76 | G.B. 1,525,541 (1978) | Poiger and Huster[326] | Roasted meat | Concentrate from steam distillation of liquid containing soluble solids only of aqueous autolysed yeast + HVP + monosaccaharide + sulfide, e.g., cysteine, cystine, methionine |
| 77 | U.S. 4,066,793 (1978) | Eguchi[327] | Meat-like/beef | Autolyzed yeast extract + 5'-nucleotides + NaCl + potassium salt ($[K^+] > 0.5 \times [Na^+]$); see also reference;[328] correction balance avoids yeast off-odors |

**Table 17 (continued)**
**SOME G.B. AND U.S. "REACTION PRODUCTS" PATENTS**

| Table entry | Patent no., (year) | Assigned to or inventor(s) | Flavor | Reaction |
|---|---|---|---|---|
| 78 | U.S. 4,076,852 (1978) | van Delft et al.[329] | Meat | Egg or enzyme digest thereof + meat powder or enzyme digest thereof + sulfur compound, e.g., cysteine, taurine + optionally thiamin and/or thiazole alkanols, amino acids, mono-, di- or polysaccharides |
| 79 | U.S. 4,161,550 (1979) | Bernhardt et al.[330] | Cooked beef | $H_2S$ precursor + dimethylsulfide precursor + protein (preferably cysteine + S-methylmethionine + soy protein) |
| 80 | U.S. 4,165,391 (1979) | Corbett[331] | Meat | HVP + yeast autolysate + soluble modified partially delactosed whey solids (as flavor enhancer) |

hydrogen sulfide and xylose reacted together under increased pressure, producing a strong odor of cooked beef. They therefore concluded that reaction between a reducing sugar and a "sulfur-donor" such as cysteine was important in addition to the already recognized Maillard reaction.[2]

More complete beef flavors were obtained when several amino acids (always including cysteine) were heated with a reducing sugar. Individual amino acids are relatively expensive but are inexpensive in the form of protein hydrolysates. These also contain free amino acids, peptides, nucleotides, reducing sugars, carbonyl compounds, and sulfur compounds.[1] Thus, improved beef flavors were prepared using acid hydrolysates from various proteins, both animal and vegetable.[2] Some of the many varieties of HVP commercially available are essentially free of reducing sugars and therefore contribute by themselves negligible Maillard-type flavors, while others contain more polysaccharide hydrolysis products,[119] and are deeply roasted, almost burned.[3] All are characterized by high salt contents and contain a broad spectrum of amino acids, including cysteine and glutamic acid. Thus, HVP not only serves as a flavoring agent, but also as a rich source of flavor precursors for thermal processing in the presence of other reactants.

These findings are summarized in Table 17, entries 1 to 4, 6, and 7. The first patent involved heating a mixture of pentose or hexose monosaccharide (ribose, xylose, glucose) with cysteine in the presence of a large excess of water.[250] Additional amino acid mixtures, other than phenylalanine and methionine could be incorporated and these could be in the form of protein hydrolysate, e.g., casein, groundnut, codfish flesh, soybean protein hydrolysate.[250] The simple reaction of ribose and cysteine gave pork-like flavor while the presence of additional amino acids gave meaty and beef-like character. Cysteine could be replaced by the tripeptide glutathione (glutamic acid/cysteine/cystine)[250] and glyceraldehyde could be used instead of the reducing sugars.[252,253] The same workers also patented at an early date the reaction of cysteine and a mixture of certain amino acids with furan or 2-substituted furan compounds.[251,255] This idea was based on the fact that furfural had previously been identified in the volatiles of cooked beef and also from heated pentoses and from simple ribose/amino acid mixtures.[2]

These early patents were followed by many others using variations on these themes

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(Table 17). In general, precursors consist of an amino and/or sulfur source on the one hand and reducing sugars or carbonyl compounds on the other.[20,29] The remainder of this discussion will therefore concentrate on significant points of interest and common innovations patented since 1961.

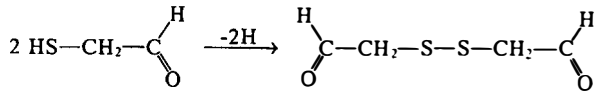
The most commonly used sulfur-containing compounds have been cysteine, thiamin, and hydrogen sulfide. Others, some of which act as $H_2S$ releasing agents (e.g., Table 17, entries 30, 36, 60, and 79) include

1. Organic thiols and sulfides: Methanethiol,[24] ethanethiol,[24] propanethiol,[24] dimethyl sulfide,[330] dimethyl disulfide,[24] methylethylsulfide,[24] Table 17, entries 29, 38, 49, 60, 72, 79; Yamamoto et al.[332]
2. Inorganic sulfides: Ammonium or sodium sulfide or hydrosulfide;[24] sodium, potassium or calcium sulfide or hydrosulfide,[24] e.g., Table 17, entries 55, 57, and 72
3. Thiocarbonates, thioamides, 2-mercaptoalkanoic acids and their amides[38]
4. Mercaptoalkylamines or aminosulfides: Ohwa et al.[333]
5. 2-Mercaptoethanol derivatives: Table 17, entry 5
6. 3-Mercaptopropan-1-ol, 3-acetyl-3-mercaptopropan-1-ol: Table 17, entries 14 and 30
7. S-acetylmercaptosuccinic acid: Table 17, entries 52 and 66; Mosher[334]
8. Methionine: Table 17, entries 11, 16, 42, 54, 62, 64, and 76; Toyoda et al.[335]
9. Taurine: Table 17, entries 17, 23, 37, 45, and 78
10. Egg protein: Table 17, entries 53 and 78; Theron et al.;[336] CPC International Inc.[337]
11. Vegetable extract: Table 17, entries 53, 54, and 75 (sulfides, thiosulfinates, thiosulfonates, etc. are converted into thiols)
12. Meat extract: Table 17, entries 25, 39, 56, 72, and 78

This consolidated the evidence that the relevance of sulfur-containing amino acids did not solely lie in their contribution as Maillard reactants, but also in the simple release of hydrogen sulfide during pyrolysis or Strecker degradation. Hydrogen sulfide is an important precursor of other sulfur-containing meat aroma constituents (see Section II.C.3.e.). It is often generated *in situ* from, e.g., inorganic sulfides, thioamides and 2-mercaptoalkanoic acids, and amides (see Table 17, entries 30, 36, 38, 57, and 60) or it may be used as such with an aqueous solution of carbonyl compounds (Table 17, entries 36, 55, and 65).

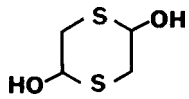
Even a cursory glance at Table 17 indicates how frequently cysteine has been selected as a component of thermally produced meat flavorings. It is the paramount source of sulfur-containing volatiles and is active either in the free form or within the tripeptide glutathione or as part of proteinaceous materials such as HVP. Of all the amino acids naturally occurring in meat, cysteine and cystine yield the meatiest odors when subjected to thermal processing,[3] although cystine is not as satisfactory as cysteine, since it does not so readily undergo Strecker degradation.[2] This unique role of cysteine is noteworthy and possible explanations of its importance have been offered.[3] The most crucial feature is the formation of many highly reactive and odorous compounds resulting from its pyrolysis, Strecker degradation and Maillard reaction (see Section II.C.3.a.c.d.e and Figures 1 and 9).

Palamand et al.[164] have suggested that the key to meat flavor formation lies in the high reactivity of the cysteine Strecker products, mercaptoacetaldehyde and the enaminol (see Figure 1). Condensation of two enaminol molecules yields pyrazines.[164] Mercaptoacetaldehyde readily dimerizes, e.g.,




mercaptoacetaldehyde (monomer) (dimer)

The dimer is also extremely reactive and can further react with animo acids or amines forming numerous products.[164] An alternative dimer is 2,5-dihydroxy-1,4-dithiane, i.e.,




which is the subject of a meat flavor patent by Broderick et al.[254] Asinger and Thiel[338] reported that at room temperature, this dimer (and its monomer) reacts with ammonia in the presence of carbonyl compounds, forming 2-substituted-3-thiazolines (see Table 1). A series of 2-alkyl-3-thiazolines for use as flavoring agents has been patented by Dubs and Pesaro.[339] In general, they have not held prominent positions in meat flavors, probably because they are thermally dehydrogenated in the presence of elemental sulfur to the corresponding thiazoles[211] (see Section II.C.3.e and Table 1).

It is clear that a great variety of potential flavor compounds can arise from cysteine-based systems (see Section II.C.3.a.c.d.e).[3] Wilson places such importance on cysteine as a reactant that he believes that, as analytical procedures improve, disclosures of potent new compounds derived from pyrolyzed cysteine and cysteine/sugar reactions will closely parallel analytical results of cooked meat flavor.[3]

Several patents stress the importance of thiamin as a meat flavor precursor (see Table 17, entries 12, 14, 19, 23, 29 to 31, 37, 45, 54, 61, 63, and 70). When heated in aqueous system with protein and a sulfur-containing compound(s), meat-like flavors are obtained;[278] carbohydrates are not necessarily included, although the presence of fat is preferable. Thiamin may be replaced by 5-hydroxy-3-mercaptopentan-2-one or by 4,5-substituted thiazoles.[340] The former is a primary product of thermal degradation of thiamin (see Section II.C.3.g and Table 16) and it further decomposes forming thiophen and furan derivatives (see Figure 15); one 4,5-substituted thiazole, i.e., 4-methyl-5-(2-hydroxyethyl)thiazole is the main product of thiamin degradation on heating and several others are secondary products of the reaction (see Table 16). The reaction in fat of 4-methyl-5-(2-hydroxyethyl)thiazole or its homologs or derivatives with amino acid mixtures comprising cysteine, produces a chicken-like flavor. Similar reaction mixtures of amino acids, sugars, fat, phosphorus compounds, and thiamin are reported to possess meat flavor.[332]

The role of thiamin in flavor production has been reviewed by Wilson.[3] Potent decomposition products of the thiazole alcohol portion of the molecule (see Section II.C.3.g) possess aroma properties described as smooth, meaty, sweet, woody, smoky, sharp, pungent, biting, harsh, and disagreeable.[3] Potentially reactive species are formed such as elemental sulfur, hydrogen sulfide, 4-methyl-5-vinylthiazole, 3-mercapto-propanol, and 5-hydroxy-3-mercaptopentan-2-one (3-acetyl-3-mercaptopropanol). The latter probably has chemical properties similar to its simplest homolog mercaptoacetal-dehyde,[3] and so its reactivity as summarized in Figure 15 is not surprising. Elemental sulfur can create many cyclic and acyclic di-, tri-, and polysulfides.

Wilson's review[3] also considered the relevance of methionine and taurine in processed meat flavorings. The use of methionine is limited to flavors in which the "potato skin" odor of methional (its Strecker aldehyde) and the "green vegetable" odor of methanethiol

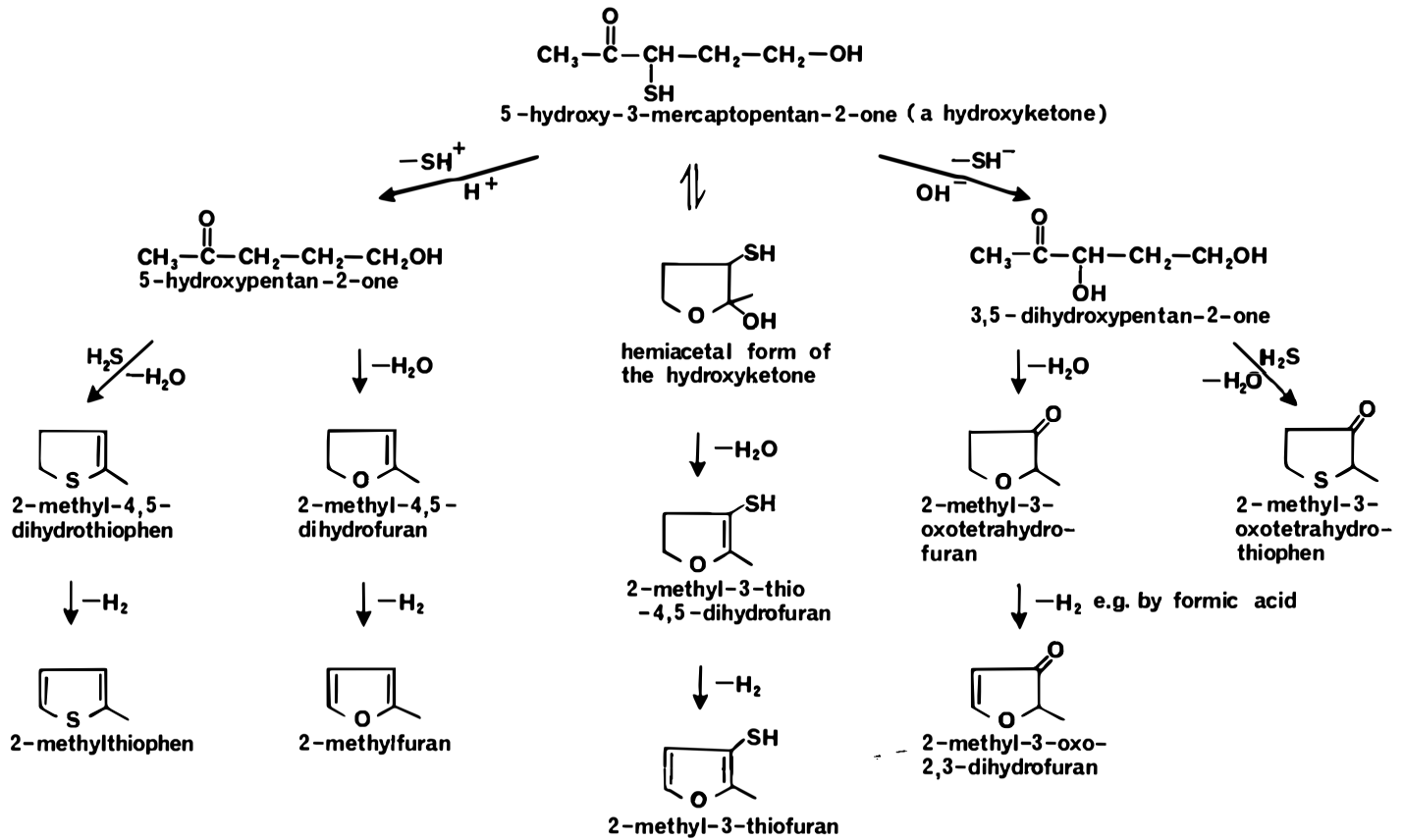



FIGURE 15. Decomposition of 5-hydroxy-3-mercaptopentan-2-one, a key intermediate in the thermal degradation of thiamin.[99]

and dimethyldisulfide (methional decomposition products) are either suppressed, tolerable, or desired.[3] A similar undesirable effect stems from phenylalanine which produces a floral flavor as well as a sweet note.[24] Methionine is the preferred amino acid for pork flavor.[24,260,262,278] Studies by Johnson et al.[341] into the biosynthesis of thiamin in yeast have shown that the thiazole moiety is derived from methionine and alanine. Thus, methionine may act as the precursor of sulfur-containing flavor compounds such as thiophens, thiazoles, 2-methylthio-5-methylfuran, 3-mercaptopropanol, and hydrogen sulfide formed via thiamin.[38]

Taurine, i.e., 2-aminoethanesulfonic acid, present in natural meat extract at approximately 1.2-1.5% by weight on a dry basis,[24] appears in several patents but its role is uncertain.[3] Although present in a wide variety of foods, no sulfur flavor components have yet been traced from it. Mecchi et al.[342] have reported that it is not a precursor of hydrogen sulfide.[342] Hack and Konigsdorf[286] described a processed meat flavoring consisting of a cysteine-free amino acid mixture, taurine and reducing sugars (see Table 17, entry 37); they stated that taurine may act as a partial replacement for cysteine. Another possible contribution of taurine is in the formation of 4-hydroxy-5-methyl-3(2H)-furanone. Although Peer and van den Ouweland[161] showed that this can be synthesised by heating ribose-5-phosphate alone in concentrated buffer systems at pH 5.5 (see Section II.C.3.b.), Tonsbeek et al.[343] reported that in a diluted natural medium such as beef broth, the reaction only occurred in the presence of pyrrolidone carboxylic acid or taurine.

Table 17 shows that a wide variety of different carbonyl compounds have been used in conjunction with the amino and/or sulfur source. Reducing sugars are widespread in the patents, and are claimed to be the most suitable.[38] Arabinose, glucose, fructose, lactose, ribose, and xylose have all been used.[24] They supply a characteristic roasted, burned, note which is both highly desirable and also difficult to obtain in their absence.[3] Pentoses are more reactive than hexoses;[2,24] sugar phosphates are more reactive than sugars.[20] Strecker degradation perpetuates the supply of carbonyl compounds in the form of Strecker aldehydes. Thus, even when it would appear from a patent that there is no carbonyl source (e.g., Table 17, entry 29),[278] such species will arise as Strecker products from the amino acids present.[24]

Some patents, recognizing the important contribution to meat flavor of carbonyl compounds, provide these from sources other than simple pentoses and hexoses; e.g.,

- Ribose-5-phosphate: Table 17, entries 16, 69, and 73
- Hydrolyzed polysaccharides: Table 17, entry 74
- Yeast autolysate/hydrolysate: Table 17, entries 11, 24, 39, 52, 56, 67, 76, 77, and 80; Tonsbeek;[344] Mosher[334]
- Aliphatic aldehydes: Glyceraldehyde, glyoxal, acetaldehyde, propanal, butanal, 2-methylpropanal, alkyl aldehydes $C_5$ - $C_8$, pyruvaldehyde, Table 17, entries 3, 4, 7, 11, 12, 31, 40, and 65
- Ketones: Table 17, entries 12, 31, and 40 (e.g., diacetyl, Table 17, entry 31; dihydroxyacetone, Table 17, entry 11; 1,3-dihydroxypropan-2-one,[306] acetylpropionyl[280])
- Nucleotide carbohydrate: Table 17, entries 9 to 11, 13, 18 to 20, 24 to 28, 32, 34, 39, 40, 43, 46, 48, 50, 52, 58, 66, and 77
- Ascorbic acid or isoascorbic acid: Table 17, entry 8
- Furanones or their precursors: Table 17, entries 27, 36, 40, and 60
- Carboxylic acids: unspecified, see Table 17, entries 14, 24, 27, 30, and 62; lactic acid, Table 17, entries 9, 13, 17, 25, 39, 46, 50, and 56; succinic acid, Table 17, entries 17, 25, 26, 32, and 50; pyruvic acid, Table 17, entry 11; $\alpha$-ketobutyric acid, Table 17, entry 18; pyrrolidone carboxylic acid or precursor, e.g., glutamine, Table 17, entries 26, 32, and 40

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The role of carboxylic acids, particularly those that are not α-dicarbonyls, is frequently to provide the low pH for release of hydrogen sulfide from the sulfur source. Hydrochloric, sulfuric, and phosphoric acids are also used.[26] Carboxylic acids which are at least partially water soluble are desirable.[24] They may be simple aliphatic acids (e.g., acetic, propionic acids) or amino acids (e.g., valine, glycine, glutamic acid) or a hydroxy acid (e.g., glycollic, malic, citric, lactic, succinic, and tartaric acids).[24,274,299] The latter also enhance Maillard browning.[123] The addition of the α-diketone pyruvic acid (or pyruvaldehyde or dihydroxyacetone) gives desirable roasted flavors.[24,278] Several acids, e.g., lactic acid, succinic acid, orthophosphoric acid, pyrrolidone carboxylic acid (and inosinic acid) also impart useful taste properties.[1] Excessive amounts of succinic acid, however, give a shell-fish like flavor.[24,274,299]

The use of aldehydes, ketones, and α-diketones in several patents is not surprising since they are well-known thermal degradation products of sugars (see Section II.C.3.b) and also since several cyclic sulfur compounds and heterocyclic compounds identified in cooked beef aroma (see Table 1) arise from a model system of α-dicarbonyls, aldehydes, hydrogen sulfide, and ammonia (see Section II.C.3.e and Figure 10).

The solubilized constituents of autolyzed yeast are amino acids, nucleotides, nucleic acids, peptides, glycogen, glucose, glucosamine, trehalose, sterols, phospholipids, and B vitamins.[246,345] This therefore acts as a source of several potential meat flavor reactants. On its own, Maillard reaction gives numerous volatiles on heating, many of which have been identified in cooked beef aroma.[345]

The frequent use of nucleotides in the patents is not only because they provide a source of carbohydrate reactant but also because of their flavor potentiating effect. Parallel reasoning applies to the use of MSG (see Table 17, entries 11, 17, 21, 49, 53, and 58), which supplies the glutamic acid amino source commonly used (see Figure 16) as well as overall flavor enhancement (see Section II.B). Certain amino acids, e.g., glycine, alanine, serine,[346] and also certain peptides, e.g., glutamic acid-lysine, glutamic acid-ornithine act synergistically with MSG or 5′-IMP or mixtures thereof.[347] More efficient potentiators than 5′-IMP are 2-furfurylthioinosine-5′-phosphate,[348] 2-allyloxyinosine-5′-phosphate,[349] 2-(lower alkoxy)inosine-5′-phosphate,[350] 2-benzylthioinosine-5′-phosphate[351] and maltobionic acid (4-glucosylgluconic acid).[352]

As might be expected (see Section II.C.3.b.d.e) furanones feature prominently in several patents, especially 4-hydroxy-5-methyl-3(2H)-furanone and its 2,5-dimethyl derivative. Precursors of the former are ribose-5-phosphate and taurine or pyrrolidone carboxylic acid;[343] the latter is readily formed on heating ammonia and glutamic acid or glutamine.[343] The reaction involving glutamine is the more rapid.[26] This explains the use of pyrrolidone carboxylic acid in several patents (see Table 17, entries 26, 32, and 40). It also imparts useful taste properties.[1] The patent described in Table 17, entry 18[267] is of interest in this context. The reactants are nucleotide, glutamate and α-ketobutyric acid. The latter, being a dicarbonyl compound, takes part in Strecker degradation of glutamic acid thus liberating ammonia. Wilson has proposed the scheme shown in Figure 16 to explain the reaction.[3] The α-ketobutyric acid reactant has been isolated from protein hydrolysates[353] and probably derives from threonine.[354] van den Ouweland and Peer prepared meat flavor mixtures by allowing hydroxyfuranones to react with hydrogen sulfide or $H_2S$-releasing agents such as cysteine, glutathione, thioacetamide, or inorganic sulfides (e.g., see Table 17, entries 36 and 60). This reaction was explained in Section II.C.3.e). Similar meat flavors were obtained by Katz et al.[355] by reacting a range of different cyclic carbonyl compounds with hydrogen sulfide or $H_2S$-releasing agents under pressure.[355] Starting materials cited were hydrofuranones, maltol, ethylmaltol, cyclotene, and 4-ethyl-3-methyl-3-hydroxy-2(5H)-furanone; $H_2S$-releasing agents used included furanthiol, 2-mercaptoethanol, methylthioglycollate, 3-mercapto-1,2-propanediol, 3-amino-2-dihydro(5H)thiophenone, 4-methyl-5(2-hydroxyethyl)thiazole,

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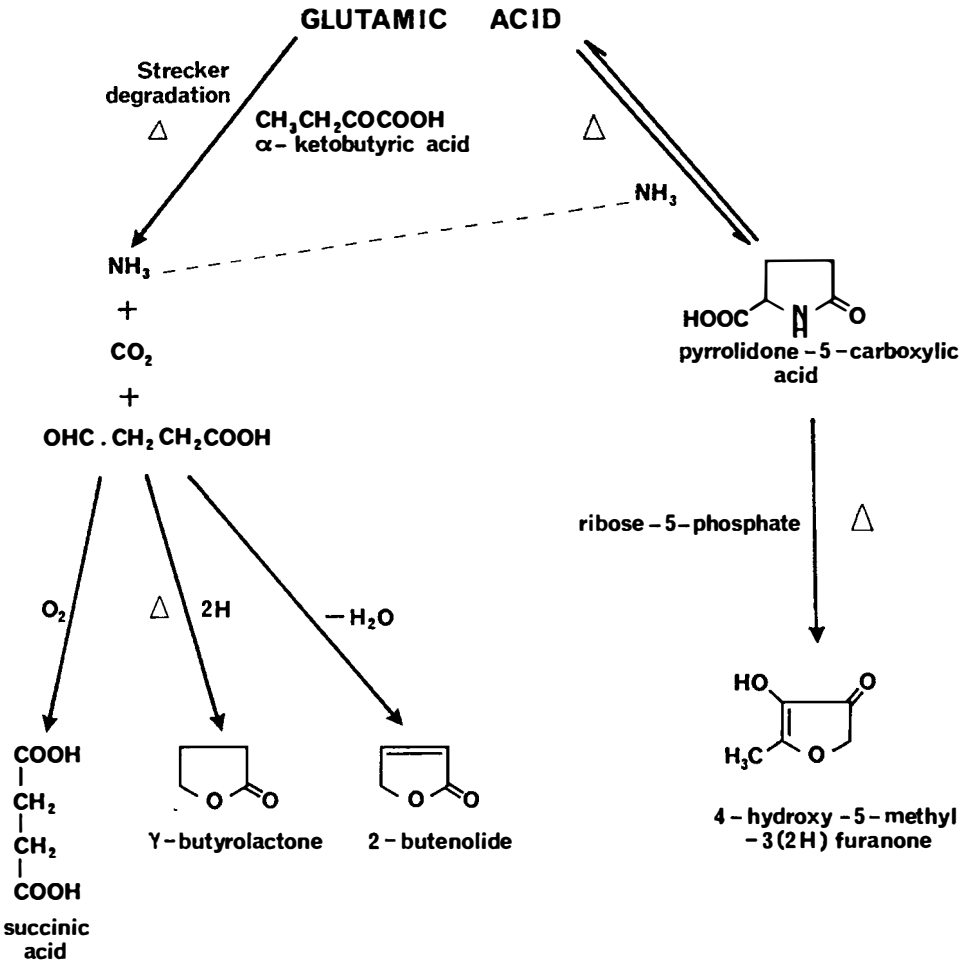


FIGURE 16. Some possible reactions of glutamic acid and α-ketobutyric acid.[3]

glutathione, 1,3-propanedithiol, acetyl methyl disulfide, and thiolacetic acid. These are powerful flavor compounds themselves.[38] In another example, a beef flavor was produced by reaction of 4-hydroxy-5-methyl-3(2H)furanone with cysteine, xylose and casein hydrolysate. This is reported to resemble much more closely than previous attempts, the authentic flavor of roasted meat.[1,356]

Many patents in Table 17 involve the addition of fat, e.g., beef fat (entries 38 and 53), chicken fat (entry 53), edible fat (entries 10, 15, 20, 21, 28, 34, 44, and 58), coconut oil (entry 21), triglyceride fat (entries 12 and 45), fatty material (entry 47) and fatty acids (entries 19 and 58). Maillard reactions in an oil or fat at temperatures up to 140° C, give roasted meat flavors.[296,323,357] A small amount of water is present in the form of crystalline water and some water is formed during the Maillard reaction. The systems are therefore not completely water-free and the presence of this small amount of water leads to attractive flavors and prevents the occurrence of burned off-flavor notes. The presence of fat is also reported to lead to more specific aromas. For instance, unsaturated fatty acids can form polyunsaturated aldehydes and γ-lactones in chicken flavor;[29] lard may also give rise to a cooked chicken flavor; palmitic acid may produce the flavor of roast pork and oleic acid the flavor of roast mutton.[264] Animal tallow gives a typical "pan drippings" note.[24] Therefore, although the Maillard reaction is undoubtedly important, the significance of lipids, especially for roast meat flavor, is recognized by several

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patents.[244] Apart from their role as precursors (see Section II.C.3.f) they may also act as reservoirs for lipid soluble compounds and direct the course of reactions occurring on heating.[244] Higher reaction temperatures, with possibly shorter reaction times, are possible and, in such apolar environments, chemical reactions can take place which do not normally occur in aqueous media.[244]

Solvents are added to "dissolve" flavor components, to induce chemical reaction and also to give a dilution suitable for easy use by the consumer. Generally, the choice of solvent depends on the manufacturing process which the product being flavored undergoes. When a relatively low temperature is used an alcoholic solvent is suitable; in other cases a solvent with a higher boiling point is needed, e.g., propane-1,2-diol (propylene glycol) or glycerol diacetate.[358,359] Such high boiling solvents anchor the more volatile flavor ingredients thereby reducing the volatility of the entire product. Apart from its solvating power and relative nontoxicity, a solvent must be odorless and tasteless.[358] Examples of solvents used are water, glycerol, propane-1,2-diol, ethanol, and ethanediol.[24] Solvent interaction products, e.g., 2-substituted-4-methyl-1,3-dioxolanes have been reported in commercial beef flavorings.[9] Their origin may be explained by reaction of propane-1,2-diol with carbonyl aroma components. These compounds have interesting odor properties and such interactions can modify the flavor characteristics of the product.

Flavor adjuvants are often added. They include stabilizers, thickeners, surface active agents, conditioners, flavorants, and flavor intensifiers.[360,361] Stabilizers include preservatives, e.g., sodium chloride, antioxidants (ascorbic acid, sodium ascorbate, BHA, BHT, propyl gallate), and sequestrants such as citric acid. Thickeners include carriers, binders, protective colloids, suspending agents, and emulsifiers. Examples are agar, carageenan, cellulose, carboxymethylcellulose, gum arabic, gum tragacanth, gelatin, pectin, and starch.[360,361] Surface active agents include emulsifying agents such as fatty acids, mono-, and diglycerides, lecithin, and also defoaming and flavor dispersing agents such as sorbitan monostearate and potassium stearate. Examples of conditioners used are bleaching and maturing agents (benzoyl peroxide, hydrogen peroxide), starch modifiers (peracetic acid, sodium chlorite, and propylene oxide), buffers and neutralizing agents (sodium acetate, ammonium bicarbonate, and citric acid), colorants, firming agents (aluminium sodium sulfate, calcium chloride, and calcium gluconate), anticaking agents (aluminium calcium sulfate and tribasic calcium phosphate), and yeast foods (iron and zinc sources and riboflavin).[360,361]

### 2. *Meat Flavorings Derived from Natural Meat*

Some of the patent examples summarized in Table 17 use meat extract or enzyme digests of meat in conjunction with various other precursors. This may be in addition to HVP and/or yeast hydrolysates, e.g., entries 39 and 56 or as alternative, e.g., entries 25, 72, and 78. Others incorporate meat enzymes in conjunction with yeast hydrolysate to hydrolyze proteins and nucleotides and to convert hexoses/pentoses into their phosphates (see Table 17, entries 54 and 67).

Landman et al.[362] produced a roasted beef flavor by heating one, two, or three fractions of cold water extract of lean beef, i.e., proteinaceous material produced by dialysis and gel filtration, lower molecular weight filtrant from gel filtration (largely a mixture of proteins, carbohydrates, and phosphorus compounds), and the effluent from a third separation (strongly positive for carbohydrates) in beef fat.

In a process assigned to General Foods Corporation, meat is liquified in the presence of moisture above 166°C at superatmospheric pressure until visible meat fibers disappear; the product is then immediately cooked at a temperature less than its atmospheric boiling point.[363]

Mabrouk et al.[364] removed fat from comminuted meat before extracting the water

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soluble meat constitutents followed by dialysis of the aqueous solution and gel permeation chromatographic fractionation and concentration of the flavor producing components of the diffusates from the dialysis. Premature degradation of the flavor precursors is minimized by maintaining temperatures below 7° C during isolation.

Dibutyl phthalate (DBP) has been used to extract meat flavor components.[365] The meat is cooked and the resulting vapor is led into the DBP via a condenser and an anhydrous calcium chloride trap, to remove water. The DBP extract is distilled under vacuum to isolate the flavor "essence".[365]

Huth and Schum[366] heated animal organs with ground beef bones, beef fat and water (e.g., 120° C/1 hr). After cooling to 35 to 70° C and removing insoluble residue, incubation with pancrease proteinase decomposes gelatinizing protein and centrifugation separates fat from the aqueous phase. The enzymes in the latter are heat inactivated and it is then evaporated under vacuum to a dry substance to which is added the obtained fat, water, and salt.[366,367] A similar method is patented by Moss and Trautman.[368]

A patent assigned to the Procter and Gamble Co. describes a meat flavor concentrate produced from heat-slurried meat, water, and ascorbic acid.[369] More recently, Japanese workers have produced a beef flavor by heating at 130° to 220° C/5 to 30 min, animal fat and brewed soy sauce (ratio 1:01 to 1.5).[370]

### 3. *Meat Flavor-Contributing Chemicals*

Because the flavors produced from reaction processes are not good enough, the trend in recent years has been toward the use of specific compounds capable of providing or improving the overall meat flavor.[1,2,241] They are either used as such or in admixture or added to a "reaction product" based flavoring. Table 18 is a summary of some meat flavor contributing compounds reported in the patent literature. Some have been isolated from cooked beef (see Table 1) and these are indicated in Table 18. Others have not yet been identified in natural meat aroma, although some have been isolated from model systems, e.g., 3-methyl-1,2,4-trithiane is present in the thermal decomposition products of cysteine and cystine in soya oil at 200° C;[375] two $\alpha$-substituted alkylidene methionals, i.e., 2-[(methylthio) methyl]-3-phenylprop-2-enal and 2,8-dithianon-4-ene-4-carboxaldehyde are naturally occurring in HVP.[376]

In an early patent, Kipins and Ornfelt[437] claimed the formation of compounds with meaty flavor by reaction of substituted glyoxals with thiols. The compounds formed, monothiohemiacetals, have the general formula $R_i$-CO-CH(OH)-S-$R_2$. When $R_1$ and $R_2$ are phenyl groups or when $R_1$ is a thiophen group, the compounds have meaty odors.[437] Broderick et al.[254] used mercatoacetaldehyde (see Section II.C.3.c. and III.B.1).[254] On reaction with reducing sugars, it generates acetals, hemiacetals, and thiohemiacetals; these compounds may also be added as such to foods.

Aldehydes, especially 4-*cis*-decanals, deca-2,4-dienals or their precursors improve chicken flavor in particular.[378,379] van Dorp et al.[378] describe the use of precursors which form aliphatic aldehydes by oxidation of corresponding alcohols, by hydrolysis of corresponding acetals and esters or by autoxidation of an unsaturated fatty acid such as arachidonic acid.

Thiols have been the subject of a series of patents (see Table 18). They are generally unstable and easily oxidize into disulfides which possess a completely different aroma. Thiols also readily volatilize and this necessitates incorporating relatively high initial quantities in foods to ensure the correct proportions at the time of consumption. This may be overcome by using a thiol protecting group which is sufficiently heat labile to cause gradual release of the thiol; this decreases the volatility or increases the threshold value of the compound.[38] Schutte and van der Heijden[438] investigated the effects of several thiol protecting groups in various flavor volatiles. They concluded that

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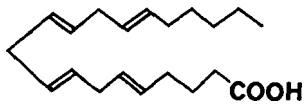
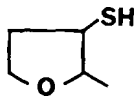
## Table 18
## SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS

I. Alcohols and aldehydes
   A. Non-2-enol; non-2-enol (meat flavor)[377] $CH_3(CH_2)_5CH{=}CHCH_2$;$CH_3(CH_2)_5CH{=}CH\ CHO$
   B. Aldehyde precursors (chicken flavor),[378] e.g., arachidonic acid

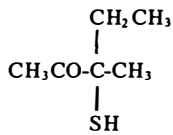



   also diethylacetal of tetradeca-2,5,8-trienal
   C. 4-*Cis*-decenals or their precursors (chicken flavor),[379] e.g., dec-4-*cis*-enal,$CH_3(CH_2)_4$ $CH{=}CH(CH_2)_2CHO$; also trideca-2-*trans*,4-*cis*, 7-*cis*-trienal, dodeca-2-*trans*,6-*cis*-dienal; precursors, e.g., diethylacetal and thiazolidine derivatives of dec-4-*cis*-enal
   D. Certain aliphatic aldehydes ($C_{11}$—$C_{17}$ and 2-4 olefinic bonds) or their precursors (chicken flavor),[380] e.g., undeca-2,5-dienal, $CH_3(CH_2)_4CH{=}CH\ CH_2CH{=}CH\ CHO$

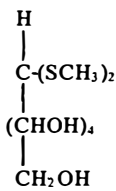
II. Sulfur Compounds
   A. Alkanedithiol derivatives (roasted meat),[381] e.g., butane-1,3-dithiol, $CH_3CH(SH)CH_2CH_2SH$ and hexane-1,6-dithiol; 2-methyl-1,3-butanedithiol; 3,3-dimethylbutane-2,2-dithiol
   B. Thiols from monocarbonate precursors (meat flavor),[372] e.g., 0-*t*-butyl-S-(1-methylthioethyl) thiocarbonate (releasing 1-(methylthio) ethanethiol, see Table 1); also 0-*t*-butyl-S-[3-(2-methyltetrahydrofuryl)] thiocarbonate (releasing 2-methyltetrahydrofuryl-3-thiol)



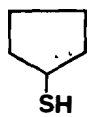

   C. Thiaalkanethiols (roasted meat),[382,383] e.g., 2-thiabutane-3-thiol, $CH_3SCH(SH)CH_3$; also 3-thiapentane-2-thiol
   D. Branched chain alkanethiols (roasted meat),[298,373] e.g., 3-methylbutane-2-thiol (see Table 1); also 2-methylpropane-1-thiol; 2-methylbutane-1-thiol (see Table 1)
   E. α-Ketothiol compounds (meat flavor),[384,385] e.g., 3-mercapto-3-methylpentan-2-one,




   also 2-mercaptobutan-3-one; 2-mercaptopentan-3-one
   F. Mercaptoacetaldehyde (meat flavor),[254] $HS\ CH_2CHO$
   G. a Sugar dialkyldithioacetal (meat flavor),[386] e.g., D-glucose dimethyldithioacetal,




   H. Cycloalkylthiols (meat flavor),[387] e.g., cyclopentylthiol (beef)

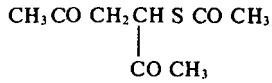



Motif Exhibit 1024, Page 112 of 133

## Table 18 (continued)
## SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS

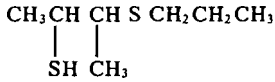
also cyclobutylthiol; 2-methylcyclopentylthiol; 1,2,3,3,4,4,5,5-octamethylcyclopentylthiol; 3,4,5-trimethylcyclohexylthiol

I. 2-Thiosubstituted-1,4-diones (roasted meat),[388–390] e.g., 3-acetylthiohexa-2,5-dione,



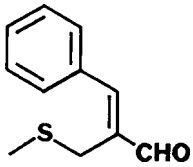
also 3-mercaptohexa-2,5-dione; 3-thiobenzoylhexa-2,5-dione; 3-mercaptobutanedial

J. Mercaptosulfides (roasted meat),[381] e.g., 2-mercapto-3-methyl-4-thiaheptane (di-α-methyl-β-mercaptopropylsulfide),

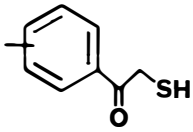


also 5-mercapto-1,2,4-trimethyl-3-thiahexan-1-ol (α-methyl-β-mercaptopropyl-α′-methyl-β′-hydroxpropylsulfide)

K. α-Substituted alkylidene methionals (meat flavor),[376] e.g., mixtures of *cis*- and *trans*-2[(methylthio)methyl]-3-phenylprop-2-enal



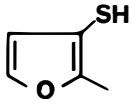

L. α-Mercaptoacetophenone and derivatives (meat flavor),[391] e.g., methylbenzoylmethanethiol (methyl-α-mercaptoacetophenone)



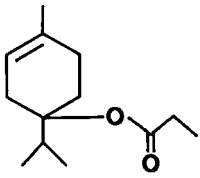

also hydroxybenzoylmethanethiol;methoxybenzoylmethanethiol;benzylbenzoylmethanethiol; chlorobenzoylmethanethiol

III. Furan derivatives

A. Alkylsubstituted furan-3-thiols; also dihydro- and tetrahydro derivatives (meat/roasted meat),[309,392–395] e.g., 2-methylfuran-3-thiol




mixture of 4-terpineolpropionate + 2-methylfuran-3-thiol[361]



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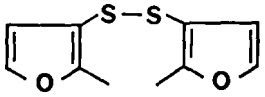
## Table 18 (continued)
## SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS

gives roast beef flavor, liver notes are suppressed; also, 2,5-dimethylfuran-3-thiol; 2-methyl-[4,5-H]-dihydrofuran-3-thiol; 2-ethyl-5-methyltetrahydrofuran-3-thiol; 3-mercapto-2-methyl-4,5-dihydrofuran;[a] 4-mercapto-2-methylfuran;[a] 4-mercapto-3-oxotetrahydrofuran[a]

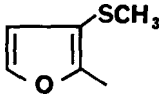
B. 3-Furylsulfides; also dihydro- and tetrahydro derivatives (roasted meat),[287,392,393,396,397] e.g., bis-(2-methyl-3-furyl)disulfide




also bis-(2-methyl-3-furyl) sulfide; bis-(2,5-dimethyl-3-furyl) sulfide; bis-(2-propyl-3-furyl) sulfide; bis-(2-methyl-3-furyl) tetrasulfide; (2-methyl-3-furyl) (2-pyridylmethyl) sulfide

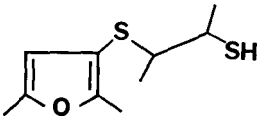
C. Dihydrofuranone derivatives (meat flavor),[276,289,395,398,399] e.g., 4-hydroxy-5-methyl-3(2H) furanone (see Table 1); 2,5-dimethyl-4-hydroxy-3(2H) furanone (see Table 1); 4-hydroxy-2-methyl-5-ethyl-3(2H) furanone; 2-alkyl-3-hydroxy-4(5H) furanone; also corresponding esters, e.g., acetates

D. 3-Furylalkyl/cycloalkyl sulfides and disulfides (meat/roast beef flavor),[287,400-404] e.g., 2-methyl-3-methylthiofuran



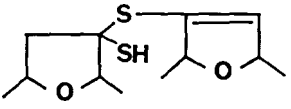

and 2,5-dimethyl-3-propylthiofuran; 2-methyl-3-(3-methylbutylthio) furan; 3-cyclohexylthio-2-methylfuran

E. 3-Furyl-$\beta$-chalcogenalkyl sulfides (meat/nutty flavor),[405,406] e.g., (2,5-dimethyl-3-furyl) (2-mercapto-2-methylpropyl) sulfide



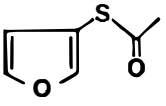

also (2,5-dimethyl-3-furyl) (2-hydroxy-l-methylpropyl) sulfide; *trans* (2-methyl-3-furyl) (2-hydroxycyclohexyl) sulfide

F. (2,5-Dimethyl-3-mercaptotetrahydro-3-furyl) (2′,5′-dimethyl-2′,5′-dihydro-3′-furyl) sulfide (meat-like),[407]




also (2-methyl-3-mercaptotetrahydro-3-furyl) (2′-methyl-4′,5′-dihydro-3′-furyl) sulfide; (2-methyl-3-mercaptotetrahydro-3-furyl) (2′-methyl-2′,5′-dihydro-3′-furyl) sulfide

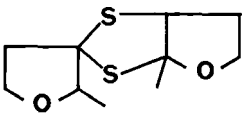
G. 3-Furyl thioesters (meat flavor),[408,409] e.g., 3-acetylthiofuran



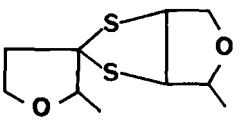

also 2-methyl-3-acetylthiofuran; 2,5-dimethyl-3-(2-ethylbutyrylthio)furan; 2-methyl-3-(2-thiofuroyl) furan

## Table 18 (continued)
## SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS

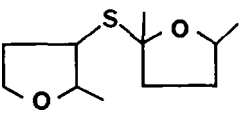
H. 2′,3-Dimethyl-3′,4-dioxa-2,8-dithiabicyclo [3.3.0] octanospirocyclopentane (meat flavor)[407]



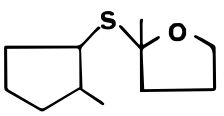
I. 2′,4-Dimethyl-3′,5-dioxa-2,8-dithiabicyclo [3.3.0] octanospirocyclopentane (meat flavor)[407]



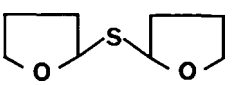
J. 2-Methyl-3-(2′,5′-dimethyl-2′-tetrahydrofurylthio) tetrahydrofuran (beef flavor)[410,411]



K. 2-Methyl-1-(2′-methyl-2′-tetrahydrofurylthio) cyclopentane (meat flavor)[410,411]



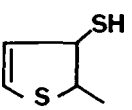
L. Bis (tetrahydrofuryl-2) sulfide (meat flavor)[412,413]



also bis (2-methyltetrahydrofuryl-2) sulfide; bis (2,5-dimethyltetrahydrofuryl-2)sulfide

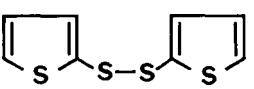
IV. Thiophen derivatives

A. Mercaptothiophen derivatives (meat flavor),[309,394] e.g., 3-mercapto-2-methyl-2,3-dihydrothiophen



also 3-mercapto-2-methylthiophen:[a] 4-mercapto-2-methyl-2,3-dihydrothiophen;[a] 3-mercapto-2-methyl-4,5-dihydrothiophen;[a] 3-mercapto-2-methyltetrahydrothiophen[a]

B. Bis (thienyl) sulfide derivatives (roasted meat),[412–414] e.g., 2,2′-bis-(thienyl) disulfide



also 3,3′-bis-(thienyl) disulfide; bis(2-methyltetrahydrothienyl-2) sulfide; thienyl-2-(2′-methyl-tetrahydrothienyl-2′) sulfide

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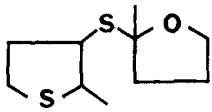
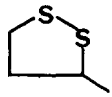
## Table 18 (continued)
## SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS

C. 2-Methyl-3-(2′-methyl-2′-tetrahydrofurylthio) tetrahydrothiophen (beef flavor)[410,411]

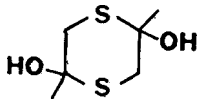


V. Heterocyclic sulfur compounds

A. 3-Methyl-1,2-dithiolane (braised beef)[415]

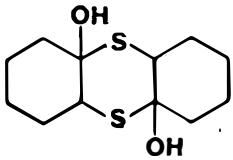


B. Dialkyldihydroxydithiane derivatives (meat flavor),[360,416] e.g., 2,5-dimethyl-2,5-dihydroxy-1,4-dithiane (cyclic dimer of mercaptoacetone)



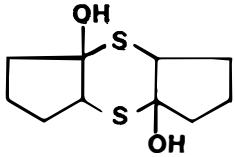
also 2,5-diethyl-2,5-dihydroxy-1,4-dithiane.

C. 1,8-Dihydroxy-2,9-dithiatricyclotetradecane and derivatives (meat/beef flavor)[417,418]



also its esters, e.g., acetate, benzoate; 4,5,6,7,11,12,13,14-octamethyl-1,8-dihydroxy-2,9-dithiatricyclo [8.4.0.0$^{3,8}$] tetradecane; these overcome heat lability of compounds in Section B

D. 1,7-Dihydroxy-2,8-dithiatricyclo [7.3.0.0$^{3,7}$] dodecane or derivatives (meat flavor),[417,418] e.g., 1,7-dihydroxy-2,8-dithiatricyclo [7.3.0.0$^{3,7}$] dodecane

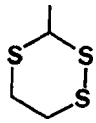


overcomes heat lability of compounds in Section B

E. 2,4,6-Trimethyl-1,3,5-trithiane (meat flavor),[371] see Table 1; (Trithioacetaldehyde)

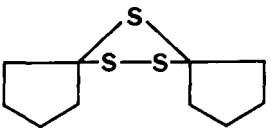
F. Hexamethyl-1,3,5-trithiane (meat flavor),[371] see Table 1

G. 3-Methyl-1,2,4-trithiane (roasted grilled meat),[419]



## Table 18 (continued)
## SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS

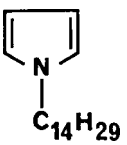
H. 3,5-Dispiro-1,2,4-trithiolanes (meat/beef flavor),[420,421] e.g., 3,5-bis (cyclopentyl) spiro-1,2,4-trithiolane




also 3,5-bis (2′-methylcyclopentyl) spiro-1,2,4-trithiolane; 3,5-bis (2′-methyltetrahydrofuryl-3′) spiro-1,2,4-trithiolane; 3,5-bis (2′-methyltetrahydrothienyl-3′) spiro-1,2,4-trithiolane.

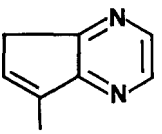
VI. Pyrrole derivatives

A. N-tetradecylpyrrole (meat flavor; also fruity, nutty).[422]



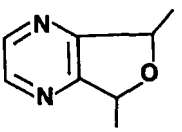

VII. Pyridine, pyrazine, and pyrimidine derivatives

A. Certain cyclopentapyrazines (meat flavor),[423–427] e.g., 5-methyl-7(H) cyclopenta [*b*] pyrazine

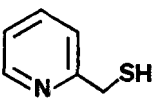



also 5-methylene-6,7-dihydrocyclopenta [*b*] pyrazine; 5-methyl-3,4,6,7-tetrahydro-2(H) cyclopentapyrazine

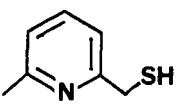
B. 5,7-Dihydro-5,7-dimethylfuro-(3,4-*b*)-pyrazine (chicken and beef flavor)[428]




C. 2-Pyridinemethanethiol (roast pork)[429]




D. Methyl-2-picolylthiols (meat flavor),[430] e.g., 6-methyl-2-picolylthiol




also 6-methyl-2-picolylallylsulfide; these compounds, unlike Section C, mask cereal aromas

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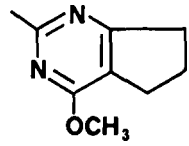
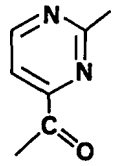
## Table 18 (continued)
## SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS

E. Cyclopentapyrimidines (meaty/nutty),[431] e.g., 4-methoxy-6,7-dihydro-5H-2-methylcyclopenta [*d*] pyrimidine




also 6,7-dihydro-5H-2-methylcyclopenta [*d*] pyrimidine; 4-isobutoxy-6,7-dihydro-5H-2-methylcyclopenta [*d*] pyrimidine

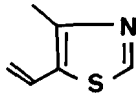
F. Acylpyrimidines (roasted, grilled meat),[432] e.g., 2-methyl-4-acetylpyrimidine

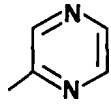



also 4-acetylpyrimidine; 4-butyrylpyrimidine; 2-methyl-4-propionylpyrimidine

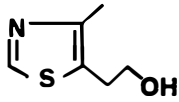
VIII. Thiazole derivatives

A. Suitable ratio of thiazoles and pyrazines (roasted meat),[303,433] e.g., 4-methyl-5-vinylthiazole and methylpyrazine



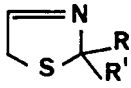




B. Thiazole alcohols (hydroxyalkyl thiazole derivatives) meat flavor,[434] e.g., 4-methyl-5-(2-hydroxyethyl) thiazole




also 4-ethyl-5-(2-hydroxyethyl) thiazole; 4-butyl-5-(2-hydroxyethyl) thiazole; 4-ethyl-5-(3-acetoxypropyl) thiazole; 4-pent-3-enyl-5-(2-hydroxybutyl) thiazole

C. 2-Substituted-3-thiazolines.[339]




D. 2-Acyl-2-thiazoline derivatives (fried, roasted meat),[374,435] e.g., 2-acetyl-2-thiazoline (see Table 1) also 2-acetyl-5-methyl-2-thiazoline; 2-acetyl-5-propyl-2-thiazoline; 2-propionyl-5-ethyl-2-thiazoline

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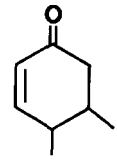
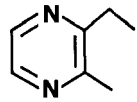
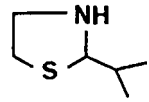
**Table 18 (continued)**
**SOME MEAT FLAVOR-CONTRIBUTING COMPOUNDS IN G.B. AND U.S. PATENTS**

E. Thiazolidines or pyrazines with cyclohex-2-enones (roasted meat, cereal, nutty),[436] e.g., 4,5-dimethylcyclohex-2-enone



plus 2-methyl-3-ethylpyrazine/2-isopropylthiazolidine





also 4,6-dimethylcyclohexen-2-one plus 2-acetylpyrazine or 2,3,5-trimethylpyrazine or 2-butylthiazolidine

IX. Miscellaneous compounds
A. 2,4,6-Trimethyl-5,6-dihydro-1,3,5-dithiazine (meat flavor),[371] (thialdine), see Table 1

[a] May be obtained from $H_2S$ + Furanones.

thioacetates were generally too stable, and that dithiocarbonates were either too stable or too unstable under subsequent heat processing conditions. The O-*t*-alkylthiocarbonates, however, possessed the correct degree of instability and the O-*t*-hexylthiocarbonates had the best flavoring characteristics; they are relatively less volatile and remain longer in the heated food, generating the thiol over a longer period. The O-*t*-butyl esters are, however, easier to prepare and are preferred in most cases. They are relatively stable in pure form; they decompose in aqueous media, probably acid-catalyzed. The relatively stable *t*-butyl carbonium ion readily splits off liberating a thio-carboxylic acid which decomposes to the thiol and carbon dioxide (see Figure 17). The advantage of monothiocarbonates as thiol precursors is shown in the following patent example.[372] When added to a dry soup, 1-(methylthio)ethanethiol is lost during boiling; when the precursor O-*t*-butyl-S-(1-methylthioethyl) thiocarbonate is added before boiling the flavor effect in the prepared soup is equal to that when an equivalent amount of thiol is added after boiling. In other examples, the precursor was shown to survive heat sterilisation in the production of canned food and the extrusion process in the preparation of textured vegetable protein.[372] The use of O-*t*-butyl-S-[3-(2-methyltetrahydrofuryl] thiocarbonate releases 2-methyltetrahydrofuryl-3-thiol which gives roast meat notes.[372]

Thiaalkanethiols are unstable in aqueous media and are very volatile. However, their degradation products have no off-flavor and overdoses may be used.[24] Stability is increased in apolar solvents such as glyceride fats or by enrobing in maltodextrin, gelatin, gum-arabic, or fat.[24,383]

Evers et al.[388,389] reported that their 2-thiosubstituted-1,4-diones (see Table 18) impart different aromas at different concentrations. For example, 3-mercaptohexa-2,5-dione has a roasted meat aroma at concentrations of 2 ppm, with a threshold value of 0.5 ppm, but it adds chicken, sulfury notes to chicken broth at 2.5 ppm. This phenomenon is not

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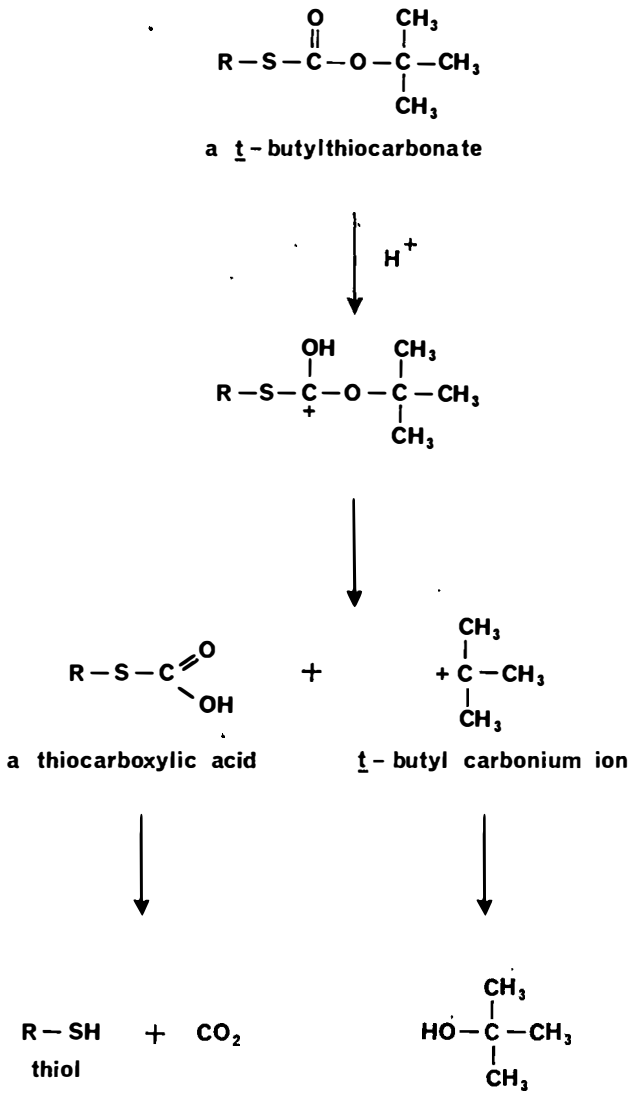


FIGURE 17. Release of thiols from *t*-butylthiocarbonates. (Reprinted with permission from Schutte, L., in *Phenolic, Sulfur and Nitrogen Compounds in Food Flavors*, ACS Symp. Ser. 26, 1976, 108. American Chemical Society.)

uncommon and in virtually all the examples quoted in Table 18 careful concentration calculations and adjustments are necessary.

Some $\alpha$-ketothiol compounds, such as 2-marcaptobutan-3-one have been identified in the volatile components of the reaction of heated protein hydrolysate with cysteine and thiamin.[385] In their work on "reaction flavors" Evers et al.[393,439] noted an intense roasted aroma of the concentrate of a similar reaction system (HVP, cysteine, thiamin, and water) and identified in it 2-methylfuran-3-thiol and bis-(2-methyl-3-furyl) disulfide (see Table 18), both of which had meaty aromas. Similar compounds were synthesised to compare their odor properties. All compounds where the sulfur atom was bound to the $\beta$ carbon atom also had meaty odors, e.g., 2,5-dimethylfuran-3-thiol; bis-(2,5-dimethyl-3-furyl)disulfide; bis-(2,5-dimethyl-3-furyl)sulfide; bis-(2-methyl-3-furyl)trisulfide; and bis-(2-methyl-3-furyl)tetrasulfide. However, when the sulfur was in the $\alpha$-position

only hydrogen sulfide-like, burned notes were detected.[439] More recently, however, some sulfides where the sulfur is at the $\alpha$-position have been patented as meat flavor compounds, e.g., bis (tetrahydrofuryl-2) sulfide (see Table 18).[412,413]

Although 2,5-dihydroxy-1,4-dithiane has meat-like flavor, it is weak, sulfurous, and egg-like.[254] Additionally this compound, together with its dimethyl and diethyl derivatives, are heat labile, degrading to the corresponding monomers, e.g., acetylmethanethiol from 2,5-dihydroxy-2,5-dimethyl-1,4-dithiane.[4] This limitation may be overcome by using instead 1,8-dihydroxy-2,9-dithia-tricyclo[8.4.0.0$^{3,8}$]tetradecane(or a derivative thereof) or 1,7-dihydroxy-2,8-dithia-tricyclo [7.3.0.0.$^{3,7}$] dodecane or its derivatives (see Table 18).

## IV. CONCLUSION

Sensory comparisons of the aromas of some commercially available simulated beef flavorings with those of genuine beef — both boiled and roasted — have revealed the former to be significantly different from and less desirable than the latter.[10] Odor descriptions were obtained for both classes of aromas. Those samples which most closely simulated the natural cooked beef aromas were more like boiled than roast beef aroma and when the simulated beef flavorings did possess burned, roasted qualities, these were undesirable and tended to obliterate any meaty quality which may have been present.[10]

Future meat flavorings will almost certainly involve the use of reaction flavors in conjunction with key compounds isolated from natural meat and subtle blending of ingredients in the correct proportions will be necessary.[1] Thus, the search for significant contributors to natural meat aroma must continue. Many are present in such small quantities that they may so far have escaped identification or even detection. Analysis therefore requires large quantities of meat as starting material, aroma isolation procedures which avoid artefact formation, high resolution separation methods and high sensitivity identification techniques in conjunction with computer data processing systems. The challenge is enticing for those who have the necessary enthusiasm and finance.

## ACKNOWLEDGMENT

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