TABLE 1 (Continued)

Classification of Flavor Ingredients by Primary Taste and Flavor Type

Flavor ingredient	Taste			Flavor type
	Sweet	Bittersweet	Bitter	
Hexyl formate	x			Plum
Hexyl furan carboxylate		x		Pear, mushroom
α-Ionone	x			Raspberry
Isoamyl acetate		x		Pear
Isoamyl formate	x			Plum
Isoamyl isobutyrate				Pineapple
Isoamyl propionate		x		—
Isoamyl salicylate		x		Strawberry
Isobutyl acetate			x	—
Isobutyl anthranilate		x		Strawberry, grape
Isobutyl butyrate	x			Rum
Isobutyl cinnamate	x			Raspberry
Isobutyl formate	x			Rum
Isobutyl phenylacetate	x			Honey
Isobutyl propionate			x	—
Isobutyl salicylate			x	—
Isopropyl acetate	x			Apple
Isopropyl benzyl carbinol		x		Peach
Isopropyl formate	x			Plum
Isopropyl isovalerate	x			Apple
Isopropyl propionate		x		Plum
Isopropyl valerate		x		Apple
Isovalerophenone		x		Grape
Linalool	x			Plum
Linalyl acetate	x			Black currant
Linalyl anthranilate	x			Orange
Linalyl butyrate	x			Honey
Linalyl formate		x		Pineapple
Linalyl isobutyrate	x			Black currant
Linalyl isovalerate			x	—
Linalyl propionate	x			Black currant
Methyl acetate			x	—
Methylacetophenone	x			Strawberry
2-Methylallyl butyrate		x		Apple, plum
2-Methylallyl caproate		x		Pineapple
Methyl amyl ketone			x	Pear
Methyl anisate	x			Melon
Methyl anthranilate			x	—
Methylbenzyl propionate		x		Cherry
Methyl butyrate	x			Apple
Methyl cinnamate	x			Strawberry
Methyl eugenol			x	Clove
Methylheptenone			x	Pear

TABLE 1 (Continued)

Classification of Flavor Ingredients by Primary Taste and Flavor Type

Flavor ingredient	Taste			Flavor type
	Sweet	Bittersweet	Bitter	
Methyl ionone	x			Raspberry, black currant
Methyl isobutyrate	x			Apricot
Methyl isoeugenol			x	Clove
Methyl isovalerate			x	—
Methyl methylanthranilate		x		Peach
Methyl-β-methylpropionate		x		Pineapple
Methyl naphthyl ketone		x		Strawberry
Methyl nonyl ketone	x			Peach
Methyl octine carbonate	x			Peach
Methyl phenylacetate	x			Honey
Methyl phenyl carbinyl acetate				—
Methyl propionate	x			Black currant
Methyl undecylate				Pineapple
Methyl undecyl ketone		x		Coconut
Musk ambrette	x			Peach
Nerol			x	Rose-like
Nerolin	x			Strawberry
Neryl acetate	x			Raspberry
Neryl butyrate	x			Cocoa
Neryl formate			x	—
Neryl isobutyrate	x			Strawberry
Neryl isovalerate			x	—
Neryl propionate	x			Plum
γ-Nonalactone		x		Coconut
Nonyl acetate			x	—
Nonyl alcohol			x	—
γ-Octalactone		x		Peach, coconut, walnut
Octyl acetate	x			Peach
Octyl butyrate	x			Melon
Octyl formate		x		—
Octyl isobutyrate	x			Grape
2-Octynoate	x			—
Phenethyl acetate		x		Honey
Phenethyl alcohol			x	Peach, rose
Phenethyl butyrate	x			Honey
Phenethyl cinnamate			x	—
Phenethyl dimethyl carbinol	x			Apricot
Phenethyl dimethyl carbinyl isovalerate		x		Rose
Phenethyl formate		x		Green plum
Phenethyl isobutyrate		x		Green plum
Phenethyl isovalerate		x		Peach
Phenethyl phenylacetate	x			Honey
Phenethyl propionate				Honey
Phenethyl salicylate	x			Peach

TABLE 1 (Continued)

Classification of Flavor Ingredients by Primary Taste and Flavor Type

Flavor ingredient	Taste			Flavor type
	Sweet	Bittersweet	Bitter	
Phenylacetaldehyde dimethyl acetal		x		—
Phenylacetic acid	x			Honey
Phenylallyl alcohol		x		Plum, peach
Phenylglycidate	x			Strawberry
Phenylpropyl acetate		x		Grape
Phenylpropyl alcohol	x			Apricot
Phenylpropyl butyrate	x			Plum
Phenylpropyl cinnamate	x			Cocoa
Phenylpropyl ether		x		Grape
Phenylpropyl isobutyrate		x		Peach
Propenyl guaethol	x			Vanilla
Propyl acetate		x		Pear
Propyl cinnamate		x		Peach, apricot
Propyl formate		x		Plum
Propyl isobutyrate	x			Pineapple
Propyl phenylacetate	x			Honey
Propyl propionate			x	—
Rhodinol			x	Rose
Rhodinyl acetate			x	—
Rhodinyl butyrate	x			Whortleberry
Rhodinyl formate		x		Cherry
Rhodinyl isobutyrate	x			Peach
Rhodinyl isovalerate		x		Cherry
Santalol	x			Woody, raspberry
Santalyl acetate		x		Apricot
Santalyl phenylacetate	x			Honey
Styralyl acetate			x	Grapefruit
Terpenyl acetate	x			Raspberry
Terpenyl anthranilate			x	—
Terpenyl butyrate		x		Plum
Terpenyl cinnamate			x	—
Terpenyl formate				—
Terpenyl isovalerate	x			Apple
Terpenyl propionate		x		—
Terpineol		x		Peach
Tetrahydrofurfuryl propionate		x		Apricot, chocolate
Tetrahydrogeraniol			x	—
Tolualdehyde (*o,m,p*)		x		Cherry, almond
γ-Undecalactone	x			Apricot, peach
Undecynoate			x	—
Vanillin			x	Vanilla
Vanillylidene acetone		x		Vanilla
Yara yara	x			Strawberry

FLORAL AND CITRUS FLAVORS

In addition to specific information concerning the formulation of flavors for various applications, a separate discussion of the characteristics, functionality, and potential use of floral (rose, jasmine, violet, orris) and citrus (orange, lemon, mandarin, cedrat) flavors may be helpful. These products are not only important technically, but they also are important from a commercial viewpoint, since they represent a very sizable portion of the world market value for flavor ingredients.[1,2]

Floral Flavors

Rose

Among all of the floral derivatives, rose is undoubtedly the most important, mainly because it is used in a wide range of flavor formulations. In addition rose is used by its producing countries and in the Middle East as the basic flavoring component in a large variety of products. Rose (*Rosa damascena* and *R. centifolia*) derivatives include the concrete, absolute, essential oil (rose otto), and the cohobation waters. The concrete is not employed as such but used only for the preparation of the absolute. Cohobation waters have only a very limited use for flavoring finished products and are never used in formulations of high yields. Sometimes the waters are used to dilute soluble, essential-oil-based flavors and to prepare syrups used in pharmaceuticals. The absolute and the essential oil exhibit different flavoring strengths. The note of the absolute is related strictly to the large phenethyl alcohol content and bears close resemblance to the rose flower note. The absolute is preferred therefore in flavor work, while the distilled essential oil is more suitable for use in perfumery.

Rose, with its intensely scented flowers, has attracted the imagination of chefs in times past; the use of rose petals is called for frequently in old recipes for sauces and other delicacies. This is also true for some classic liqueur and sweet cordial formulations, a few of which have been retained until the present time (*e.g.*, rosolio, alkermes). Also rose-flavored sherbets have found a certain degree of acceptance.

On examination of rose-based flavors for various culinary and liqueur formulations, it is apparent that the most interesting results have been obtained from the following combinations:

1. Rose with citrus notes: cedrat, lemon, orange, bergamot
2. Rose with floral notes: orange flowers, violet, jasmine, orris
3. Rose with spicy notes: nutmeg, clove, cinnamon
4. Rose with other notes: angelica, rosemary, bitter almond

Rose is employed successfully in the formulation of *compounded flavors*, such as sour cherry, mango, raspberry, sweet cherry, strawberry, tutti-frutti, pistachio, and millefiori (thousand flowers). The mellow-flavored rose is a very important element, conferring roundness to flavors that often exhibit a harshness from the absence of certain unidentified constituents. In many instances economic considerations limit the use of rose absolute in flavors, and its replacement as part of the formulation is required. Replacement with other flavor ingredients should follow certain criteria; even an excellent rose composition formulated for use in fragrances cannot be adapted for flavoring food products. Many constituents that are highly functional in perfumes are unpalatable or exhibit at least a taste quite foreign to the aroma. Therefore, flavor substitutes for true rose must contain only those constituents of rose absolute with a pleasant flavor. A rose-like composition fulfilling the above requirements can be formulated according to the following general guidelines:

Imitation Rose Flavor

Ingredients	Parts by weight
Geraniol	4.0
Phenethyl alcohol	3.0
Linalool	1.25
Rhodinol	1.25
Citronellol	0.5
Aldehyde C_9	0.05
Citral	0.04

The resulting product can be used as is for flavoring baked goods, while the addition of 5–10% true rose absolute is advisable for candy; this should be increased further when flavoring liqueurs. Whenever a rose note is desired for products soluble in very low-strength alcohol, the use of a 3:1 mixture of phenethyl alcohol and citronellol may suffice if properly dosed.

Jasmine

Jasmine absolute and its substitutes (which must be formulated with the same precautions employed for rose absolute) have very limited use. The absolute should be employed only in minimal doses and limited mainly to liqueurs, candy, special tannings, and fruital aromas. Jasmine absolute also may be replaced entirely or partially by other less expensive flavor compositions. The following guideline formulation, especially suitable for baked goods, may be usefully employed:

Jasmine Formulation

Ingredients	Parts by weight
Benzyl acetate	10.0
Linalyl acetate	4.0
Benzyl butyrate	1.5
Phenethyl butyrate	1.5
Phenethyl alcohol	1.0
α-Amyl cinnamaldehyde	1.0
Hydroxycitronellal	0.3

Violet and Orris

In addition to the violet-flowers note (ionone and methylionone), the characteristic aroma exhibited by the derivatives of orris rhizomes (the butter, absolute, and resinoid) also should be considered for flavors. Violet and orris aromas are extremely important and find application in wines, liqueurs, and fruital flavors used for candy and pastry. While violet and orris aromas are caused chiefly by irone, the fragrance of violet leaf absolute consists of entirely different aromatic principles and does not find application in flavors; however, the aroma of orris derivatives is considered fundamental in flavors. Fresh violet flowers once were candied with a certain degree of acceptance; this practice has nearly disappeared with the exception of a few compounded aromas. Dried violet flowers are used currently to prepare tinctures for liqueurs and, when blended with other dried herbs, for compounded flavors used in carbonated beverages.

The aroma of fresh violet flowers can be approximated using a guideline formulation similar to the following:

Ingredients	Parts by weight
x-Ionone (colorless)	55–58%
Phenethyl alcohol	28–32%
Bergamot	5%
Vanillin	3%
Orris butter	2–3%
Ylang-ylang	1–2%
Guaiac wood	1%

The above formulation is rather simple, has a satisfactory taste, and can be employed either as a base flavor or as a modifier. It is also heat stable and has a harmonious bouquet, especially on dilution.

Citrus Flavors

Citrus essential oils require modification in order to be formulated into flavors that are readily absorbed by the food substrate without yielding objectionable separations or agglomerates during the shelf-life of the product. While food manufacturers have at their disposal more stable and functional essential oils with good solubility, this creates additional problems for the flavorist; the full flavor of the natural essential oil is deprived of a number of complementary notes that are no longer reproducible even when the soluble oil is used for flavoring in combination with large amounts of natural juices. There is no easy solution to this problem at the present time, and the possibility of reproducing the aroma of freshly expressed fruit juice using various aroma formulations does not seem readily attainable. Therefore, the following alternatives (equally applicable to the use of citrus aromas in flavors) remain open in the field of beverage concentrates (syrups, slushes, etc.) and finished ready-to-market carbonated beverages.

Terpeneless and Sesquiterpeneless Citrus Oils

Should citrus oils be employed as is, or should terpeneless and sesquiterpeneless oils be used instead? Paste flavors (for carbonated beverages) usually employ raw or rectified essential oils, while the soluble oils for syrups and liqueurs consist mainly of hydroalcoholic solutions of citrus oils largely deprived of terpene and sesquiterpene fractions by a manufacturing process similar to cold-extracted terpeneless oils. These two product types yield entirely different flavor values. Although flavor judgments are subjective, undoubtedly beverages flavored with paste flavors (all other flavor components remaining the same) duplicate the aroma of freshly expressed juices better than soluble oils. However, paste flavor formulations cannot be prepared with all citrus oils; flavorwise, the most successful paste flavor is orange. Because of the poor stability of lemon (and cedrat) essential oils, the use of the more stable soluble oil is preferred to obtain longer lasting and more consistent flavor effects.

The beverage industry, with a world consumption of several thousand tons of citrus oils, does not represent the only outlet for citrus-based flavors. Statistical figures on the exact ratio of citrus-oil consumption between the beverage and confection industries generally are not available. However, this ratio is estimated between 3:1 and 4:1 for the European market (*e.g.*, Italy) but perhaps 16:1 in the United States. The Italian pastry industry, for example, has attained world-wide acceptance with its important product panettone, a traditional Italian fruitcake. This has created a need for the characteristic flavor of panettone derived from citrus oils; the flavor duplicates the fruitcake aroma obtained by adding candied citron, raisins, etc. to the dough.

The panettone aroma is not the only type for which an industrial need exists; several other products that are employed for pastry flavoring can be considered variations of the panettone theme. All types may contain an additional butter-like note. Independent of the presence of the butter-like note and of the varying ratios of the constituents in the flavor, the characteristic notes of panettone and other similar flavors include the citrus and vanilla notes. The citrus note is subdivided further into

citron-like and "fantasia" types. Citron-like essential oils are duplicated with a blend of lemon, orange, and bergamot essential oils. The formulation of such blends varies widely according to the composition of natural citron essential oil, but only limonene, dipentene, citral, and citroptene are important to the aroma. Therefore, a good lemon essential oil with a citral content that has been increased from 3–4% to 5–6% should suffice for good duplication.

In practice organoleptic requirements have led to more complex formulations. The organoleptic requirement, *i.e.*, the desired aromatic result, is usually satisfied by the use of flavor formulations with the following minimum and maximum values, together with all possible intermediate values:

Oil	Formulation types				
	A	B	C	D	E
Lemon	12	2	1	1	80
Orange	1	2	1	2	20
Bergamot	0.5	1	—	2	0.25

In the above formulations having the citrus note, type D can be eliminated from further contention as a flavor, since it is used only in perfumery; with slight modifications it is a good starting material for colognes. Type A is a good starting material for the preparation of a soluble oil useful for flavoring carbonated beverages. Type B is a magnificent flavor base for preparing compounded oils for liqueurs and syrups, especially if the lemon concentration is decreased slightly by 10% and the orange concentration increased by 30% (*i.e.*, final formulation 62, 22, 16). Finally, formulations E and C are extremely suitable for use in pastry. Mandarin oil also may be added to the above bases to sweeten the flavor note; when added to formulation A, B, C, or E, it should never exceed 0.5% based on the level of orange oil. Referring once again to panettone, this flavor type may be formulated with or without bergamot. In either case a rounding of the citrus-citron note is required by the addition of a good mandarin oil—one part to formulation E or one-half part to formulation C (with or without the use of bergamot). The finishing touches to the formulation are rendered by dosing with 1 part of vanillin (25% maximum).

The remarkable evolution in taste over the past 60 years for lemon-flavored carbonated beverages should be noted. At the beginning of this century, a typical lemon-flavored beverage consisted of a soluble lemon oil dissolved in ordinary syrup and diluted with carbonated water. Today cola beverages have attained widespread acceptance; they are bittersweet, fantasia-type, lemon-based beverages whose formulation originated in the United States at the end of the nineteenth century and was introduced into Europe during World War I. The flavor composition is complex and based chiefly on the following components: cola-nut extract, lemon oil or juice, lime, sweet orange, neroli, traces of spicy oils, caffeine, caramel, and phosphoric acid. The lime, lemon, and orange essential oils, modified to a slightly bitter flavor, represent the citrus note in the syrup. Other flavor ingredients only complement the characteristic note. The introduction of cola beverages has radically modified the consumers' taste and has created in a matter of a few years a much wider acceptance for bitter-flavored beverages. On the continent, for example, grapefruit and bitter-orange flavored beverages (scarcely accepted until a few years ago) and other bitter tonics based on a citrus undernote (vermouth-rhubarb) have captured large portions of the consumer market. The degree of carbonation has undergone a parallel change, and highly carbonated beverages are currently preferred.

Bitter and Sweet Orange

Sweet orange essential oil is employed as is for flavoring both non-alcoholic beverages and liqueurs. Bitter orange oil, however, is never used alone or in concentrations exceeding 50% of the aroma formulation (maximum levels are used in liqueurs). A blend of bitter and sweet orange oils containing

approximately 50% each of the two oils (also ratios varying between 90:10 and higher) is used to prepare bitter-flavored beverages and aperitifs. In fact the flavor of certain aperitifs consists of more than 95% sweet and bitter orange together with the corresponding peel extracts, traces of vanillin, and complementary bitter notes. The sweet orange note is widely employed in compounded oils for liqueurs and fruital aromas (apricot, pineapple, benedictine, banana, cherry, chartreuse, strawberry, peach and benevento).

Lemon

The widespread acceptance of the new lemon-flavored beverages together with citron-like combinations has already been mentioned. Lemon essential oil is used alone, especially in beverages and candy. Alone or in combination with lime (distilled lime oil has an aroma entirely different from the cold-expressed product), lemon oil finds use in the flavor composition of several bittersweet beverages. In the formulation of compounded oils and fruital aromas, lemon oil is used less extensively than sweet orange oil, but it can be utilized (found) in the following liqueurs and fruital aromas: apricot, pineapple, benedictine, banana, curaçao, strawberry, apple, currant, and benevento.

Mandarin

The mandarin note is used alone to flavor candies and liqueurs. Usually it finds very limited use in the formulation of compounded aromas with the exception of the very important flavors for baked goods and pastry (panettone). The rum-mandarin note is a very interesting aroma combination for mandarin punch.

FRUITAL FLAVORS

Introduction

One of the most interesting areas of flavor formulation is the imitation of fruital aromas. It is well known that man retains a strongly conservative predilection for natural flavors. The attraction for fruital flavors probably occurs during youth, at which time most persistent organoleptic preferences are developed. This psychological need, associated with the lack of available natural fruit aromas with the strength to flavor food products or at least to partially duplicate the pleasant fruit flavor sensation, has compelled the flavorist to concentrate his efforts in the imitation of fruit aromas.

Originally the flavor ingredients of choice were very limited in number and consisted chiefly of essential oils. The resulting flavor was scarcely attractive. A renewed impulse to create fruital formulations was brought about by the introduction of the so-called "fruit ethers." These are the highly volatile esters readily prepared by esterification of aliphatic acids with ethyl, methyl, butyl, propyl, or amyl alcohols. For several years thereafter fruit flavor formulations were based almost exclusively on essential oil and fruit ether flavor blends.

The systematic identification of constituents in natural flavors is a more recent development. Until recently all attempts to reformulate a natural aroma were limited to the analytical organoleptic perceptiveness of the flavorist. Science was not interested in such marginal problems, and the enthusiasm of a few pioneers was not sufficient to make flavor chemistry progress at the same fast pace as other industry-oriented branches of chemistry. As investigations gradually expanded, new flavor ingredients became available to the flavorist. However, the accidental discovery of a flavor component with a definite aroma was kept highly secret by those few better-equipped researchers. Such products were made commercially available as complex mixtures under a variety of trade names or arbitrarily qualified as "aldehydes" (*e.g.*, aldehydes C_{15}, C_{17}, C_{19}, C_{21}, C_{25}, C_{27}, C_{29}, C_{30}, and C_{31}). Other suppliers traded the pure product under imaginative names or used the misnomer of aldehyde (*e.g.*, aldehyde C_{14} for γ-undecalactone, aldehyde C_{18} for γ-nonalactone, and aldehyde C_{16} for ethyl methylphenylglycidate). More advanced flavors could be formulated with the use of these new products, especially strawberry, peach, coconut, plum, and apricot. In recent years studies of the constitution of flavors have progressed markedly by the introduction of instrumental analysis; most of the chemically defined components of the more important fruital flavors and their relative ratios have been identified.

As a result of the acquired knowledge, increasing attention has been paid to a number of synthetic chemicals with regard to their potential use in small percentages in modern fruital flavors. A list of the most recurrent chemicals, grouped by functional classification, is shown below. When properly chosen and employed in appropriate amounts, these products play a very important role in the formulation of fruital flavors, such as apple, banana, bilberry, grape, grapefruit, guava, orange, peach, pear, pineapple, raspberry, strawberry, tomato, and tea. Often close duplication of the natural flavor notes is achieved. Those chemicals marked with an asterisk are either specific aroma components identified in one of the above-mentioned natural flavors or common to a number of the above flavors. In all cases, they are the most widely employed in the formulation of well-balanced fruital flavors.

Alcohols and Esters

1-Penten-3-ol*
cis-2-Pentenal*
cis-3-Pentenal*
Pentenyl caproate (hexanoate)*
1-Hexen-3-ol*
cis-2-Hexenol*
cis-2-Hexenyl acetate
cis-2-Hexenyl caproate (hexanoate)
trans-2-Hexenol*
trans-2-Hexenyl acetate*
trans-2-Hexenyl propionate
trans-2-Hexenyl butyrate*
trans-2-Hexenyl caproate (hexanoate)*

Alcohols and Esters *(continued)*

trans-2-Hexenyl caprylate (octanoate)*
cis-3-Hexenol*
cis-3-Hexenyl acetate*
cis-3-Hexenyl butyrate
cis-3-Hexenyl propionate*
cis-3-Hexenyl formate
cis-3-Hexenyl valerate
cis-3-Hexenyl isovalerate
cis-3-Hexenyl 2-methylbutyrate
cis-3-Hexenyl tiglate
cis-3-Hexenyl caproate (hexanoate)*
cis-3-Hexenyl hepatonoate
cis-3-Hexenyl caprylate (octanoate)*

Alcohols and Esters *(continued)*

cis-3-Hexenyl caprate (decanoate)
cis-3-Hexenyl lactate
cis-3-Hexenyl pyruvate
cis-3-Hexenyl benzoate*
cis-3-Hexenyl phenylacetate
cis-3-Hexenyl cinnamate
cis-3-Hexenyl salicylate
cis-3-Hexenyl anthranilate
trans-3-Hexenol*
trans-3-Hexenyl acetate*
trans-3-Hexenyl caproate (hexanoate)
trans-3-Hexenyl caprylate (octanoate)*
β, α,Hexenol (mixture of *cis*- and *trans*-3-hexenol)
β, α-Hexenyl acetate
β, α-Hexenyl formate
β, α-Hexenyl isobutyrate
trans, trans-2,4-Hexadienol
trans, trans-2,4-Hexadienyl acetate
cis-3-Heptenol*
cis-3-Heptenyl acetate*
cis-4-Heptenol
1-Octen-3-ol*
1-Octen-3-yl acetate
1-Octen-3-yl butyrate
1-Octen-3-yl propionate
trans-2-Octenol*
trans-2, *cis*-6-Octadienol
trans-2, *cis*-6-Octadienyl acetate
2-Nonanol*
1-Nonen-3-ol*
1-Nonen-3-yl acetate
trans-2, *cis*-6-Nonadienol
trans-2, *cis*-6-Nonadienyl acetate
2-Decanol*

Acetals

Acetaldehyde ethyl-(*cis*-3-hexen)-yl acetal*
Acetaldehyde ethyl-(*trans*-3-hexen)-yl acetal*
Acetaldehyde (*cis*-3-hexen)-yl acetal*
trans-2-Hexenal diethyl acetal
cis-4-Heptenal diethyl acetal
trans, trans-2,4-Hexadienal diethyl acetal
trans-2, *cis*-6-Nonadienal diethyl acetal

α-Ethylenic Aldehydes

trans-2-Pentenal*
trans-2-Hexenal*
trans-2-Heptenal*
trans-2-Octenal*
trans-4-Octenal*
trans-2-Nonenal*
trans-2-Decenal*

α-Ethylenic Aldehydes *(continued)*

trans-2-Undecenal*
trans-2-Dodecenal*

Monoethylenic Aldehydes

cis-4-Heptenal

Diethylenic Aldehydes

trans, trans-2,4-Hexadienal*
trans, trans-2,4-Heptadienal*
trans-2, *cis*-6-Octadienal
trans-2, *cis*-6-Nonadienal

Ketones

Nootkatone*

Acids and Esters

2-Methylbutyric acid*
Methyl 2-methylbutyrate*
Ethyl 2-methylbutyrate*
Propyl 2-methylbutyrate*
Butyl 2-methylbutyrate*
Isobutyl 2-methylbutyrate*
Amyl 2-methylbutyrate*
Isoamyl 2-methylbutyrate
Hexyl 2-methylbutyrate*
Octyl 2-methylbutyrate
Ethyl-3-hydroxy hexanoate*
trans-2-Hexenoic acid*
Ethyl *trans*-2-hexenoate
Methyl *trans*-2-hexenoate*
cis-3-Hexenoic acid*
Ethyl *cis*-3-hexenoate
trans-3-Hexenoic acid
Ethyl *trans*-3-hexenoate
Methyl *trans*-3-hexenoate*
Methyl *cis*-4-octenoate*
trans-2-Octenoic acid*
Ethyl *trans*-2-octenoate*
Methyl *trans*-2-octenoate*
trans-3-Octenoic acid
Ethyl *trans*-3-octenoate
Methyl *trans*-3-octenoate
trans-2-Decenoic acid
Ethyl *trans*-2-decenoate*
Methyl *trans*-2-decenoate*
trans-3-Decenoic acid
cis-4-Decenoic acid
Ethyl *cis*-4-decenoate*
Methyl *cis*-4-decenoate*
Ethyl *trans*-2, *cis*-4-decadienoate*
Ethyl *trans*-2, *trans*-4-decadienoate*
Methyl methylthiopropionate

Finally, the flavor effects obtainable by the addition to fruital formulation of flavor components such as C_6 to C_{12} gamma and delta lactones should not be overlooked. These components, occurring naturally in many pit fruits, contribute to create flavor fullness by arousing sensations reminiscent of fruit pulp. Therefore, they are considered essential in the formulation not only of peach and apricot flavors, but also of pear, raspberry, and many other fruital flavors.

Will it be possible with this detailed knowledge to duplicate exactly the various fruital flavors? A positive answer should be expected based on analogy with the excellent results obtained in duplicating essential oil flavors. In a few cases not only the flavor but exact physical-chemical constants have been elucidated. However, even perfectly rebuilt essential oils exhibit somewhat apparent organoleptic deficiencies. Similar results in the sector of rebuilt fruital aromas are probably quite a long distance away. For example, gas chromatographic analysis using capillary and semi-capillary columns, together with other refined instrumental techniques, yields flavor compositions that appear easily duplicable. In other cases the analysis reveals an exceedingly large number of components. Simply mixing components based on gas chromatographic data has led to disappointing results; on the other hand, results of a more general and positive nature have been obtained using these techniques. Such work has led to the formulation of flavor bases and in this respect contributed to products that duplicate the natural types much more closely than possible with prior flavor art.

The causes determining the organoleptic deficiencies in a rebuilt aroma, even when all of the constituents are identified and available, are manifold and complex. Formation of "artifacts" during isolation of the flavor complex or during the analytical investigation cannot be overlooked. Degradation products formed during the time elapsed between harvesting and working-up the fruit to isolate the aroma should also be considered, since the maturation process may have been interrupted, giving way to a degenerative process. Present knowledge does not allow definite conclusions. Considering, however, that natural flavor components are produced by constructive and destructive mechanisms functioning concomitantly, it has been impossible (at least to date) to rebuild flavors under conditions of biogenesis. Based on present knowledge, the only choice is to duplicate natural flavors as closely as possible with good imitations.

In the following pages the more important fruit flavors will be discussed together with specific formulation guidelines and aroma compositions, if available, as identified by more recent analytical studies. Formulations will be based on readily available raw materials; specific components whose use is subject to government regulations that vary from country to country will be omitted. The formulations list all probable components with potentially useful alternatives indicated in parentheses ( ) or as separate entries. *Only those marked with an asterisk* (*) *comprise the guideline formulation.* The formulation guideline should *not* be considered in any way finished; it must be further refined by the flavorist to meet specific end-use requirements.

Apple

The complexity and the continuing changes in the innumerable types of apple aromas have caused quite different approaches to the formulation of the aroma imitations. In addition to amyl acetate, amyl butyrate, amyl valerate, and ethyl butyrate, which comprise up to 50% of the total aroma formulation, a fairly large number of aliphatic esters (especially the C_5 to C_{10} acid esters) are often employed in the formulation. Although natural apple aroma contains many of the above esters, the proper blending of the esters in the formulation is extremely difficult, especially when aroma imitations of specific cultivars rather than generic and polyvalent aroma formulations must be prepared.

Products most frequently added to modify or characterize the various apple aroma formulations (in addition to the above-mentioned flavor ingredients) follow: ethyl acetate, ethyl valerate, ethyl isovalerate, ethyl pelargonate, vanillin, lemon essential oil, citral, citronellal, rose absolute, geraniol, orange essential oil, geranium essential oil, aldehyde C_{10}, ethyl heptanoate, acetaldehyde, so-called aldehydes C_{14} and C_{16}, styralyl acetate, dimethyl benzyl carbinyl acetate, benzyl formate, phenyl ethyl isobutyrate, cinnamyl isovalerate, anise essential oil, and the methyl esters of colophony and benzaldehyde.

The use of butyl isovalerate, isopropyl acetate, and methyl butyrate (naturally occurring products) has also been found of interest in apple aroma imitations. Encouraging results have been obtained by using the following products not yet identified in natural apple aroma but most likely occurring in other natural products: terpenyl isovalerate, isopropyl isovalerate, citronellyl isovalerate, geranyl isovalerate, benzyl isovalerate, cinnamyl formate, isopropyl valerate, butyl valerate, and methyl allyl butyrate.

Synthetic products not yet found in nature whose use in apple aroma formulations is governed (as the above compounds) by specific regulations in different countries include: cyclohexyl acetate, allyl butyrate, allyl cyclohexylvalerate, allyl isovalerate, and cyclohexyl butyrate. The aroma of these products blends very well with natural apple aroma.

Several analytical investigations have broadened the present knowledge of apple aroma. The first of these studies dates back to 1920. To date, about 40 researchers have contributed to the investigation. From the combined results 90 components have been identified in various natural apple aromas; these have been sub-divided in the following table according to their chemical functionality.

Components of Natural Apple Aroma

Hydrocarbons	Esters *(continued)*	Free and Esterified Acids
1-Butoxy-1-ethoxyethane	Ethyl acetate	Acetic
1,-1-Diethoxyethane	Ethyl butyrate	Benzoic
1-Ethoxy-1-hexoxyethane	Ethyl formate	Butyric
1-Ethoxy-1-methoxyethane	Ethyl hexanoate	Formic
1-Ethoxy-1-(2-methylbutoxy)-ethane	Ethyl 2-methylbutyrate	Hexanoic
1-Ethoxy-1-propoxyethane	Ethyl 2-methylpropionate	*n*-Hexenoic
1-Methyl-naphthalene	Ethyl octanoate	3-Methylbutyric
2-Methyl-naphthalene	Ethyl pentanoate	4-Methylpentanoic
2,4,5-Trimethyl-1,3-dioxolane	Ethyl 2-phenylacetate	2-Methylpropionic
	Ethyl propionate	Octanoic
Free and Esterified Alcohols	*trans*-2-Hexen-1-yl-acetate	Pentanoic
Butanol	Hexyl acetate	Propionic
Ethanol	Hexyl butyrate	
Geraniol	Hexyl propionate	Aldehydes and Ketones
Hexanol	Methyl acetate	Acetaldehyde
n-Hexenol	2-Methylbutyl acetate	Acetone
trans-2-Hexen-1-ol	3-Methylbutyl acetate	Acetophenone
3-Hexen-1-ol	3-Methylbutyl 3-methylbutyrate	Butanal
Methanol	Methyl butyrate	2-Butanone
2-Methylbutan-1-ol	Methyl formate	Diacetyl
3-Methylbutan-1-ol	Methyl hexanoate	Formaldehyde
2-Methylpropan-1-ol	Methyl 2-methylbutyrate	Furfural
Pentanol	Methyl 3-methylbutyrate	Hexanal
Propanol	2-Methylpropyl acetate	2-Hexanone
2-Propanol	2-Methylpropyl propionate	2-Hexenal
	Pentyl acetate	2-Methylbutanal
Esters	Pentyl butyrate	3-Methylbutanal
Benzyl acetate	Pentyl 2-methylbutyrate	2-Methylpropanal
Butyl acetate	2-Phenylethyl acetate	Nonanal
Butyl butyrate	Propyl acetate	Pentanal
Butyl hexanoate	2-Propyl acetate	2-Pentanone
Butyl propionate	Propyl butyrate	3-Pentanone
	Propyl pentanoate	Propanal
	Propyl propionate	

Apple Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Acetaldehyde	13.0	Ethyl isovalerate	
Acids (formic, acetic, butyric*)	4.0	Ethyl methylphenylglycidate*	12.0
Aldehyde C_{10}*	5.0	Ethyl pelargonate	
Allyl butyrate		Ethyl phenylacetate	
Allyl cyclohexylvalerate		Ethyl valerate	
Allyl isovalerate		Geraniol*	21.0
Amyl acetate*	240.0	Geranium essential oil*	14.0
Amyl butyrate*	170.0	Geranyl acetate*	100.0
Amyl valerate*	570.0	Geranyl isovalerate	
Anise essential oil (anethol*)	3.0	Isopropyl isovalerate (isopropyl valerate)	
Benzaldehyde		Lemon essential oil*	24.0
Benzyl formate*	1.1	Maltol*	7.0
Benzyl isovalerate		Methyl acetate	
Butyl valerate		Methyl allyl butyrate	
Cinnamyl formate		Orange essential oil*	11.2
Cinnamyl isovalerate*	35.7	Phenethyl isobutyrate*	28.4
Citral	15.0	Rhodinol*	5.0
Citronellal*	13.0	Rose, absolute*	0.6
Citronellyl isovalerate		Styralyl acetate*	10.0
Cyclohexyl acetate		Terpenyl isovalerate	
Cyclohexyl butyrate		γ-Undecalactone*	14.0
Dimethyl benzyl carbinyl acetate*	34.0	Vanillin* (ethyl vanillin)	50.0
Ethyl acetate*	80.0	Solvent	455.0
Ethyl butyrate			
Ethyl formate		**Total**	2,000.0
Ethyl heptanoate	64.0		

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

Apricot

Apricot flavor, although varying somewhat from cultivar to cultivar, exhibits a characteristic note, *i.e.*, a very pronounced floral note with a citrus-like undernote that becomes more intense with incipient ripening. The various imitation apricot flavors have originated from an association with violet, rose, and jasmine, together with other suitable ingredients. Historically the formulation of imitation apricot flavor has evolved through the following stages:

1. Essential oils of bitter almond, orange, geranium, and cognac, vanilla, ethyl acetate, ethyl valerate, and ethyl butyrate were combined.
2. Amyl acetate, amyl valerate, and amyl butyrate were then added to the base ingredients in No. 1.
3. Coumarin was the next major ingredient to be added.
4. New formulations based on the ingredients in Nos. 1, 2, and 3 contained α-ionone, orris butter, jasmine absolute, ethyl caproate, and ethyl caprylate.
5. Finally ethyl methylphenylglycidate, γ-nonalactone, γ-undecalactone, traces of eugenol, angelica essential oil, and petitgrain bigarade were employed (all or only a few of these products in varying combinations).

Although the above combinations attained a certain degree of success, in most instances they are too complicated. The constituents of a rather simple but effective formulation include the following: amyl acetate, amyl butyrate, amyl formate, amyl valerate, benzaldehyde, cinnamaldehyde, ethyl caproate, ethyl heptylate, ethyl valerate, geraniol, α-ionone, neroli, γ-undecalactone, and vanillin.

An examination of current formulation capabilities not only confirms the usefulness of almost all the constituents employed in the evolution of the apricot aroma formulation, but it also points out the usefulness of a few products previously identified in nature and found to be extremely functional in the formulation. These include cinnamic acid, phenyl propyl alcohol, geraniol, ethyl cinnamate, citronellyl acetate, geranyl isobutyrate, geranyl butyrate, propyl butyrate, methyl isobutyrate, and butyl propionate. A few additional products, such as benzyl propionate, heptyl acetate, methyl isobutyrate, citronellyl isobutyrate, propyl cinnamate, santalyl acetate, and isoamyl phenylacetate, may also find practical use in the formulation; their natural occurrence, although very probable, has not yet been reported. New synthetic molecules have been prepared whose notes blend well with apricot aroma; among these the following are noteworthy: allyl cyclohexylvalerate, allyl cyclohexylcapronate, tetrahydrofurfuryl propionate, allyl butyrate, and allyl propionate. The use of such synthetic products is subject to government regulations by which the formulator must abide.

Studies of the composition of natural apricot aroma have not solved the problem of reconstituting the exact aroma. While the analytical results would indicate the sure presence of certain components in the aroma, these results are partially conditioned by the potential formation of artifacts. Gas chromatography, aided by other instrumental techniques, has identified about 15 of the approximately 40 components of a natural apricot aroma absorbed on activated carbon. The identified products include myrcene, limonene, *p*-cymene, *trans*-2-hexanol, acidic acid, linalool, terpinolene, geranial, 2-methylbutyric acid, α-terpineol, γ-octalactone, γ-decalactone, and γ-nonalactone. This preliminary identification may explain to some extent the floral note and citrus undernotes originally recognized in apricot aroma.

Apricot Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Allyl butyrate		Isoamyl phenylacetate*	0.1
Allyl cyclohexylcaproate*	0.2	Jasmine, absolute (benzyl acetate*)	9.5
Allyl cyclohexylvalerate		Lemon essential oil* (citral)	5.0
Allyl propionate		Methyl cinnamate	
Almond, bitter* (benzaldehyde)	11.5	Methyl isobutyrate	
Amyl acetate*	7.5	Neroli* (petitgrain bigarade sur fleurs)	18.5
Amyl butyrate*	7.5	γ-Nonalactone	
Amyl formate*	10.0	γ-Octalactone	
Amyl valerate*	15.0	Orange essential oil*	10.5
Benzyl propionate		Orris butter (α-irone)	
Ceylon cinnamon (cinnamaldehyde)	0.5	Phenethyl butyrate	
Citronellyl isobutyrate		Propyl butyrate	
γ-Decalactone		Propyl cinnamate*	0.2
γ-Dodecalactone		Rose, absolute*	3.0
Ethyl acetate*	14.5	Tetrahydrofurfuryl propionate	
Ethyl butyrate*	4.5	γ-Undecalactone	200.0
Ethyl hexanoate	10.0	Vanillin* (ethyl vanillin, propenyl guaethol, vanilla absolute)	85.0
Ethyl octanoate		Solvent	527.0
Ethyl valerate*	50.0		
Geranium (rhodinol, geraniol, *l*-citronellol, linalool,* α-terpineol)	0.5		
Heptyl acetate			
α-Ionone*	9.5	**Total**	1,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

Banana

Imitations of banana flavors have attained success for some time. Amyl and isoamyl acetate together with amyl butyrate (the presence of these components in the natural aroma was subsequently ascertained) were found to be extremely suitable in banana formulations and closely duplicated the natural aroma. The specific note of these esters is usually rounded off by the addition of a green, woody note together with a more volatile fruity note (amyl butyrate alone also exhibits a fruity note). Flavorists have attempted to further improve the aroma formulation by means of various esters, a few essential oils (mainly citrus oils), and vanillin.

A cursory examination of formulations perfected around 1920 for candy flavoring with a yield of approximately 3,000 shows that about 50% of the aroma formulations consisted of amyl acetate and amyl butyrate usually in a 2:3 ratio, while an additional 20% consisted of amyl valerate. Other esters, such as ethyl caprylate and ethyl heptanoate, were employed at lower levels; the addition of citrus oils and vanillin did not exceed a total of 10% in the formulation. The above ratios were largely increased in the absence of essential oils to the following upper limits: 44% amyl butyrate, 43% amyl acetate, 8% ethyl butyrate, 1% geranyl propionate, and 4% vanillin. Some flavorists recommended the use of approximately 10% acetaldehyde in formulations containing about 50% amyl acetate and, in addition, strong floral, rose-violet notes, coumarin, vanilla, and heliotropin (10% total).

Based on the above description, it is apparent that imitations of banana aroma were rather simple, containing only a limited number of components. In practice the basic schemes have not been abandoned altogether, although significant qualitative improvements have been introduced in the formulation subsequent to the commercial availability of esters having much higher purity.

A more recent approach to rounding off the banana aroma containing mainly amyl acetate, isoamyl acetate, and isoamyl butyrate consists of using benzyl butyrate, 2-ethylbutyl acetate, methyl heptanone, isopropyl benzyl carbinol, methyl amyl ketone, ethyl heptanoate, ethyl valerate, hexyl acetate, and cyclohexyl esters (butyrate, isovalerate, propionate). Not all of the above products have been identified in the constituents of the natural aroma; therefore, their use is conditioned by certain limitations. Butyl acetate and butyl butyrate might also be used.

Several studies of the constituents of banana aroma have been published, especially since 1950. Because the aroma of bananas from various cultivars and at varying stages of the ripening process were studied, analytical results were significantly different. Although the common constituents were always found to be present, their relative ratios in the aroma varied widely from type to type. Two banana cultivars (Gros Michel and Valery) have been the subject of extensive investigation. Approximately four–five constituents of the banana aroma remain unidentified; two are found among the low-volatile components. The following components have been identified in Gros Michel banana aroma:

Components of Gros Michel Banana Aroma

Amyl acetate	*n*-Hexyl acetate
1-Butanol	Isoamyl acetate
2-Butanol	Isoamyl alcohol
n-Butyl acetate	Isoamyl butyrate
Ethanol	Isobutyl acetate
Ethyl acetate	2-Pentanone
1-Hexanol	2-Pentyl acetate
trans-2-Hexenal	2-Pentyl butyrate
1-Hexyl acetate	1-Propanol

It is interesting to note the presence of alcohols in this aroma. Prior to their identification alcohols were never taken into consideration, although they produced interesting aromatic effects by imparting a woody, somewhat mold-like note often associated with the green note typical of several natural banana aromas.

Banana Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Acetaldehyde*	0.75	Heliotropin*	7.20
Alcohol C_6		2-Hexenal*	0.5
Amyl acetate*	300.50	Hexyl acetate	
Amyl butyrate*	206.0	Isoamyl acetate*	70.0
Amyl valerate*	18.0	Isoamyl alcohol*	0.50
Benzyl butyrate		Isoamyl butyrate*	40.0
Benzyl propionate*	6.6	Isobutyl acetate	
Butyl acetate*	1.0	Isopropyl benzyl carbinol	
Butyl butyrate		Lemon essential oil*	1.30
Cyclohexyl butyrate		Methyl amyl ketone	
Cyclohexyl isovalerate		Methyl heptenone*	1.0
Cyclohexyl propionate*	2.0	Orange essential oil*	0.30
Ethyl acetate		Rose (linalool,* rhodinol, geraniol,	
2-Ethyl butyl acetate		citronellol)	12.0
Ethyl butyrate*	30.0	Vanillin*	9.0
Ethyl capronate*	7.20	Violet flowers	
Ethyl caprylate		(or α-ionone,* α-irone,	0.25
Ethyl heptanoate		△-methyl ionone*)	2.0
Ethyl valerate		Solvent	277.9
Geranyl propionate*	6.0		
		Total	1,000.00

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

Currant

The two most characteristic notes of currant aroma, namely the red and black varieties, have been the subject of several attempts at imitation. The main effort was directed toward the imitation of black currant aroma, the type in the greatest demand throughout central European countries because of the large number of flavor applications. Very few chemically defined flavor ingredients exhibit organoleptic characteristics that blend well with currant flavor. In the case of black currant aroma, the naturally occurring methyl propionate can be employed together with linalyl propionate, whose presence in nature, although most likely, has not yet been confirmed. More generic flavor ingredients include linalyl acetate, guaiol acetate, and γ-ethylionone (the last product is synthetic). The use of diphenyl ether also may be used in the formulation.

Old formulations for non-specific imitation currant aromas (but mainly attempting to duplicate red currant aroma) were based chiefly on the use of citrus essential oils. Of the 100 parts of the aroma formulation, approximately 45 parts consisted of lemon essential oil complemented by 5–6 parts of sweet orange essential oil. Amyl acetate, amyl butyrate, amyl formate, and ethyl acetate rounded off by orris, rose, and vanilla notes were also employed; recent aroma imitations still retain most of these products. New formulations also contain the constituents of rose—namely citronellol, ethyl benzoate, ethyl butyrate, ethyl heptanoate, α-ionone, sometimes menthol of mint essential oil, petitgrain bigarade or neroli, rum ether, and strawberry complex aromas.

Grape

The preparation of a reconstructed grape flavor is an extremely difficult task because of the great variety of grape species, each having its own characteristic note. The flavor also can vary significantly within each species, depending on whether the whole fruit (including the peel) or only the pulp is utilized. The flavor of grape juice tends to change quickly (apart from fermentation) and, if not properly inhibited, produce off-flavors. With these factors in mind, it is apparent that there are only limited

formulation possibilities, in light of present knowledge, for the reconstruction of specific grape flavors. Nonetheless, imitation grape flavors or grape juice fortified with approximately 50–100 ppm of complementary flavor ingredients is extremely important to the beverage industry.

Currant Flavors

Ingredient	Parts by weight		Ingredient	Parts by weight	
	Red currant	Black currant		Red currant	Black currant
Amyl acetate*	430.0	184.0	Lemon essential oil*	40.0	44.6
Amyl butyrate	4.0	96.0	Linalyl propionate		
Amyl formate	2.0		γ-Methylionone		
Benzyl acetate*		2.8	Methylphenylglycidate*		3.2
Ceylon cinnamon essential oil* (cinnamaldehyde)		1.0	Methyl propionate*		125.0
			Methyl salicylate*	6.0	
Chinese cinnamon essential oil* (cassia)		40.0	Mint essential oil* (menthol)		20.0
			Neroli essential oil (petitgrain bigarade sur fleurs)		22.0
Cognac essential oil* (ethyl heptanoate)	44.0		Orange essential oil		64.0
Ethyl acetate*	64.0	64.0	Orris resinoid*	16.0	
Ethyl benzoate*		40.0	Rose, absolute (citronellol*)	1.0	
Ethyl butyrate*	146.0	120.0	Rum ether*	690.0	
Guaiol acetate			Vanillin*	162.0	40.0
α-Ionone*	17.0		Solvent (alcohol)	378.0	1,051.0
β-Ionone*		2.4			
Isobutyl acetate		80.0	**Total**	2,000.0	2,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

Among the various types of grape aromas, the muscatel is considered the most characteristic and functional for various flavor applications. Muscatel aroma is in fact recurrent also in muscat wines. The characteristic flavor is imitated in sparkling wine-based beverage formulations (*spume*) typical of the Italian market by means of infusions of coriander seeds, violet flowers, clary sage flowering tops, and elder flowers. Imitations of muscat grape aroma can be obtained also by the use of essential oils.

Volatile Constituents of *Vitis vinifera* Aroma

Hydrocarbons
- Cyclohexane
- *p*-Ethyl toluene
- Hexane
- *n*-Propyl benzene
- Toluene
- *o*-Xylene
- *p*-Xylene

Alcohols
- 2-Heptanol
- 1-Hexanol
- *trans*-2-Hexen-1-ol
- *trans*-3-Hexen-1-ol or *cis*-3-hexen-1-ol
- 2-Methyl-1-butanol
- 3-Methyl-1-butanol

Esters
- *n*-Amyl acetate
- Butyl phthalate
- Ethyl acetate
- Ethyl butyrate
- Ethyl propionate

Aldehydes and Acetates
- 1,1-Diethoxyethane
- Hexanal
- *cis*-2-Hexanal or *trans*-2-hexanal
- 2-Methylbutanal
- 2,4,5-Trimethyl-1,3-dioxolane

Ketones
- Acetone
- 2-Heptanone
- 3-Heptanone
- 2-Pentanone

In addition to the essential oils of coriander and clary sage, which form the main body of the formulation, the essential oils of rose, cognac, celery, and orange, together with vanilla absolute are employed to introduce complementary notes. Whenever an ethereal note is desired, the following naturally occurring ingredients are commonly used: amyl acetate, ethyl butyrate, and ethyl isobutyrate. Additional products used for the same purpose but not yet identified in nature include cinnamyl anthranilate, phenyl *p*-tolyl ether, decyl formate, allyl salicylate, and isovalerophenone.

A few grape flavor formulations are based on the use of methyl anthranilate, ethyl capronate, benzyl propionate, benzylideneacetone or dimethyl anthranilate, ethyl acetate, ethyl anthranilate, methyl naphthyl ketone, rum ether, cinnamyl alcohol, so-called aldehydes C_{16} and C_{14}, ethyl heptanoate, α-ionone, and terpeneless lemon or lime essential oil. Isobutyl anthranilate blends well with the American Concord grape aroma (*Vitis labrusca* L.).

A typical grape flavor formulation carrying the Concord variety note (methyl anthranilate) and suitable for hard candies, confections, baked goods, and soft beverages includes the following ingredients:

Grape Flavor Formulation

Ingredient	Parts	Ingredient	Parts
Amyl isovalerate	8	Ethyl oenanthate	8
Cinnamyl alcohol	5	Ethyl pelargonate	3
Cinnamyl isovalerate	3	Hydroxycitronellal	1
Cinnamyl propionate	3	Methyl anthranilate	132
Citral	1	Methyl salicylate	12
Ethyl acetate	62	Paraguay petitgrain	1
Ethyl benzoate	3	Terpinyl acetate	10
Ethyl butyrate	15	Tolylaldehyde	3
Ethyl caproate	3	Solvent	718
Ethyl methylphenylglycidate	9		
		Total	1,000

Peach

Peach aromas vary widely depending on their cultivar. The various aromas, however, can be reduced to a single basic type; various formulations of imitation aromas are discussed below.

Originally the formulation called for use of the following constituents in suitable ratios: the essential oils of bay, bitter almond, cinnamon, clove, coriander, neroli, and sweet and bitter orange, with ethyl and methyl cinnamate when intended primarily for flavoring liqueurs rather than candy or pastry. The peach aroma imitation commonly offered for a long period for flavoring candy and pastry was a simple mixture consisting of aldehyde C_{14} (γ-undecalactone) and small amounts of amyl acetate and ethyl butyrate. An aroma formulation midway between the above compositions consisted of the following ingredients: aldehyde C_{14}, amyl acetate, amyl butyrate, amyl valerate, ethyl acetate, ethyl caprylate, ethyl cinnamate, ethyl heptanoate, ethyl nitrate, ethyl phenylacetate, ethyl vanillin, and the essential oils of Ceylon cinnamon, clary sage, lemon, pimenta, and sweet orange.

A step forward in peach aroma imitations was represented by the following formulation: aldehyde C_{14}, amyl acetate, amyl butyrate, amyl formate, ethyl capronate, ethyl valerate, vanillin, the essential oils of bitter almond, cinnamon, geranium, neroli, and valerian, and subsequently a small percentage of aldehyde C_{18} (more correctly defined as γ-nonalactone).

Considering that the flavorist had at his disposal few raw materials together with his organoleptic capability for evaluation (only a few studies of the constitution of natural peach aroma had been carried out), it is understandable that early flavorists could not attain a peach aroma beyond a certain quality. Formulations hinged chiefly on flavorists' ability of flowering, spicing, fruitening, and sweetening the fundamental benzaldehyde note, almost the only constituent positively identified in the natural peach aroma complex. This was achieved by using products not entirely compatible with the aroma formulation, such as ethyl and methyl cinnamate (exhibiting a honey or fruital raspberry-like note) or the

newly available aldehyde C_{14}, which modified a slight ester note. Independent of the closeness of the imitation to the natural aroma, the following observations can be made by examining a list of constituents selected for various specific formulations: (1) citrus notes were largely used in formulations destined for flavoring liqueurs, and (2) the amount of volatile esters employed decreased for those formulations used in baked goods. The use of a lactone, together with a trace amount of esters, yielded functional formulations exhibiting the required chemical-physical compatibility between the various constituents of the aroma as well as between the aroma and food substrate. Among the flavor ingredients mentioned thus far, only γ-undecalactone, in addition to the fundamental benzaldehyde note, blends well with peach aroma. The other ingredients impart only secondary notes, especially when harmoniously modified by the addition of essential oils or even vanillin.

Products having notes similar to peach and considered suitable for blending in formulations include those identified as constitutents of natural peach aromas: methyl methylanthranilate, terpineol, octyl acetate, phenethyl alcohol, butyl propionate, anisyl butyrate, and *l*-citronellol. Others, most likely occurring in the natural products but not as yet identified, include propyl cinnamate, phenylethyl cinnamate, amyl phenylacetate, benzyl propionate, and phenyl salicylate. Several synthetics of value include allyl cyclohexylcapronate, allyl cyclohexylvalerate, methyl octyl carbonate, and phenyl allyl alcohol. All of the above products may be useful in the formulation of peach aroma imitations for liqueurs or pastry flavoring.

Recent gas chromatographic studies (conducted with the help of other instrumental techniques) of the aroma of Red Globe peaches indicate that while various peach aromas exhibit the same components, the relative ratios vary widely with different types. These studies give information on those constituents listed below in order of increasing retention time: acetaldehyde, methyl acetate, ethyl

Peach Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Acetaldehyde		Ethyl phenylacetate	
Allyl cyclohexylcaproate		Ethyl valerate*	226.0
Allyl cyclohexylvalerate		Geranium essential oil (linalool*)	0.5
Amyl acetate*	140.0	γ-Heptalactone	
Amyl butyrate*	40.0	γ-Hexalactone	
Amyl formate*	82.0	Hexyl formate	
Amyl phenylacetate		α-Ionone*	10.0
Amyl valerate*	75.0	Lemon essential oil* (citral)	5.0
Anise essential oil (anethol)		Mandarin essential oil*	300.0
Anisyl butyrate		Methyl cinnamate	
Bay essential oil		Methyl methylanthranilate	
Benzaldehyde*	30.0	Methyl octine carbonate	
Benzyl acetate*	9.5	Neroli essential oil (petitgrain bigarade sur fleurs*)	136.0
Benzyl propionate		γ-Nonalactone	
Bitter almond essential oil*	30.0	γ-Octalactone	
Cinnamon essential oil (cinnamaldehyde*)	2.0	Octyl acetate	
Cognac essential oil (ethyl heptanoate)		Orange, bitter, essential oil*	
Coriander essential oil		Orange, sweet, essential oil*	310.0
γ-Decalactone		Phenethyl cinnamate	
Ethyl acetate*	16.0	Rose, absolute* (*l*-citronellol, phenethyl alcohol)	13.0
Ethyl butyrate*	4.5	Rum ether*	40.0
Ethyl capronate*	86.0	Terpineol (geraniol)	1.5
Ethyl caprylate		γ-Undecalactone*	900.0
Ethyl cinnamate		Vanillin* (ethyl vanillin)	440.0
Ethyl methylphenylglycidate		Solvent	1,103.0
Ethyl nitrate		**Total**	4,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

acetate, ethyl alcohol, hexyl formate, hexyl acetate, *trans*-2-hexen-1-ol, benzaldehyde, isovaleric acid, ethyl benzoate, γ-hexalactone, benzyl acetate, γ-heptalactone, caproic acid, benzyl alcohol, γ-octalactone, γ-nonalactone, hexyl benzoate, γ-decalactone, α-pirone, and Δ-decalactone. The following comments can be made on examination of the gas chromatogram:

1. Nature has combined benzaldehyde with a low volatility nucleus consisting of γ-lactones (hexa- to deca- lactones).
2. Contemporarily, the presence of highly volatile components (*e.g.*, esters having an aroma outside the peach note) increases the total volatility of the peach aroma.
3. The presence of acids modifies the flavor of peach aroma.
4. The presence of a few aromatic compounds, such as benzoates, benzyl esters, and benzyl alcohol, is responsible for the floral fragrance of the natural aroma.

Pear

With a good quality amyl acetate, the formulation of an imitation pear aroma would appear to be a simple task. Amyl acetate is commercially available under the trade names "pear oil" and "banana oil." However, to obtain flavor results of real interest, more complex formulations are necessary. The problem is further complicated by the large number of pear aromas that vary widely, depending on the cultivar; for example, the characteristic aroma of Williams pears is used to prepare an excellent liqueur by direct fermentation and distillation. The large water content of the fruit yields an aromatic sensation so specific that even the transfer of a well formulated pear aroma from one food substrate to another causes a much greater negative shift in organoleptic sensations as compared to other imitation aromas.

In early formulations the amyl acetate note was rounded off by the addition of essential oils. Specifically, lemon and bergamot essential oils were blended into an imitation pear flavor consisting of more than 90% by weight of amyl acetate; vanillin, rose absolute, and sometimes a trace of raspberry aroma were also added to better balance the resulting formulation. A few esters—geranyl propionate, amyl valerate, ethyl acetate, and ethyl butyrate—were added for special effects. Some formulations also call for the use of aldehyde C_{14} (γ-undecalactone).

Today pear aroma imitations are still based on traditional schemes, together with the following useful, naturally occurring products: hexyl acetate, propyl acetate, methylheptanone, ethyl heptylate, and hexanoic, octanoic, and decanoic acid ethyl esters. Benzyl butyrate and hexyl phenyl carbonate (probably present but not yet identified in natural pear) may be of interest in the aroma formulation, together with 2-ethylbutyl acetate, a synthetic product not found in nature.

Components of Natural Pear Aroma

Amyl acetate	Hexanol
n-Butyl acetate	*cis*-Hexenyl acetate
Butyl alcohol	Hexyl acetate
Butyl *trans*-2-*cis*-6-dodecadienoate	Methyl acetate
trans-2-*trans*-4-Decadienoate	Methyl *cis*-2-*trans*-4-decadienoate
Ethyl acetate	Methyl *trans*-2-*cis*-4-decadienoate
Ethyl alcohol	Methyl decanoate
Ethyl *trans*-2-*trans*-4-decadienoate	Methyl *cis*-4-decanoate
Ethyl decanoate	Methyl 3-hydroxyoctanoate
Ethyl *cis*-4-decanoate	Methyl *trans*-2-octenoate
Ethyl *trans*-2-decenoate	Methyl *cis*-8-tetradecenoate
Ethyl dodecanoate	*n*-Octanol
Ethyl *trans*-2-dodecenoate	Octyl acetate
Ethyl *cis*-6-dodecenoate	Pentanol
Ethyl 4-hydroxy-*trans*-butenoate	Propyl acetate
Ethyl 3-hydroxyoctanoate	Propyl alcohol
Ethyl octanoate	Propyl *trans*-2-*trans*-4-decadienoate
Ethyl tetradecenoate	Terpene, unsaturated
Ethyl *cis*-8-tetradecenoate	
Heptyl acetate	

Studies of identification of the constituents of natural pear aroma are very recent. In the past ten years these studies have been concerned almost exclusively with Bartlett, Williams, and Winter pear cultivars. Components that have been identified are shown in the preceding table (p. 662).

Pear Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Amyl acetate	1,340.0	α-Ionone (1% solution in alcohol*)	1.0
Amyl valerate	130.0	Isoamyl acetate	
Benzyl acetate (10% solution in alcohol)	25.0	Isoamyl valerate	
		Lemon essential oil* (citral)	3.0
Benzyl butyrate		Methyl acetate	
Bergamot essential oil		Methyl heptenone	
n-Butyl acetate		Orris butter (orris resinoid, 1% solution in alcohol*)	5.0
Ethyl acetate*	80.0		
Ethyl butyrate*	13.0	Propyl acetate	
Ethyl decanoate*	2.0	Rose, absolute (citronellol, 1% solution in alcohol*)	1.0
Ethyl heptylate*	2.0		
Ethyl hexylate*	1.0	γ-Undecalactone	
Ethyl octanoate*	2.0	Vanillin	5.0
Geranyl propionate*	100.0	Solvent	288.0
Hexyl acetate*	2.0		
		Total	2,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

Pineapple

The exotic sour pineapple aroma (whose main components have been identified) found some acceptance in the past by flavorists in Europe, although consumer acceptance remained somewhat limited for quite a long time. The original aroma imitations were all based on the use of amyl and ethyl butyrate (more than 50% of the total formulation) together with traces of terpeneless lemon essential oil (sometimes citral) and approximately 2% by weight of vanillin. Subsequently, although amyl and ethyl butyrate were retained as basic raw materials, the aroma formulations became more complex. Butyric acid, amyl acetate, ethyl acetate, acetaldehyde, allyl capronate, allyl caprylate, ethyl caprylate, and orange and angelica essential oils found use in the aroma formulations.

Following the introduction of allyl cyclohexylpropionate, allyl phenoxyacetate, and other synthetic products, formulators further developed the aroma formulations. The following represented a typical aroma composition:

Ingredient	Per cent
Ethyl butyrate	18%
Ethyl isovalerate	18%
Allyl heptylate	14%
Butyl acetate	10%
Allyl capronate	10%
Ethyl propionate	8%
Allyl cyclohexylpropionate	6%
Ethyl heptanoate	6%
Amyl acetate	2%
Allyl phenoxyacetate	1%
Orange essential oil	
Lemon essential oil	
Vanillin traces	

The above formulation together with the addition of naturally occurring products, such as ethyl

Components of Pineapple Aroma

Acetaldehyde	Formaldehyde
Acetic acid	Furfural
Acetone	5-Hydroxy-2-methyl furfural
p-Allyl phenol	Isobutanol
Amyl *n*-capronate	Methanol
γ-Caprolactone	Methyl acetate
Diacetyl	Methyl *n*-butyrate
2,5-Dimethyl 4-hydroxy-3-(2H)-furanone	Methyl *n*-capronate
Ethanol	Methyl *n*-caprylate
Ethyl acetate	Methyl isocapronate
Ethyl acrylate	Methyl isovalerate
Ethyl *n*-butyrate	Methyl β-methylthiopropionate
Ethyl *n*-capronate	Methyl *n*-propyl ketone
Ethyl *n*-caprylate	Methyl *n*-valerate
Ethyl isovalerate	*n*-Pentanol
Ethyl lactate	*n*-Propanol
Ethyl β-methylthiopropionate	

Pineapple Flavor

Ingredient	Parts by weight	Ingredients	Parts by weight
Acetaldehyde		Ethyl butyrate*	45.0
Acetic acid		Ethyl capronate	
Allyl capronate*	21.4	Ethyl *n*-caprylate	
Allyl caprylate		Ethyl heptanoate	12.7
Allyl cyclohexylacetate		Ethyl hexandienoate	
Allyl cyclohexylbutyrate		Ethyl isovalerate*	36.0
Allyl cyclohexylpropionate*	16.4	Ethyl lactate	
Allyl heptylate		Ethyl propionate	16.0
Allyl-2-nonylenate		Formaldehyde	
p-Allyl phenol		Hexyl butyrate	
Allyl phenoxyacetate*	2.0	Isoamyl isobutyrate	
Allyl undecylenate		Lemon essential oil (citral*)	0.6
Amyl acetate*	28.6	Methyl acetate	
Amyl butyrate*	112.0	Methyl allyl caproate*	2.5
Amyl *n*-caprylate		Methyl butyrate	
Angelica essential oil		Methyl *n*-caproate	
Bornyl acetate*	0.1	Methyl *n*-caprylate*	1.0
Butyl acetate*	105.0	Methyl isocapronate	
Butyl isobutyrate		Methyl isovalerate	
Butyric acid*	8.0	Methyl-β-methylthiopropionate*	2.0
Cinnamyl acetate*	0.3	Methyl propyl ketone	
Citronellyl butyrate*	4.0	Methyl undecylenate	
Cognac essential oil* (ethyl heptanoate)	0.3	Methyl valerate	
		Orange essential oil*	22.5
Decyl acetate		Propyl isobutyrate	
Diethyl sebacate*	20.0	Vanillin*	5.6
Ethyl acetate*	376.0	Solvent	162.0
Ethyl acrylate			
		Total	1,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

isovalerate and ethyl butyrate (main constituents of natural pineapple aroma), is of definite current interest (with the exception of allyl cyclohexylpropionate and ethyl phenoxyacetate).

The examination of a number of products identified in nature or prepared synthetically provides an additional list of flavor ingredients whose aroma is of interest in the formulation of pineapple flavors:

A. **Naturals**—Decyl acetate, butyl isobutyrate, methyl allyl capronate, cinnamyl acetate, *n*-butyl acetate, hexyl butyrate, propyl isobutyrate, methyl *β*-methylthiopropionate, and bornyl acetate.

B. **Synthetics**—Allyl cyclohexylacetate, allyl cyclohexylbutyrate, 2-allyl nonylenate, ethyl hexandienoate, methyl undecylenate, allyl undecylenate, and isoamyl isobutyrate.

Consultation with official regulatory lists on the use of the above products is highly recommended.

Since the original study of the composition of pineapple aroma by Haagen-Smit and collaborators in 1945, extensive knowledge of the components of the aroma has been acquired. An updated list of components positively identified in pineapple aroma appears on page 664.

Plum

Old formulations for imitation plum aroma duplicated the complex fragrance of the various plum types by a simple and unique association of 4 parts of amyl acetate, 1 part benzaldehyde, 1.33 parts ethyl heptanoate, 0.25 part vanillin, and a light trace note of orris butter. The resulting aroma imitation had a harsh flavor that would no longer find acceptance by the consumer who today is educated to extremely well formulated bouquets closely reminiscent of the various types of natural plum aromas, such as Mirabelle, Reine Claude (yellow plum), and blue plum. All of the original raw materials find application in today's formulations; only their relative ratios in the formulation have changed. Many

Plum Flavors

Ingredient	Parts by weight			Ingredient	Parts by weight		
	Yellow plum	Blue plum	Common plum		Yellow plum	Blue plum	Common plum
Amyl acetate	52.0	55.0	—	Mandarin essential oil*	40.0	10.0	
Amyl butyrate*	38.0	—	20.0	Neroli essential oil* (petitgrain bigarade sur fleurs)		1.0	
Bitter almond essential oil* (benzaldehyde)	62.0	290.0	175.0	γ-Nonalactone	2.0	32.0	5.0
Butyl formate*	5.0	5.0	10.0	Orange essential oil	20.5		15.0
Butyric acid*	10.0	—	—	Orris butter (orris resinoid)			
Citronellol	1.0	1.0	1.0	Phenethyl alcohol*		8.0	
Citronellyl butyrate				Phenethyl butyrate			
Citronellyl formate*	15.0	5.0		Phenethyl formate			
Ethyl butyrate (ethyl acetate)	200.0	2.0	50.0	2-Phenyl-1-propyl butyrate*	20.0	200.0	100.0
Ethyl heptanoate* (cognac essential oil)	3.5			Propyl formate*	8.0		
Ethyl pelargonate	22.0			Rose, absolute		1.0	
Ethyl valerate*	29.0		15.0	Rum ether*	36.0	28.0	—
Heptyl butyrate				Terpenyl butyrate*		5.0	
Isoamyl formate*	6.0			γ-Undecalactone	1.0	4.0	3.0
Isoamyl propionate*			10.0	Vanillin*	44.0	2.0	10.0
Lemon essential oil* (citral)		15.0		Solvent	385.0	336.0	586.0
Linalool				Total	1,000.0	1,000.0	1,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

additional products also are used to impart characteristic notes. Mirabelle plum aroma, for instance, is formulated by adding rose, orange, and peach notes to the basic ingredients. The Reine Claude plum aroma has a characteristic wine-like note enhanced by adding ethyl butyrate, ethyl acetate, and some other esters. Coumarin derivatives, mandarin oil, and a few other ingredients play an important role in imparting the sweet, raisin-like background note characteristic of the aroma of dried plums.

In addition to the above products, several other naturally occurring constituents may find use in the formulation of various plum aroma formulations. These include isoamyl formate, isoamyl propionate, butyl formate, propyl formate, linalool, citronellyl butyrate, citronellyl formate, and phenethyl *n*-butyrate. Also used are constituents probably occurring in natural products but not yet identified, such as terpenyl butyrate, isopropyl propionate, phenethyl butyrate, neryl propionate, phenylpropyl butyrate, heptyl butyrate, and methyl allyl butyrate. The last product exhibits an aromatic note that blends very well with plum aroma.

Raspberry

The significant aroma difference existing between cultivated and wild raspberry has spurred the flavorists' efforts. At the onset, however, very few useful products were at the disposal of formulators to achieve satisfactory results. Among the available constituents orris butter represented an ideal base especially associated with rose and jasmine notes. However, the use of these, together with large amounts of amyl acetate and amyl butyrate in the presence of a little vanillin, was insufficient to produce aroma imitations similar to the valuable natural aroma. The use of ethyl methylphenylglycidate and α-ionone brought a decisive contribution to raspberry aroma formulations. These guidelines remain valid today.

By careful dosing of the ester content in the formulation and by working around the basic ionone note, it is possible to obtain satisfactory aroma results using the following ingredients in the proper ratios: orris butter, orris resinoid, α- and β-ionone, jasmine absolute, vanillin, aldehyde C_{14}, anethol, celery essential oil, aldehyde C_{16}, citral, methyl sulfide, maltol, dimethyl anthranilate, diethyl succinate, ethyl valerate, ethyl acetate, benzyl salicylate, isobutyl cinnamate, terpenyl acetate, and methyl β-naphthyl ketone.

The following table of naturally occurring components has been prepared by examining several studies of the constitution of natural raspberry aroma. It is interesting to note that current studies are now always in agreement with the presence of certain *esters*.

Components of Natural Raspberry Aroma

Acids	Carbonyl Compounds *(continued)*	Alcohols *(continued)*
Acetic	2-Hexenal	1-Pentanol
Butyric	*cis*-3-Hexenal	1-Penten-3-ol
Caproic	4-(*p*-Hydroxyphenyl)-2-butanone (raspberry ketone)	
Caprylic	α-Ionone	Esters
Formic	β-Ionone	Butyl acetate
2-Hexenoic	2-Pentanone	Ethyl acetate
3-Hexenoic	2-Pentenal	Ethyl butyrate
Isobutyric	Propanal	Ethyl crotonate
Isovaleric		Ethyl propionate
Propionic	Alcohols	2-Hexenyl acetate
Valeric	1-Butanol	2-Hexenyl butyrate
	trans-2-Buten-1-ol	Hexyl acetate
Carbonyl Compounds	Ethanol	Hexyl butyrate
Acetaldehyde	Geraniol	Isoamyl acetate
Acetone	1-Hexanol	Isopropyl butyrate
Acetyl methyl carbinol	*cis*-3-Hexen-1-ol	Methyl butyrate
Acrolein	Methanol	Methyl caproate
Diacetyl	3-Methyl-3-buten-1-ol	Methyl caprylate
β,β-Dimethylacrolein		Propyl acetate
Hexanal		

In the preceeding table note the following:

1. 4-(*p*-Hydroxyphenyl)-2-butanone exhibits the characteristic raspberry taste and odor.
2. The ratio of 2-hexenyl acetate, acetone, acetaldehyde, and the ethyl acetate esters are considered most important toward the aroma formulation.

Raspberry Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Acetic aldehyde		Hexyl butyrate	
Acetone		4-(*p*-Hydroxyphenyl-2-butanone)	16.0
Acids (formic, acetic, butyric, valeric)		α-Ionone* (β-ionone)	210.0
		Isobutyl cinnamate	
Amyl acetate*	500.0	Jasmine, absolute (10% solution in ethanol*)	7.0
Amyl butyrate*	15.0		
Anethol*	0.5	Lemon essential oil (citral*)	13.0
Benzyl salicylate		Maltol*	3.0
Diacetyl (acetyl methyl carbinol)		Methyl butyrate	
Dimethyl anthranilate*	1.0	Methyl capronate	
Ethyl acetate*	60.0	Methyl disulfide*	1.0
Ethyl butyrate*	74.0	Methyl *p*-naphthyl ketone	
Ethyl methylphenylglycidate*	20.0	Orris butter (orris resinoid,* α-irone)	60.5
Ethyl succinate			
Ethyl valerate		Rose, absolute* (rhodinol)	10.0
Geraniol*	13.0	Terpenyl acetate	
Hexanal		γ-Undecalactone*	10.0
cis-3-Hexen-1-ol		Vanilla* (ethyl vanillin)	86.0
2-Hexenyl acetate		Solvent	900.0
2-Hexenyl butyrate			
		Total	2,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

Sour Cherry

Morello sour-cherry aroma differs widely from marasca sour cherry. The aroma of morello cherries is largely imitated for use in pastry and beverages; concentrated morello cherry juice often is used in syrups, beverages, and other food products. The aroma of marasca cherries is not imitated, since the fruit distillate is preferred for flavoring liqueurs because of the particular fragrance.

Sour-cherry aroma imitations are based primarily on the use of benzaldehyde and bitter-almond essential oil, together with a few complementary flavor ingredients responsible for "fruitening" and sweetening the note of the aroma formulations. The choice and the per cent ratio of these complementary flavor ingredients are conditioned by the end-use of the aroma. Candy aromas may contain a high level and number of esters; the use of a few essential oils is recommended in the formulation of aromas for non-alcoholic beverages. For example, with benzaldehyde representing from 20–35% by weight of the aroma formulation, ethyl acetate is frequently employed in an approximately identical weight ratio. Additional esters commonly used include amyl acetate, amyl valerate, anisyl acetate, ethyl benzoate, and ethyl butyrate. Vanillin also is added in fairly large amounts (2–5%) together with a trace of heliotropin. Cinnamaldehyde, eugenol, rhodinol, citronellol, ethyl heptanoate, and α- or β-ionone also exhibit interesting notes and may be replaced (if necessary) by cinnamon, clove, and cognac essential oils, rose absolute, and orris butter. Some aroma formulations employ the essential oils of mace, coriander, and lemon, while the presence of γ-undecalactone has been reported in other cases. A few synthetic products not found in nature also exhibit cherry-like aromas highly suitable

Sour Cherry Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Allyl isovalerate*		Heliotropin	
Amyl acetate*	103.0	α-Ionone*	4.0
Amyl butyrate*	1.0	β-Ionone	
Amyl valerate		Jasmine, absolute* (benzyl acetate)	1.0
Anisyl acetate		Lemon essential oil* (citral)	10.0
Bitter almond* (benzaldehyde)	380.0	Mace essential oil	
Ceylon cinnamon essential oil* (cinnamaldehyde)	1.6	Neroli essential oil* (petitgrain bigarade sur fleurs)	1.8
Clove bud essential oil* (eugenol)	0.8	Orange essential oil*	6.0
Cognac oil*		Orris butter (α-irone)	2.4
Coriander essential oil	0.5	Orris resinoid*	16.4
Cyclohexyl cinnamate		Rose*	1.4
Cyclohexyl formate		Rum ether*	90.0
Ethyl acetate*	38.5	*o,m,p*-Toluic aldehyde	10.0
Ethyl benzoate		γ-Undecalactone	
Ethyl butyrate*	6.8	Vanillin*	55.0
Ethyl heptanoate	7.4	Solvent	259.8
Geranium essential oil (rhodinol, citronellol*)	2.6	**Total**	1,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

for blending with sour-cherry imitations; these are cyclohexyl cinnamate, cyclohexyl formate, *o*-, *m*-, and *p*-toluic aldehydes, and the less important allyl isovalerate. No significant studies of the identification of the natural constituents of sour-cherry aroma (morello or marasca) have been reported.

Strawberry

Millions of tons of strawberry aromas have been consumed by the candy and beverage industries. This large consumption has prompted the flavor industry to find the best solution to the vital problem of imparting a strawberry flavor to food products where it is impossible to use the fruit derivatives directly.

Originally, classic imitations of strawberry aroma consisted of the following cor pounds:

Ingredient	Parts
Amyl acetate	12.5
Amyl valerate	3.5
Bulgarian rose (or imitation)	2
Ethyl acetate	15
Ethyl butyrate	2
Ethyl nitrate	4
Methyl benzoate	1
Methyl cinnamate	0.5
Phenethyl alcohol	5
Yara yara (20% solution in benzyl benzoate)	3.5

Following the discovery of ethyl methylphenylglycidate (so-called aldehyde C_{16}, a product not found in nature), the flavor industry made commercially available literally hundreds of strawberry aromas. In addition to the above products, the following flavoring ingredients in varying ratios are employed: amyl butyrate, butyric acid, ethyl cinnamate, ethyl heptanoate, ethyl propionate, heliotropin, α-ionone, isobutyl butyrate, lemon and mint essential oils, methyl salicylate, neroli, orris butter, orris resinoid, raspberry base, rum ether, and vanillin.

When maltol (a product identified in 1964 in natural strawberry aroma) was synthesized and became commercially available, the aroma formulations acquired a different physiognomy. The large portions of aliphatic esters previously used were replaced by more complex products resulting in formulations with much higher yields. Formulations that became available consisted of the following:

A. Acetic acid, anethol, benzyl acetate, diacetyl, ethyl methylphenylglycidate, β-ionone, maltol, methyl anthranilate, methyl cinnamate, methyl heptine carbonate, methyl salicylate, γ-undecalactone, and vanillin.

B. Cinnamyl isobutyrate, cinnamyl isovalerate, diacetyl, dipropyl ketone, ethyl heptanoate, ethyl lactate, ethyl methylphenylglycidate, ethyl valerate, ethyl vanillin, maltol, methyl amyl ketone, and γ-undecalactone.

These aroma formulations also contain products not found in nature. Other flavoring ingredients might eventually find use in the above compositions, such as cumic alcohol (cuminol) and anisyl formate (among the naturals); isobutyl anthranilate, benzyl isobutyrate, neryl isobutyrate (probably occurring in nature but not as yet identified); and methyl naphthyl ketone, 4-methyl acetophenone, and ethyl 3-phenylglycidate (among the synthetics).

The economic importance of aroma has compelled the research chemist to know more about the flavor components present in the natural product. The following table of naturally occurring components in strawberry aroma is based on the results of such investigations. (Although the table has been prepared from carefully checked bibliographic references, it lends itself to some doubts because of disagreements among the various investigators concerning the presence of certain components. However, this may be explained by taking into account the different strawberry cultivars studied and the use of various analytical techniques for separating the natural aroma components.)

Naturally Occurring Components of Strawberry Aroma

Alcohols
- Benzyl alcohol
- 1-Borneol*
- Butanol*
- 2-Butanol
- Ethanol*
- 2-Heptanol*
- Hexanol*
- *trans*-2-Hexenol*
- *p*-Hydroxyphenyl-2-ethanol
- Isoamyl alcohol
- Isobutanol
- Isofenchyl alcohol
- Methanol*
- 1-Pentanol
- Penten-1-3-ol*
- Phenyl-2-ethanol
- *n*-Propanol
- *d-l*-α-Terpineol
- *cis*-Terpineol hydrate

Carbonyl Compounds
- Acetaldehyde
- Acetophenone
- Acetone

Carbonyl Compounds *(continued)*
- Acrolein
- *n*-Butanal
- Crotonal
- Diacetyl
- 2-Heptanone
- *cis*-3-Hexal
- Hexanal
- 2-Hexenal
- Methyl-3-butanone
- 2-Pentanone
- 2-Pentenal
- Propanal

Esters
- Butyl acetate
- Ethyl acetate
- Ethyl acetoacetate
- Ethyl benzoate
- Ethyl butyrate
- Ethyl capronate
- Ethyl cinnamate
- Ethyl crotonate
- Ethyl formate

Esters *(continued)*
- Ethyl isobutyrate
- Ethyl isovalerate
- Ethyl α-methylbutyrate
- Ethyl propionate
- Ethyl salicylate
- Ethyl valerate
- *trans*-2-Hexenyl
- *trans*-2-Hexenyl acetate
- Hexyl acetate
- Hexyl butyrate
- Isoamyl acetate
- Isopropyl butyrate
- Methyl acetate
- Methyl butyrate
- Methyl capronate
- Methyl isobutyrate
- Methyl α-methylbutyrate
- Propyl acetate

Free Acids
- Acetic
- Benzoic
- Butyric
- Caproic

Free Acids *(continued)*
- Cinnamic
- Formic
- Isobutyric
- Isovaleric
- α-Methylbutyric
- Propionic
- Salicylic
- Succinic*
- *n*-Valeric

Others
- Acetals
- Acetoin
- γ-Decalactone
- 1,1-Diethoxyethane
- 1,1-Dimethoxyethane
- Dimethoxymethane
- Dimethyl sulfide
- 1-Ethoxy-1-propoxyethane
- Hydrogen sulfide
- Maltol
- 1-Methoxy-1-ethoxyethane
- Methyl sulfide

* Asterisked alcohols are definitely present.

The following comments apply to the preceding table:

1. Based on more recent discussions, the number of alcohols found in the references should, in practice, be smaller. Those alcohols marked with an asterisk (*) are definitely present.
2. Several esters evidenced by gas chromatographic analysis have not as yet been identified.
3. The characteristic strawberry aroma is probably caused by carbonyl compounds, esters, and a few other products rather than the alcohols.

Studies of a complete identification of the strawberry aroma constituents continue, together with the search for an improved reconstruction of the aroma based on the increasing analytical information.

Strawberry Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Amyl acetate*	34.0	α-Ionone (β-ionone*)	6.5
Amyl butyrate*	15.0	Isobutyl anthranilate	
Amyl valerate*	15.0	Isobutyl butyrate	
Anethol*	1.5	Lemon essential oil* (citral)	1.0
Anisyl formate		Maltol*	70.0
Benzyl acetate* (jasmine absolute)	85.0	4-Methylacetophenone	
Benzyl isobutyrate		Methyl anthranilate*	6.5
Butyric acid (acetic acid*)	15.0	Methyl benzoate	
Cinnamyl isobutyrate*	7.0	Methyl cinnamate*	35.5
Cinnamyl valerate*	9.5	Methyl heptine carbonate*	0.5
Cognac essential oil* (oenanthic ether)	1.5	Methyl naphthyl ketone	
Diacetyl*	10.0	Methyl salicylate*	6.5
Dipropyl ketone		Mint essential oil (menthol)	
Ethyl acetate*	50.0	Neroli essential oil* (petitgrain	
Ethyl amyl ketone	15.0	bigarade sur fleurs)	0.5
Ethyl butyrate*	30.0	Nerolin (yara yara)	
Ethyl cinnamate*	52.0	Neryl isobutyrate	
Ethyl heptanoate		Orris butter* (orris resinoid)	1.5
Ethyl heptylate*	2.5	Phenethyl alcohol	
Ethyl lactate		Rose (rhodinol-citronellol)	
Ethyl methylphenylglycidate*	260.0	Rum ether	
(ethyl 3-phenylglycidate)		γ-Undecalactone*	58.5
Ethyl nitrate		Vanillin* (ethyl vanillin)	70.0
Ethyl propionate*	15.0	Solvent	1,060.0
Ethyl valerate*	60.0		
Heliotropin		**Total**	2,000.0
Hydroxyphenyl-2-butanone (10%			
solution in alcohol)	5.0		

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

Sweet Cherry

Imitations of sweet-cherry aroma are frequently and erroneously prepared in an analogous manner to sour-cherry aroma by simply adding an excess of bitter-almond essential oil. It is true that the benzaldehyde note must be predominant in this flavor, but this must be modified by a fairly large amount of *p*-toluic aldehyde or by a mixture of *o*-, *m*-, and *p*-toluic aldehydes used in a 4:1–5:1 ratio and at maximum not to exceed 40% total in the formulation. Both *p*-toluic aldehyde and the mixture of *o*-, *m*-, and *p*-toluic aldehydes are not found in nature.

A formulation that has attained a certain degree of acceptance contains, in addition to the mixture of the above aldehydes, amyl butyrate, anisic aldehyde, anisyl acetate, benzyl acetate, cinnamaldehyde, ethyl butyrate, ethyl heptanoate, ethyl methylphenylglycidate (a product not found in nature), eugenol,

and vanillin. Outside the above guidelines, satisfactory aromatic results become questionable; it is necessary to follow traditional formulation schemes consisting of bitter almond, the complex of the natural constituents of raspberry, a rose-like note, and vanillin. Other than the above products, there are no other natural products of interest for the imitation of sweet-cherry aroma.

Allyl benzoate is a potentially interesting product, but its toxicity is not yet sufficiently known. Anisyl propionate, anisyl butyrate, rhodinyl formate, and rhodinyl isovalerate, whose aromas blend well with sweet-cherry aroma, have not yet been identified in nature, although their presence is most likely. While other functional products, such as allyl isovalerate, cyclohexyl cinnamate, and cyclohexyl formate, have not yet been reported in the natural product, they may nonetheless prove useful.

Sweet Cherry Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Allyl isovalerate		Ethyl methylglycidate*	100.0
Amyl butyrate*	200.0	Geranium (rhodinol-citronellol*)	60.0
Anisic aldehyde*	37.0	α-Ionone* (β-ionone)	4.0
Anisyl acetate*	25.0	Jasmine, absolute*	13.0
Anisyl butyrate		Lemon (citral)	1.0
Anisyl propionate		Maltol (5% solution in ethanol*)	1.0
Benzyl acetate*	50.0	Orris butter*	30.0
Bitter almond essential oil* (benzaldehyde)	4,640.0	Orris resinoid*	160.0
Ceylon cinnamon (cinnamaldehyde*)	18.0	Rhodinyl formate*	1.0
Clove buds (eugenol*)	7.0	Rhodinyl isovalerate	
Cyclohexyl cinnamate		Rose, absolute*	1.0
Cyclohexyl formate		*o*-, *m*-, and *p*-Toluic aldehydes*	500.0
Ethyl acetate*	680.0	Vanillin*	400.0
Ethyl butyrate*	152.0	Solvent	2,920.0
		Total	10,000.0

Notes:
1. An asterisk denotes the guideline formulation.
2. Parentheses indicate potentially useful alternatives.

"Fantasia" Formulations Based on Fruit Flavors

By properly compounding the various fruit aroma imitations, additional flavor products having a characteristic but normal taste can be formulated. An example of the most characteristic and intriguing fantasia aroma is the tutti-frutti. This aroma may be formulated by complex recipes, such as pineapple, banana, orange, lemon, raspberry, vanilla, or by using much less complex compositions. The following formulation of fruit blends is suitable for flavoring pastry and baked goods. Using natural fruit juices for beverage flavors, the following blend can be prepared: pear, apple, peach, apricot, raspberry,

Tutti-Frutti Flavor

Ingredient	Parts by weight	Ingredient	Parts by weight
Amyl acetate	300.0	Rose, imitation (10% solution in alcohol)	28.0
Amyl butyrate	48.0	Rum ether	100.0
Ethyl butyrate	36.0	γ-Undecalactone	18.0
α-Ionone	120.0	Vanillin	11.0
Jasmine (10% solution in alcohol)	1.0	Solvent	257.0
Lemon essential oil	1.0		
Orris resinoid	80.0	Total	1,000.0

strawberry, Mirabelle plum, and cherry. There is no limitation in preparing identical formulations using the corresponding fruit aroma imitations as long as a citrus note is added to the final formulation.

Another fantasia fruit aroma somewhat resembles pomegranate. This aroma is formulated for either pastry flavors or syrups using the following basic notes: vanilla, neroli, raspberry, and orange. Needless to say, imitation fruit aromas, essential oils, terpeneless oils, or natural juices may be employed for such formulations depending on the end-use; care should be taken to soften the more stable notes and to enhance the least stable ones in baked goods.

Pomegranate Flavor

Ingredient	Parts by weight
Amyl acetate	150.0
Amyl butyrate	2.4
Ethyl butyrate	20.0
Ethyl pelargonate	1.5
α-Ionone	6.0
Jasmine, imitation (10% solution in alcohol)	0.4
Orris resinoid	4.3
Petitgrain bigarade sur fleurs	2.5
Rose, imitation	1.4
Terpeneless sweet orange essential oil	100.0
Vanillin	15.5
Solvent	196.0
Total	500.0

BITTER FLAVORS

The creation of bitter aromas represents one of the most difficult and fascinating problems in formulating flavors. The flavorists' creativity as well as ingenuity and tradition become intriguingly entwined with the most advanced technology. The fields of application are vast; only a few can be covered by a general text on flavors. However, an attempt will be made to group and classify for ready reference not only various problem areas but also to suggest suitable solutions.

A word of caution with respect to bitter flavors. Probably no other flavor group is more bound by tradition than the bitter aroma. The term *bitters* is quite generic and hardly apt in describing the broad range of bitter flavors known the world over. To western European consumers the bitter aroma is often represented by a high degree of astringency over a strong wine base. The development of vermouths and aperitifs in France and Italy is a typical example. For many years such products were not very popular in the United Kingdom, and for the most part they were rejected in the United States. On the other hand, the bitter principle delivered by quinine has evolved through years of use from an apparently disagreeable medicinal to a universal mix for gin and vodka. This type of bitter is accepted throughout the English-speaking world. Additional examples become readily apparent when one considers more specific national preferences in bitter beverages.

To the flavorist the term *bitter* is intended as the *base* flavor or taste and really represents only one component in the formulation of bitters. In fact, flavorists speak of tonics as *aperitifs* or *digestives*. These concepts were discussed at the *Colloques des Plantes Aromatiques* held at Milly-LaForet in 1966.[3]

Table 2 illustrates the best known herbs and derivatives commonly employed in the formulation of bitters. (The individual plants, botanical sources, derivatives, and physical-chemical constants are detailed in Part II of this book.) The 72 botanical sources listed in Table 2 provide the utmost flexibility

TABLE 2

Herbs and Derivatives Used to Formulate Bitters

Common name	Botanical name	Parts of plant used
Aloe	*Aloe* species	Concentrated leaf juice
Ambrette	*Hibiscus abelmoschus* L.	Seeds
Angelica	*Angelica archangelica* L.	Roots
Angostura	*Galipea cusparia* DC.	Bark
Anise	*Pimpinella anisum* L.	Fruits
Artichoke	*Cynara scolymus* L.	Leaves
Balm (lemon balm)	*Melissa officinalis* L.	Leaves and flowering tops
Blessed thistle	*Cnicus benedictus* L.	Leaves and flowers
Calamus	*Acorus calamus* L.	Rhizomes
Calumba	*Jatrorrhiza palmata* (Lam.) Miers	Roots
Camomile, Hungarian or German	*Matricaria chamomilla* L.	Flowers
Camomile, Roman or English	*Anthemis nobilis* L.	Flowers
Cardamom	*Elettaria cardamomum* Maton	Fruits
Cascarilla	*Croton eluteria* Benn.	Bark
Catmint	*Nepeta cataria* L.	Flowering tops
Centaury	*Erythraea centaurium* Pers.	Whole plant
Chicory	*Cichorium intybus* L.	Roots
Chinotti	*Citrus myrtifolia* Risso	Peels or the whole fruit
Chirata	*Swertia chirata* (Roxb.) Buch.-Ham.	Whole plant
Cinchona	*Cinchona* species	Bark
Cinnamon, Ceylon	*Cinnamomum zeylanicum* Nees	Bark
Clary sage	*Salvia sclarea* L.	Flowering tops

TABLE 2 (continued)

Herbs and Derivatives Used to Formulate Bitters

Common name	Botanical name	Parts of plant used
Clove	*Eugenia caryophyllata* Thunb.	Buds
Condurango	*Marsdenia condurango* Reichenb. f.	Bark
Coriander	*Coriandrum sativum* L.	Fruits
Dandelion	*Taraxacum officinale* Weber	Leaves and roots
Dittany of Crete	*Origanum dictamnus* L.	Leaves and flowering tops
Elder	*Sambucus nigra* L.	Flowers
Elecampane	*Inula helenium* L.	Rhizomes
Galanga	*Alpinia officinarum* Hance	Rhizomes
Genepi	*Artemisia glacialis* L.	Whole plant
Gentian	*Gentiana lutea* L.	Rhizomes and roots
Gentian, stemless	*Gentiana acaulis* L.	Whole plant
Germander	*Teucrium chamaedrys* L.	Flowering tops
Ginger	*Zingiber officinale* Rosc.	Rhizomes
Grains of paradise	*Aframomum melegueta* Rosc.	Seeds
Hyssop	*Hyssopus officinalis* L.	Leaves and flowers
Imperatoria	*Peucedanum osthruthium* (L.) Koch.	Rhizomes
Juniper	*Juniperus communis* L.	Berries
Larch agaric	*Polyporus laricis* Jacq.	Inner portion of the thallus
Lemon	*Citrus limonum* (L.) Risso	Peels
Liatris (wild vanilla)	*Trilisa odoratissima* (Walt.) Cass.	Leaves
Licorice	*Glycyrrhiza glabra* L.	Roots
Mace	*Myristica fragrans* Houtt.	Arillodes
Marjoram, sweet	*Marjorana hortensis* Moench.	Flowering tops
Melilotus	*Melilotus officinalis* (L.) Lam.	Flowers
Mugwort	*Artemisia pontica* L.	Leaves and flowering tops
Myrrh	*Commiphora* species	Gum resin
Nutmeg	*Myristica fragrans* Houtt.	Fruits
Orange, bitter	*Citrus aurantium* L. subspecies *amara* L.	Peels
Orange, sweet	*Citrus sinensis* L. Osbeck	Peels
Orris	*Iris pallida* L. and *I. germanica* L.	Roots
Peppermint	*Mentha piperita* L.	Flowering tops
Quassia	*Picrasma excelsa* (Sw.) Planch.	Wood
Rhubarb	*Rheum* species	Rhizomes
Rue	*Ruta graveolens* L.	Leaves
Saffron	*Crocus sativus* L.	Stems
St. Johnswort	*Hypericum perforatum* L.	Flowering tops
Savory, summer	*Satureja hortensis* L.	Flowering tops
Southernwood	*Artemisia abrotanum* L.	Leaves and flowering tops
Star anise	*Illicium verum* Hook. f.	Fruits
Thyme	*Thymus vulgaris* L.	Whole flowering plant
Tonka bean	*Coumarona odorata* Aubl.	Seeds
Valerian	*Valeriana officinalis* L.	Rhizomes and roots
Vanilla	*Vanilla* species	Pods
Walnut	*Juglans regia* L.	Leaves and green nuts
Woodruff, sweet	*Asperula odorata* L.	Whole plant
Wormwood	*Artemisia absinthium* L.	Leaves and flowering tops
Wormwood, mountain	*Artemisia valesiaca* L.	Leaves and flowering tops

TABLE 2 (continued)

Herbs and Derivatives Used to Formulate Bitters

Common name	Botanical name	Parts of plant used
Yarrow	*Achillea millefolium* L.	Whole flowering plant excluding the root
Yarrow, musk	*Achillea moschata* Jacq.	Leaves and flowering tops
Zedoary	*Curcuma zedoaria* Rosc.	Bark

TABLE 3

Classification of Bitter Flavors

Bitter flavors		Complementary flavors		
Aromatic-bitter	**Bitter**	**Aromatic**	**Pungent**	**Sweet**
Angelica	Aloe	Ambrette	Cardamom	Anise
Balm	Angostura	Clary sage	Cinnamon, Ceylon	Licorice
Calamus	Artichoke	Coriander	Clove buds	Star anise
Camomile, Hungarian	Blessed thistle	Imperatoria	Ginger	Vanilla
Camomile, Roman	Calumba	Lemon	Grains of paradise	
Cascarilla	Centaury	Liatris	Juniper	
Catmint	Chicory	(wild vanilla)	Mace	
Chinotti	Chirata	Melilotus	Nutmeg	
Condurango	Cinchona	Myrrh	Peppermint	
Dittany of Crete	Dandelion	Orange, sweet	Thyme	
Elder	Gentian	Orris		
Elecampane	Gentian, stemless	Saffron		
Galanga	Larch agaric	St. Johnswort		
Genepi	Quassia	Savory, summer		
Germander	Rhubarb	Tonka bean		
Hyssop	Southernwood	Valerian		
Marjoram, sweet	Walnut	Woodruff, sweet		
Mugwort				
Orange, bitter				
Rue				
Wormwood				
Wormwood, mountain				
Yarrow				
Yarrow, musk				
Zedoary				

in the formulation of flavors for bitters. In addition to the extracts and the tinctures, in some cases the soluble (terpeneless) essential oils are frequently employed (*e.g.*, bitter orange, sweet orange, and mint essential oils). The following essential oils are used occasionally as modifiers: angelica root, anise, calamus, cinnamon, clary sage, clove bud, coriander, ginger, lemon, and nutmeg.

The derivatives of the above listed products generally exhibit a definite bitter or aromatic-bitter flavor. Exceptions are vanilla, licorice, star anise, and anise, all of which have a characteristic *sweet* flavor and are used as either basic flavor ingredients or as sweeteners to yield contrasting effects in

slightly *pungent* or *sharp* flavors, such as thyme, peppermint, Ceylon cinnamon, nutmeg, grains of paradise, clove buds, cardamom, juniper, mace, and ginger. The following 16 plants yield derivatives with a definite *aromatic* flavor: woodruff, liatris, melilotus, clary sage, coriander, summer savory, orris, ambrette, tonka bean, sweet orange, imperatoria, lemon, valerian, saffron, St. Johnswort, and myrrh.

The remaining 42 products all exhibit varying degrees of bitter flavor, of which 17 yield exclusively bitter flavors: southernwood, chirata, gentian, blessed thistle, cinchona, rhubarb, aloe, angostura, larch agaric, artichoke, chicory, calumba, walnut, quassia, dandelion, gentian (stemless), and centaury. These are sometimes defined as "characteristic," while the derivatives of the additional 25 plants exhibit an *aromatic-bitter* flavor.

Finally attention is called to some of the secondary flavor notes encountered in bitter principles, such as the *sweet notes* associated with the aromatic flavor of tonka bean, sweet orange, lemon, liatris, and melilotus. *Tonic action* is associated with the aromatic-bitter flavors of mugwort, bitter orange, marjoram, angelica root, cascarilla, catmint, condurango, and genepi or with the *bitter* flavor of centaury, angostura, blessed thistle, and cinchona. This classification is shown in Table 3.

ALCOHOLIC BEVERAGES

Vermouth

In 1786 Antonio and Benedetto Carpano prepared the first typical vermouth formulation, using herbs harvested in the mountains and the plains of Piedmont, Asti muscat wine, sugar, and alcohol. The name *vermouth*, today generic, is derived from *Wermuth*,* the original German name for wormwood (*Artemisia absinthium*), one of the aromatic herbs employed in the formulation.

According to definition and standards set by Italian law, the name *vermouth* is reserved exclusively for the finished product prepared using genuine wine of national production in combination with aromatic and bittering ingredients permitted under the regulations issued by the Italian Department of Health. The finished product must have an alcohol and sugar content within the following limits:

Red and white vermouths. Not less than 15.5% alcohol by volume and not less than 13% by weight total invert sugar (calculated following the inversion of sucrose).

Dry vermouth. Not less than 18% alcohol by volume and not more than 4% by weight total invert sugar (calculated following the inversion of sucrose).

In the preparation of Italian vermouths, the addition of sucrose, pure and rectified ethyl alcohol, and coloring matter (sucrose-caramel or burnt sugar) is permitted. The ingredients added (flavors, bittering substances, alcohol, sucrose, and caramel) must not exceed 30% by volume; the finished product also must be perfectly clear.

Constituents of Vermouth

Sucrose, free of active decolorizing agents, and good-tasting ethyl alcohol are obviously the products of choice for vermouth formulations. This leaves only the wine, the flavoring-bittering ingredients, and the caramel. The choice of the most suitable caramel type for coloring is not limited simply to selecting the best caramel type prepared from sucrose for use in alcoholic beverages; it is usually complemented by a number of coloring, aging, and flavor panel tests to determine the following:

1. The total absence of secondary reactions among the various ingredients in the vermouth formulation that might cause flavor degradation, formation of deposits, or turbidity.
2. The color stability.
3. The palatability of the resulting flavor, remembering that caramel not only adds color but also flavor to the finished product. The latter is strongly dependent on the other ingredients present because of varying synergistic effects.

The choice of the wine deserves particular attention. Originally pure Asti muscat wine of a certain type was the only product prescribed for use in vermouths to obtain the desired flavor effects. Because of the increasing industrialization of vermouth production and the growing demand for the specific wine type, wine specialists selected certain cuts of wines from both Asti and other neighboring areas to formulate an alternative but nonetheless suitable product. This resulted in the *bianco carta* (paper white) that is used almost exclusively in today's qualified production of Italian vermouths. This compounded wine has a higher alcohol content than the original Asti variety.

The bitter flavor ingredients consist mainly of derivatives (tinctures, extracts, etc.) of the following herbs or dried spices:

**Vermut-vein* is the medieval German name for wormwood-flavored wine.

Flavor Ingredients of Vermouth

Aromatic	Pungent	Sweet
Ambrette	Cardamom	Anise
Clary sage	Ceylon cinnamon	Licorice
Coriander	Clove	Vanilla
Ginger	Grains of paradise	
Imperatoria	Juniper	
Lemon	Mace	
Liatris (wild vanilla)	Nutmeg	
Melilotus	Peppermint	
Myrrh	Saffron	
Orange, sweet	Thyme	
Orris		
St. Johnswort		
Savory, summer		
Tonka bean		
Valerian		
Woodruff		

The choice and the dosage of the flavor ingredients together with the extraction procedures from the botanical source represent not only a typical challenging problem for the flavorist, but they are also responsible for the following classification of vermouths:

White dry vermouths
White, highly aromatic vermouths
White, lightly aromatic vermouths
Red vermouths
Red bitter vermouths
Cinchona-flavored red vermouths

Formulation of Vermouth Flavors

Before discussing criteria for vermouth formulations, some attention must be given to fundamental concepts of the extraction of the herbs, since the extractive technique employed directly affects the resulting flavor of the finished product.

Traditional methods for the preparation of vermouths prescribed the use of a blend of aromatic herbs in suitable predetermined ratios. The herbs were comminuted and subsequently macerated for a predetermined length of time in the wine of choice. The wine was fortified with added amounts of ethyl alcohol necessary to prepare a finished product having the required alcohol strength. Care was taken to account for evaporation losses and slight dilution effects by the residual moisture in the herbs. The sugar content was adjusted optionally before or after maceration. Following maceration and filtration of the herb residue, the infusion was aged and finally bottled.

Other methods of preparation consist of adding typical compounded flavor extracts to the fortified wine mixture. These compounded flavors are obtained (1) by hydro-alcoholic maceration of properly formulated blends of herbs or (2) by hydro-alcoholic extracts of the individual herbs that are subsequently blended together.

It is apparent from the above descriptions that the "flavor yield" of the individual aromatic herb depends on the different preparatory techniques. Since the basic operation consists of an extraction, not only the extractive power of the solvent but also the solubility of the flavor constituents of the herbs must be considered. In the original method a large number of synergistic effects may occur in

the blend of herbs that are extracted with a low-strength solvent. In the second method the extraction is still carried out on a blend of herbs; the only difference is that a solvent with a higher strength is employed to prepare a flavor concentrate of the required yield. In the third method the extraction is carried out on the individual herbs using a solvent of strength similar to that used in the second method. Experience shows that if the same amounts and types of herb(s) are extracted in each of the three methods, three different flavors are obtained. Therefore, if one wishes to duplicate the flavor resulting from the first extraction method by using the second or third extraction procedure, respectively, it may be necessary to consider the higher solubility of the aromatic principles as well as the lower solubility of the water-soluble components.

Regardless of the flavorists' personal preference for the direct use of the aromatic herbs, the use of tinctures prepared from fluid extracts and distillates should not be neglected. Using tinctures not only insures a controlled reproducibility of the active flavor principles in the formulation, but it may be absolutely necessary in those formulations containing flavor ingredients of quite different solubility characteristics. Similarly distillates (derivatives usually distilled from alcoholic infusions of the aromatic herbs) are highly functional to impart specific flavor notes. They are used also in the preparation of white vermouths and special bitters. Approximately 1,000 kilograms (2,205 pounds) of finished vermouth or bitter may be prepared using a blend of aromatic herbs in amounts varying between 3–6 kilograms (7–13 pounds); *i.e.*, the aromatic herbs have a flavor yield of approximately 1 × 200 to 1 × 400.

Of the 72 bittering plants used by the flavor industry that were listed in Table 2 (see p. 673), only a few find use as flavor ingredients in vermouth formulations. The flavor ingredients employed in vermouth formulations and their preferential use in various types of vermouth are listed in Table 4.

The products listed in Table 4 should be interpreted with a certain degree of flexibility. The fact that specific herbs have not been reported used in certain types of vermouth does not imply their categoric exclusion from other formulations; a relative degree of freedom may be permitted to obtain specific flavor effects. For the sake of thoroughness (and with reference to the choice and blending of herbs for the various vermouth formulations shown in Table 4), it must be pointed out that the following herbs are included in the formulation of almost all vermouth types and are therefore the most important:

Angelica	Germander
Calamus	Marjoram
Cinnamon	Mugwort
Clove	Summer savory
Coriander	Wormwood
Dittany of Crete	Wormwood, mountain

Apart from the characteristic aromatic notes rendered by calamus, dittany of Crete, coriander, summer savory, cinnamon, marjoram, angelica, and clove, the reader should note the use of germander (an absolutely irreplaceable product of great potential), mountain wormwood, wormwood, and mugwort as basic flavor ingredients in vermouth formulations. For example, by keeping constant the desired concentration levels of germander and mountain wormwood, the concentration ratio of wormwood to mugwort can be increased or decreased to impart a more or less bitter-aromatic note to the resulting vermouth formulation.

TABLE 4

Flavor Ingredients in Vermouth Formulations

Flavor ingredients	Vermouths					
	White, dry	White, highly aromatic	White, lightly aromatic	Red	Red, bitter	Red, cinchona-flavored
Ambrette		x		x		
Angelica	x	x	x	x	x	x
Balm (lemon balm)				x		
Blessed thistle				x		
Calamus	x	x	x	x	x	x
Camomile		x		x		
Cascarilla*		x			x	
Centaury			x	x	x	x
Chirata*		x			x	x
Cinchona						x
Cinnamon	x	x	x	x	x	x
Clary sage	x		x	x		x
Clove		x	x	x	x	x
Coriander	x	x	x	x		x
Dittany of Crete	x	x	x	x	x	
Elder		x			x	
Elecampane		x	x		x	
Galanga			x		x	
Gentian			x		x	x
Gentian, stemless			x		x	
Germander		x	x	x	x	
Grains of paradise*		x	x		x	
Hyssop	x				x	
Imperatoria*					x	x
Licorice*				x		
Marjoram		x	x	x	x	x
Melilotus				x		
Mugwort	x	x	x	x	x	x
Nutmeg	x	x		x	x	
Orange, bitter	x	x	x			
Orange, sweet		x				
Orris		x				
Peppermint	x					
Savory, summer	x	x		x	x	x
Southernwood	x				x	
Tonka bean		x	x			
Thyme	x		x	x	x	x
Vanilla		x				
Wormwood	x	x	x	x	x	x
Wormwood, mountain	x	x	x	x	x	x
Yarrow			x	x	x	x
Yarrow, musk				x	x	x

* Rarely used.

A typical vermouth formulation is shown below. This formulation, however, is intended only as a guideline for the preparation of a white vermouth by direct infusion of the herbs in wine fortified with alcohol.

White Vermouth Formulation

Ingredient	Parts	Ingredient	Parts
Clary sage	2	Orange, bitter	1
Wormwood	2	Southernwood	1
Calamus	1.5	Thyme	1
Germander	1.5	Mugwort	0.5
Coriander	1	Summer savory	0.5
Dittany of Crete	1	Ceylon cinnamon	0.25
Hyssop	1	Nutmeg	0.25
Mountain wormwood	1	Vanilla	0.1

The comminuted herbs are macerated in the fortified wine for at least 15 days; the resulting infusion is pressed, sugar is added, and the infusion is finally filtered.

Bitters

This category of products is extensive and includes several characteristic examples. The following classification may be useful in defining this product category.

1. Alcoholic bitters (typical)
2. Alcoholic aperitifs with special flavors in mixture with citrus notes
3. Alcoholic aperitifs with a characteristic flavor note (*e.g.*, rhubarb, gentian, artichoke, etc.)
4. Tonics and digestives with a characteristic flavor note (anise, cinchona, genepi, etc.)
5. Tonics and digestives with a mixed flavor note (*e.g.*, centerbe, fernet, mint fernet, felsina bitter, etc.).

Following criteria similar to those used for vermouth formulations, a list of dried herbs useful for the formulation of bitters is given in Table 5. In addition to the herbs listed, soluble essential oils extracted from the same herbs are also employed in the formulation of special and digestive-tonic bitters. A "complex" typical bitter flavor can be added to round off the flavor note in tonics and digestives. It is also possible to employ flavor distillates in all bitter formulations to create special effects. Note that raspberry distillate and violet tincture are not included in Table 5 because of their very limited, specific use.

A guideline to a typical basic bitters formulation is shown below. A 40% tincture having an approximately 1 × 100 yield is prepared by maceration of the herbs for 15–20 days in approximately 60% alcohol.

Basic Bitters Formulation

Ingredient	Parts
Aloe	0.2
Cascarilla	3
Chinotto	2
Cinnamon	1
Gentian	16
Germander	11
Orange, bitter	11
Orange, sweet	13
Rhubarb	6
Wormwood	6

TABLE 5

Herbs Used in Bitters Formulations

Flavor ingredient	Typical bitters	Special bitters	Tonics and digestives	Flavor ingredient	Typical bitters	Special bitters	Tonics and digestives
Aloe	x	x	x	Imperatoria	x		x
Ambrette		x		Juniper	x	x	x
Angelica	x	x	x	Larch agaric		x	
Angostura		x		Lemon		x	
Anise			x				
				Liatris (wild vanilla)	x	x	
Artichoke		x		Licorice		x	
Balm (lemon balm)	x			Mace		x	
Calamus	x	x	x	Melilotus	x	x	
Calumba		x	x	Myrrh			x
Camomile, Hungarian		x	x				
				Nutmeg		x	
Camomile, Roman		x	x	Orange, bitter	x	x	x
Cardamom		x		Orange, sweet	x	x	
Cascarilla	x			Orris		x	
Catmint		x		Peppermint	x		x
Centaury	x	x	x				
				Quassia		x	
Chicory		x		Rhubarb	x	x	x
Chinotto	x	x	x	Rue		x	x
Chirata	x		x	Saffron			x
Cinchona	x	x	x	St. Johnswort			x
Cinnamon	x		x				
				Southernwood	x		
Clove	x	x	x	Tonka bean		x	
Condurango		x		Valerian		x	
Coriander			x	Vanilla		x	x
Dandelion		x		Walnut		x	x
Galanga	x						
				Woodruff		x	
Genepi		x	x	Wormwood	x		x
Gentian	x		x	Wormwood, mountain	x		
Gentian, stemless	x	x	x	Yarrow	x		
Germander	x			Yarrow, musk	x	x	
Grains of paradise	x						
Hyssop			x	Zedoary		x	x

In the aromatic blending of very bitter flavors, the following combinations are preferred:

Angelica with: balm, cardamom, coriander, hyssop, marjoram, mint, thyme, vanilla.

Calamus with: cardamom, cinnamon, mace or nutmeg, zedoary; **or:** calumba, camomile, cascarilla, cinchona, larch agaric, and rhubarb.

Camomile with: artichoke, bitter orange, cinchona, genepi, gentian, gentian (stemless), mint, summer savory.

Cascarilla with: bitter and sweet orange, calamus, chinotti, cinnamon, grains of paradise, lemon, nutmeg, thyme.

Centaury with: calamus, cinchona, condurango, gentian, gentian (stemless); **or:** bitter and sweet orange, cardamom, clove, lemon, licorice, mace.

Condurango with: bitter orange, cardamom, chicory, cinchona, dandelion, lemon, rhubarb.

The operative technique for the preparation of flavors for bitters consists of (1) production of the individual tinctures and their subsequent mixing to prepare the so-called "compounded alcoholic essence," having a yield varying between 3 × 100 and 1 × 100, and (2) preparation of the compound tincture by direct extraction of properly ratioed blends of the various herbs. All alcoholic extracts are added to water, alcohol, and sugar to prepare the finished products. The alcohol content of tinctures usually varies between 21–30%. In aromatic-bitter flavor formulations the total alcohol content should also be considered, as this may enhance certain notes. The sugar content in various formulations plays an important role; in all cases the sugar level is balanced against the bitter bouquet.

The aromatic note of so-called American bitters results from mixing two–three parts of good quality red vermouth with one part of bitter. The conclusions that may be drawn from this for formulative purposes are quite obvious.

The flavors obtained from bitter formulations vary widely as the result of carbonation. While flavor ingredients used are generally the same (*i.e.*, individual or compounded flavor extracts), the relative doses should be modified accordingly to counteract the two-fold effects of carbon dioxide. In addition to causing a partial desensitization of the taste buds following an initial temporary stimulative effect, carbon dioxide also reacts chemically with the constituents of the flavor complex. Therefore, the contribution by the reaction products to the resulting flavor must be taken into account, especially after prolonged storage. As in the case of non-carbonated bitters, the alcohol content plays an important role.

Regarding the formulation of aperitifs, tonics, and digestives, the topic differs somewhat from the basic considerations presented so far. As mentioned above, not only the various herbs and corresponding derivatives (extracts and tinctures) but also essential oils and sometimes distillates play an important role in the flavor of the final formulation. Therefore, formulations in most cases are hinged on the combination either of bitter flavors with citrus notes or of aromatic notes with bitter flavors. Specific examples of the above formulating techniques are represented by products such as aperol, select, and fernet. In the latter formulation the flavor contrast lies between mint and saffron and related variations, such as anise and saffron. In aperol, select, and other similar products, the basic flavor ingredient consists of a blend of soluble essential oils of sweet and bitter orange together with added amounts of vanilla or vanillin; the bitter principle consists of a complex bitter flavor formulated by using some of the herbs listed in Table 5.

In fernet, which is flavored with the characteristic aromatic note based on saffron and mint combinations, neither citrus nor other essential oils are used (except for mint essential oil). The bitter flavor usually is obtained with a few herbs used in suitable ratios, such as angelica (roots), calamus, calumba, camomile, centaury, cinchona, gentian, imperatoria, larch agaric, rhubarb, St. Johnswort, and zedoary to which aloe and myrrh resinoid are added. A large mint-to-bitter-complex ratio yields mint-flavored fernet types, whereas lower ratios yield bitters exhibiting flavor characteristics less reminiscent of typical fernets. The flavor of products with a definite basic note (anise, artichoke, cinchona, gentian, rhubarb, etc.) is rounded and upgraded using notes strictly dependent on the background note. This leaves very little room for variations and, therefore, permits only the addition of notes to refine and characterize the finished product.

Once the various flavors for alcoholic and non-alcoholic bitters and special aperitifs have been properly formulated, the suggested use levels for most typical products shown in Table 6 can be followed. The suggested formulations are suitable for the preparation of approximately 100 liters of finished product.

TABLE 6

Formulations of Various Bitters

Finished product	95% alcohol, l	Sugar, kg	Distilled water, l	Flavor complex	Color
Alpine herbs	33	15	59.2	q.s.*	q.s.*
Amarone	30	1	70.7	q.s.	q.s.
American, red and white	17	25	67.6	q.s.	q.s.
Artichoke	16.2	25	67.6	q.s.	q.s.
Centerbe	47	20	43.1	q.s.	q.s.
China-china	30	10	65	q.s.	q.s.
Cinchona bitter	30	10	65.5	q.s.	q.s.
Dutch bitter	32	25	54	q.s.	q.s.
Felsina bitter	31	14	61	q.s.	q.s.
Fernet	42	—	60	q.s.	q.s.
Fernet, mint	41.7	31	41	q.s.	q.s.
Ferro-china	21.5	10	73	q.s.	q.s.
Genepi	36	30	47	q.s.	q.s.
Milan bitter	26	24	60	q.s.	q.s.
Orange bitter	35	10	60.5	q.s.	q.s.
Tourin bitter	26	30	56	q.s.	q.s.
Venetia bitter	30	25	55.7	q.s.	q.s.
White bitter	36	20	53.2	q.s.	q.s.

* A sufficient quantity (*quantum sufficiat*).

Sweet Liqueurs

Parallel to bitters, the liquor industry manufactures a series of sweet liqueurs largely using traditional recipes from a great variety of ethnic sources. Sweet liqueurs consist of water, sugar, alcohol, and blends of flavor principles obtained by various extractive techniques from aromatic plants. Sweet liqueurs, therefore, differ from distilled liquors, which build up the aromatic principles and alcohol content during the fermentation of sugars present in the juices of fruit and other plants.

Prior to examining liqueurs from the standpoint of specific flavoring, a classification of the various categories of products is necessary. Only the most important products will be included in the following classification; wherever possible, synonyms will be used rather than trade names to designate commercially available products.

1. **Sweet liqueurs with definite fruity aromas:** apricot, banana, bitter and sweet orange, cedrat, cherry, mandarin, marasca cherry, peach, plum.
2. **Sweet liqueurs with definite floral, seedy, fruity, or herbaceous aromas:** anise, cocoa, coffee, kümmel, mint, rose, vanilla, vervain.
3. **Sweet liqueurs with a mixed, or fantasia, aroma:** alkermes, amaretto, arquebus, benedictine, benevento, certosa, cordial, goccia d'oro, goldwasser, millefiori, perfetto amore, ratafia.
4. **Elixirs (with a bittersweet note):** china (cinchona), rhubarb, walnut (nocino).

Basic Ingredients

Specific flavor ingredients (regardless of the preparation method) are the basic building blocks of liqueur formulations; consequently, the resulting flavor is strictly dependent on their use in the formulation. The flavorist also should be cautious in his choice of other basic ingredients, such as water, sugar, alcohol, and colorants. The functional importance of the above ingredients should in no way be underestimated.

Water. Although the choice of water is not as critical in the formulation of liqueurs as in carbonated beverages, the quality of water should be properly selected. Spring or tap water is usually good but not recommended; distilled or deionized water is preferred.

Sugar. Fine granulated sugar from reputable sources (cane or beet sugar) is preferred. Good manufacturing practice involves dissolving the sugar in distilled water, then adding colorants to the resulting syrup, and finally filtering.

Alcohol. The alcohol used must be free of off-flavors. Alcohol from the fermentation of fruit advantageously replaces alcohol from vinous fermentation in several liqueur types. The aromatic principles are dissolved or mixed in the required amount of alcohol; the resulting solution is added to the syrup. The resulting mixture is left standing for an extended period of time to allow an intimate blending of the flavor ingredients. Filtration of the finished liqueur prior to bottling is necessary to remove any residual haziness that is absolutely unacceptable in good commercial products.

Sweet Liqueurs with Definite Fruity Aromas

Apricot

In addition to alcoholic extracts (sometimes distilled) of fresh and dried fruits or concentrated juices, compound flavors prepared by mixing aldehyde C_{14} with various aromatic principles are frequently employed. These impart the following:

1. flowery notes—benzyl acetate, α-ionone, jasmine absolute, neroli essential oil, orris butter, and petitgrain bigarade essential oil;
2. walnut flavor—bitter almond, aldehyde C_{18}; and
3. slight ether notes—ethyl acetate.

Such flavor bases have very high yields ranging from 1 × 10,000 to 1 × 30,000, based on the weight of the finished product. Therefore, the use of tinctures prepared from fruit distillates is highly recommended to round off the flavor of the alcohol used for dilution.

Two basic types of liqueurs with an apricot flavor are prepared: (1) a sweet type, and (2) a somewhat less sweet type generally known as apricot brandy. Typical formulations for the preparation of 100 liters of finished product include the ingredients shown in the table below; the 96% alcohol can be replaced with a wine distillate (brandy, cognac) having a high (60–65%) alcohol content, with the water adjusted accordingly to maintain the desired alcoholic level in the finished product.

Apricot Liqueurs

Ingredient	Quantity	
	Sweet apricot	Apricot brandy
96% alcohol	30 l	33 l
Sugar	40 kg	36 kg
Distilled water	46.3 l	41.5 l
Compound flavor 1 × 100*	1 kg	1 kg
Concentrated apricot juice	3 kg	3 kg
Colorant	q.s.†	q.s.†

* The concentration of flavor ingredient is proportional to the yield.
† Sufficient quantity.

Banana

Banana liqueur is not currently in demand and is generally of limited consumption. The compounded essential oil used exclusively in the preparation of banana liqueur results from the blending of amyl and benzyl acetate and amyl and ethyl butyrate; the mixture is rounded off by the

addition of essential oils (orange, lemon) and vanillin. The so-called "cream of banana" formulation consists of the following (recipe for 100 liters of finished product):

Cream of Banana

Ingredient	Quantity
96% alcohol	30 l
Sugar	40 l
Distilled water	46.4 l
Compound flavor 1 × 100*	1 kg
Colorant	q.s.

* The amount of flavor is proportional to the yield.

Bitter and Sweet Orange

Bitter and sweet orange are not commercially used names; curaçao and triple sec are those most frequently employed. These products can be prepared by directly using the tincture from the peels of bitter orange and mandarin, to which small amounts of chinotti tincture and spices, such as cinnamon and clove, can be added.

When the compounded essential oil (prepared from the individual essential oils and having a yield of approximately 1 × 10,000) is used for flavoring, a small amount of orange peel tincture can be added to improve the flavor. The compounded essential oil consists of a blend of sweet and bitter orange essential oils, rounded off by small additions of lemon, neroli, and petitgrain bigarade essential oils, and spiced with a flavor complex consisting of clove, cinnamon, coriander, and mace (or nutmeg) essential oils. A guideline to the formulation of compounded oil for flavoring curacao follows:

Ingredient	Parts
Bitter orange essential oil	190
Cinnamon essential oil	4
Clove essential oil	3
Coriander essential oil	1
Lemon essential oil	22
Neroli essential oil	5
Nutmeg essential oil	2
Rum ether	5
Sweet orange essential oil	350
Alcohol	418
Total	1,000

A guideline to the formulation of orange-flavored liqueurs sufficient for the preparation of 100 liters of finished product is shown below:

Ingredient	Curaçao	Curaçao and triple sec
96% alcohol	36 l	36 l
Sugar	35 kg	38 kg
Distilled water	44.3 l	42.5 l
Compound flavor 1 × 200	0.5 kg	0.5 kg
Colorant	q.s.	q.s.

Sweet orange is also employed alone in the formulation of liqueurs; it is known under the generic name *cream of orange*. The soluble essence (used for flavoring syrups), more or less modified by the addition of tinctures, is usually employed for flavoring this type of liqueur. The following guideline formulation is suitable to prepare 100 liters of finished product:

Cream of Orange

Ingredient	Quantity
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.4 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

A cream of mandarin is obtained by dilution similar to cream of orange. Mandarin soluble essence or the tincture is prepared from fresh mandarin peels, to which a small amount of vanilla is added.

Cedrat

The tincture from fresh peels is used in the preparation of this liqueur. Direct use of the essential oil is excluded because the resultant product is somewhat flavorless and because the essential oil is not produced industrially. The use of citrus-flavored blends prepared from the soluble essential oils of orange, lemon, and bergamot reminiscent of the cedrat flavor is of some interest from a technical viewpoint but is limited by the use of products of undefined origin.

The liqueur having a cedrat note is commercially available in two basic types: sweet citron water and strong citron water. These types usually are formulated by the following guideline formulations:

Cedrat-flavored Liqueurs

Ingredient	Quantity*	
	Sweet citron water	Strong citron water
96% alcohol	26.4 l	32 l
Distilled water	59.5 l	57.5 l
Compound flavor 1 × 200†	0.5 kg	0.5 kg
Colorant	q.s.	q.s.

* Preparation sufficient for 100 liters of finished product.
† The amount of compound flavor is proportional to the yield.

Cherry

Two techniques may be employed for the preparation of this liqueur, commercially available under the names *cherry* or *cherry brandy*. One method utilizes cherry juice, cherry distillate, alcohol, water, and sugar exclusively; the second method consists of diluting compounded essential oils in water, alcohol, and sugar, and adding cherry juice and cherry distillate. The amount of 96% alcohol in this formulation can be advantageously replaced, partially or totally, with a wine distillate, such as brandy or cognac, having a high (60–65%) alcohol content. The amount of water to be added should be adjusted based on the alcohol content in the finished product. The compounded oil contains bitter almond essential oil rounded off and finished with raspberry and rose notes (see discussion of sweet cherry flavor). The above-mentioned products may be prepared by the following guideline formulations:

Cherry-flavored Liqueurs

Ingredient	Quantity*	
	Cherry	Cherry brandy
96% alcohol	30 l	30 l
Distilled water	40 l	40 l
Compound flavor 1 × 100†	0.5 kg	0.5 kg
1:5 concentrated cherry or amarelle juice	—	ca. 3 kg
Colorant	q.s.	q.s.

* Preparation sufficient for 100 liters of finished product.
† The amount of compound flavor is proportional to the yield.

Mandarin

The use of mandarin essential oil is not always recommended for the preparation of the liqueur. The product resulting from the simple dilution of the essential oil with alcohol is rather flavorless; the use of alcoholic extract or tincture (usually 10% in 60% or 70% alcohol) prepared from fresh mandarin peels is preferred. The mandarin note can be rounded off by small additions of natural vanilla or vanillin solutions and neroli and petitgrain bigarade essential oils. The liqueur known by the generic name *cream of mandarin* can be prepared as follows:

Cream of Mandarin

Ingredient	Quantity*
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.4 l
Compound flavor 1 × 100†	1 kg
Colorant	q.s.

* Quantities are sufficient for 100 liters of finished product.
† The amount of compound flavor is proportional to the yield.

Marasca Cherry

A typical formulation for this type of liqueur employs the distillate from Dalmatian marasca cherry, which is usually obtained by recovering the fractions distilling around 70°C from a tincture prepared as follows: (1) with water (20%), alcohol (60%), and marasca cherries (approx. 20%), and (2) directly from marasca cherries (20%) and 95% alcohol (80%). In the latter case the liqueur is prepared by diluting the distillate to the required alcohol content and adding sufficient amounts of sugar and flavor modifiers. The rose note plays a very important role in the aromatic maraschino complex.

When the use of compounded essential oils is desired (to decrease the use of marasca distillates), the corresponding product exhibits a basic bitter-almond note, as in cherry- and peach-flavored liqueurs; it can be formulated by using deacidified bitter almond or cherry laurel essential oils rounded off with neroli or petitgrain bigarade, citrus notes (orange, lemon), coumarin notes (tonka bean, melilotus, liatris, or coumarin), a slight cognac note, and rose absolute. The rose derivative is used generally at the 0.5% level based on the benzaldehyde content of the other ingredients (see discussion of sour cherry flavor, p. 668). When essential oils are used, the following guideline formulation is useful for preparing 100 liters of finished product:

Marasca Cherry Liqueur

Ingredient	Quantity
96% alcohol	33 l
Sugar	40 kg
Distilled water	44.1 l
Compound flavor 1 × 200	0.5 kg

Peach

The use of alcoholic peach extracts or tinctures yields only limited flavor results in peach liqueur. It is, therefore, necessary to use a compounded essential oil duplicating the flavor characteristics by modifying the bitter almond note fundamental in peach-flavored liqueurs. This compounded essential oil results from the blending of esters, such as methyl and ethyl cinnamate, with essential oils (clove, neroli, cinnamon, and coriander) imparting a floral, spicy note; it is sweetened by the addition of citrus essential oils, such as sweet and bitter orange, and sometimes small amounts of anise or anethol. The basic flavor resulting from a suitable blend of the above constituents has a yield of approximately 1 × 8,000. The use of aldehyde C_{14} yields excellent results in the formulation of flavors for pastry, even when used in massive doses; however, it may yield entirely different results in the formulation of liqueurs (see discussion of peach flavor, p. 660).

A typical product having a peach note (Persico Reale) may be formulated as follows:

Ingredient	Quantity*
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.9 l
Compound flavor 1 × 200†	0.5 kg
Colorant	Only if required

* Quantities are sufficient for 100 liters of finished product.
† The amount of flavor is proportional to the yield.

Peach brandy can be formulated as follows:

Peach Brandy

Ingredient	Quantity*
96% alcohol	33 l
Sugar	36 kg
Distilled water	44.8 l
Compound flavor 1 × 100†	1 kg
Concentrated peach juice	3 kg
Colorant	q.s.

* Quantities are sufficient for the preparation of 100 liters of finished product.
† The amount of flavor is proportional to the yield.

Plum

Plum-flavored liqueurs are usually formulated by using compounded essential oils prepared by rounding off the bitter-almond note. The rounding off of this note employs several essential oils (*e.g.*, capsicum, cinnamon, clove, cognac), esters (amyl and ethyl acetate, ethyl butyrate, and ethyl and methyl cinnamate), ionones, and vanillin (see discussion of plum flavor, p. 665). The distillate and plum juice are also employed in the formulation of the best quality types, *i.e.*, sweet and dry plum liqueurs. Liqueurs formulated using essential oils exhibit varying compositions depending on the type. General guidelines are given below:

Plum-flavored Liqueurs

Ingredient	Quantity*			
	Plum, sweet	Plum, dry	Plum, regular (prunella)	Plum brandy
96% alcohol	30 l	50 l	30 l	33 l
Sugar	35 kg	1 kg	40 kg	36 kg
Distilled water	49.5 l	51.5 l	45.0 l	44.5 l
Compound flavor 1 × 100†	1 kg	0.5 kg	3 kg	3 kg
Concentrated plum juice	3 kg	—	—	3 kg
Colorant	q.s.	q.s.	q.s.	q.s.

* Quantities are sufficient for the preparation of 100 liters of finished product.
† The amount of flavor is proportional to the yield.

Sweet Liqueurs with Definite Floral, Seedy, Fruity, or Herbaceous Aromas

Anise

The liqueur industry uses anise flavor in a wide variety of finished products. The widespread acceptance of anise-flavored liqueurs is illustrated by the popularity of the following throughout the Mediterranean: Turkish raki, mastic of chio, Greek onyo, Egyptian arak-el balah, Lebanese arak, Moroccan mahia, and Tunisian nukha. Another classic series of anise-flavored liqueurs is *anisette*, originally prepared by distillation of green anise seeds macerated in a water-alcohol mixture. This liqueur also contains trace amounts of bitter principles or a floral note in order to impart a characteristic bouquet to the finished product.

In contrast to the traditional manufacturing techniques, there is regular use of compounded essential oils consisting mainly of anise essential oil (congealing point, 15°C), green anise essential oil, or anethol. Based on the percentage of anethol present in the formulation, the optional addition of trace quantities of characterizing flavors, the degree of the milky appearance of the liqueur on dilution with water, the amount of sugar, and the alcohol content, the various anise-flavored products may be classified into the following basic types: anisette, anice forte, sambuca, sambuca coffee, anesone, mastic of chio, anici lattanti, and sassolino. Typical formulations characteristic of the different type products are shown in the following table:

Anise-flavored Liqueurs

Ingredient	Anice forte	Anici lattanti	Anisette	Mastic of chio	Sambuca	Sassolino	Sambuca coffee	Anesone
96% alcohol	41.6 l	46.9 l	33 l	50 l	43.5 l	36 l	43.2 l	36 l
Sugar	1 kg	1 kg	40 kg	1 kg	38 kg	32 kg	38 kg	20 kg
Distilled water	60.3 l	55.1 l	44 l	51.6 l	35.3 l	45.7 l	35 l	53.7 l
Compound flavor 1 × 1000	0.5 kg	0.5 kg	0.5 kg	0.5 kg	0.5 kg	1 kg	1 kg	1 kg
Colorant	—	—	—	q.s.	—	—	q.s.	—

Anici lattanti flavored with wormwood was extremely popular during the nineteenth and early twentieth centuries for use in liqueurs in France. After the barring of wormwood, similar formulations were introduced in which wormwood was replaced by alternate bitter principles to satisfy the demand for this type of product. The use of cinnamon, camomile, lemon balm, lemon, orange, and coriander in such liqueurs as complementary flavor ingredients is maintained in such formulations. The effective yield of anethol, based on the finished liqueur "as is," is approximately 1 × 2,000.

Cocoa

This product is known commercially by the generic name *creme de cacao*; it is produced as both a colorless and a cocoa-like brown product. It is prepared directly from cocoa distillates or tinctures obtained either from roasted and ground cocoa beans or from bitter, defatted cocoa. Cocoa distillates are prepared by distilling an alcohol-water mixture of macerated cocoa beans (ca. 30%) and recovering the distilled fraction having a 60–65% alcohol content. The yield of the distillate, based on the finished liqueur, ranges between 1 × 25 and 1 × 33; distillates having a larger yield may be prepared by adding reinforcing flavors. The tincture consists of the above mixture after maceration and has a yield of 1 × 20 maximum.

The rounding off of the cocoa note using small amounts of vanilla (approximately 1 × 10,000 vanillin) in the finished liqueur is recommended. Compounded essential oils based on isolates or synthetic products are not commonly used in the formulation of liqueurs. A guideline formulation for creme de cacao is shown below; the formulation may also be used for the preparation of white or brown cream of chocolate liqueurs.

Creme de Cacao

Ingredient	Quantity*
96% alcohol	24 l
Sugar	40 kg
Distilled water	51.8 l
Compound flavor 1 × 100	1 kg
Colorant	If required

* This formulation yields 100 liters of finished liqueur.

Coffee

The discussion of coffee-flavored liqueurs parallels cocoa as to both the name *cream of coffee* and the use of tinctures and distillates. The amount of coffee beans used in the preparation of the flavor intermediates is analogous to cocoa beans, but greater emphasis is placed on the degree of roasting and the choice of coffee blends; highly aromatic and not too bitter coffee qualities are preferred. Modifying flavors are not usually added, except for a slight ether note (*e.g.*, traces of rum or vanilla flavor) in a few cases. The resulting formulation will be intensely colored by the addition of caramel. Similar considerations to those made for cocoa-flavored liqueurs are valid for the use of compounded essential oils or compound flavors with a definite coffee-like note. A guideline formulation for cream of coffee sufficient for 100 liters of finished product is given below:

Cream of Coffee

Ingredient	Quantity
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.4 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

Crystallized Liqueurs

In a liqueur containing 42–43% alcohol, a 40% sugar content already yields crystallization. Whenever the alcohol content is decreased, the sugar content must be increased to insure crystallization. For example, in order to deposit sugar crystals on the branchlets of heath (as in a typical millefiori liqueur) without depositing it on the glass walls of the container, the amount of sugar must be very accurately dosed, based on the corresponding alcohol content so as to exceed only slightly the minimum amount yielding incipient crystallization. The following operative technique is suggested:

1. Dissolve the compound oil in the alcohol required for the preparation of a predetermined amount of finished liqueur. Aliquots of the alcohol solution are then divided into the various containers.
2. Prepare the sugar syrup (usually containing 550–650 g sugar per liter of finished liqueur) by heating; then add the colorant if required, and filter the solution immediately. Fill the bottles with the hot syrup and seal them temporarily.
3. Allow the bottles to cool without disturbing. Adjust the final volume by adding a small amount of hot syrup to replace volume losses caused by contraction of the mass on cooling.
4. Again cool the bottles, seal, and store them in a cool place for 15 days minimum without disturbance.

Kümmel

Kümmel is also known by other names, such as double kümmel or crystallized kümmel, based on the amount of sugar present in the finished liqueur. The basic ingredient for flavoring kümmel is caraway essential oil (rectified), imparting the characteristic anise-like note to the finished product. The preparation of the compounded oil calls for about 90% rectified caraway essential oil; the remaining 10% consists of a blend of spicy notes, such as cinnamon, nutmeg, clove, and coriander, together with small amounts of orange and lemon (sometimes in combination with a small amount of anethol).

Kümmel Flavor

Ingredient	Parts
Rectified caraway essential oil	350
Rum ether	20
Anethol	3
Rectified fennel essential oil	2
Lemon essential oil	2
Coriander essential oil	1
Solvent (alcohol)	122
Total	500

It is also possible to employ the alcohol distillate of caraway seeds as the basic ingredient. A guideline formulation for the preparation of 100 liters of liqueur is shown below:

Kümmel

Ingredient	Quantity
96% alcohol	38 l
Sugar	60 kg
Distilled water	28 l
Compound flavor 1 × 200	0.5 kg

Lemon

The production of lemon liqueur today is of limited domestic use only. The commercial product is often called by the corresponding French name *verveine*. In the latter case, however, the flavor is somewhat different and may be defined as a blend of flavors used in certain types of liqueurs, such as certosa and benedictine, together with a lemon-like flavor (lemon verbena). Homemade liqueurs are prepared by direct infusion of the green lemon verbena leaves in 40% alcohol without further addition of complementary flavors; the resulting infusion is sweetened with sugar (q.s.) to personal taste.

The liqueur flavored with essential oils can be prepared by using the guideline formulation shown below:

Lemon Verbena

Ingredient	Quantity*	
	Strong	Sweet
96% alcohol	32 l	32 l
Sugar	36 kg	40 kg
Distilled water	48.5 l	45 l
Compound flavor 1 × 200	0.5 kg	0.5 kg

* Formulation is sufficient for 100 liters of finished liqueur.

Mint

Mint-flavored liqueurs are usually prepared by diluting a good quality tri-rectified peppermint essential oil (approximate yield, 1 × 4,000) or the soluble essence (approximate yield, 1 × 2,000) with alcohol and syrup. Small amounts of flavor modifiers, such as citrus essential oils, may be added as optional ingredients; however, these should not exceed 3.5%, based on the amount of peppermint essential oil employed, in order to obtain good flavor results.

Green and white mint liqueurs may be prepared by using the following guideline formulation, sufficient for 100 liters of finished product:

Mint Liqueurs

Ingredient	Quantity	
	Green mint	White mint
96% alcohol	32 l	32 l
Sugar	36 kg	40 kg
Distilled water	48.5 l	45 l
Compound flavor 1 × 200	0.5 kg	0.5 kg
Colorant	q.s.	—

Rose

The importance of this flavor ingredient is described in the discussion of Floral Flavors (see p. 573). The following description, therefore, will be limited to the formulation of creme de rose, or rosolio. The basic note in rose liqueurs is obviously the rose flavor that, when formulated as a compounded essential oil free of additional diluents, has an approximate yield of 1 × 8,000 based on the finished product. The choice of a rose absolute rich in phenethyl alcohol is recommended for the formulation of the compound flavors. The note of rose absolute alone is too sweet, however, and citrus notes (sweet orange) must be added in small amounts; this is rounded off by the addition of vanillin and spiced

with a blend of cinnamon and nutmeg. If necessary to decrease formulating costs, only one part of true rose absolute can be employed together with massive doses of rose derivatives; it is advisable to add a small amount of rose distillation water to dilute the alcohol content. The following guideline formulation may be employed. Note that rosolio has approximately the same formulation as alkermes (see p. 622).

Rosolio

Ingredient	Quantity*
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.4 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

* Formulation is sufficient for 100 liters of finished product.

Vanilla

White creme de vanilla is generally used as a flavor modifier when added in varying amounts to creme de mocha, rhubarb elixir, and a few other products, depending on traditional customs. The brown quality is used mainly as a liqueur. Creme de vanilla is prepared with vanilla tincture obtained by macerating vanilla pods in approximately 50% alcohol. The hydro-alcoholic solution of vanillin or vanilla absolute may be used for less expensive products. Both white and brown creme de vanilla can be prepared by the following formulation:

Creme de Vanilla

Ingredient	Quantity*	
	White	Brown
96% alcohol	24 l	24 l
Sugar	14 kg	40 kg
Distilled water	51.8 l	51 l
Compound flavor 1 × 100	1 kg	1 kg
Colorant	—	q.s.

* Formulation is sufficient for 100 liters of finished liqueur.

Sweet Liqueurs with Mixed, or Fantasia, Flavors

The formulation of these liqueurs varies widely and includes a certain number of basic flavor notes. The formulations discussed in the following pages represent examples of the individual categories of products apparently developed as variations of a single flavor theme. These liqueur varieties found wide acceptance at the beginning of the century and are still rather popular today.

Alkermes

The formulation of alkermes is rather typical. The characteristic bouquet results from a nearly equal-weight mixture of a strong citrus flavor (orange and lemon) together with a blend of spices (clove, cinnamon, and mace). The resulting flavor is strongly influenced by the spicy note, which can

be reinforced for specific uses, as in *bagne** for pastry. A rose note that can be quite pronounced gives a flavor effect similar to rosolio. Other products also are used to round off the flavor note, such as coriander, calamus, and vanillin; the latter ingredient is usually present in a 1:15 ratio based on the citrus essential oils.

A guideline formulation for the preparation of a suitable compounded oil for alkermes is given below:

Ingredient	Parts
Clove essential oil	780
Lemon essential oil	400
Orange essential oil	300
Cinnamon essential oil	250
Mace essential oil	180
Vanillin	150
Neroli essential oil	10
Citronellol	2
Rose absolute	1
Solvent (alcohol)	927
Total	3,000

The liqueur is usually prepared according to the following formulation:

Alkermes

Ingredient	Quantity*
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.8 l
Compound flavor 1 × 200	0.5 kg
Colorant	q.s.

* Formulation sufficient for 100 liters of finished liqueur.

Amaretto

Amaretto is a sweet, floral variation of bitter almond liqueurs. Its flavor results from using citrus flavors (*e.g.*, lemon, bitter orange, etc.) and then adding vanillin, cocoa distillate, and a trace of neroli. A guideline formulation for the preparation of amaretto follows:

Amaretto

Ingredient	Quantity*
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.5 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

* Formulation for 100 liters of finished liqueur.

* *Bagne* are liqueur sauces used for soaking pound cakes, such as baba rum.

Arquebus

The characteristic flavor note of this product results from blending five basic notes: thyme, clary sage, rosemary, lavender, and anise. These might ultimately be blended in equal amounts. Other minor ingredients, such as fennel, orange or lemon, angelica, and oregano, enhance the thoroughness of the blend by bringing out certain characteristic notes of any one of the five basic flavors. The compounded essential oil is formulated by using only the individual essential oils; it has an approximate yield of 1 × 2,000. A guideline formulation is shown below:

Ingredient	Parts
Lavender essential oil	105
Clary sage essential oil	100
Rosemary essential oil	100
Thyme essential oil	90
Fennel essential oil	40
Mint essential oil	25.9
Angelica essential oil	5
Anise essential oil	5
Lemon essential oil	4
Wormwood essential oil	2
Cinnamon essential oil (10% in alcohol solution)	0.1
Solvent (alcohol)	523
Total	1,000.0

In place of the essential oils, the same liqueur can also be prepared by distillation of the hydroalcoholic infusion made by macerating the corresponding dried herbs. The approximately 60% alcohol distillate has a yield of about 1 × 50 after the addition of small amounts of angelica and lavender essential oils in alcohol solution. A liqueur acceptable to traditional market requirements may be prepared by the following guideline formulation:

Arquebus

Ingredient	Quantity*
96% alcohol	46.9 l
Sugar	1 kg
Distilled water	55.1 l
Compound flavor 1 × 200	0.5 kg

* Formulation for 100 liters of finished liqueur.

Benedictine

Benedictine is prepared in countless flavor variations, especially in France, although it consists basically of the blending of three flavors: the citrus note (orange), angelica, and juniper together with coriander. The large number of flavor ingredients that may be added to the basic formulation greatly influences the flavor of the finished product. From an old formulation prepared by distillation of infusions of dried herbs comes the following list of flavor ingredients: coriander, cardamom, angelica seeds, angelica roots, lemon verbena, yarrow, arnica, hyssop, lemon balm, marjoram, cinnamon, mace, oregano, clove, juniper berries, pine buds, and peppermint. To obtain certain flavor results, the use of distillates and tinctures rather than the essential oils of the above herbs are preferred for benedictine formulations. Essential oils may be employed only in solution and in trace amounts to round off the

flavor note. Benedictine is formulated according to the guideline values given for the preparation of green certosa liqueurs (see p. 625).

Benevento

The characteristic flavor of benevento results from cardamom, coriander, angelica, and some calamus in specific cases. To these basic ingredients, mint, cinnamon, ginger, a pronounced citrus note, and a touch of anise flavor must be added. Although the basic ingredients for the product have been listed, the potential variations of the basic formulation are numerous. A typical variation consists of angelica seeds, angelica roots, or mixtures of the two in varying ratios. The amount of calamus used depends on flavor variations.

Citrus flavors consisting of compound oils formulated exclusively with the individual essential oils must be properly selected. In specific cases the terpeneless oils are preferred because of their better solubility. Such compound flavors have an approximate yield of 1 × 8,000. A guideline for the preparation of the compound flavor is given below:

Ingredient	Parts
Cardamon essential oil	100
Coriander essential oil	100
Ginger essential oil	30
Angelica seeds	25
Angelica roots essential oil	20
Anethol	10
Lemon essential oil	8
Menthol	7
Ceylon cinnamon essential oil	5
Solvent (alcohol)	695
Total	1,000

The distillate from the hydro-alcoholic infusion prepared by macerating the corresponding dried herbs can also be used in the liqueur preparation. The distillate has a yield of approximately 1 × 50; the flavor is usually reinforced by small amounts of essential oils in alcoholic solution to enhance the sharp, citrus-anise note. The possible variations with respect to alcohol and sugar content in the formulation are somewhat limited and usually do not vary much from the following values:

Benevento

Ingredient	Quantity*
96% alcohol	36 l
Sugar	30 kg
Distilled water	47.5 l
Compound flavor 1 × 200	0.5 kg
Colorant	q.s.

* Suitable for the preparation of 100 liters of finished product.

Certosa

Certosa exhibits a flavor very similar to benedictine; in certosa the citrus flavors also are associated with angelica and juniper. The ingredient ratios, however, are entirely different from benedictine; two additional flavor notes are present—anise and wormwood. The latter can be replaced by a vermouth compound flavor.

Certosa liqueurs are produced in two types—green certosa and yellow certosa. The anise note is most pronounced in the yellow certosa, whereas it is somewhat subdued in green certosa. Rum and cognac notes may be used in green certosa formulations, while only trace amounts of these flavors should be used in the formulation of yellow certosa. Following are essential oils used exclusively for the preparation of a compound certosa flavor having a yield of approximately 1 × 5,000:

Compound Certosa Flavor

Ingredients	Parts
Lemon essential oil	60
Anethol	20
Juniper essential oil (rectified)	15
Clary sage essential oil	7.1
Hyssop essential oil	4
Bitter orange essential oil	3
Mint essential oil (tri-rectified)	3
Petitgrain bigarade	3
Coriander essential oil	2.5
Angelica essential oil	2.1
Mace essential oil	2.1
Wormwood essential oil	2.1
Sweet orange essential oil	2
Caraway essential oil	1
Ceylon cinnamon essential oil	1
Lavender essential oil	Trace

The above values should be considered as approximate, with anethol, lemon, and juniper comprising the bulk of the formulation.

Certosa may also be formulated by using the corresponding dried herbs in place of the essential oils. However, the resulting flavor effects will not be entirely satisfactory unless additional quantities of soluble essential oils are added to the compound flavor. In general, an infusion followed by distillation of a blend of cinnamon, mace, bitter orange, clary sage, juniper, angelica, coriander, wormwood, and hyssop could be prepared. The distillate then could be added with a suitable blend of essential oils, such as lemon, sweet orange, mint, petitgrain bigarade, and anise.

Yellow certosa and green certosa differ slightly as to flavor, color, and alcohol content. Both liqueurs may be prepared according to the following guideline formulations:

Yellow and Green Certosa

Ingredient	Quantity*	
	Yellow certosa	Green certosa
96% alcohol	36 l	38 l
Sugar	30 kg	30 kg
Distilled water	47.5 l	45.6 l
Compound flavor 1 × 200	0.5 kg	0.5 kg
Colorant	q.s.	q.s.

* Formulation for 100 liters of finished product.

Cordial

This liqueur exhibits chiefly floral and fruital flavors. In formulations considered nearly typical, the flavor results from a blend of violet and cherry notes. To obtain satisfactory flavor results, it is necessary to blend the characteristic irone note of orris butter present in raspberry distillate with that of kirsch and maraschino present in sweet and marasca cherry distillates, respectively. The addition of a small amount of cognac and sweet orange essential oil imparts a slightly tart, spicy, citrus-like flavor to the compounded essential oil that has an approximate yield of 1 × 4,000. A guideline formulation for the preparation of the compounded oil follows:

Ingredient	Parts
Rum ether	100
Vanillin	100
Cognac essential oil	62
Ethyl acetate	60
Sweet orange essential oil	35
Amyl acetate	20
Bitter almond essential oil	13
Cherry laurel essential oil	4
Orris butter	1.8
Lemon essential oil	1.4
α-Ionone	0.5
Rose absolute	0.3
Solvent (alcohol)	602
Total	1,000.0

A guideline formulation for the preparation of cordial follows:

Cordial

Ingredient	Quantity*
96% alcohol	36 l
Sugar	30 kg
Distilled water	47 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

* Formulation for 100 liters of finished liqueur.

Goldwasser

This type of liqueur is also known as gold-drop, goldwater, and danzig water. The name *goldwasser* derives from the tiny gold leaflets suspended in the finished liqueur. The characteristic flavor results from a mixed citrus note (orange and lemon, 1 : 2) blended with a spicy flavor complex consisting mainly of calamus, ginger, cinnamon, and nutmeg. Cardamom is sometimes added; lavender, neroli, and sometimes spearmint are frequently added to impart particular bouquets to the finished product. A guideline to the formulation of the compound flavor is given on the following page.

Goldwasser Flavor

Ingredient	Parts
Lemon essential oil	200
Orange essential oil	100
Cinnamon essential oil	100
Nutmeg essential oil	50
Calamus essential oil	25
Cardamon essential oil	12
Neroli essential oil	3
Rosemary essential oil	2
Solvent (alcohol)	508
Total	1,000

A guideline formulation for the preparation of 100 liters of finished liqueur follows:

Goldwasser

Ingredient	Quantity
96% alcohol	14 l
Sugar	25 kg
Distilled water	46.8 l
Compound flavor 1 × 200	0.5 kg
Colorant (to create gold leaflet effect)	q.s.

Millefiori

The name *millefiori* is intended to represent an association with countless floral notes. The basic flavor notes of this liqueur consist of bitter orange flowers (neroli), rose, orris, vanillin, and a trace amount of spices. Two liqueur types are formulated: one contains large amounts of sugar, the other has a small amount of sugar and is called "frosted." To create special effects, a small amount of ambrette seed tincture may be added to subdue the spicy cinnamon and cardamom notes (sometimes employed also in blends with coriander). A guideline formulation for the preparation of a suitable compounded oil is given below:

Ingredient	Parts
Neroli essential oil	115
Rose flavor imitation	75
Vanillin	60
Bitter orange essential oil	10
Clove essential oil	6
Ceylon cinnamon essential oil	5
Nutmeg essential oil	5
Orris butter	4
Solvent (alcohol)	720
Total	1,000

Following the guidelines discussed for the preparation of crystallized liqueurs (see p. 689), millefiori frosted or crystallized liqueurs may be formulated as follows:

Millefiori

Ingredient	Quantity*	
	Frosted	Crystallized
96% alcohol	35.5 l	30 l
Sugar	60 kg	40 kg
Distilled water	28.7 l	46.6 l
Compound flavor 1 × 100	1 kg	1 kg
Colorant	q.s.	q.s.

* Formulation for 100 liters of finished product.

Perfetto Amore

Liqueurs of this type have been formulated under the same name but with entirely different flavors in several European countries. Among the most characteristic formulations, one is specifically reminiscent of benevento liqueurs; it consists of lemon, coriander, mace, clove, and a trace of cinnamon. A few other products exhibit an anise flavor. The liqueur may be prepared according to the following formulation:

Perfetto Amore

Ingredient	Quantity*
96% alcohol	30 l
Sugar	40 kg
Distilled water	46.9 l
Compound flavor 1 × 200	0.5 kg
Colorant	q.s.

* Formulation for 100 liters of finished product.

Ratafia

The traditional formulation of this liqueur can be considered a spice-flavored variation of bitter almond liqueurs. Cherry laurel once was the basic ingredient in the compounded essential oil together with clove, cinnamon, mace, and coriander. The resulting flavor was complemented by a good red Barbera wine.

Although these product types have almost completely disappeared from the market, a flavor formulation free of cherry laurel (an oil that must be rendered completely free of prussic acid) can be prepared by replacing cherry laurel essential oil with that of bitter almond, to which small amounts of benzyl alcohol and citronellol are added. A guideline formulation follows:

Ratafia

Ingredient	Quantity*
96% alcohol	24 l
Wine	20 l
Sugar	40 kg
Distilled water	31.7 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

* Formulation for 100 liters of finished liqueur.

Elixirs

This category includes liqueurs prepared by dissolving the aromatic principles of specific herbs in water, alcohol, and sugar. The resulting flavor consists of a sugar flavor blended with the usually bitter note of the herb. The oldest and most typical liqueur formulations are representative of elixirs.

Rhubarb Elixir

The basic raw material for this preparation is Chinese rhubarb (flat or round). The comminuted rhizome is extracted with a mixture of water and alcohol (according to some preparation procedures: 1 part rhubarb, 1 part water, and 1 part alcohol). After a few days the tincture is drained off and filtered; small amounts of essential oils (calamus, coriander, wormwood, etc.) are added to impart the characteristic bouquet. Alternatively, a compound tincture of rhubarb with other herbs can be prepared using traditional preparatory methods. Rhubarb-flavored elixir is prepared according to the following guideline formulation:

Rhubarb Elixer

Ingredient	Quantity*
96% alcohol	16.5 l
Sugar	27 kg
Distilled water	65 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

* Formulation for 100 liters of finished product.

China (Cinchona-flavored Elixer)

Cinchona-flavored elixir is prepared usually from cinchona tinctures. Individual or compounded tinctures may be prepared by extracting the flavor principles from the individual herbs or from a blend. Cinchona bark is the most important raw material; characteristic flavor effects are obtained by adding clove, cinnamon, coriander, and sweet orange. Sometimes the bitter flavor is reinforced by the addition of gentian and chirata (the latter may be employed up to approximately equal weight of cinchona), whose flavors blend well with cinchona. Cinchona-flavored elixir may be prepared according to the following guideline formulation:

China

Ingredient	Quantity*
96% alcohol	32.2 l
Sugar	34 kg
Distilled water	47.4 l
Compound flavor 1 × 100	1 kg
Colorant	q.s.

* Formulation for 100 liters of finished product.

Nocino (Walnut-flavored Elixer)

Nocino, often found in old recipe books for liqueurs, today is produced primarily in Italy. The characteristic bitter flavor is obtained by the extraction of green walnuts harvested at the end of June according to Italian tradition. A recipe for a homemade liqueur for approximately 2.5 liters of finished product prescribes the extraction of about 30 walnuts in 70% alcohol, to which sufficient sugar is added. The addition of a few grams of cinnamon, clove, and lemon peel is optional.

By using specifically prepared compounded oils, 100 liters of liqueur may be formulated according to the following guideline:

Nocino

Ingredient	Quantity
96% alcohol	24 l
Sugar	40 kg
Distilled water	52.3 l
Compound flavor 1 × 200	0.5 kg
Colorant	q.s.

Distilled Liquor Imitations and Their Composition

The large market demand for distilled liquors has prompted the study and formulation of the corresponding imitations to satisfy widely divergent consumer needs. An additional factor that has stimulated the search for suitable imitations is the relevant difference in production costs between natural and imitation distillates; these high costs are attributed to the lengthy aging required by natural distillates together with the relatively large capital investment for cellar space and equipment. It should be stressed that the potential use of imitation distillates for flavoring pastry is high; well formulated imitations, in fact, have been proven to yield highly satisfactory flavor results. From the standpoint of regulations governing the production of natural distillates, a discussion of the comparative value of commercial distillate imitations is beyond the scope of the book.

Rum

Rums and tafias are obtained by distillation of raw or slightly cooked and concentrated fermented juices expressed from sugar canes (*Saccharum officinarum* L.) or by distillation of fermented molasses (black strap) residue from the refining of cane sugar. The production site of these distillates, together with the name *rum* or *tafia*, has always been employed to differentiate the various commercial qualities. Specific reference will be made, for example, in the text to the following types: Jamaica rum, Martinique rum, white or Antilles rum, and Demerara or British Guiana rum. Countries that produce rum distillates include Brazil, British Guiana, Cuba, Haiti, Jamaica, Puerto Rico, Santo Domingo, Trinidad, Madagascar, the United States (Kentucky, Massachusetts, and Hawaii), and the Virgin Islands. The Hawaiian production started only recently and follows production methods quite "new" from certain points of view, although concentrated sugar-cane juices are still used as the primary source of raw material.

The flavor complex of natural rum has been the subject of several analytical studies. The reader can refer to a comprehensive bibliography on the subject[7] and to a more recent gas-chromatographic study using capillary columns.[5,6] The characteristic rum flavor is dependent on the total impurities coefficient expressed as total impurities content in milligrams based on 100 cc anhydrous alcohol; the commercial classification based on the above coefficient is in practice the resulting sum of acids, ethers, alcohols, aldehydes, and furfural content. The most important free acids are formic, acetic, butyric, and caproic. For the weight composition of volatile components in rum flavor, the reader again is referred to the above study.[5,6]

The need for an imitation rum distillate was created in Europe by the unavailability of either cane sugar or molasses. From the end of the nineteenth century to the beginning of the twentieth century, sugar beet molasses, barley and other meals, and various fruit concoctions were employed as raw materials for the distillation together with flavor formulations containing old leather scrapings, black minced truffles, and other substances. Aging was carried out artificially by various expedients, such as singeing the inner walls of oak barrels with tarred straw. The evolution of the chemical studies led to preparation methods of a certain interest, such as the recipe below suitable for the preparation of 100 liters of 70% rum using only 8 liters of genuine Jamaica rum. The following ingredients are mixed in a still:

Imitation Rum Distillate

Ingredient	Quantity
90% alcohol	34 l
Water	20.5 l
Choice wine vinegar	1.5 l
Bleached sugar syrup	1 kg
Tannin	375 g
Sulfuric acid	190 g
Powdered carbon black	250 g

Preparation:

1. The mixture is distilled slowly until 35 liters of distillate is obtained; the following ingredients are added:

Peru balsam	130 g
Ethyl acetate	65 g
Candied brown sugar	2 kg
Genuine Jamaica rum	8 kg

2. The distillate is then diluted to 100 liters with water and sufficient alcohol to yield a 70% total alcoholic content.

Formulations similar to the above may be found by the hundreds in old formularies for liqueurs; all are different, however, because of the relentless search by flavorists for the characteristic flavor note. Some flavorists identified the note with Malaga wine flavor; a few others with that of green tea, vanilla, or cinnamon, but all failed to formulate a characteristic bouquet.

Rum Ether

A milestone in the formulation of rum imitations is the fabrication of rum ether, whose composition in volatile substances is qualitatively very similar to rum distillates.[8] To the flavorist this product represents the building block in the imitation of distillates. In the following sections various flavor ingredients suitable for addition to rum ether to formulate the most characteristic bouquets will be discussed.

Today's manufacture of rum ether is based on the use of the following ingredients: ethyl alcohol (95%), sulfuric acid (66 Be), manganese dioxide, and piroligneous acid. The method of preparation consists of first adding the alcohol and manganese dioxide to the still, then the piroligneous acid, and finally the sulfuric acid (slowly, with stirring, to prevent the temperature in the reaction mass from exceeding 40–50 C). The resulting mixture is distilled under atmospheric pressure, and the fraction distilling between 60–100 C is collected. The distillate is subsequently rectified.

A survey of the relative amounts of the various ingredients used in the preparation shows upper and lower limits (indicated as Type A and Type B, respectively, in the following table) as well as all possible intermediate values being used.

Ingredient	Type A		Type B
95% alcohol	12 kg	to	20 kg
Piroligneous acid (12% sol in acetic acid)	10 kg	to	16 kg
Sulfuric acid	3 kg	to	8 kg
Manganese dioxide	2 kg	to	5 kg
Or, placing ethyl alcohol equal to 100			
95% ethyl alcohol	100 kg		100 kg
Piroligneous acid (12% sol in acetic acid)	83 kg	to	80 kg
Sulfuric acid	25 kg	to	40 kg
Manganese dioxide	16.6 kg	to	25 kg

The average yield of rectified rum ether from various preparations is about 98% calculated from the amount of alcohol used. The rectified fraction has a distillation range between 65–87°C.

The distillate is sometimes divided into two main fractions suitable for specific applications in liqueur formulations based on the higher or lower acetaldehyde content. More often, two or more types of rum ether are distilled by varying the amount of the starting materials in order to prepare products more suitable in specific liqueur applications. A few manufacturers add ingredients such as starch, meals, birch tar, sugar beet or sugar cane molasses, sucrose, etc. to the basic mixture, but this is not commonly practiced. Some authors also suggest the addition of acetic acid, wood coal, and Peru balsam.[9]

Rum ethers prepared by different methods contain qualitatively the same volatile principles but in varying ratios. Therefore, the most suitable product can be selected for specific uses. The addition of other flavor ingredients will follow parallel guidelines by observing that the same ingredients are often used in more than one formulation. The ingredients most widely used in distillate imitations are as follows:

1. Tinctures: carob, raisin, saffron, vanilla (or vanillin)
2. Essential oils: cinnamon, cognac
3. Orris absolute

Among the above ingredients a few are recurrent in most formulations because of their functionality. Saffron tincture is the most significant example and is used to impart the flavor note characteristic of aged distillates. Cognac oil imparts the flavor experienced when swallowing the liquor, while cinnamon essential oil adds a characteristic spicy note.

Jamaica Rum

In addition to the above major ingredients, equal amounts of raisin and carob tincture and slightly less saffron tincture are used for flavoring Jamaica rum distillate imitation; for example, 1 part raisin tincture, 1 part carob tincture, and 0.04 part saffron tincture are added to 6 parts rum ether.

Martinique Rum

Natural Martinique rum is characterized by a low total impurities coefficient if distilled from fermented cane sugar juice and not from molasses. This is reproduced in the distillate imitation by avoiding the use of carob and raisin tinctures, while using only trace amounts of saffron tincture in proportioned blends with the essential oils and vanillin.

White Antilles Rum

The flavor composition of white Antilles rum is very similar to Martinique rum. The finished imitation should not be colored with caramel to avoid confusion with the less valuable Martinique rum from molasses. The ratio between rum ether and other flavor ingredients is usually 90:2 in this product as compared to the somewhat lower 90:3–3.5 in Martinique rum.

Demerara Rum

This distillate could be classified in flavor midway between Jamaica and Martinique rum. However, it exhibits a characteristic sweet, less spicy note; it also has a somewhat higher volatile content. Therefore, Demerara imitation distillates contain more than the usual amounts of carob tincture and rum ether, fewer essential oils, and more saffron tincture to improve the flavor of the blend, which is less aromatic than other rum types.

Following this rather cursory examination of the aroma notes characteristic of different rum distillates, it should be stressed that rum ether in blends with flavor ingredients (in suitable doses) may be diluted 200 to 400 fold with alcohol of the selected strength. Products with yields varying between approximately 1 × 100 and 1 × 200 on dilution with 70% alcohol are suitable for distillate imitations for pastry use.

Cognac and Brandy

Cognac is a distillate of French wines native to the Charentes region. From the white wine of another French district, namely the hilly area separating the Garonne from the Adour basin, Armagnac distillates are produced. The aging process of wine distillates in oak barrels is as important as the use of specific grapes and wines in order to obtain good distillates. Countries other than France also have started the production of wine distillates. Since the name *cognac* has been reserved exclusively for distillates of French production, several other names are used to designate wine distillates from other sources. The generic name *brandy* has been adopted to designate those distillates of other nations.

Aside from personal preferences for natural cognac or brandy types, there is no significant difference in the number and nature of the basic components in the volatile aroma of the various products. However, definite quantitative differences as well as characteristic undertones are detectable; these determine the personal preference and allow the classification of wine distillates according to quality. A quantitative comparison of a cognac and brandy with a 40% alcohol strength shows the following:

1. a large ester (methyl formate plus ethyl acetate) content in cognac
2. an approximately equal aldehyde content, which is sometimes slightly higher in brandy
3. equal acetal content (acetaldehyde plus propionaldehyde), and
4. a larger acetone, *n*-propyl alcohol, isobutyl alcohol, and isoamyl alcohol content in brandy.

These observations have been confirmed by gas-chromatographic analysis using capillary columns that may yield additional differences such as to pinpoint with sufficient precision why each individual cognac exhibits a characteristic bouquet.

Cognac and brandy have long been imitated by using formulations based on essential oils and spirits suitable for imparting flavors closely duplicating those typical to diluted alcohol solutions. The demand for cognac and brandy imitations is attributable mainly to economic considerations. Originally, the raw material widely employed for such imitations was cognac oil; subsequently cognac oil was replaced with oenanthic ether, commercially available as a mixture of esterified coconut fatty acids. Today both products are employed in liquor distillate imitations. While cognac oil consists mainly of ethyl caprylate and ethyl palmitate, oenanthic ether contains a larger number of ethyl esters, such as ethyl caproate, ethyl caprylate, ethyl caprate, ethyl laurate, ethyl myristate, and ethyl palmitate. This implies significant flavor differences, although the presence of trace free alcohols in the intimate blend of notes tends to level off such flavor differences.

Economic and qualitative considerations govern the use of the individual flavor ingredients or blends thereof. Usually the above flavor ingredients alone are not sufficient to rebuild the classic bouquet of the distillates; it is, therefore, necessary to add other flavor ingredients. The choice and the use level of complementary flavor ingredients is subordinate to the cognac or brandy being imitated. The selection of ingredients extends to several categories, such as essential oils, tinctures, distillates, isolates, and synthetic products, as follows:

Essential Oils. Cognac, bitter almond, bay, clove, cinnamon, orris, birch, and neroli.

Absolutes. Vanilla, tonka bean, and oakmoss.

Isolates and Synthetic Products. Vanillin, irone, oenanthic ether, ethyl pelargonate, benzaldehyde, coumarin, ethyl acetate, ethyl formate, ethyl butyrate, acetaldehyde, and rum ether.

Tinctures. Saffron, oak bark, raisin, carob, and tea.

The basic formulation guidelines are often modified by the individual creativity of the flavorist as follows:

1. To formulate a flavor having an approximate yield of 1 × 500 to 1 × 600, 1 kg cognac oil (or cognac oil and oenanthic ether mixture) is blended with approximately 200–250 g essential oils, 60–80 g vanillin plus coumarin (or equivalent products), 7–8 kg rum ether, 1 kg esters (or more if rum ether is not included in the formulation), and 12–15 kg tincture (saffron tincture is used only in trace amounts based on the finished product).
2. To formulate fantasia rum, cognac, or brandy imitations using essential oils, tinctures, and distillates, the formulations shown in the following table may be a useful starting point:

Ingredient	96% alcohol, l	Sugar, kg	Distilled water, l	Colorant and compound flavor
Various types fantasia rum (with/without the addition of natural rum distillate)	50	0.5–1	52	q.s.
Whisky (imitation)	41.6	1	60.3	q.s.
Various brandy types	45	1	56.6	q.s.
Vodka (imitation)	50	0.5	52	

A few products such as calvados, whisky, vodka, and arrak are not usually imitated. Calvados is a cider distillate aged in oak barrels.

Gin and Kirschwasser

Gin and kirschwasser are two liquors generally obtained by direct distillation of juniper berries and cherries, respectively; these liquors are successfully imitated by means of compound flavors and alcohol (both liquors contain only a very small amount of sugar). Juniper essential oil is obtained as a by-product in the distillation of gin. A soluble essential oil can be prepared by a very careful rectification of the essential oil, which can be dissolved in alcohol of the required strength to yield imitation gin. The formulation of the kirsch note is somewhat more complex; also in this case the flavor note is obtained by using cherry kernels distillate. A guideline formulation follows:

Ingredient	Quality*
96% alcohol	50 l
Sugar	1 kg
Distilled water	52.1 l
Compound flavor 1 × 200	0.5 kg

* Formulation for 100 liters of finished product.

Fruit Distillates

The imitation of fruit distillates and their flavoring are also important; grappa, for example, is obtained by distillation of the expressed grape residue. The most widely used flavors for the above applications are muscat wine, pear, gentian (bitter), mint, plum, and bitter almond.

Muscat Flavor. Muscat flavor is prepared by distillation of a water-alcohol infusion of coriander, clary sage, and elder. The 50-proof distillate flavor has a yield of 1 × 100 or more.

Almond-plum Flavor. Almond-plum flavor is prepared by blending a plum tincture with bitter-almond essential oil (free from prussic acid) or benzaldehyde (free from hydrochloric acid) rounded off by small additions of cherry distillate or cognac oil.

Pear Flavor. Pear flavor is a product of very limited use basically prepared with esters (amyl acetate and a few others having similar notes) imparting to the compound flavor a note reminiscent of Williams pear.

Bitter Flavor. The bitter flavor of rue is obtained by direct infusion of the herb in the distillate. Gentian bitter flavor is quite frequently encountered and is prepared by the addition of small amounts of gentian tincture to the distillate.

Mint Flavor. Trirectified mint essential oil is used.

Punch

Liquors of this type are diluted with hot boiling water immediately prior to use; therefore, an alcohol content suitable for dilution is required. From a flavor standpoint, the various punches may be considered as variations of a basic rum flavor note.

Rum-flavored punches represent the classic beverage consumed piping hot in cold winter months; all other products consist of rum flavor combined with citrus notes (orange and mandarin punch), spicy notes (alkermes punch), or other flavors such as coffee, camomile, etc. For the preparation of the above products, orange or mandarin soluble essential oils, the compounded essential oil of alkermes, or the tinctures of coffee or camomile are added to rum distillate. Guideline formulations are shown below:

Punch Formulations*

Ingredient	Rum	Orange	Mandarin	Alkermes	Coffee	Camomile
96% alcohol, l	33	33	33	33	33	33
Sugar, kg	25	25	25	25	25	25
Distilled water, l	53.5	53.5	53.5	53.5	46	53.5
Compound flavor 1 × 200, kg	0.5	0.5	0.5	0.5	1†	0.5
Colorant	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.

* The formulations are sufficient for 100 liters of finished product.
† (1 × 100).

NON-ALCOHOLIC BEVERAGES

Syrups

Syrups for non-alcoholic beverages consist of solutions containing sufficient sugar and flavor to achieve a 4–5 fold dilution with cold water or soda immediately prior to use. Syrups must be clear, yield clear solutions (with the exception of products such as orzata*), and exhibit good storage stability in containers repeatedly uncorked during use. To fulfill these physical requirements and to have a pleasant taste, syrups should contain 65% sugar and 35% fruit juice. Since the manufacturer seldom has fresh fruit at his disposal for expression of the juice in which sugar may be dissolved at room temperature, it is common practice to use 5–7 fold concentrated juice diluted with the required amount of syrup prior to use.[10] When fresh juices are employed, the addition of colorant and, sometimes, citric acid may not be required. The above represents optimum guidelines for the preparation of syrups for beverages.

While the presence of 65% sugar inhibits the growth of molds and bacteria, fermentation or degradation of the syrup may still occur, even when the above precautions are taken.[11] Syrup degradation may occur because of the sugar or water quality employed, lack of cleanliness, and a disregard for elementary hygienic practice during manufacturing. While preparation of syrups is a rather simple task, it requires good manufacturing practice and good quality raw materials. Independent of existing regulations concerning manufacturing practice and marketing of all types of syrups, it is always advisable to practice the following basic rules:

1. Wash and sterilize all containers prior to bottling the syrup.
2. Wash and sterilize all containers used in the preparation, filtering, and bottling of syrups.
3. Use refined sugar.
4. Use distilled, purified, or boiled water.
5. Use pasteurized juices.
6. Thoroughly filter the syrup.

As previously mentioned fresh fruit juices are seldom available for the preparation of syrups. In some cases concentrated juices are used after diluting as required; in other cases juices are used only in limited amounts or omitted from the formulation. In the latter case the basic steps for the preparation of syrup are as follows:

1. Preparation of the sugar syrup
2. Acidification of the sugar syrup
3. Coloring the sugar syrup
4. Flavoring the syrups with or without the addition of concentrated juice
5. Addition of preservatives where permitted.

65 kg of sugar are soluble in 35 kg of water, yielding 100 kg of syrup (or 75.8 l)

or

85.7 kg of sugar are soluble in 46.2 l of water, yielding 100 l of syrup (or 131.9 kg)

Preparation of Sugar Syrups at 65° Brix

1. Refined sugar is dissolved in pure (preferably distilled) water in a stainless steel container equipped with a stirrer and steam jacket.
2. When distilled water is used, dissolution of the sugar can be carried out at a low temperature.
3. Otherwise, the water is heated to boiling, and the sugar is added and stirred at 80°C until completely dissolved. The solution is then allowed to cool to room temperature.
4. When a crystal-clear syrup (instead of a yellowish product) is desired, the residual color may be removed by mixing approximately 0.1–0.2 kg activated charcoal (of the same quality used in wines) with the syrup. The syrup is then cooled overnight and finally filtered using asbestos or felt-lined filters for complete removal of the charcoal.[1]

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* Orzata is a mixture of comminuted almonds, sugar, and water yielding milky solutions.

The syrup prepared as above must have the following specific gravity: (1) by refractive index values, 65° Brix, or (2) by hydrometer values, 34.5° Be = 1.319 kg/l.

Preparation of Sugar Syrups at 68° Brix

Operate as in the preceding method, using the following formulation:

sugar	68.00 kg
water	31.95 kg
citric acid	0.05 kg
syrup	100.00 kg

The above syrup must have the following specific gravity: (1) by refractive index values, 68° Brix, or (2) by hydrometer values, 36° Be = 1.3324 kg/l.

Acidification of Sugar Syrups

Citric acid or tartaric acid is used to acidify sugar syrups. The amount of added acid varies from 150 g per ton in citron-mint flavored syrup to as much as 1,400 g per ton in champagne-flavored syrup. Usually the acid is dissolved in the minimum amount of boiling water; the resulting solution is added to the syrup with brisk stirring to insure uniform dispersion. Guidelines for the acidification of syrups are shown in Table 7.

TABLE 7

Guidelines to the Acidification of Syrups

Grams of Acid per 100 kg of Finished Syrup*

Syrup	Acid	Quantity, grams
Apricot, 35% juice	Citric acid or tartaric acid	500
Apricot, 10–15% juice	Citric acid or tartaric acid	700
Apricot, juiceless	Citric acid or tartaric acid	800
Amarelle, 35% juice	Citric acid or tartaric acid	500
Amarelle, 10–15% juice	Citric acid or tartaric acid	700
Amarelle, juiceless	Citric acid or tartaric acid	800
Pineapple, 35% juice	Citric acid —	500
Pineapple, 10–15% juice	Citric acid —	700
Pineapple, juiceless	Citric acid —	800
Orange, 35% juice	Citric acid —	700
Orange, 10–15% juice	Citric acid —	1,000
Orange, juiceless	Citric acid —	500
Chinotti, juiceless	Citric acid —	750
Cherry, 35% juice	— Tartaric acid	500
Cherry, 10–15% juice	— Tartaric acid	700
Cherry, juiceless	— Tartaric acid	800
Strawberry, 35% juice	Citric acid —	500
Strawberry, 10–15% juice	Citric acid —	700
Strawberry, juiceless	Citric acid —	700

* The use of tartaric, ascorbic, malic, and other acids is regulated by present regulations. Modifications of the above listed doses may be required.

TABLE 7 (continued)

Guidelines to the Acidification of Syrups

Syrup	Acid		Quantity, grams
Raspberry, 35% juice	Citric acid	—	500
Raspberry, 10–15% juice	Citric acid	—	700
Raspberry, juiceless	Citric acid	—	700
Lemon, 35% juice	Citric acid	—	—
Lemon, 10–15% juice	Citric acid	—	500
Lemon, juiceless	Citric acid	—	1,300
Mandarin, 35% juice	Citric acid	—	700
Mandarin, 10–15% juice	Citric acid	—	1,000
Mandarin, juiceless	Citric acid	—	1,000
Apple, 35% juice	—	Tartaric acid	500
Apple, 10–15% juice	—	Tartaric acid	550
Apple, juiceless	—	Tartaric acid	600
Mint, juiceless	Citric acid (q.s.) or tartaric acid		30
Pear, 35% juice	Citric acid or tartaric acid		500
Pear, 10–15% juice	—	Tartaric acid	600
Pear, juiceless	—	Tartaric acid	600
Peach, 35% juice	Citric acid	—	500
Peach, 10–15% juice	Citric acid	—	600
Peach, juiceless	Citric acid	—	600
Plum, 35% juice	Citric acid	—	500
Plum, 10–15% juice	Citric acid	—	600
Plum, juiceless	Citric acid	—	600
Currant, 35% juice	Citric acid	—	—
Currant, 10–15% juice	Citric acid	—	500
Currant, juiceless	Citric acid	—	800
Rose, juiceless	Citric acid	—	35

Coloring of Sugar Syrups

The addition of colorants to syrup is permitted as long as certified colorants are employed. For best results it is advisable to weigh the colorant, place it in a glass-lined or enameled container with approximately 5–10 times its weight of distilled or deionized water, and then mix thoroughly with a glass rod until the colorant is completely dissolved. The resulting solution is added to the syrup. When crystalline caramel color must be used, follow the above procedure, using boiling water to achieve solution. If fluid caramel is used, mix the colorant thoroughly with a little syrup.

Flavoring of Sugar Syrups

The colored or colorless syrup (acidified or not) is added with the required amount of compound flavor or concentrated juice plus compound flavor to yield the desired aroma effects. For best flavor

results and independent of the concentrated juice levels employed, soluble compound essential oils for syrups are added as flavor reinforcers. Such oils (having yields varying between 1 × 100 and 1 × 200) are formulated by the basic guidelines for typical fruit-flavored formulations and tailored specifically to yield the required solubility for use at room temperature. Prior to adding the flavor, it is important to make sure that the syrup is cooled completely. Then add the compound flavoring with agitation for homogeneous distribution of the flavor in the mass; avoid drawing air into the syrup. The latter may be accomplished by slow agitation without turbulence. After a few hours standing, the syrup is filtered over felt liners or filter-press. Orzata and tamarind syrups are usually filtered prior to flavoring.

Addition of Preservatives

To prevent oxidation of syrups, Italian law permits the use of ascorbic acid "300" or sodium *l*-ascorbate "301" (150 mg/l or 115 mg/kg syrup). These chemicals can be used also in combination with citric or tartaric acid during the acidification step, or they can be dissolved separately in hot water prior to addition to the finished syrup. Fruit juices stabilized with sulfur dioxide are also permitted (in Italy) provided that the amount of sulfur dioxide does not exceed 100 mg/kg of finished syrup. In the United States ascorbate can also be used for its antioxidant effect. When stabilizers are used, it is advisable to consult with the supplier of colorants. Both ascorbic acid and sulfur dioxide react with dyes (especially red and green dyes), causing color fading and, sometimes, complete decoloration of the syrup in a rather short length of time.

Guideline formulations for the preparation of syrups sufficient for about 100 kg of finished product are shown in Table 8.

Soft Drinks and Carbonated Beverages

Waters

This category includes products with different characteristics, such as tonic water, sparkling water, seltzer water, soda, Vichy water, carbonated water, and others.

Sparkling Waters

The generic term *sparkling waters* applies to all carbonated beverages consisting of carbonated water with or without the addition of salts (sodium carbonate, sodium bicarbonate, sodium chloride, sodium sulfate). The salt may be added as a concentrated solution during bottling, as in the case of

TABLE 8

Formulations for Syrups

Ingredient	30–35% fruit juice	10–15% fruit juice	Soluble[1] flavoring oils
Sugar syrup at 65° Brix, kg	90.2 92.9[2]	96.3 96.8[3]	98.2[4] 99.5[4]
Colorant	q.s.	q.s.	q.s.
Acid (if required)	q.s.	q.s.	q.s.
Concentrated juice, 1:5–1:8 fold	q.s.	q.s.	—

[1] Soluble flavoring oils only having a yield of 1 × 100 to 1 × 200.
[2] 95.5 kg for lemon-flavored syrup.
[3] 97.3 kg for lemon-flavored syrup.
[4] 96 kg for tamarind-flavored syrup (yield, about 1 × 25).

syrups. Sparkling waters are carbonated by using carbon dioxide at high pressures. Club soda, Vichy waters, and slightly bitter-tonic-flavored waters (tonic water) are included in this group.

Carbonated Waters

The term *carbonated waters* applies only to those products consisting exclusively of distilled, deionized, or treated carbonated water. While these products may also be defined as sparkling waters, the name *soda* (which implies the addition of sodium salts) cannot be used. In England carbonated waters are also called aerated waters; in Italy this definition encompasses all carbonated waters.

Soda

Soda is a generic term commonly used in the United States and England as a synonym for carbonated soft beverages. More specifically the term defines carbonated waters containing soda (sodium bicarbonate). British soda contains 5 grains minimum of sodium bicarbonate (approximately 0.33 g per pint). In the manufacture of soda water, the hardness of the water used should be taken into account.

Seltzer Water

Originally seltzer water was an imitation of natural mineral waters. Therefore, the number of salts added is larger than in the case of soda waters. Typical seltzer water also contains considerably more sodium chloride than soda water.

Fruit-flavored Beverages

With regard to composition, these beverages can be subdivided into two categories: (1) beverages flavored with fruit juices (with or without fruit pulp), and (2) beverages flavored with fruit flavor imitations or with natural or mixed flavor ingredients. The first group includes citrus (orange, lemon, grapefruit) and other fruit-based beverages—grape, apple, pineapple, etc. All of these contain sugar, acids (citric or tartaric), and sometimes colorants.

Carbonated Beverage Ingredients

The preparation of carbonated beverages in general calls for use of the following main ingredients: water, carbon dioxide, sugar, salts, acids, flavors (including fruit juices), and colorants.

Water

Spring, well, and tap waters may be used in the manufacture of carbonated beverages provided that the salt composition is compatible (or rendered such) with the flavor ingredients being used. The amount of calcium and magnesium salts in the water is responsible for the hardness. This is measured in French degrees as grams of salt as calcium carbonate present in 100 liters of water or in German degrees as grams of salt as calcium oxalate present in 100 liters of water. Water hardness is classified as total, permanent, or temporary. *Total hardness* is the hardness determined directly in a sample of the water. *Permanent hardness* defines the hardness retained by the water boiled for about 30 minutes, *i.e.*, calcium and magnesium salts left in solution after boiling. *Temporary hardness* is the difference between total and permanent hardness, *i.e.*, the hardness removed with boiling. Salt composition and water hardness can affect the addition of organic acids as well as the solubility of certain flavor ingredients.

Carbon Dioxide

Like many other gases, the solubility of carbon dioxide in water increases with decreasing temperature: one unit volume of carbon dioxide is soluble in 0.6 unit volumes of water at 0°C, while 13 unit volumes of water is required to dissolve the same amount at 25°C. As shown in the following table, the solubility of carbon dioxide in sugar solutions varies depending on the sugar content.

Solubility of Carbon Dioxide in Sugar Solutions
At 15.5°C and 760 mm Hg

Dissolved sugar, g	Dissolved carbon dioxide, ml	Dissolved sugar, g	Dissolved carbon dioxide, ml
1.0	0.995	8.0	0.943
2.0	0.989	9.0	0.936
3.0	0.982	10.0	0.928
4.0	0.975	11.0	0.918
5.0	0.967	12.0	0.907
6.0	0.959	13.0	0.902
7.0	0.951		

Commercial carbon dioxide contains not less than 99% (by volume) CO_2.

Preparation of Carbon Dioxide

In the past carbon dioxide for use in the carbonated-beverage industry was produced directly by the beverage manufacturer by contacting some carbonates, such as gypsum, sodium bicarbonate, etc., with sulfuric or hydrochloric acid. The largest and most consistent yields were obtained using calcium bicarbonate, whereas varying yields were obtained with gypsum. As both liquid and solid carbon dioxide became commercially available several decades ago, they are no longer produced directly by the beverage manufacturer.

Carbon dioxide is obtained usually as a by-product in the following processes: (1) the manufacture of calcium, (2) the combustion of coke, coal, or natural gases, and (3) the fermentation of beer. Carbon dioxide from the fermentation of beer, unless further purified, retains a characteristic odor and can be used only for the carbonation of beer.

Carbon Dioxide Content in Beverages

The volume of carbon dioxide in the finished product is an extremely important factor determining, together with the temperature, the length of sparkling in the beverage. The carbonated beverage and bottling industries have adopted a standard unit volume, defined as the amount of gas in milliliters absorbed by a given volume of water at 15.5°C under atmospheric pressure (760 mm Hg). The above unit is used to measure the volumes of carbon dioxide in carbonated beverages.

Measurement of Carbon Dioxide Volume

In order to measure the volume of carbon dioxide dissolved in a carbonated beverage, it is necessary to know the temperature and the pressure in the container. Special measuring instruments are available based on the following principle: a needle perforates the cork of the bottle, allowing the outflow of the head pressure until a bubble develops in the liquid. The valve is then closed, and the container is shaken until the instrument gauge no longer registers an increase in pressure. The temperature of the liquid is measured at this point.

Addition of Carbon Dioxide

In view of the better solubility of carbon dioxide in cold water, several methods are available to the bottler for cooling the water. Usually liquid carbon dioxide is employed in the manufacture of carbonated beverages; the liquid is contained in a stainless steel cylinder connected to an automatic gassing equipment of metal tubings. A large water surface comes in contact with carbon dioxide under pressure in the gassing apparatus, allowing a fast rate of absorption of the gas by the cooled water. Carbonation is made continuous by means of a valve that regulates the gas flow in the gassing equipment as required. The carbonated water flows into the filling machine.

Gassing machines must be made of corrosion-resistant metal and specifically designed to avoid potential contamination. Two types of machines are commercially available. In the first type the syrup is cooled and carbonated in the gassing equipment, mixed with cooled and carbonated water in a separate mixing tank, and transferred to a collecting tank and then to the filling machine. In the second type the syrup is measured directly into the individual bottles and diluted with carbonated water. The latter system is usually employed in automatic and semi-automatic bottling equipment.

Pressure–Temperature Relationship

An increase in temperature causes a corresponding pressure increase in carbonated-beverage containers. This in turn may cause leakage through the bottle seal or deformation of cans. This danger increases when carbonated beverages are pasteurized directly in the container.

Losses of Carbon Dioxide

The decrease of gas pressure during the filling operation or subsequent to unsealing the container represents a major problem for the carbonated-beverage industry. Adequate cooling of the water and syrup prior to carbonation is helpful in preventing gas losses during filling. Gas losses upon unsealing the container are attributable to various factors, such as presence of nuclei, excessive air content in the beverage, excessive agitation, or inadequate storage.

Nuclei tend to form from unclean bottles, mold-covered seals, and residues from bottle-washing operations. It has been reported that black nylon brushes do not tend to accumulate particles, are easier to clean, and have readily identifiable bristles. Thorough cleaning and maintenance of the bottling equipment is of primary importance to decrease the formation of nuclei.

Sugar and Syrup

A good quality sugar (sucrose—specific gravity, 1.588; specific volume, 0.630) must yield clear solutions in the water used for syrup preparation. The preparation of the syrup is the first operation in the manufacture of carbonated beverages; acids, colorants, and flavor ingredients (including fruit juices) are then added to the syrup. The sugar solution must be prepared with stirring (avoiding the drawing of air into the solution) and at the lowest feasible temperature to avoid the appearance of a brown color from caramelization.

The acids, predissolved in a small amount of water, are added to the cooled sugar solution to avoid inversion. Concentrated colorant solutions, juices, and flavor ingredients also must be dispersed in the cooled syrup solutions.

Density of Sugar Solutions

Density	Degrees, Bé	Water, kg	Sugar, kg
1.1249	16	71	29
1.1418	18	67.5	32.5
1.1796	22	60	40
1.1898	23	58	42
1.2003	24	56	44
1.2328	27	50	50
1.2637	30	44.5	55.5
1.2958	33	39	61
1.3078	34	37	63
1.3199	35	35	65
1.3322	36	33	67

The various non-volatile substances dissolved in the syrup and, in turn, the beverage determine the *dry residue* in the beverage, which is expressed either in weight per cent (grams of residue on evaporation

of 100 cc of beverage) or in degrees Brix. The sugar content in the syrup can be measured by a refractometer or a polarimeter. The sugar content also determines variations in the density of sugar solutions (also expressed in degrees Baumé).

Flavor Ingredients for Carbonated Beverages

The flavoring of carbonated beverages represents one of the most important tasks in aroma formulations. In addition to technical and specific formulation problems (*e.g.*, the formulation of bitters), the basic requirement of carbonated-beverage flavors is complete solubility in syrup. The flavored syrup must in turn be completely soluble in the carbonated water. The finished product must not develop haze on storage (except when this is desirable), even in cold weather.

There are several products that are useful for flavoring carbonated beverages: (1) individual or compounded soluble essential oils, (2) individual soluble extracts or compounded flavors from soluble tinctures, alcoholic extracts, and distillates from herbs (with or without the addition of soluble essential oils), and (3) flavoring pastes and fruit juices.

The various soluble oils and soluble extracts have yields ranging between 1 × 50 and 1 × 400 (based on the syrup). The relative amounts of sugar, acids, and carbon dioxide vary, depending on the flavor and the chemical nature of the flavor ingredient. Variations in the dry residue of various types of beverages are expected, depending on the amount of sugar, juices, salts, and acids employed. In certain types of juice-based beverages, minimum dry residue specifications are set by law.

Carbonated Beverage Formulations

Guideline formulations commonly employed in the preparation of a few carbonated-beverage types follow:

Gazzosa

Syrup

Sugar	50 kg
Citric acid	2.7 kg
Water	47 l
Soluble lemon essential oil	q.s. (depending on the yield)

Beverage

The beverage is usually prepared in 200 cc glass containers (saturation pressure = 5 atm).

1. By diluting 26 cc of the above syrup to 200 cc total, a carbonated beverage with approximately 8% dry residue is obtained.
2. By diluting 33 cc of the above syrup to 200 cc total, the resulting beverage contains approximately 10% dry residue.

Orange Soda

Syrup

Sugar	48 kg
Citric acid	0.8 kg
Water	40 l
Orange juice, 15° Brix (7.5 fold concentrated)	7.2 kg
Colorant	q.s.
Soluble oil or flavoring paste	q.s. (depending on the yield)

Beverage

The beverage is usually prepared in 200 cc glass containers (saturation pressure = 4 atm). By diluting approximately 40 cc of the above syrup to 200 cc total, a carbonated orange soda is obtained with an approximate 12% dry residue.

Citron Soda

Syrup

Sugar	50 kg
Citric acid	1 kg
Colorant	q.s.
Water	48.5 l
Soluble oil	q.s. (depending on the yield)

Beverage

The beverage usually is prepared in 200 cc glass containers (saturation pressure = 5 atm).

1. By diluting 36 cc of the above syrup to 200 cc total, a carbonated citron soda is obtained with an approximately 12% dry residue.
2. By diluting 32 cc of the above syrup to 200 cc total, the resulting beverage contains approximately 10% dry residue.

Cola

Syrup

Sugar	50 kg
Citric acid	0.5–0.8 kg
Caramel	q.s.
Water	46.5 l
Soluble flavor or extract	q.s. (depending on the yield)

Beverage

Cola is usually prepared in 200 cc glass containers (saturation pressure = 6 atm). By diluting 40 cc of the syrup to 200 cc total, a carbonated cola beverage is obtained with an approximate 12.5% dry residue.

Non-alcoholic Aperitifs

The formulation ingredients of non-alcoholic aperitifs duplicate closely those used in alcoholic aperitifs. The lack of a functional alcoholic content in the finished product, however, is of basic importance regarding the flavor results as well as the formation and preservation of the flavor in the beverage. Flavor formation in particular undergoes very pronounced changes.

The aromatic herbs used for alcoholic aperitifs are also employed in non-alcoholic aperitifs as individual or compounded hydro-alcoholic extracts; however, the yields are rather different. Often it may be necessary to reinforce the aroma by the addition of soluble essential oils to attain the desired flavor effects. In a few cases the soluble essential oils are the basic ingredients in the formulation and are reinforced by tinctures.

While finished alcoholic aperitifs are ideally neutral products, non-alcoholic aperitifs are usually acid. Citric (or tartaric) acid is present from 4–7% by weight, depending on the amount of sugar in the syrup and the degree of carbonation. The presence of citric acid may cause flavor problems that, if not readily overcome, may be further complicated by the presence of carbon dioxide. Acids and carbon dioxide, individually or synergistically, react with the flavor ingredients and often yield off-flavors that break the flavor balance in a fairly short period of time.

It is not possible to present general theoretical formulation guidelines, since both the quality and quantity of flavor ingredients may undergo unpredictable changes directly related to the chemical nature as well as to the varying acid and carbon dioxide ratios in the beverage.

Successful formulations used world-wide are based mainly on the tailored blend between a complex citrus background note and characteristic bitter flavor ingredients together with slightly spicy, sharp notes. The following flavor ingredients are usually employed: sweet and bitter orange, chinotti, vanilla, cinnamon, calamus, wormwood, gentian, and rhubarb.

The following procedure is usually employed in the preparation of non-alcoholic aperitifs:

Syrup

Sugar	50 kg
Citric acid	0.2 kg
Water	49.150 l
Colorant	q.s.
Soluble extract	q.s. (depending on the yield)

Beverage

The beverage is usually prepared in 100 cc glass containers (saturation pressure = 5 atm). By diluting 26 cc of the above syrup to 200 cc total, a non-alcoholic aperitif is obtained with an approximate 16% dry residue.

Bitter Non-alcoholic Beverages

In bitter, refreshing, non-alcoholic beverages, such as gingers, chinotto, spume, and tonic waters, the problem of the presence of carbon dioxide and citric acid is identical to aperitifs. The flavor ingredients used in the formulations are quite different from those used in bitter, alcoholic beverages. Guideline formulations for flavoring the above beverage types are given below.

Chinotto (Bitter Orange Soda)

The introduction of chinotto represents undoubtedly the new flavor line for carbonated beverages in Italy. The bittersweet characteristic flavor note represents a break from traditional citrus-flavored beverages as well as from the less aromatic but very well known cola beverages. Although the customer's taste has been educated to the bitter note through other commercial bitter-flavored beverages, the original creativity expressed in the beverage chinotto should not be underestimated.

The basic flavor of the beverage may be defined as the vermouth note (a red, slightly aromatic, and somewhat bitter vermouth) associated with the chinotti citrus flavor rounded off by the addition of an orange note.

Syrup

Sugar	48 kg
Citric acid	0.6–1.2 kg
Caramel for acids	q.s. (intense color)
Water	46 l
Soluble extract	q.s. (depending on the yield)

Beverage

The beverage is usually prepared in 200 cc glass containers (saturation pressure = 4 atm). By diluting approximately 40 cc of the above syrup to 200 cc total, a chinotto beverage with approximately 12% dry residue is obtained.

Tonic Waters

This beverage type exhibits a rather simple note obtained by a combination of bitter flavor with a citrus note. The flavor variations are somewhat limited, since the finished beverage must be colorless or only slightly colored. Quinine chlorhydrate (or a concentrated bitter tincture) is the water-soluble, bitter flavor principle. Soluble lemon essential oil in suitable dose (sometimes in combination with soluble orange essential oil) adds the complementary note to the aroma of the most simple beverage types of widespread consumption. In addition tonic waters yield an excellent refreshing cocktail when consumed with gin or vodka.

Syrup

Sugar	50 kg
Citric acid	2.35 kg
Water	46.65 l
Soluble flavor	q.s. (depending on the yield)

Beverage

The beverage is usually prepared in 200 cc glass containers (saturation pressure = 6 atm). By diluting 32 cc of the above syrup to 200 cc total, a tonic water with an approximate 10% dry residue is obtained.

Gingers

The spicy ginger note is indispensable to the flavor of certain internationally known gingers. The ginger flavor is associated with the citrus note in this beverage type. A typical ginger ale formulation, for example, employs ginger and capsicum oleoresin together with ginger essential oil, lime distilled essential oil, and cold-expressed lemon and orange essential oils.

The Italian type of ginger differs somewhat from the above flavor note; the following flavor ingredients are chiefly employed: sweet and bitter orange, lemon, vanilla, calamus, cinnamon, ginger, clove, and traces of additional bitter flavors.

Syrup

Sugar	50 kg
Citric acid	0.140 kg
Water	49 l
Colorant	q.s.
Soluble flavor	q.s. (depending on the yield)

Beverage

Ginger is usually prepared in 200 cc glass containers (saturation pressure = 5 atm). By diluting 48 cc of the above syrup to 200 cc total, a ginger beverage with approximately 15% dry residue is obtained. A ginger with approximately 14% dry residue is also prepared by diluting 46 cc of the syrup to 200 cc total.

Spume

Spume are non-alcoholic, carbonated, champagne-type beverages. They comprise a large number of white or dark carbonated beverages with a basic aromatic wine flavor (muscat) associated with a bitter note (sometimes a citrus undertone). It is also characterized by a slightly tart flavor. The possible flavor variations are countless. The basic muscat flavor note is imparted by the use of tinctures or distillates from clary sage, elder, coriander, violet, and orris. Clary sage is the most important flavor ingredient for this product.

White Spuma

Syrup

Sugar	50 kg
Citric acid	1 kg
Water	48 l
Caramel for acids	q.s. (traces only)
Soluble flavor extract	q.s. (depending on the yield)

Beverage

The beverage is usually prepared in 1,000 cc glass containers (saturation pressure = 5 atm). A

white spuma with approximately 11% dry residue is obtained by diluting 180 cc of the above syrup to 1,000 cc total.

Dark Spuma

Syrup

Sugar	50 kg
Citric acid	0.7 kg
Water	47 l
Caramel for acids	q.s. (dark color)
Soluble flavor extract	q.s. (depending on the yield)

Beverage

The beverage is usually prepared in 1,000 cc glass containers (saturation pressure = 5 atm). By diluting 165 cc of the above syrup to 1,000 cc total, a dark spuma with an approximate 10% dry residue is obtained. A dark spuma with a 12% dry residue is also prepared by diluting 195 cc of the above syrup to 1,000 cc total.

Preservation and Alteration of Carbonated Beverages

The manufacture of carbonated beverages is not particularly difficult from a technological standpoint. The use of good quality raw materials and suitable bottling equipment is for the most part a guarantee to successful operation. However, the observance of strict hygienic conditions throughout the manufacturing process is indispensable. Carbonated beverages are extremely delicate and susceptible to degradation and fermentation due to several and quite different causes. These are not always predictable or controllable in spite of the extreme care observed during manufacture. The observance of absolutely hygienic manufacturing practices and the use of preservatives (wherever permitted) and/or pasteurization are of paramount importance.

In addition to the above precautions, the following are also recommended:

1. Avoid sugar inversion during the preparation of the syrup.
2. Add sufficient acid to the beverage.
3. Store finished products in cool, aerated places.
4. Avoid discoloration in the beverage from prolonged exposure to sunlight during shipping or storage.

In view of the commercial as well as the alimentary importance of carbonated beverages, a more detailed discussion of the potential causes of alteration in carbonated beverages encompasses very important theoretical and practical considerations.

Carbonated beverage consumption has increased steadily over the years. What was considered at one time a seasonal (summer) production today is distributed quite uniformly throughout the year. For readily apparent commercial reasons carbonated beverages may remain in storage for extended periods of time prior to consumption. Prolonged storage considerably increases the possibility of alteration, although the manufacturing technology has made remarkable advances in recent years.

Sometimes finished beverage stocks ready for shipment are stored by the manufacturer in refrigerators. Significant temperature changes during storage and subsequent shipment may affect beverage stability. In more recent years the carbonated-beverage industry has increased the consumption of fruit juices for the preparation of beverages. Juices are, in fact, extremely susceptible to deterioration from the action of various microorganisms. The addition of fruit juice enriches the content of vitamins, mineral salts, and nitrogenous compounds in the beverage. All of these ingredients create a favorable ground for bacterial growth with consequent spoilage of the beverage by bacteria. The potential causes of alteration may be present not only in the finished products but also during manufacturing, in the equipment and containers used, or even in the starting raw materials; all of these potential alterations can shorten shelf-life.

Alterations occurring in carbonated beverages are phenomena of physical, chemical, biochemical, and microbiological nature.

Physical Alterations

Light is undoubtedly the main physical source of alteration in carbonated beverages. Sunlight may induce terpenization of citrus flavors (especially orange and lemon flavors), which in turn causes the development of a characteristic, unpleasant, oily off-flavor reminiscent of turpentine. Light may also unpleasantly shift the acid taste or induce off-odors and off-flavors especially in beverages containing natural fruit aromas. Light also may cause partial discoloration of synthetic dyes, leading, especially in the case of dark or brown colors, to unsightly chromatic effects. Some food, drug, and cosmetic dyes are particularly sensitive to sunlight in the presence of ascorbic acid. Hence, it is necessary to preserve carbonated beverages (orange- and lemon-flavored beverages in particular) in dark places if extensive storage is required.

High temperatures may also affect the quality of carbonated beverages. Beverages accidentally subjected to temperatures higher than 40°C may undergo losses of carbon dioxide from the well known inverse solubility of carbon dioxide in water at higher rather than lower temperatures. Extended storage at low temperatures also may have adverse effects. Certain flavors and colorants, much less soluble at low temperatures, can readily precipitate out and do not redissolve completely even when the temperature is increased to normal values. Even when the components redissolve, the products in solution are different from the starting materials because of irreversible changes taking place during cooling.

Precipitation and flocculation may occur when hard water is employed unless the water is pretreated by resin (ion) exchange. The same source may also induce alteration of the colorants in the finished beverage, causing partial but highly objectionable discoloration.

An additional physical change may be caused by the rapid loss of carbon dioxide through imperfect seals, although the latter alteration should be considered as accidental only and seldom involves a large portion of the production. With canned carbonated beverages, corrosion of the lining is an important aspect.

Chemical Alterations

Sometimes various components present in carbonated beverages may react chemically with (1) the atmospheric oxygen dissolved in the water phase or present in the container, and (2) among themselves because of chemical incompatibility. The presence of the dispersing aqueous phase creates favorable conditions for the potential occurrence of chemical reactions throughout the beverage. For instance, the terpene or rancid flavor sometimes perceptible in beverages of old production is caused by the action of oxygen dissolved in the water phase or present in the head space of the container between the seal and the liquid surface. In addition to terpenes, a few aldehydes (present especially in fruit flavors) may readily undergo oxidation, thus accelerating the degradation process in beverages.

The presence of air in the carbon dioxide used for carbonation, caused by imperfect functioning of the automatic filling equipment or the non-observance of proper manufacturing techniques, may also be a problem. A recent survey reported that out of 340 carbon dioxide samples tested, 105 samples had an air content of 30% or more. Therefore, alterations attributable to this cause are in general much larger and occur much more frequently than expected from a cursory examination of the problem. It must be added that all oxidation reactions induced by atmospheric oxygen are catalyzed by sunlight and temperature. It is apparent that, to avoid such possibilities, it is necessary to deaerate the water for carbonation prior to use.

A very important role in the chemical alteration of beverages is attributed to heavy metals, such as iron and copper. Water used in the manufacture of beverages must contain less than 3 ppm iron. If larger amounts are present, iron may precipitate as a salt or a complex, or it may form yellow to reddish-brown rings consisting of iron hydroxide on the surface of the liquid. Iron also may react with

dyes, causing the precipitation of insoluble lacquers, or with flavor ingredients, causing the development of disagreeable metallic off-flavors in the beverage. Therefore, the use of water containing iron, usually as soluble iron bicarbonate, is not recommended. The ferrous ion is readily oxidized to trivalent iron in the presence of atmospheric oxygen, yielding highly insoluble iron hydroxide. Whenever it is necessary to use waters containing iron in excess of 3 ppm, the iron can be easily removed by various methods including direct ion-exchange or complexed with chelating agents such as EDTA. Copper also plays an important role in catalyzing corrosion reactions in canned beverages.

Chlorides and alkaline substances may be detrimental to an effective preservation of carbonated beverages. Spoilage is also caused by an excessively acid pH that can cause sugar inversion. Invert sugar has a flavor quite different from regular sucrose. This last type of alteration is considered rare due to the length of time required for the inversion of sugar; it has been included only as an illustrative example of the many factors affecting the storage stability of carbonated beverages.

Excessive water hardness may cause chemical alterations (in addition to the previously mentioned physical changes) because of the presence of calcium. Calcium salts in the presence of tartaric acid used to acidify beverages may yield precipitation of insoluble calcium tartrates.

Biochemical Alterations

The main form of biochemical alteration consists of enzymatic activity. Enzymes are soluble or colloidal substances produced by living organisms and capable of catalyzing specific reactions. Chemically, enzymes may be considered simple or conjugated proteins. As to specific activity, only two enzymes are of interest to the carbonated beverage industry—carbohydrase and lipase. The former catalyzes hydrolysis carbohydrates or sugars, while the latter catalyzes the scission of fats and esters. One should remember that enzymes produced by the metabolism of microorganisms may exhibit activity long after the death of the enzyme-producing organism; they are therefore resistant to common preservatives.

Enzymes may be found in the raw materials employed by the beverage industry, such as fruit juices, fruit concentrates, and natural gums. The presence of lipase may be particularly harmful because of selectively attacking and breaking ester molecules (so-called esterase), a very important category of flavor ingredients in the formulation of aromas. Ester breakage by lipase may reduce the flavor yield or produce off-odors and flavors incompatible with the original note.

Microbiological Alterations

Undoubtedly alterations caused by the activity of microorganisms represent the gravest and most serious single source of preoccupation by the manufacturer of carbonated beverages. Microorganisms responsible for spoilage of beverages include fungi, yeasts, bacteria, algae, and protozoa. Statistically, yeasts are responsible for spoilage in most cases, whereas degradation from molds and bacteria (especially lactic acid bacteria) is encountered in relatively few instances. In general, the degradation phenomenon may be compared to an alcoholic fermentation characterized by (1) flavor changes, (2) a pressure increase in the container, (3) discoloration, and (4) the formation of sediments and precipitate usually considered the first and most visible indication of the incipient alteration of the beverage.

The largest number of alterations is attributable to yeasts, which require very few nutrients to survive and grow as compared to bacteria (autotrophic bacteria, however, are capable of surviving with the little nutrient present in water). In addition yeasts, although sensitive to high carbon dioxide pressures, are fairly resistant to the acid conditions prevalent in most carbonated beverages; certain types continue to grow even at pH 2.5 as compared to bacteria, which are much less resistant under acid conditions.

Any beverage based on fruit juice containing vitamins, proteins, and mineral salts provides an extremely favorable substrate for the growth of microorganisms and much more so than a clear beverage. Therefore, utmost attention must be given to the preparation of beverages flavored with natural juices. The various categories of microorganisms causing spoilage and the conditions influencing their specific activity are reviewed below.

Fungi

The groups of interest include ficomycetes, ascomycetes, and basidiomycetes. Spoilage caused by these fungi closely resembles that by yeasts and molds.

Yeast

This generic term defines a large class of substances. *Saccaromyces cervisiae* (beer yeast) is the best illustrative example in the class. Yeasts, when examined under the microscope, appear as very tiny, egg-shaped cells with small lateral humps (buds). They reproduce at an extremely high rate and grow freely in sugar syrups, acid solutions (optimum growth occurs at pH 4–4.5), and flavored non-alcoholic solutions. Reproduction of yeast on the above substrates occurs at a much faster rate than other categories of microorganisms.

F. Hale points out that 90% of the microbiological alterations occurring in beverages is attributable to yeasts.[12] The presence of this organism should not be underestimated, and great care must be exercised to control the yeast population for better preservation of beverages.

The vehicles through which yeast may find their way into beverages are countless—damp sugar bags (especially those made of canvas), dyes, pre-contaminated juices, dirty equipment and pipes, dust or dirt collected during manufacturing, and non-sterile containers and seals. The last factor, according to a study presented at the Third International Conference on the Microbiology of Food Products (Avian, 1960), is the major source of alteration in food products. Therefore, a strict control of the operative efficiency of the washing machines and a thorough sterilization of bottles and caps (leaving the least possible number of microorganisms, excluding the species capable of proliferating under acid conditions) is highly recommended.

The need for continuous microbiological analyses is the limiting factor to the practical implementation of the controls, since a well equipped laboratory and specialized personnel are required to perform the analyses. It is often sufficient, however, to overcome contamination problems by strictly implementing the hygienic measures required by good manufacturing practice.

In addition to observable phenomena caused by the growth of yeasts in the beverage, spoiled beverages also exhibit a typical fermentation flavor and a bitter taste. Flavor changes are strictly dependent on microbial activity and are, therefore, more or less directly dependent on the substances influencing growth, such as sugar, acid, and carbon dioxide.

Experiments conducted by U.S. scientists have shown that low-strength (5–10°$_0$) sugar solutions, such as carbonated beverages, provide an excellent substrate for the growth of yeasts proliferating to 400 fold the original value in a very short period of time (5 days). Such growth occurs at a much slower rate in syrups whose activity increases with the increasing sugar concentration.

As to the influence of pH, an increase in the concentration of inorganic acids (citric, tartaric, malic) added to a 10% sugar solution decreases the potential growth of yeasts. This is not absolutely valid, however, since yeasts show great adaptability to different environmental conditions. Therefore, the concept of improving the beverage stability by increasing the acidity is of limited application.

Studies by N. F. Insalata have shown that carbon dioxide has an inhibiting effect on yeast growth.[13] Three beverages having a 12% dry residue and a pH of 4.5 were carbonated with 3, 4, and 5 volumes, respectively, of carbon dioxide and inoculated with 150 cells of yeast. Sterilization occurred after 20, 13, and 10 days, respectively, thus proving that an increase in the carbon dioxide content corresponds to an increase of the anti-yeast activity in the beverage. It should be pointed out, however, that this study applied to yeast only; the results are of limited value to the manufacturer of carbonated beverages, who should in no way be induced to relax his regular hygienic controls.

Molds

This category of microorganisms is seldom encountered in spoiled beverages. Molds generally develop in oxygen-rich beverages, as oxygen is indispensable for their metabolism; mold growth is strongly inhibited by the presence of carbon dioxide. Usually molds proliferate on caps, canvas bags, and wood and cardboard containers used for packaging the raw materials; from these they subsequently

are transferred into beverages. In addition to causing flocculation and precipitation, molds impart an unpleasant odor and flavor.

Bacteria

An additional potential source of contamination, although very rare in practice, is bacteria. Several species of bacteria are known, but only a few are pathogenic. Some bacterial species thrive only under optimum ambient conditions; others thrive also in oxygen-poor and carbon-dioxide-rich environments in the presence of rather acid pH values (3–4). The most visible phenomena in a beverage spoiled by bacteria are discoloration and the formation of off-flavors. The possibility of pathogenic bacterial contamination, such as *Escherichia coli* or *Salmonella typhosa*, in beverages should be considered remote if proper manufacturing practices are observed.

Algae and Protozoa

Algae comprise a heterogeneous group of substances that may be present as contaminants in the water used for bottling. Similarly, protozoa (microscopic unicellular organisms) may be introduced into the beverage through the use of contaminated well water. Both algae and protozoa may cause off-flavors.

Dry Beverage Bases

The formulation of dry beverage bases as a means of imparting an acceptable flavor to water represents an old challenge to the flavorist. Originally, dry beverage bases were developed to partially fill an increasing consumer's demand for prepared carbonated water that was usually high-priced and in scarce supply. A solution was found by using sodium bicarbonate and tartaric acid (prepared in individual packets in approximately stoichiometric ratios) dissolved in water shortly before use. Usually the packets were sufficient to prepare 1 liter of carbonated water. Tablets containing sodium bicarbonate and tartaric acid in a 3:1 ratio found use in the preparation of seltzer water imitations. The well known Vichy water was imitated by adding small amounts of other salts together with the above mentioned basic components in order to improve the flavor characteristics. A typical Vichy-water formulation consisted of the following:

Imitation Vichy Water

Ingredient	Quantity, grams
Packet 1	
Sodium bicarbonate	4.0
Sodium chloride	0.10
Sodium sulfate	0.25
Magnesium sulfate	0.07
Ferrous sulfate	0.05
Packet 2	
Tartaric acid	1.0

The above ingredients have remained basically unchanged. The carbonation principle based on the chemical reaction between sodium bicarbonate and tartaric acid yielding carbon dioxide is still valid. Only the slightly tart or salty flavor resulting from a deficiency or an excess in the amount of sodium bicarbonate used has slowly changed in order to impart the desired note to different products. Therefore, increasing emphasis was placed on the addition of salts, such as lithium carbonate, to the bicarbonate base. While the use of ascorbic and malic acids, together with tartaric acid was considered, citric acid did not make an inroad in these type formulations because of technical shortcomings. With

the increasing availability of anhydrous chemicals, improved mixing and packaging techniques, and air-tight seals, the need for individual packets was overcome; today single-package dry beverage bases are marketed.

As an extension of the above evolution in the preparation of Vichy water imitations, new ideas were developed to make carbonated water imitations into flavorful and thirst-quenching beverages replacing the syrup-based beverages and even carbonated waters.

A few products that served to create a favorable market for the development of dry beverage bases into flavored products included the so-called "effervescent granular mixtures" or "effervescent magnesia." No longer popular, these products consisted chiefly of an intimate mixture of sugar (about 50% by weight), citric or tartaric acid (sometimes also a blend of these acids), sodium bicarbonate, and terpeneless or soluble citrus oils dissolved and thoroughly mixed with a little hot syrup (usually not exceeding 85°C). The mixture was then manually or mechanically worked into granules and finally dried. Such formulations, together with almost countless modifications, were developed to produce inexpensive, well accepted granular dry flavor bases yielding sparkling, usually fruit-flavored, soft beverages. After several technically unsuccessful attempts to extend the concept of a two-packet product to the introduction of a third packet containing flavors, colorants, and sweeteners, single-package, flavored, dry beverage bases were developed by utilizing manufacturing techniques used for granular products.

Flavored dry beverage bases are formulated in two different types:

1. Dry beverage bases yielding carbon dioxide on dissolution in water.
2. "Still" dry beverage bases.

Both formulations may contain sugar (q.s.), synthetic sweeteners, or mixtures of natural and synthetic sweeteners. In order to generate carbon dioxide, a mixture of sodium bicarbonate and sodium tartate is used together with additional salts, acids, and colorants to complement the organoleptic characteristics of the flavored dry base.

The flavor ingredients are powders consisting either of spray-dried oils or lyophilized juices usually reinforced by spray-dried aromas. "Still" formulations are generally prepared from a large variety of fruit types, including the citrus flavors. They do not contain sodium bicarbonate, but only acids, colorants, and various salts. Citrus-flavored still beverages are prepared in the same manner as those producing carbonation, whereas spray-dried compounded flavors are used in place of the corresponding lyophilized fruit juices when the latter are unavailable. The amount of lyophilized juice must be properly dosed in the dry beverage base in order to reproduce the characteristic flavor of beverages prepared with natural fruit juices. It is worthwhile to note that flavor effects in dry beverage bases prepared with and without sugar or synthetic sweeteners (diet beverages) and containing identical flavor ingredients differ widely.

Teas and Tisanes

Teas

A certain confusion exists in the botanical classification of tea by both botanists and growers. The two varieties *Thea sinensis* L. and *Camelia sinensis* (L.) Kun. are considered almost equivalent with a slight preference for the latter. *Camelia sinensis* belongs to the family *Theaceae*. The plant is native to China; its cultivation and commercial development spread from China to Japan, then to India, Ceylon, Java, Africa (Kenya, Uganda, Tanzania), Sumatra, the Azores, Formosa, and Trans-Caucasian Russia (Georgia, Black Sea).

For the preparation of commercial tea, leaves harvested from three-year-old (minimum) plants are used. The plants are usually produced over a period of ten years. Commercial tea is classified into two important types: green and black teas. The differences consist in methods of treating the leaves prior to commercialization. Green tea is prepared by the following method: the harvested leaves are steam treated, dried, lightly roasted, rolled, again roasted, sieved, and aerated. The preparation of black tea follows the same procedure, with the addition of fermentation. This step is carried out after drying the leaves; fermentation favors the development of a particular flavor. The various leaf qualities (par-

tially or completely ripe), the method of rolling the leaves (manually or mechanically), the age of the plant, and other factors are the elements on which an extremely fine classification of commercial green and black teas is based.

The method of preparation as well as the different sources of tea leaves tends to impart a characteristic aroma, which can be modified by the addition of complementary flavors to the finished product. Green tea, usually much less aromatic than fermented black tea, is sometimes flavored during manufacturing with jasmine or orange flowers. The flavoring operation is often continued by the consumer, who may add other herbs or dried flowers to the tea infusion. The flavoring of fermented black tea is carried out largely by the manufacturer. Well known specialties are flowery pekoe and orange pekoe, which are flavored with jasmine and orange flowers, respectively. Various tea manufacturers have marketed other products flavored with various characteristic aromas, including rose, lavender, ripe peach, mandarin, muscat grape, clove, orris, and sometimes a smoky aroma. Properly diluted essential oils, sprayed on the product according to traditional methods or to other undisclosed proprietary procedures, also are employed for tea flavoring.

Tisanes

This name designates those concoctions prepared by treating aromatic plants with hot water. Camomile, linden, mint, and karkade are the aromatic plants chiefly used for tisanes. Camomile has picked up new momentum in the consumer market in recent years. It is interesting to mention that, in a few cases, the characteristic camomile flavor has been modified by the addition of aromatic herbs in an attempt to create new flavors.

Cocoa

It is extremely probable that sugar, amino acids, and flavonoids are the precursors in the flavor complex of roasted cocoa. Defatted cocoa forms the familiar chocolate base. Often cocoa flavor is confused with chocolate flavor, although chocolate is derived from cocoa by subsequent treatments and the addition of other flavors, such as vanillin.

Cocoa flavor is not related to the so-called cocoa red, which is isolated as an oil from roasted arriba beans and has an extremely high flavoring strength (12–13 ppm). The extremely difficult reconstruction of cocoa flavor, although not as complex as coffee flavor, was originally obtained by tentatively reinforcing the flavor of extracts, tinctures, and cocoa distillates by addition of trace vanillin or aldehyde, benzyl butyrate, and amyl phenylacetate. These products together with aldehyde C_{18}, neryl butyrate, phenylpropyl cinnamate (floral note), ethyl benzoate, dimethylresorcin, linalool, cyclotene, diacetyl, maltol, dihydrocoumarin, resinoids, and balsams (Tolu and Peru) are the products most frequently used to formulate cocoa flavor imitations with high flavor yields. Careful attention must be given to the addition of vanilla in the formulation, as it tends not only to sweeten but also to shift the cocoa note toward chocolate. The potential use of phenylacetic acid and its esters should also be considered.

Studies of the constitution of natural cocoa aroma dating back to 1921 have received great impetus in more recent years. These studies have supplied a very extensive list of components reported present in solvent extracts, steam distillates, or cocoa butter; they have prompted considering the use of quaternary, alicyclic, aromatic, and heterocyclic compounds for cocoa flavor imitations. Products identified thus far in natural cocoa aroma are listed in the following table:[14]

Compounds in Natural Cocoa Aroma

Compounds	References
Hydrocarbons	
Undecane	37, 43
Dodecane	37
Tridecane	37
Tetradecane	37
Octadecane	37
β-Myrcene	37, 43
Limonene	41, 42, 43
β-Elemene	41, 42, 43
β-Pinene	41, 42, 43
Valencene	41, 42, 43
Caryophyllene	41, 42, 43
Benzene	29, 31, 35, 42
Toluene	29, 31, 35, 42
1,2-Dimethylbenzene	41, 42, 43
1,3-Dimethylbenzene	41, 42, 43
1,4-Dimethylbenzene	41, 42, 43
1,2,4-Trimethylbenzene (pseudocumene)	41, 42, 43
1,3,5-Trimethylbenzene (mesitylene)	41, 42, 43
1,2,3,5-Tetramethylbenzene	41, 42, 43
Vinylbenzene (styrene)	41, 42, 43
1-Ethyl-2-methylbenzene	41, 42, 43
1-Ethyl-3-methylbenzene	41, 43
1-Ethyl-4-methylbenzene	41, 42, 43
2-Ethyl-1,4-dimethylbenzene	41, 42, 43
2,4-Dimethyl-1-vinylbenzene	41, 42, 43
Propylbenzene	41, 42, 43
Isopropylbenzene (cumene)	41, 42, 43
1-Isopropyl-4-methylbenzene	41, 42, 43
Methylbiphenyl	37
Naphthalene	37, 43
2-Methylnaphthalene	37, 43
Dimethylnaphthalene	37
Trimethylnaphthalene	37
Tetramethylnaphthalene	37
Alcohols	
Methanol	28, 29, 31, 42
Ethanol	28, 29, 31, 35, 42
1-Propanol	28, 31, 35, 42
2-Propanol	28, 31, 35, 42
2-Methylpropan-1-ol (isobutanol)	28, 35, 39, 42
1-Butanol	31, 39
2-Butanol	31
3-Methylbutan-1-ol (isoamyl alcohol)	28, 35, 39, 40, 43
1-Pentanol	31, 35, 37, 39
2-Pentanol	39, 40
1-Hexanol	35, 39, 42
2-Heptanol	39
1-Octanol	39, 41, 42, 43
1-Octen-3-ol	35, 39, 42
Geraniol	28, 31, 35, 42, 43
Linalool	25, 28, 31, 35, 37, 40, 42, 43
Benzyl alcohol	35, 39, 43
1-Phenylethanol	35, 37, 39, 40, 43
2-Phenylethanol	35, 37, 39, 40, 43
2-Phenylpropan-2-ol	35, 39
2-Methyl-3-phenylpropan-2-ol	41, 42
Menthol	41, 42, 43
α-Terpineol	41, 42, 43
Terpineol-1	41, 42, 43
Terpineol-4	41, 42, 43
Borneol	41, 42, 43
Furfuryl alcohol	28, 31, 35, 39, 40, 42, 43
2,3-Butanediol	31, 35, 39, 42, 43
Carbonyls	
Acetaldehyde	28, 29, 31, 35, 40, 42
Propanal	29, 31, 35, 42
2-Propenal (acrolein)	35, 42
2-Methylpropanal	29, 31, 35, 40, 42, 43
2-Methylprop-2-enal (methacrolein)	41, 42
Butanal	29, 31, 35, 42
2-Butenal (crotonaldehyde)	35, 39, 42, 43
2-Methylbutanal	37, 43
3-Methylbutanal	29, 31, 35, 37, 40, 42, 43
Hexanal	41, 42, 43
5-Methyl-2-isopropylhex-2-enal	40
Octanal	41, 42, 43
2,4-Octadienal	35, 42
Nonanal	41, 42, 43
Decanal	41, 42, 43
Citronellal	28, 31, 35, 42, 43
Benzaldehyde	31, 35, 39, 40, 42, 43
Phenylacetaldehyde	35, 39, 40, 42, 43
Phenylbutenal	39
2-Phenylbut-2-enal	40
4-Methyl-2-phenylpent-2-enal	40
5-Methyl-2-phenylhex-2-enal	40
2-Propanone	29, 31, 35, 42, 43
Acetol acetate	35, 39, 42
2-Butanone	40
3-Hydroxybutan-2-one	31, 35, 37, 39, 40, 42, 43
2,3-Butanedione (diacetyl)	26, 28, 29, 31, 35, 40, 42, 43
trans-3-Penten-2-one	40
2,3-Pentanedione	35, 39, 40, 42
5-Methylhexan-2-one	41, 42, 43
2-Heptanone	37, 43
6-Methyl-5-hepten-2-one (2-methyl-2-hepten-6-one)	28, 31, 35, 37, 42
2-Octanone	37, 43
5-Hydroxyoctan-4-one	41, 42, 43

Compounds in Natural Cocoa Aroma (continued)

Compounds	References
4,5-Octanedione	41, 42, 43
2-Nonanone	37
2-Dodecanone	37
3-Heptadecanone	31, 35, 42
Acetophenone	31, 35, 37, 39, 40, 42, 43
2-Hydroxyacetophenone	35, 37, 39, 42, 43
4-Methylacetophenone	41, 42, 43
1-Phenylpropan-2-one	41, 42, 43
3-Methylcyclopentan-1,2-dione (cyclotene)	35, 39, 42
2-Acetyl-4-isopropenylcyclopent-1-ene	41, 42
Menthone	41, 42, 43
Camphor	41, 42, 43
Furfural	26, 35, 39, 40, 42
5-Methylfurfural	40, 41, 42, 43
2-Acetylfuran	35, 37, 39, 40, 42, 43
2-Acetyl-5-methylfuran	41, 42, 43
2-Propionylfuran	41, 42, 43
2-Methyltetrahydrofuran-3-one	35, 39, 40, 41 42, 43
Tetrahydrofuran-2-one	40
Acids	
Formic acid	35, 42, 43
Acetic acid	25, 31, 35, 40, 42, 43
Propanoic acid	25, 35, 40, 42, 43
2-Hydroxypropanoic acid (lactic acid)	31, 43
2-Methylpropanoic acid	39, 40
Butanoic acid	25, 31, 35, 42
2-Butenoic acid (crotonic acid)	40
2-Methylbutanoic acid	31, 35, 37, 42, 43
3-Methylbutanoic acid	37, 40, 43
2-Hydroxy-3-methylbutanoic acid	41, 42
Pentanoic acid	31, 35, 40, 42, 43
4-Methylpentanoic acid	40
2-Hydroxy-3-methylpentanoic acid	41, 42, 43
2-Hydroxy-4-methylpentanoic acid	41, 42, 43
Hexanoic acid	25, 31, 35, 40, 42, 43
Heptanoic acid	40
Octanoic acid	25, 31, 35, 40
Nonanoic acid	25, 35, 40, 42
Decanoic acid	31, 40, 42
Dodecanoic acid (lauric acid)	40
Tetradecanoic acid (myristic acid)	40
Hexadecanoic acid (palmitic acid)	40
2-Hydroxy-3-methylglutaric acid	41, 42, 43
Benzoic acid	40, 43
2-Methoxybenzoic acid	41, 42, 43
4-Hydroxybenzoic acid	30, 31, 32, 35, 42
4-Methoxybenzoic acid (anisic acid)	30, 31, 35, 42, 43
4-Hydroxy-3-methoxybenzoic acid (vanillic acid)	30, 31, 32, 35, 42
3,5-Dimethoxy-4-hydroxybenzoic acid	32, 35, 42
3,4-Dihydroxybenzoic acid (protocatechuic acid)	33, 35, 42
Phenylacetic acid	30, 31, 32, 35, 40, 42
2-Hydroxyphenylacetic acid	30, 31, 32, 35, 42
4-Hydroxyphenylacetic acid	30, 31, 32, 35, 42
4-Hydroxyphenylpropanoic acid	32
4-Hydroxycinnamic acid	32, 35, 42
4-Hydroxy-3-methoxycinnamic acid (ferulic acid)	32, 35, 42
2-Methoxyphenylacetic acid	30
4-Methoxyphenylacetic acid	30
Esters	
Methyl acetate	29, 31, 35, 42
Ethyl acetate	28, 31, 35, 40, 42
Propyl acetate	26, 28, 31, 35, 42
Isopropyl acetate	26, 28, 31, 35, 42
Butyl acetate	26, 28, 31, 35, 42
Isobutyl acetate	26, 28, 31, 35, 40, 42
2-Methylbutyl acetate	41, 42, 43
Amyl acetate	25, 26, 28, 31, 35, 42
Isoamyl acetate	35, 37, 40, 42, 43
2-Pentyl acetate	35, 40, 42
Neryl acetate	41, 42, 43
Geranyl acetate	41, 42, 43
Linalyl acetate	25, 28, 31, 35, 42, 43
Benzyl acetate	35, 37
Phenyl acetate	31, 35, 42
Phenethyl acetate	31, 35, 37, 39, 40, 42, 43
3-Phenylpropyl acetate	41, 42, 43
Furfuryl acetate	35, 39, 42
Ethyl propanoate	28, 31, 35, 42
Amyl propanoate	25, 28, 31, 35, 42
Hexyl propanoate	25, 35, 42
Ethyl 2-oxopropanoate	41, 42, 43
Amyl butanoate	25, 28, 31, 35, 42
Hexyl butanoate	25, 35, 42
Ethyl 2-butenoate (crotonate)	41, 42, 43
Ethyl 3-methylbut-2-enoate	41, 42, 43
Ethyl 4-oxopentanoate	41, 42, 43
Ethyl 4-methylpent-2-enoate	41, 42, 43
Ethyl 4-methylpent-3-enoate	41, 42, 43
Ethyl hexanoate	31, 35, 37, 39, 42, 43
Ethyl 3-heptenoate	41, 42, 43
Ethyl octanoate	37, 43
Ethyl decanoate	37, 43
Ethyl dodecanoate	37
Ethyl tetradecanoate	37

Compounds in Natural Cocoa Aroma (continued)

Compounds	References
Isobutyl benzoate	42, 43
Ethyl benzoate	37, 39, 42, 43
Isoamyl benzoate	40
Methyl phenylacetate	31, 35, 42, 43
Ethyl phenylacetate	31, 35, 39, 42, 43
Ethyl cinnamate	37
4-Hydroxybutanoic acid lactone	35, 39, 42
4-Hydroxy-2-methylbutanoic acid lactone	35, 42
4-Hydroxypentanoic acid lactone	35, 39, 42
4-Hydroxyhexanoic acid lactone	35, 39, 42
4-Hydroxynonanoic acid lactone	37
Bases	
Methylamine	27, 35, 42
Dimethylamine	27, 35, 42
Trimethylamine	27, 35, 42
Ethylamine	27, 35, 42
Triethylamine	27, 35, 42
Isobutylamine	27, 35, 42
sec-Butylamine	27, 35, 42
Isoamylamine	23, 31, 35, 42
Phenethylamine	31, 35, 42
Pyrrole	35, 39, 42
Methylpyrazine	35, 38, 39, 40, 42, 43
2,3-Dimethylpyrazine	35, 37, 38, 39, 40, 42, 43
2,5-Dimethylpyrazine	35, 37, 38, 39, 40, 42, 43
2,6-Dimethylpyrazine	31, 35, 37, 38, 39, 40, 42, 43
Trimethylpyrazine	35, 37, 38, 39, 40, 42, 43
Tetramethylpyrazine	31, 35, 37, 38, 39, 40, 42, 43
Ethylpyrazine	40
2-Methyl-5-ethylpyrazine	38, 39, 40, 43
2-Methyl-6-ethylpyrazine	35, 42, 43
2-Methyl-6-isoamylpyrazine	41, 42, 43
2-Methyl-6-(2-methylbutyl)-pyrazine	41, 42, 43
2,3-Dimethyl-5-ethylpyrazine	40, 43
2,3-Dimethyl-5-isoamylpyrazine	37
2,3-Dimethyl-5-(2-methylbutyl)-pyrazine	37
2,5-Dimethyl-3-ethylpyrazine	35, 37, 38, 39, 40, 42, 43
2,5-Dimethyl-3-propylpyrazine	37
2,5-Dimethyl-3,6-diethylpyrazine	41, 42, 43
2,6-Dimethyl-3-ethylpyrazine	38, 43
2,6-Dimethyl-3-isoamylpyrazine	41, 42, 43
2,6-Dimethyl-3,5-diethylpyrazine	41, 42, 43
Dimethyl-isopropylpyrazine	37
Trimethyl-ethylpyrazine	34, 39, 40, 43
Trimethyl-isoamylpyrazine	37
S-Compounds	
Methylthiomethane	29, 35, 39, 40, 42
Methyldithiomethane	29, 35, 37, 40, 42, 43
Methyldithioisopropane	41, 42, 43
Methyldithiobenzene	41, 42, 43
Methyltrithiomethane	40, 42
Methyltrithiopropane	35, 43
Propyltrithiopropane	42
Isobutyl thiocyanate	41, 42, 43
3-Methylthiopropanal	40
2-Methylthio-2-methylpropanal	41, 42, 43
5-Methylfurfurylthiomethane	35, 39, 42
4-Methyl-5-(β-hydroxyethyl)-thiazole	36
4-Methyl-5-vinylthiazole	36
Benzothiazole	37, 43
Miscellaneous	
3-Methylbutane nitrile	41, 42, 43
Benzonitrile	35, 39, 43
Phenol	31, 35, 37, 39, 40, 42
Methylphenol (cresol)	31, 35, 42
2,3 Dimethylphenol	40
4-Ethylphenol	31, 35, 42
2-Methoxyphenol (guaiacol)	31, 35, 37, 39, 40, 42, 43
2-Methoxy-4-methylphenol	31, 35, 37
4-Allyl-2-methoxyphenol (eugenol)	31, 35, 37, 42
1-Allyl-3,4-methylenedioxy benzene (safrole)	41, 42, 43
6,7-Dihydroxycoumarin	32, 35, 42
1,4-Cineole	41, 42, 43
1,8-Cineole	41, 42, 43
2-Formylpyrrole	35, 39, 40, 42
2-Formyl-1-methylpyrrole	35, 39, 42, 43
2-Formyl-5-methylpyrrole	35, 39, 42
1-Ethyl-2-formylpyrrole	41, 42, 43
2-Formyl-1-pentylpyrrole	41, 42, 43
2-Acetylpyrrole	31, 35, 39, 40, 42, 43
2-Acetyl-1-pentylpyrrole	41, 42, 43
2-Propionylpyrrole	41, 42, 43
2-Methoxycarbonylpyrrole	41, 42, 43
2-Methyltetrahydrofuran	40
cis-5-(2-Hydroxy-isopropyl)-2-methyl-2-vinyltetrahydrofuran = *cis*-2,6-dimethyl-3,6-epoxy-2-hydroxyoct-7-ene = linalool-oxide II	35, 39, 42, 43
Furan	29, 35, 42
2-Methylfuran	29, 35, 42
3-Phenylfuran	41, 42, 43
3-Hydroxy-2-methyl-4-oxo-1,4-pyran (maltol)	31, 35, 42
Pentanal	43

Compounds in Natural Cocoa Aroma (continued)

Compounds	References	Compounds	References
2-Pentanone	43	Ethyl 2-furancarboxylate	43
3-Hexanone	43	2,5-Dimethyl-3-isobutyl-pyrazine	43
1-Acetyl-4-isopropenylcyclo-pent-1-ene	43	2,5-Dimethyl-3-(2-methylbutyl) pyrazine	43
4-Phenylbutan-2-one	43	2,5-Dimethyl-3-isoamyl pyrazine	37, 43
α-Terpinyl acetate	43	Isopropylpyrazine	43
Ethyl 2-hydroxypropanoate (lactate)	43	Methylthioethane	43
Ethyl 2,2-diethoxypropanoate	43	1,1-Diethoxyethane	43
Ethyl 3-ethoxypropanoate	43	1,1-Diethoxy-2-methylpropane	43
Ethyl 3-methylbutanoate	43	1,1-Diethoxy-2-methylbutane	43
Ethyl 2-hydroxy-3-methyl-butanoate	43	1,1-Diethoxy-3-methylbutane	43
Ethyl 4-methylpentanoate	43	1-Ethoxy-1-isobutoxy-3-methyl-butane	43
Ethyl 2-hydroxy-4-methyl-pentanoate	43	1,1-Diethoxy-3-oxobutane	43
Ethyl heptanoate	43	1,1-Dimethoxyphenylethane (acetal)	43
Ethyl nonanoate	43	Diisoamyl ether	43
Methyl 4-methoxybenzoate	43	Benzyl-ethyl ether	43
Ethyl acid succinate	43	Benzylcyanide	41, 42, 43
Diethyl succinate	43	*trans*-Linalooloxide I	43
Methyl 2-furancarboxylate	43		

Coffee

Whenever the distillate, tincture, or soft or dried extract of roasted coffee fails to adequately flavor any given food substrate because of technical limitations, it may be necessary to use coffee flavor imitations. The imitation of coffee flavor represents indeed an extremely difficult and complex problem to the flavorist. The green coffee bean almost lacks any flavor whatsoever; yet once roasted, it turns into an endless source of flavor sensations.

Furfural, long known to be present in roasted coffee aroma through the caramelization of carbohydrates and the decomposition of pentosans, is nearly useless for the reconstruction of natural coffee aroma. Coffee aroma, in fact, is the resulting product not only of the caramelization of sugars, but also of the (1) simultaneous drastic hydrolysis of plant tissues, (2) partial elimination of volatile products, (3) carbonization of cellulose, (4) decomposition of glucosides and fats, and (5) hydrolysis of proteins. All of these reactions cause the development of the characteristic coffee aroma; they are dependent both qualitatively and quantitatively on the method of roasting and the blend of coffee beans.

The initial attempts to imitate coffee aroma were limited to reinforcing the aroma of complex coffee extracts by the addition of a small amount of distillate to hydro-alcoholic tincture. Attempts were also made to strengthen the aroma of concentrated aqueous coffee extracts containing small amounts of propylene glycol or propylene glycol ethyl ester to improve the solubility of the flavor ingredients. The most functional products for such purposes were ethyl formate, acetaldehyde, diacetyl, furfural, pyridine, thional (condensation product of tolyl aldehyde with *n*-hexylmercaptan), and cyclotene or equivalent products (to sweeten the note). The formulations suggested by H. Staudinger and T. Reichstein provided guidelines for the preparation of the so-called "concentrated bases of mocha coffee imitations."[16] The following formulation represents a valuable starting point in the study of coffee-flavored imitations.

Imitation Coffee Formulation

Ingredient	Parts	Ingredient	Parts
Ethyl methyl glyoxal	4	Phenol	1
2-Methylbutanal	4	Isoeugenol	1
Acetaldehyde	3	Methyl mercaptan	0.6
Pyridine	3	α-Methylcyclopentenolone	0.5
α-Methylfurfural	2	Thioguaiacol	0.4
Isovaleric acid	2	Furfuryl mercaptan	0.3
Diacetyl	1	*n*-Octyl alcohol	0.3
Furfural	1		

Knowledge of the components present in coffee aroma does not imply the ability to rebuild the natural aroma via imitations. However, an examination of the components identified in coffee aroma by M. Stoll *et al.* may yield very valuable information.[17] According to the authors, the list may be quantitatively inaccurate and may also contain potential artifacts. The flavorist should keep in mind that coffee aroma is probably the most complex aroma and, therefore, the most difficult to imitate satisfactorily.

Components of Coffee Aroma

Hydrocarbons

p-Cymene
Dimethylnaphthalene
Diphenyl
2-Ethylnaphthalene
Fluorene
Indene
p-Isopropenyltoluene
p-Menthadiene (1,8)
3-Methyl diphenyl
1-Methylnaphthalene
2-Methylnaphthalene
Myrcene
Naphthalene
Styrene
1,2,4,5-Tetramethylbenzene
Tetramethylnaphthalene
Toluene
1,2,4-Trimethylbenzene
Trimethylnaphthalene

Alcohols and Esters

3,4-Dimethoxystyrene
Ethanol
2-Heptanol
1-Hexanol
Linalool
Methanol
3-Methyl-1-butanol
3-Methyl-2-buten-1-ol
3-Octanol
1-Octen-3-ol
1-Pentanol
α-Terpineol

Aldehydes

Acetaldehyde
Benzaldehyde
Butyraldehyde
Hexanal
Isobutyraldehyde
Isopentanal
2-Methyl-2-butanol
2-Methylbutyraldehyde
Phenyl acetaldehyde
Propionaldehyde
Salicylaldehyde
o-Toluic aldehyde

Ketones

Acetone
Butanone
Cyclopentanone
2-Decanone
6,10-Dimethyl-2-undecanone
2-Heptanone
3-Hexanone
Mesityl oxide
6-Methyl-5-hepten-2-one
2-Nonanone
2-Octanone
3-Octanone
2-Pentanone
3-Pentanone
Propiophenone (ethyl phenyl ketone)
2-Tridecanone
6,10,14-Trimethyl-2-pentadecanone
2-Undecanone

Ketoalcohols

1-Butanol-2-one
2-Butanol-2-one
3-Pentanol-2-one
2-Pentanon-3-one
1-Propanol-2-one

Diketones

2,3-Butanedione
3,4-Heptanedione
2,3-Hexanedione
3,4-Hexanedione
5-Methyl-3,4-heptanedione
6-Methyl-3,4-heptanedione
5-Methyl-2,3-hexanedione
4-Methyl-2,3-pentanedione
2,3-Octanedione
2,3-Pentanedione
1-Phenyl-1,2-propanedione

Acids and Anhydrides

Acetic acid
2,3-Dimethyl maleic anhydride
2-Ethyl-3-methyl maleic anhydride
Formic acid
Hexanoic acid
Isovaleric acid
2-Methylbutyric acid
Propionic acid

Esters and Lactones

Benzyl formate
γ-Butyrolactone
2-Isopentenyl acetate

Components of Coffee Aroma (continued)

Esters and Lactones *(continued)*

Methyl acetate
Methyl benzoate
Methyl formate
Methyl palmitate
2-Phenethyl formate

Mercaptans and Sulfides

Carbon disulfide
Methyl ethyl sulfide
Methyl mercaptan
Methyl sulfide
Methylthiobenzene
1-Methyl-2-thio-2-butanone
2-Methylthiophenol

Phenols

o-Cresol
2,3-Dimethylphenol (*o*-Xylenol)
2,5-Dimethylphenol (*p*-Xylenol)
2,6-Dimethylphenol (*m*-Xylenol)
3,4-Dimethylphenol (*o*-Xylenol, unsy.)
4-Ethyl-2-methoxyphenol
2-Ethylphenol
o-Ethylphenol
2-Hydroxyacetophenone
o-Methoxyphenol
5-Methyl-2-hydroxyacetophenone
Methyl salicylate
Phenol
2,3,5-Trimethylphenol

Furan Derivatives

2-Acetyl furane
2-Acetyl-5-methyl furane
2-Amyl furfurane
Benzofuran
2-Butyryl furane
2-Cyano-5-methyl furane
Difurfuryl ether
2,3-Dihydro benzofurane
Di-(5-methylfurfuryl) ether

Furan Derivatives *(continued)*

Furan
Furfural
Furfuryl acetate
Furfuryl alcohol
Furfuryl alcohol, methyl ester
Furfuryl butyrate
Furfuryl crotonate
Furfuryl, β,β-dimethyl acrylate
Furfuryl formate
2-Furfuryl furfurane
Furfuryl isobutyrate
Furfuryl isovalerate
Furfuryl mercaptan
Furfuryl 2-methylbutyrate
Furfuryl methylsulfide
Furfuryl propionate
Furfuryl sulfide
Furfuryl thioacetate
2-Furyl-1,2-butanedione
2-Furyl-2-butanone
2-Furyl-3-butanone
2-Furyl furfurane
Furyl methyl thiocarbonate
2-Furyl-1,2-propanedione
2-Furyl-2-propanone
5-Methyl furfural
2-Methyl furfurane
2-(5-Methylfurfuryl)furfurane
2-(5-Methylfurfuryl)5-methyl furfurane
5-Methylfurfuryl methylsulfide
5-Methylfuryl-1,2-butanedione
5-Methylfuryl-2-butanone
5-Methylfuryl-3-butanone
5-Methylfuryl-1,2-propanedione
5-Methylfuryl-2-propanone
2-Methyl-5-propionyl furane
3-Phenyl furfurane
2-Propionyl furane

Thiophene Derivatives

2-Acetyl-3-methyl thiophene
2-Acetyl-4-methyl thiophene

Thiophene Derivatives *(continued)*

2-Acetyl-5-methyl thiophene
Benzo-b-thiophene
4-Ethyl-2-methyl thiophene
2-Formyl-5-methyl thiophene
2-Formyl thiophene
2-Propionyl thiophene
Thienyl acetate
Thienyl alcohol
Thienyl formate
2-Thienyl-methyl carbonate
2-Thienyl-1,2-propanedione
3-Thienyl-1,2-propanedione
3,2[b] or 2,3[b]-Benzothiophene
3-Vinyl thiophene

Pyrrole Derivatives

1-Acetyl furfuryl-2-pyrrole
1-Ethylformyl-2-pyrrole
1-Formylfurfuryl-2-pyrrole
1-Furfuryl pyrrole
1-Isoamylformyl-2-pyrrole
1-Isoamyl pyrrole
1-Methyl acetyl-2-pyrrole
1-(2-Methyl butyl)formyl-2-pyrrole
2-Methyl butyl-1-pyrrole
1-Methylformyl-2-pyrrole
5-Methyl furfuryl-1-pyrrole
1-(2-Pyrrolyl)-1,2-butanedione

Thiazoles

2-Acetyl-4-methyl thiazole
2-Propionyl-4-methyl thiazole

Other Products

Anhydrous linalool oxide
cis-Linalool oxide
Maltol
2-Methyl-3-hydrofuranone
t-Methyl-quinoxaline
2-Methyl-3-tetrahydrothiophenone
Tetrahydrothiophene

Research on the identification of those components responsible for the aroma of roasted coffee has continued after 1967, date of the publication of the above list. An updated list of products identified thus far in coffee aroma is reported in the following table.

Recently Identified Components of Coffee Aroma

Compounds	References
Hydrocarbons	
Methane	58, 66
Ethylene	66
Butene	58, 66
2-Methylbuta-1,3-diene	46, 52, 55, 58, 61, 65, 66
Pentane	58, 66
Pentene	58, 66
Pentadiene	45, 58, 61, 66
Hexene	58, 66
Hexadiene	58, 66
Octane	58, 66
Octene	58, 66
Octyne	58, 66
Nonane	58, 66
Tetradecane	62, 66
Pentadecane	62, 66
Heptacosane	61, 66
Myrcene	59, 60, 66, 67
1-Methylcyclohexa-2,4-diene	58, 66
Limonene	60, 66
Benzene	56, 58, 66
Toluene	55, 56, 58, 60, 61, 66
Dimethylbenzene	56, 58, 66
1,2,4-Trimethylbenzene (pseudocumene)	60, 66
1,2,4,5-Tetramethylbenzene	60, 66
Ethylbenzene	58, 66
Vinylbenzene (styrene)	56, 60, 66
1-Isopropyl-4-methylbenzene	60, 66
1-Isopropenyl-4-methylbenzene	60, 66
Silvestrene	61, 66
Indene	60, 66
Biphenyl	60, 66
3-Methylbiphenyl	60, 66
Naphthalene	60, 61, 66
1-Methylnaphthalene	60, 66
2-Methylnaphthalene	60, 66
Dimethylnaphthalene	60, 66
Trimethylnaphthalene	60, 66
Tetramethylnaphthalene	60, 66
2-Ethylnaphthalene	60, 66
Fluorene	60, 66
Phenanthrene	57
Anthracene	57
Fluoranthrene	57
Pyrene	57
Chrysene	57
1,2-Benzanthrene	57
1,2-Benzopyrene	57
3,4-Benzopyrene	57
1,12-Benzperylene	57
Alcohols	
Methanol	44, 45, 46, 48, 52, 53, 55, 58, 60, 61, 65, 66
Ethanol	44, 45, 46, 48, 52, 55, 58, 60, 61, 65, 66
2-Propanol	64, 65, 66
2-Methylpropan-1-ol (isobutanol)	58, 66
2-Methylpropan-2-ol	58, 66
2-Methylbutan-1-ol (isoamyl alcohol)	60, 66
3-Methylbut-2-en-1-ol	60, 65, 66
2-Methylbutan-2-ol	58, 66
1-Pentanol	58, 60, 66
1-Hexanol	56, 58, 60, 66
2-Heptanol	60, 66
3-Octanol	60, 66
1-Octen-3-ol	60, 66
Linalool	59, 60, 65, 66, 67
α-Terpineol	59, 60, 66
Furfuryl alcohol	51, 54, 55, 60, 61, 65, 66
Carbonyls	
Formaldehyde	55, 61, 66
Acetaldehyde	44, 45, 46, 47, 48, 52, 53, 54, 55, 58, 60, 61, 65, 66
Propanal	44, 45, 46, 47, 48, 52, 53, 54, 55, 56, 58, 60, 61, 65, 66
2-Propenal (acrolein)	44, 48, 61, 66
2-Methylpropanal	45, 46, 47, 52, 53, 54, 55, 56, 58, 60, 61, 65, 66
Butanal	45, 46, 52, 56, 58, 60, 61, 65, 66
2-Butenal (crotonaldehyde)	56, 66
2-Methylbutanal	45, 47, 53, 54, 55, 58, 60, 61 65, 66
3-Methylbutanal	44, 45, 46, 47, 48, 52, 53, 54, 60, 61, 65, 66
2-Methylbut-2-enal	44, 48, 60, 65, 66
Pentanal	45, 58, 61, 66
2-Methylpent-2-enal	44, 48, 61, 66
Hexanal	58, 60, 66
Benzaldehyde	60, 66, 67
2-Methylbenzaldehyde	60, 66
3-Methylbenzaldehyde	64, 65, 66
2-Hydroxybenzaldehyde (salicylaldehyde)	60, 66
Phenylacetaldehyde	60, 66

Recently Identified Components of Coffee Aroma (continued)

Compounds	References
2-Propanone	44, 45, 46, 47, 48, 52, 53, 54, 55, 56, 58, 60, 61, 65, 66
1-Hydroxypropan-2-one (acetol)	53, 55, 60, 61, 65, 66
Acetol acetate	53, 54, 55, 56, 61, 65, 66
2-Butanone	44, 45, 46, 48, 52, 53, 54, 55, 56, 58, 60, 61, 65, 66
3-Buten-2-one (1-buten-3-one)	44, 48, 61, 66
1-Hydroxybutan-2-one	60, 66
3-Hydroxybutan-2-one	53, 54, 55, 60, 61, 65, 66
3-Methylbutan-2-one	58, 66
2,3-Butanedione (diacetyl)	44, 45, 46, 48, 52, 53, 54, 55, 58, 60, 61, 65, 66
2-Pentanone	58, 60, 66
3-Pentanone	44, 49, 58, 60, 61, 66
trans-3-Penten-2-one (2-penten-4-one)	64, 65, 66
3-Hydroxypentan-2-one	55, 60, 61, 66
2-Hydroxypentan-3-one	55, 60, 61, 66
4-Methyl-3-penten-2-one (2-methyl-2-penten-4-one)	60, 66
2,3-Pentanedione	46, 52, 53, 54, 55, 56, 60, 61, 65, 66
2,4-Pentanedione	44, 48, 61, 66
4-Methylpentane-2,3-dione	60, 66
3-Hexanone	56, 60, 65, 66
2,3-Hexanedione	53, 54, 60, 65, 66
2,5-Hexanedione	64, 65, 66
3,4-Hexanedione	60, 66
5-Methylhexane-2,3-dione	60, 66
2-Heptanone	60, 66
6-Methyl-5-hepten-2-one (2-methyl-2-hepten-6-one)	60, 66
2,5-Heptanedione	64, 65, 66
3,4-Heptanedione	60, 66
5-Methylheptane-3,4-dione	60, 66
6-Methylheptane-3,4-dione	60, 66
2-Octanone	60, 66
3-Octanone	60, 66
2,3-Octanedione	60, 66
2-Nonanone	60, 66
trans-2-Nonenal	71
2-Decanone	60, 66
2-Undecanone	60, 66
6,10-Dimethylundecan-2-one	59, 60, 66
2-Tridecanone	60, 66
6,10,14-Trimethylpentadecan-2-one	59, 60, 66
2-Hydroxyacetophenone	60, 65, 66
2-Hydroxy-5-methylacetophenone	60, 66
2,3-Dihydroxyacetophenone	55, 61, 66
4-Hydroxy-3-methoxyacetophenone	61, 66
1-Phenylpropan-1-one (propiophenone)	60, 66
1-Phenylpropane-1,2-dione	60, 66
Cyclopentanone	55, 60, 61, 65, 66
Cyclopentan-1,2-dione	66
3-Methylcyclopentan-1,2-dione (cyclotene)	49, 55, 61, 65, 66
3,4-Dimethylcyclopentan-1,2-dione	49, 55, 61, 65, 66
3,5-Dimethylcyclopentan-1,2-dione	49, 55, 61, 66
3-Ethylcyclopentan-1,2-dione	49, 55, 61, 65, 66
Cyclopent-2-en-1-one	62, 66
2-Methylcyclopent-2-en-1-one	62, 66
2-Ethylcyclopent-2-en-1-one	62, 66
2,3-Dimethylcyclopent-2-en-1-one	67
2,3,5-Trimethylcyclopent-2-en-1-one	62, 66
3-Methylcyclohexan-1,2-dione	49, 55, 61, 65, 66
Cyclohex-2-en-1-one	67
2-Methylcyclohex-2-en-1-one	62, 66
2-Acetyltetrahydrofurane	67
Furfural	45, 51, 53, 54, 55, 58, 60, 61, 65, 66
5-Methylfurfural	51, 53, 54, 55, 60, 61, 65, 66
5-Hydroxymethoxyfurfural	68
3-(Furyl-2)propanal	64, 65, 66
3-(Furyl-2)prop-2-enal	58, 64, 65, 66
2-Acetylfuran	51, 53, 54, 55, 56, 60, 61, 65, 66
2-Acetyl-5-methylfuran	51, 55, 60, 61, 65, 66
2-Propionylfuran	60, 65, 66
5-Methyl-2-propionylfuran	60, 65, 66
1-(Furyl-2)propan-1,2-dione	51, 55, 60, 61, 65, 66
1-(5-Methylfuryl-2)propan-1,2-dione	51, 55, 60, 61, 65, 66
2-Acetonylfuran	60, 65, 66
2-Acetonyl-5-methylfuran	60, 66
2-Furfuryloxyacetone	64, 65, 66
2-Butyrylfuran	60, 65, 66

Recently Identified Components of Coffee Aroma (continued)

Compounds	References
2-Isobutyrylfuran	65
1-(Furyl-2)butan-2-one	60, 66
1-(5-Methylfuryl-2)butan-2-one	60, 66
1-(Furyl-2)butan-3-one	60, 65, 66
1-(5-Methylfuryl-2)butan-3-one	60, 65, 66
1-(Furyl-2)but-1-en-3-one	64, 65, 66
1-(Furyl-2)butan-1,2-dione	51, 55, 60, 61, 65, 66
1-(5-Methylfuryl-2)butan-1,2-dione	60, 66
2-Methyltetrahydrofuran-3-one	50, 53, 54, 55, 56, 60, 61, 65, 66
2,5-Dimethyl-(2H)-furan-3-one	67
2,4,5-Trimethyl-(2H)-furan-3-one	62, 66
Acids	
Formic acid	45, 55, 60, 61, 63, 65, 66
Acetic acid	45, 53, 55, 60, 61, 63, 65, 66
Propanoic acid	45, 53, 55, 60, 61, 63, 65, 66
2-Methylpropanoic acid	55, 61, 65, 66
2-Methylpropenoic acid	64, 65, 66
Butanoic acid	63, 65, 66
cis- and *trans*-2-Butenoic acid	55, 61, 64, 65, 66
2-Methylbutanoic acid	55, 60, 61, 66
3-Methylbutanoic acid	53, 55, 60, 61, 65, 66
2-Methylbut-2-enoic acid (tiglic acid)	64, 65, 66
3-Methylbut-2-enoic acid (senecioic acid)	55, 61, 65, 66
Pentanoic acid	63, 66
Hexanoic acid	60, 62, 66
Heptanoic acid	63, 66
Octanoic acid	63, 66
Nonanoic acid	63, 66
Decanoic acid	63, 66
Hexadecanoic acid (palmitic acid)	61, 66
3-Ethyl-2-methylmaleic anhydride	55, 60, 61, 64, 65, 66
2,3-Dimethylmaleic anhydride	55, 60, 61, 65, 66
Esters	
Methyl formate	44, 45, 46, 48, 52, 53, 54, 55, 56, 58, 60, 61, 65, 66
Ethyl formate	45, 46, 52, 61, 65, 66
Isopropyl formate	64, 65, 66
Benzyl formate	60, 66
Phenethyl formate	60, 65, 66
Furfuryl formate	51, 55, 60, 61, 65, 66
Methyl acetate	44, 45, 46, 48, 52, 53, 54, 55, 56, 58, 60, 61, 65, 66
Ethyl acetate	55, 58, 61, 65,
Butyl acetate	56, 66
2-Oxobutyl-1 acetate	62, 64, 65, 66
3-Methylbut-2-enyl acetate	60, 66
2-Oxopentyl-1 acetate	64, 65, 66
3-Oxopentyl-2 acetate	64, 65, 66
Isoamyl acetate	64, 65, 66
Furfuryl acetate	51, 53, 54, 55, 56, 60, 61, 65, 66
Methyl propanoate	56, 58, 65, 66
Acetonyl propanoate	62, 66
Furfuryl propanoate	60, 65, 66
Furfuryl 2-methylpropanoate	60, 66
Furfuryl butanoate	60, 66
Furfuryl 2-butenoate	60, 66
Furfuryl 3-methylbut-2-enoate	60, 65, 66
Methyl-3-methylbutanoate	56, 66
Furfuryl 3-methylbutanoate	60, 66
Methyl hexadecanoate (palmitate)	60, 66
Methyl benzoate	60, 66
Methyl phenylacetate	64, 65, 66
Methyl salicylate	60, 65, 66
Methyl nicotinate	55, 61, 65, 66
4-Hydroxybutanoic acid lactone	53, 54, 55, 60, 61, 65, 66
4-Hydroxy-2-methylbutanoic acid lactone	64, 65, 66
4-Hydroxybut-2-enoic acid lactone (crotonic)	55, 61, 66
4-Hydroxy-2,3-dimethylbut-2-enoic acid lactone	64, 65, 66
4-Hydroxypentanoic acid lactone	64, 65, 66
4-Hydroxy-3-methylpent-2-enoic acid lactone	64, 65, 66
4-Hydroxy-2,3-dimethylpent-2-enoic acid lactone	64, 65, 66
Furfuryl 2-methylbutanoate	60, 66
Bases	
Ammonia	66
Methylamine	66
Trimethylamine	66
Pyrrole	44, 48, 51, 55, 61, 65, 66
Dimethylpyrrole	44, 48, 58, 66
1-Methylpyrrole	44, 48, 51, 53, 54, 55, 56, 58, 61, 65, 66
2-Ethylpyrrole	56, 66
1-(2-Methylbutyl)pyrrole	60, 66
1-Butylpyrrole	58, 66
1-Pentylpyrrole	62, 66

Recently Identified Components of Coffee Aroma (continued)

Compounds	References
1-(3-Methylbutyl-1)pyrrole	60, 66
Pyrazine	53, 54, 55, 56, 60, 61, 62, 65, 66, 70
Methylpyrazine	53, 54, 55, 56, 60, 61, 62, 65, 66, 70
2,3-Dimethylpyrazine	53, 54, 55, 61, 62, 65, 66, 70
2,5-Dimethylpyrazine	53, 54, 55, 60, 61, 62, 65, 66, 70
2,6-Dimethylpyrazine	55, 60, 61, 62, 65, 66, 70
Trimethylpyrazine	60, 62, 65, 66, 70
Tetramethylpyrazine	64, 85, 66, 67, 70
2-Methyl-3-ethylpyrazine	60, 62, 65, 66, 70
2-Methyl-5-ethylpyrzaine	60, 62, 65, 66, 70
2-Methyl-6-ethylpyrazine	60, 62, 65, 66, 70
2-Methyl-5-vinylpyrazine	60, 62, 66, 70
2-Methyl-6-vinylpyrazine	60, 62, 66, 70
2-Methyl-5-propylpyrazine	67, 70
2-Methyl-6-propylpyrazine	60, 66, 70
2-Methyl-5-isopropylpyrazine	60, 62, 66, 70
2-Methyl-6-isopropylpyrazine	70
2-Methyl-3-isobutylpyrazine	60, 66, 70
2,3-Dimethyl-5-ethylpyrazine	67
2,5-Dimethyl-3-ethylpyrazine	60, 62, 65, 66, 70
2,6-Dimethyl-3-ethylpyrazine	60, 62, 65, 66, 70
2,5-Dimethyl-3-isobutylpyrazine	67, 70
Trimethylethylpyrazine	64, 65, 66, 67, 70
Ethylpyrazine	60, 62, 66, 70
Vinylpyrazine	62, 66, 70
2-Ethyl-6-vinylpyrazine	67, 70
2-Ethyl-6-propylpyrazine	67, 70
2,3-Diethyl-5-methylpyrazine	62, 65, 66, 70
2,5-Diethylpyrazine	60, 66, 67, 70
2,5-Diethyl-3-methylpyrazine	67
2,6-Diethylpyrazine	60, 62, 66, 70
3,5-Diethyl-2-methylpyrazine	62, 66, 70
Propylpyrazine	60, 62, 66, 70
trans-1-Propenylpyrazine	62, 66, 70
2-Methyl-5-(*trans*-1-propenyl) pyrazine	62, 66, 70
2-Methyl-6-(*trans*-1-propenyl) pyrazine	62, 66, 70
2-Isobutyl-3-methoxypyrazine	67, 70
2-(Furyl-2)pyrazine	67, 70
Pyridine	53, 54, 55, 56, 58 60, 61, 65, 66
2-Methylpyridine (α-picoline)	60, 66
3-Methylpyridine (β-picoline)	55, 60, 61, 65, 66
3-Ethylpyridine	60, 66
5-Methylquinoxaline	59, 60, 66
S-Compounds	
Hydrogensulfide	46, 55, 61, 65, 66
Carbondisulfide	44, 45, 46, 48, 52, 58, 60, 61, 65, 66
Methanethiol	45, 46, 47, 52, 55, 58, 60, 61, 65, 66
Ethanethiol	47, 64, 65, 66
1-Propanethiol	64, 65, 66
Methylthiomethane	44, 45, 46, 47, 48, 52, 55, 56, 60, 61, 65, 66
Methylthioethane	44, 60, 61, 65, 66
Methyldithiomethane	44, 48, 56, 58, 65, 66
Methyldithioethane	44, 48, 56, 58, 61, 66
Ethyldithioethane	56, 66
Methylthiobenzene	60, 66
1-Methylthiobutan-2-one	60, 66
Thiophene	45, 55, 56, 58, 59, 61, 65, 66
2-Methylthiophene	56, 66
3-Vinylthiophene	60, 66
2-Methyl-4-ethylthiophene	60, 66
Benzo(b)thiophene	60, 66
2-Furylmethanethiol	56, 60, 61, 66
Furfurylthiomethane	51, 55, 59, 60, 61, 65, 66
5-Methylfurfurylthiomethane	59, 60, 66
(5-Methylfuryl-2)thiomethane	59, 60, 66
Furoylthiomethane	59, 60, 66
Furfurylthiolacetate	59, 60, 66
Difurfurylsulfide	59, 60, 66
(2-Thienyl)methanol (thenyl alcohol)	56, 60, 65, 66
Thenyl formate	60, 66
Thenyl acetate	60, 65, 66
2-Formylthiophene	60, 65, 66
5-Methyl-2-formylthiophene	60, 66
Tetrahydrothiophen-2-one	64, 65, 66
Tetrahydrothiophen-3-one	60, 66
2-Methyl-tetrahydrothiophen-3-one	60, 66
2-Acetylthiophene	55, 60, 61, 65, 66
3-Acetylthiophene	64, 65, 66
2-Acetyl-3-methylthiophene	60, 65, 66
2-Acetyl-4-methylthiophene	60, 66

Recently Identified Components of Coffee Aroma (continued)

Compounds	References
2-Acetyl-5-methylthiophene	60, 65, 66
2-Propionylthiophene	60, 65, 66
1-(Thienyl-2)propane-1,2-dione	60, 66
1-(Thienyl-3)propane-1,2-dione	60, 66
Methyl 2-thiophenecarboxylate	60, 66
2-(Methylthio)phenol	60, 66
2-Thiophenothiophene	59, 60, 66
2-Acetyl-4-methylthiazole	60, 66
2-Propionyl-4-methylthiazole	60, 66
2-Methyl-3-oxa-8-thiabicyclo-(3.3.0)	69
1,4-Octadiene (kahweofuran)	
Miscellaneous	
1,1-Dimethoxyethane	61, 66
Propenenitril	44, 48, 56, 61, 66
3-Butenenitril	44, 48, 61, 66
Phenol	53, 54, 55, 56, 60, 61, 65, 66
2-Methylphenol (*o*-cresol)	60, 65, 66
3-Methylphenol	55, 60, 61, 66
4-Methylphenol	60, 66
2,3-Dimethylphenol	60, 66
2,5-Dimethylphenol	60, 66
2,6-Dimethylphenol	60, 65, 66
3,4-Dimethylphenol	60, 66
2,3,5-Trimethylphenol	60, 66
2-Ethylphenol	60, 66
4-Ethylphenol	60, 66
2-Methoxyphenol (guaiacol)	53, 54, 55, 61, 65, 66
4-Ethyl-2-methoxyphenol	55, 60, 61, 65, 66
2-Methoxy-4-vinylphenol	55, 59, 60, 61, 65, 66
4-Allyl-2-methoxyphenol (eugenol)	61, 66
1,2-Dihydroxybenzene	61, 66
1,3-Dihydroxybenzene (resorcinol)	66
1,4-Dihydroxybenzene (hydrochinone)	66
4-Vinyl-1,2-dihydroxybenzene	66
3,4-Dimethoxystyrene	54, 60, 66
2-Formylpyrrole	51, 55, 56, 61, 65, 66
2-Formyl-1-methylpyrrole	51, 55, 60, 61, 65, 66
2-Formyl-5-methylpyrrole	51, 55, 61, 65, 66
1-Ethyl-2-formylpyrrole	60, 65, 66
1,5-Dimethyl-2-formylpyrrole	51, 55, 61, 65, 66
2-Formyl-1-(2-methylbutyl-1) pyrrole	60, 66
2-Formyl-1-(3-methylbutyl-1) pyrrole	60, 66
2-Formyl-1-furfurylpyrrole	60, 66
2-Acetylpyrrole	51, 53, 55, 61, 65, 66
2-Acetyl-1-methylpyrrole	51, 55, 60, 61, 65, 66
2-Acetyl-1-ethylpyrrole	64, 65, 66
2-Acetyl-1-furfurylpyrrole	60, 66
2-Propionylpyrrole	51, 55, 61, 66
1-(Pyrryl-2)butan-1,2-dione	60, 66
1-Furfurylpyrrole	50, 51, 55, 60, 61, 65, 66
1-(5-Methylfurfuryl) pyrrole	60, 65, 66
Tetrahydrofuran	56, 64, 65, 66
2-Methyltetrahydrofuran	64, 65, 66
5-Isopropenyl-2-methyl-2-vinyltetrahydrofuran	59, 60, 66
cis-(2-Hydroxy-isopropyl)-2-methyl-2-vinyltetrahydrofuran = *cis*-2,6-dimethyl-3,6-epoxy-2-hydroxyoct-7-ene = *cis*-linaloöloxyde[4,8]	59, 60, 65, 66, 67
trans-linaloöloxyde[4,8]	64, 65, 66
Furan	44, 45, 46, 48, 51, 52, 53, 54, 55, 56, 58, 59, 60, 61, 65, 66
2-Methylfuran	44, 45, 46, 48, 51, 52, 53, 54, 55, 56, 58, 59, 60, 61, 65, 66
3-Methylfuran	56, 66
2,5-Dimethylfuran	44, 48, 51, 55, 56, 58, 61, 65, 66
2-Ethylfuran	56, 66
2-Propylfuran	44, 48, 51, 56, 58, 61, 66
3-Propylfuran	56, 66
2-Butylfuran	44, 48, 61, 66
2-Pentylfuran	60, 66
3-Phenylfuran	59, 60, 65, 66
Bi-(furyl-2)	59, 60, 66
Bi-(furyl-2)methane	51, 55, 59, 60, 61, 65, 66
(Furyl-2)-(5-methylfuryl-2) methane	59, 60, 65, 66
Bi-(5-methylfuryl-2)methane	59, 60, 66
Benzofuran	60, 66
2,3-Dihydrobenzofuran	60, 66
2-Methylbenzofuran	60, 66
Methylfurfuryl ether	60, 65, 66
Difurfuryl ether	59, 60, 65, 66
5-Methylfurfuryl-furfuryl ether	59, 60, 66
2-Methyl-5-cyanofuran	60, 66
3-Hydroxy-2-methyl-4-oxo-1,4-pyran (maltol)	53, 55, 60, 61, 65, 66
5-Acetyl-2-methyloxazole	64, 65, 66
N, α-Dimethylbutanimide	64, 65, 66
Butyraldoxime	67

BAKED GOODS

Bread

The characteristic fragrance of freshly baked bread has intrigued investigators of natural aromas not only to identify the precursors but also to rebuild flavors capable of imparting this aroma to other food products and to bread itself (when the particular flavor is lacking for various reasons). By examining the nature of bread ingredients, it is assumed that the transformation process of the various flavor components is dependent on the manufacturing process that consists of two basic operations—fermentation and baking. Bread flavor after fermentation, which is quite different from that of freshly mixed dough, yields the characteristic freshly baked bread flavor on baking. Although bread loses a portion of its flavor on cooling, the flavor may be partially restored by reheating. This peculiar behavior is attributed to a "locking in" process (with subsequent liberation on reheating) of a certain portion of the volatile constituents by the linear fraction of wheat starch. The flavor of stale bread is believed to be caused by the oxidation of the aldehyde fraction present in fresh bread and the formation of large amounts of acids. During the fermentation of the dough, amino acids and sugars are formed together with alcohols, whose presence may also be detected organoleptically in the brew. By baking the leavened dough, Maillard's reaction between amino acids and sugars is triggered; this takes place preferentially in the bread crust.

Investigation of bread flavor has thus far identified the following components:

Components of Bread Flavor

Acids	Alcohols	Aldehydes	Ketones
Acetic	*d*-Amyl alcohol	Acetaldehyde	Acetoin
Benzilic	Ethanol	Benzaldehyde	Acetone
Butyric	Isoamyl alcohol	2-Butanal	Diacetyl
Capric	Isobutanol	Crotonaldehyde	Ethyl *n*-butyl
Caproic	*n*-Propanol	2-Ethylhexanal	Maltol
Formic		Formaldehyde	Methyl ethyl
Heptanoic	Esters	Furfural	Methyl ethyl *n*-butyl
Hydrocinnamic		*n*-Hexanal	
Isobutyric	Ethyl acetate	Hydroxymethylfurfural	
Isocaproic	Ethyl hydrocinnamate	Isobutanaldehyde	
Itaconic	Ethyl itaconate	Isovaleral	
Lactic	Ethyl lactate	2-Methylbutanal	
Levulinic	Ethyl levulinate	Propionaldehyde	
Nonanoic	Ethyl pyruvate	Pyruvaldehyde	
Octanoic	Ethyl succinate	*n*-Valeraldehyde	
Propionic			
Pyruvic			
Valeric			

Studies of the reconstruction of bread flavors have been partially oriented toward the formation of complex flavors by Maillard's reaction between certain amino acids and glucose. Several experimental data are reported by Colombo.[18] The addition of amino acids to the bread dough may enhance the bread flavor during baking. In our opinion, however, the esters and alcohols directly related to the fermentation process should also be considered in the reconstruction of the bread flavor.

Cookies

The gamut of food products belonging to this category is quite extensive and varied. These products have attained an importance almost equal to that of bread. Uniformity in size, manufacturing and packaging, minimum moisture content, extended shelf-life without loss of appetence (although dependent on the raw materials used, baking procedure, and adequate storage facilities) are the basic requirements that determine the widespread universal acceptance of cookies of various types and shapes.

The formulation, consistency of the dough (hard, soft, and liquid), and manufacturing process differ for various types of cookies. Although these differences are somewhat marginal, they are sufficient, together with the differences in shape, appearance, friability, and palatability, to differentiate the various products. The flavoring of almost all products is substantially indentical and based on the use of vanilla and butter. Amaretti (made with minced almonds and sugar) belongs to the category of tea pastry and includes croccanti biscuits (crunchy, made of almonds and sugar) whose flavoring is almost exclusively obtained by the use of vanilla and other specific ingredients such as bitter and sweet almond, custards, zabaglione, and chocolate. Savoiardi and Savoy biscuits (spongecake) belong, instead, to the category of pound cakes.

Wafers are cookies consisting of thin layers and filling. The wafer is prepared with water, flour, milk, sugar, and eggs; the filling consists of a pound custard or fat that requires flavoring. Although the types of flavor in the filling (and therefore in the wafers) are countless, three basic flavors are usually employed: vanilla, lemon, or chocolate. Sometimes chocolate is used for a partial or total frosting of the wafer. A salty type of wafer is also produced whose flavoring is more a gastronomic problem.

Frosted cakes, egg cookies, and sweets in general are not included in this work, since their flavoring is the specific domain of the baker rather than of the flavorist. The flavoring of vanilla and lemon custards is obtained using vanillin and lemon essential oil, respectively; chocolate custards are flavored by direct addition of cocoa or chocolate.

Pound Cakes

In this category are included all those bakery products obtained by mixing eggs and sugar until a complete, light, well aerated suspension is formed. Flour, leavening, molten fats, and flavors are added to the suspension by simple blending. The resulting mixed product is poured into molds and baked. The oven temperature is kept at approximately 160 C, and the "pounding" is carried out for about 25 minutes. Recently products have been introduced on the market useful for the industrial manufacture of pound cakes by cutting the pounding time to 4–5 minutes: the basic ingredients and the accessory ingredients are mixed in one step. The pound mix does not "break" readily and allows better flexibility for the mechanical pouring into molds. Well known products in this category include plum cakes, angel food, Savoy biscuits, and spongecake. For products containing fats, the fats are emulsified together with sugar, then the eggs are added, and finally the flour.

Pound cakes can be consumed as is and therefore require adequate flavoring during production. Vanillin and candied fruit (plum cakes) complemented by a vanilla-flavored sugar dusting may be employed for flavoring or may be used as a base for more elaborate flavoring. Finishing requires filling and decoration by the use of custards containing fats and of bagne sauces that are spread on the whole or the cut pound cake. Aside from the innumerable custard formulations containing milk, eggs, and butter, the most frequently used flavors are vanilla and lemon, obtained by the use of vanillin and soluble lemon essential oil, respectively. Whipped cream (vanilla-flavored), chocolate, and zabaglione may also be employed. *Bagne* (sauces) are alcoholic (about 16 %) products of various flavors obtained by dilution of commercial liquors or bagne bases, which are high-proof liquors for pastry use. Pastry flavoring is quite varied, but the most frequently used flavors in the filling are rum, strega, curaçao, alkermes, and maraschino. Bagne-based formulations are typical of the corresponding liqueur imitations.

Leavened Doughs

Fruit cake, brioche, croissant, krapfen, and baba are products included in this category. The leavened doughs owe their name to the leavening effect of the fermenting flour dough itself or to that of barm and baking powders (dry yeasts) added to the dough. A perfect knowledge of the delicate natural leavens requiring particular attention during preparation and storage (the leaven must be freshened every 3–4 hours by addition of flour and tepid water to retain its strength) is extremely difficult. Dough preparation is strongly time-dependent and consequently dependent also on the temperature, moisture content, and other factors of both the atmosphere and the raw materials.

Freshly prepared yeast must be elastic and must be kept stored at 25–30°C under odorless and low-humidity conditions to prevent weakening and the development of a strong acid flavor. Yeast yields acetic and butyric acids instead of alcohols during fermentation. A good yeast has an alcohol-like odor. Sugar is added to weak yeasts (thus increasing the carbon dioxide content), whereas the addition of flour dilutes the activity of strong yeasts. A gluten-rich flour is required to prepare leavened doughs, since it must raise a mixture rich in eggs, fats, and sugar in addition to candied fruit. As salt stops the leavening process, its addition must be carefully controlled. Industrial yeasts, barm, and baking powders do not exhibit the above shortcomings but they yield results inferior to natural yeasts.

A typical example of leavened dough is fruit cake, such as panettone Milano. The ingredients are whole wheat flour, natural yeast, butter, sugar, whole eggs, egg yolk, raisins, citron, orange peel, candied fruit, water, salt, milk, and powdered dry malt. The most recent manufacturing process calls for the use of two doughs prepared separately. The first dough contains yeast, flour, sugar, and butter; it is allowed to rise and is then introduced into a mechanical dough mixer with the second dough, which consists of flour, sugar, butter, eggs, salt, raisins, candied fruit, malt, milk, and flavor ingredients. The flavor ingredients are added last and dosed according to the instructions for use of the compounded flavor. The mixture is allowed to rise further, and then the fruit cake is baked. Guidelines for the preparation of compound flavors suitable for panettone flavoring are shown below:

Panettone Flavor

Ingredient	Parts
Sweet orange essential oil	180
Lemon essential oil	160
Mandarin essential oil	160
Bergamot essential oil	30
Ethyl vanillin	80
Solvent	890
Total	1,500

Note: Sometimes vanilla is also added to the above compound flavor.

Similar manufacturing processes using somewhat different techniques and raw materials are employed for the preparation of *colomba* and *pandoro*. As in other baked goods of this type, compounded flavors are used. The classical note in all such compound flavors is citrus together with vanilla and butter notes. The ingredient ratios in the flavor vary from product to product yielding characteristic flavor effects. The citron note is predominant in panettone, and butter (cocoa butter) is predominant in pandoro; a slight lemon or orange note characterizes the colomba flavor. The following guidelines may be useful for the preparation of pandoro and colomba compound flavors:

Colomba Flavor

Ingredient	Parts
Sweet orange essential oil	180
Lemon essential oil	130
Mandarin essential oil	40
Ethyl vanillin	25
Solvent	125
Total	500

Pandoro Flavor

Ingredient	Parts
Colomba aroma	100
Cream flavor, 1 × 2,000	3
Cocoa distillate, 65%	22
Solvent	125
Total	250

Specific flavor ingredients added to the dough during the mixing are required for other products included in this category. The most interesting flavor combinations include lemon essential oil for *Bussola Bresciana*; vanilla for *Veneziana*; orange, clove, cinnamon, orris, and kirsch for *Focaccia Veneziana*; fennel for *Pan Dolce di Genova*; lemon, citron, or vanilla in flavored marsala wine for *Panettone* and *Focaccia Piemontese*; citron, cinnamon, clove, coriander, and nutmeg for *Pan Giallo alla Romana*; nutmeg, cardamom, vanilla, and lemon for *Dresden stollen*; and orange for *Provenzal Focaccia.*

The above flavor recipes are often prepared at home with the addition of ground spices and fresh citrus peels. Brioches, krapfens, and croissants usually are not flavored or only slightly flavored with panettone flavors. The baked babas are usually soaked in aromatic wines and frequently in rum and cognac.

Crackers

Crackers are similar in composition to cookies, except that they taste salty rather than sweet. In the last few decades crackers with their countless varieties have attained world-wide acceptance. Originally salted crackers and unsalted, unsweetened crackers were produced only as a replacement for bread. Subsequently, salted crackers, either naturally leavened or prepared with yeast, were established in the consumer market. Those leavened with yeast lend themselves to many flavor variations, among which are the well known salted cheese-flavored crackers (biscuits au Rochefort). The introduction of the more easily digested Anglo-Saxon salted crackers took over the consumer market; these products may be classified as follows:

1. *Soda crackers*: leavened, containing sodium bicarbonate and salt
2. *Salt crackers*: similar to soda crackers, but having a saltier flavor
3. *Cream crackers*: containing whipped or butter cream

Crackers are usually small in size, thin, and sometimes leavened with barm. English salt crackers differ from the U.S. soda-cracker counterpart in their larger salt content (almost twice as much). However, the basic raw materials are present in almost identical ratios. Hydrogenated fats and special shortenings are used to prepare the dough. Sometimes malt is added together with a thin fatty layer (caprate esters) spread on the cracker surface to impart an appealing shiny appearance.

In the last two decades there has been a growing market for new crackers to serve with aperitifs and cocktails. These products have surpassed the sales of soda crackers and are continuously presented to the consumer with new and original flavors, such as cheese, soybean, bacon, ham, tomato, onion, caraway, and roasted sesame seeds. Flavor ingredients plated on a salt carrier, spice oleoresins, and compounded fantasia flavors may find interesting applications in the preparation of the above products.

BREAD FLAVOR

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INTRODUCTION

Various forms of bread-like products have been consumed for thousands of centuries by the vast majority of the world popluation. Thus, the acceptability of bread products is well documented. One of the key factors in promoting this acceptability is the influential role of bread flavor and odor, especially of baking or freshly baked products. Through the centuries bread types have evolved mainly because of their unique flavor and odor and the successful production of most breads was considered to be an art. However, during this century bread production, by the necessity of the modern world, has become more of a science and technology related food production and distribution system. In the transition, scientists have attempted to unravel the complex nature of bread flavor and odor. Few scattered reports of these studies are available before 1955. However, during the following decade numerous reports appeared, all contributing a small piece to the puzzle. These studies were promoted by the introduction of controversial mechanical techniques into the baking industry in an effort to more rapidly and economically mass produce acceptable bread products.

Most all would agree that the pleasing aroma and flavor of freshly baked bread is quite shortlived; the flavor chemist has found himself attempting to duplicate these delicate and fleeting sensory properties, which has resulted in a better understanding of bread flavor. However, to date no imitation bread product has had the commercial success of other imitation foods, indicating that additional work in the bread flavor area is needed to more fully understand and appreciate total bread flavor.

One of the major problems in understanding bread flavor is that it may originate from a wide variety of factors in the bread making process, including such areas as ingredients, fermentation, and baking. Researchers have had to devote much time and effort to a portion of the entire bread flavor forming process, only to discover that their area of interest was responsible for but a fraction of total bread flavor. Such discoveries have discouraged some investigators from continuing research in the area.

The relative importance of bread flavor to the food scientist and technologist can best be appreciated by citing a portion of the vast number of reviews that have appeared dealing with various phases of bread flavor. These include the works of Coffman (1967a,b), Collyer (1964), DeFigueiredo (1964), Drapron (1970a,b; 1971), Jackel (1969), Jakubezyk and Haber (1968), Johnson (1967), Johnson et al. (1966), Pomeranz and Shellenberger (1971), Pence (1967), Otterbacher (1959) and Wiseblatt (1961a,b).

This review will attempt to cover the subject by acknowledging both American and European workers, and by covering all areas of bread flavor formation, information lacking in most previous reviews.

Specific areas to be covered include:

1. The flavor components reportedly isolated, and where reported; the quantities found and their possible flavor contribution based on available threshold data.
2. Methods of bread flavor isolation, including comments on the merits and limitations of the techniques employed; suggestions for improved techniques that could be applicable in bread flavor research.
3. Formation of bread flavor, including detailed discussion on the role of ingredients, fermentation, mechanical and enzymatic degradation, mixing procedures, and baking techniques.
4. Effects of compositional and processing factors on impaired bread flavor.
5. Methods of enhancing bread flavor, including the use of condensates, addition of flavoring materials and precursors, and the pretreatment of ingredients.

FLAVOR COMPONENTS

Introduction

The whole area of bread flavor is clouded by the fact that researchers have reported on the isolation of numerous volatile flavor compounds from various phases of bread systems, but no one has attempted to tie all of the pieces together. For example, numerous data exist on the presence of volatile flavor compounds found in brews of pre-ferments, bread dough, oven gases, and bread crust and crumb. A great majority of these compounds may only serve as other flavor precursors, or may not even be present in the final product. The volatiles emitted from a loaf of bread during baking may not have any direct bearing on the flavor properties of the same bread eaten three days later. The author does not mean to imply that studies of this nature are not valuable; they can shed light on volatile flavor compound formation resulting from the baking process, which may in turn assist the baker in producing a more flavorful loaf of bread. However, it would appear that at this stage in the study of bread flavor a research group would be able to follow bread flavor formation and destruction through the entire breadmaking process. Research efforts with this goal in mind are to be encouraged.

Another area of bread flavor investigation that requires interpretation with reservation is that few researchers have quantitated their findings. Thus, in reading the literature one has difficulty establishing the possible flavor or odor contribution of specific compounds. To date, over 100 volatile flavor compounds have been detected in bread and only one study (Mulders, 1973) has attempted interpreting the overall flavor role of certain compounds found in bread.

Two areas of bread flavor that have received little attention include the possible role of nonvolatile compounds and the flavor of toast. Perhaps separation problems associated with nonvolatile compounds have discouraged researchers in this area. In regard to toast, it would be a simple task to isolate and quantitate flavor compounds formed during toasting, including those lost to the atmosphere and those retained in the product.

Various classes of compounds have been detected and the occurrence of each individual class reported during the bread making process will be discussed.

Acids

As can be seen from Table 1, most of the acids reported in bread systems have been isolated in pre-ferments, while few investigators have detected acidic compounds from oven vapors. The value of investigating the composition of oven vapors may be questioned in that it becomes extremely difficult to establish the relative importance of compounds that are no longer in the product in question.

Due to the large number of reports involved, only several in each bread system area will be discussed. In the area of pre-ferments, one of the most detailed studies was that reported by Hunter et al. (1961). They employed programmed flash exchange gas-liquid chromatography and found at least 44 compounds. They concluded that these compounds included mono-, di-, and other types of carboxylic acids. Also, dicarboxylic acids appeared both as mono- and di-esters. Among the compounds identified were 17 acids ranging from methanolic (formic) to hexadecanoic (palmitic). The authors concluded that these acids could significantly contribute to bread flavor possibly in two ways. First, the higher-boiling fatty acids could hinder the volatility of lower-boiling compounds, thus increasing the time required for their evaporation from bread. Secondly, it was noted that the acid fraction found, when heated, gave an aroma similar to bread. However, no actual sensory or analytical data were provided to substantiate these claims. It might well be that the solvent used (dichloromethane) in the original organic acid extraction from the pre-ferment also extracted other volatile compounds that were detected in the separation and contributed to the characteristic flavor of the extract.

Another interesting study dealing with the keto acids associated with pre-ferments was reported by Cole et al. (1966). A total of eight keto acids were identified in pre-ferments. The major keto acids were pyruvic, α-ketoisovaleric, and α-ketoglutaric acid. The concentrations of these three acids as influenced by time of fermentation were measured and these data are summarized in Table 2.

Pyruvic acid was the most prevalent and was also found before fermentation. Its high level is probably due to a decarboxylase deficiency in the yeast (Suomalainen and Oura, 1959). In most cases maximum keto acid concentrations were reached in three to five hours.

TABLE 1

Acids Reported in Bread Systems

Acid	Pre-ferment	Oven vapor	White bread	Rye products
Methanoic	Hunter et al. (1961)		Mulders and Dhont (1972)	Markova (1970)
Ethanoic	Johnson (1925)	Baker et al. (1953)	Wiseblatt (1960b)	von Sydow and Anjou (1969)
	Johnson and Miller (1957)	Wiseblatt (1960a)	Wick et al. (1964)	Markova (1970)
	Johnson et al. (1958)	Wiseblatt (1960b)	Mulders and Dhont (1972)	
	Drews (1960)		Mulders et al. (1973)	
	Drews (1960)			
	Wiseblatt (1960b)			
	Hunter et al. (1961)			
Propanoic	Hunter et al. (1961)		Mulders and Dhont (1972)	
2–Methylpropanoic	Hunter et al. (1961)		Mulders and Dhont (1972)	von Sydow and Anjou (1969)
2 Oxopropanoic	Cole et al. (1962)		Wiseblatt and Kohn (1960)	Markova (1970)
	Cole et al. (1966)			
Butanoic	Wiseblatt (1960b)		Wiseblatt (1960b)	von Sydow and Anjou (1969)
	Hunter et al. (1961)		Mulders and Dhont (1972)	
	Korolkova et al. (1968a,b)			
3–Methylbutanoic	Wiseblatt (1960b)	–	Wiseblatt (1960b)	von Sydow and Anjou (1969)
	Hunter et al. (1961)		Mulders and Dhont (1972)	
3–Oxobutanoic	–	Baker et al. (1953)	–	–
2–Butenoic	Hunter et al. (1961)	–	–	–
Pentanoic	Hunter et al. (1961)	–	Mulders and Dhont (1972)	von Sydow and Anjou (1969)
4–Methylpentanoic	Hunter et al. (1961)	–	–	–
4–Oxopentanoic	–	–	Wiseblatt and Kohn (1960)	–
Hexanoic	Wiseblatt (1960b)	–	Mulders and Dhont (1972)	von Sydow and Anjou (1969)
	Hunter et al. (1961)			
Heptanoic	Hunter et al. (1961)	–	–	–
Octanoic	Hunter et al. (1961)	–	Mulders and Dhont (1972)	von Sydow and Anjou (1969)
Nonanoic	Hunter et al. (1961)	–	–	–
Decanoic	Hunter et al. (1961)	–	Mulders and Dhont (1972)	von Sydow and Anjou (1969)
Dodecanoic	Hunter et al. (1961)	–	Mulders and Dhont (1972)	von Sydow and Anjou (1969)
Tetradecanoic	Hunter et al. (1961)	–	–	–
Hexadecanoic	Hunter et al. (1961)	–	–	–
Benzoic	–	–	Mulders and Dhont (1972)	–

TABLE 1 (Continued)

Acids Reported in Bread Systems

Acid	Pre-ferment	Oven vapor	White bread	Rye products
2–Hydroxypropanoic	Johnson and Miller (1957) Johnson et al. (1958) Drews (1960) Drews (1961) Korolkova et al. (1968a,b) Permilovskaya and Berzina (1973)	–	Mulders and Dhont (1972)	Drews (1960)
Tetrahydroxypentanoic	–	–	–	Markova (1970)
Hydroxyethanolic	–	–	–	Markova (1970)
2–Hydroxy–1,2,3–propanetricarboxylic	Drews (1960) Drews (1961) Kazanskaya and Bezruchenko (1963) Korolkova et al. (1968a) Permilovskaya and Berzina (1973)	–	–	Kazanskaya and Bezruchenko (1963) Markova (1970)
Ethanedioic	Korolkova et al. (1968b) Permilovskaya and Berzina (1973)	–	–	–
Propanedioic	Korolkova et al. (1968b)	–	–	–
Butanedioic	Kazanskaya and Bezruchenko (1963) Permilovskaya and Berzina (1973)	–	–	Kazanskaya and Bezruchenko (1963) Markova (1970)
Hydroxybutanedioic	Drews (1960) Drews (1961) Kazanskaya and Bezruchenko (1963) Korolkova et al. (1968a) Permilovskaya and Berzina (1973)	–	–	Kazanskaya and Bezruchenko (1963)

TABLE 1 (Continued)

Acids Reported in Bread Systems

Acid	Pre-ferment	Oven vapor	White bread	Rye products
Dihydroxybutanedioic	Kazanskaya and Bezruchenko (1963) Korolkova et al. (1968a) Korolkova et al. (1968b) Permilovskaya and Berzina (1973)			Kazanskaya and Bezruchenko (1963)
Cis- butenedioic				Markova (1970)
Trans- butenedioic	Permilovskaya and Berzina (1973)			Markova (1970)
Propanedioic	Korolkova et al. (1968b)	–		–
α–Ketoglutaric	Cole et al. (1962) Suomalainen and Ronkainen (1963) Cole et al. (1966)		–	–
α–Ketoisovaleric	Cole et al. (1966)	.		–
β–Hydroxypyruvic	Cole et al. (1966)	–	–	
α–Keto–γ–methiol–butyric	Cole et al. (1966)	–	–	–
ρ–Hydroxyphenyl–pyruvic	Cole et al. (1966)	–	–	–
α–ketoisocaproic	Cole et al. (1966)	.	–	–
α–Keto–β–Methyl–valeric	Cole et al. (1966)	–	–	–

TABLE 2

Influence of Fermentation Time on Keto Acid Production in Pre-ferments

Time (hr)	Pyruvic	α–Ketoisovaleric	α–Ketoglutaric
0	0.11*	0	0
1	7.1	0.21	0.17
2	14.0	0.48	0.20
3	18.0	0.80	0.22
4	20.0	0.74	0.25
5	19.0	0.62	0.26
6	17.0	0.78	0.25

*Mmol/liter of pre-ferment.
From Cole et al. (1966).

TABLE 3

Amino Acids Formed by Hydrogenation of Keto Acids

Keto acid	Amino acid
Pyruvic	Alanine
α–Ketoglutaric	Glutamic acid
α–Ketoisovaleric	Valine
β–Hydroxypyruvic	Serine
α–Keto–γ–methiolbutyric	Methionine
ρ–Hydroxyphenylpyruvic	Tyrosine
α–Ketoisocaproic	Leucine
α–Keto–β–methylvaleric	Isoleucine

From Cole et al. (1966).

TABLE 4

Volatile Organic Acids in Dough and Bread

Acid	Dough	Bread
Acetic	198.0 mg/1,000 g flour	150.0 mg/1,000 g flour
Butyric	23.1	10.6
Isovaleric	13.1	6.1
Caproic	6.2	–

From Wiseblatt (1960b).

Another phase of their study dealt with the hydrogenation of the keto acid derivatives isolated from pre-ferments into their corresponding amino acids. This information is summarized in Table 3.

They reported that alanine, glutamic acid, and valine occurred in sizeable amounts. They postulated that although most of the keto acids were present in small quantities, they could contribute to the sensory properties of bread, especially in the case of sulfur-containing keto acid, α-keto-γ-methiolbutyric acid.

Various investigators have reported on the presence of 15 acids in baked bread. The most comprehensive study in this area was by Mulders and Dhont (1972). They identified 13 acids, 8 of which had not been previously reported. It should be noted that one of the acids they reported finding was benzoic acid, this is the only report of benzoic acid being a bread constituent. They postulated that it was probably derived from the bleaching agent benzoyl peroxide, which was added to the flour used in the study.

In an earlier study, Wiseblatt (1960b) used gas-liquid chromatography and found acetic, butyric, and isovaleric acids in bread. Attempts were made to quantitate these acids and these values are summarized in Table 4.

There was a reduction in concentration of organic acids during baking. Wiseblatt (1960b) postulated that these reductions were probably due to hydrolysis during baking, or possibly due to esterification. He also pointed out that the role of these acids in bread flavor varied with changes during storage of baked bread.

In the case of acids in rye products, two major reports have appeared. The findings of von Sydow and Anjou (1969) are summarized in Table 5.

Of the nine acids found, caproic acid was the most prevalent. The entire acid fraction represented approximately 13% of the total volatile flavor fraction recovered. They postulated that the aliphatic acids probably are important to the aroma of rye crispbread, but no supportive data were given.

Another interesting report associated with the acids in rye was authored by Markova (1970). A portion of these data is summarized in Table 6.

The greatest number of acids was found in the flour itself. The role of flour on bread flavor will be discussed in a later section. Three of the ten acids were found in the flour only. Generally, acid levels decreased during the baking of the dough.

TABLE 5

Aliphatic Acid Composition of Rye Crispbread

Compound	Percent*
Acetic acid	2.8
Isobutyric acid	2.1
Butyric acid	0.3
Isovaleric acid	–
Valeric acid	0.05
Caproic acid	3.4
Caprylic acid	1.4
Capric acid	1.0
Lauric acid	1.7

*Percent of flavor fraction isolated.
From von Sydow and Anjou (1969).

TABLE 6

Influence of Baking Procedures on Organic Acid Distribution in Rye, Flour, Dough, and Bread

Compound	Flour	Dough	Bread
Acetic	0.05*	0.36	0.37
Arabonic	0.04	0.03	0.09
Lactic	0.10	1.22	0.76
Glycolic	0.02	0.14	0.05
Formic	0.10	0.11	0.15
Succinic	0.02	–	0.16
Malic	0.08	–	–
Citric	0.05	–	–
Fumaric	0.04	–	–
Pyruvic	0.01	0.18	0.03
Total:	0.51	2.04	1.61

*Percent dry matter.
From Markova (1970).

TABLE 7

Amino Acid Precursors in Alcohol Production

Amino acid	Resulting alcohol
Tyrosine	Tyrosol
Tyrptophan	Tryptophol
Phenylalanine	β–Phenylethanol
Valine	2–Methyl–1–propanol
Leucine	1–Pentanol
Alanine	Ethanol

From Otterbacher (1959).

Alcohols

The fact that ethanol and carbon dioxide are the primary end products of bread fermentation is well established. It is also known that alcohols can result from amino acid fermentation. Typical examples of such transformations are summarized in Table 7.

As can be seen, an alcohol containing one less carbon results, along with ammonia which, in turn, is utilized by the yeast. Alcohols such as 2-methyl-1-propanol and 1-pentanol, as well as those possessing an aromatic ring structure, have characteristic odors and tastes which in turn can contribute to the aroma and flavor of bread. A total of 19 alcohol derivatives have been reported in various bread systems. These are summarized in Table 8.

Among the 27 compounds they detected, Smith and Coffman (1960) found seven alcohols in bread pre-ferments. The most predominant were ethanol and two isomeric forms of 2,3-butanediol. The two butanediols amounted to approximately 85% of the extractable neutral fraction. Another uncommon alcohol that they found was 2-phenylethanol.

Coffman (1966) detected four alcohols in oven vapors. These were 1-propanol, 2-methyl-1-propanol, 1-pentanol and β-phenylethanol in the approximate ratios of 1:9:30:2, respectively.

In the case of bread, the group headed by Mulders has reported on the occurrence of 15 alcohols (Mulders et al., 1972; Mulders, 1973; Mulders et al., 1973). To date they are the only group reporting on the occurrence of ten such compounds in bread. The report of von Sydow and Anjou (1969) has dominated concerning the alcohols found in rye products. They have reported on the presence of nine such compounds, including the compound eugenol (4-allylguaiacol). A portion of their data is shown in Table 9.

TABLE 8

Alcohols Reported in Bread Systems

Alcohol	Pre-ferments	Oven vapor	White bread	Rye products
Ethanol	Smith and Coffman (1960) Miller et al. (1961) Cole et al. (1962) Permilovskaya and Berzina (1973)	Baker et al. (1953) Wiseblatt (1960a)	Ocker (1961) Wiseblatt and Kohn (1960) Ocker (1964) Wick et al. (1964) Mulders et al. (1972) Rothe et al. (1972) Mulders (1973)	Rothe (1971) Rothe et al. (1972)
1–Propanol	Smith and Coffman (1960)	Coffman (1966)	Wick et al. (1964) Mulders et al. (1972) Mulders (1973) Mulders et al. (1973)	–
2–Propanol	–		Wiseblatt and Kohn (1960)	
2-Methyl–1–propanol	Smith and Coffman (1960) Miller et al. (1961)	Coffman (1966)	Wick et al. (1964) Mulders et al. (1972) Mulders (1973) Mulders et al. (1973)	von Sydow and Anjou (1969)
1–Butanol			Mulders et al. (1972)	
2 Methyl–1 butanol			Wick et al. (1964) Mulders et al. (1973)	
3 Methyl 1 butanol	Smith and Coffman (1960) Miller et al. (1961)		Wick et al. (1964) Mulders et al. (1972) Mulders (1973) Mulders et al. (1973)	von Sydow and Anjou (1969)
1–Pentanol	–	Baker et al. (1953) Coffman (1966)	Mulders et al. (1972) Mulders et al. (1973)	von Sydow and Anjou (1969)
2–Pentanol	–		Mulders et al. (1973)	–
3–Pentanol			Mulders et al. (1973)	–
1–Hexanol	–	–	Mulders et al. (1972) Mulders et al. (1973)	von Sydow and Anjou (1969)

TABLE 8 (Continued)

Alcohols Reported in Bread Systems

Alcohol	Pre-ferments	Oven vapor	White bread	Rye products
1–Octanol	–	–	–	von Sydow and Anjou (1969)
2,3–Butanediol	Smith and Coffman (1960)	–	Mulders et al. (1973)	–
1–Penten–3–ol	–	–	–	von Sydow and Anjou (1969)
Benzyl alcohol	–	–	Mulders et al. (1973)	von Sydow and Anjou (1969)
Furfuryl alcohol	–	–	Mulders et al. (1972)	–
			Mulders et al. (1973)	
2–Phenylethanol	Smith and Coffman (1960)	Coffman (1966)	Mulders et al. (1973)	von Sydow and Anjou (1969)
1,3–Propanediol monoacetate	Smith and Coffman (1960)	–	–	–
4–Allylguaiacol	–	–	–	von Sydow and Anjou (1969)

TABLE 9

Alcohol Distribution in Rye Crispbread

Alcohol	Percent*
2-Methyl-1-propanol	0.9
3-Methyl-1-butanol	2.9
1-Pentanol	0.1
1-Hexanol	0.3
1-Octanol	0.02
1-Penten-3-ol	0.2

*Percent of total flavor fraction evaluated.
From von Sydow and Anjou (1969).

In relation to the total flavor fraction, the alcoholic fraction represented 4.4% of the total, with 3-methyl-1-butanol being the most prevalent alcohol found. It should be noted that the shorter chain alcohols (ethanol-butanol) present in white bread were not detected in the rye product, probably due to the volatility of these compounds.

Aldehydes

This class of compounds contains the largest number (33) of flavor compounds reported in various bread systems. The specific compounds are summarized in Table 10.

Major emphasis has been placed by the bread flavor chemist on aldehydes and ketones as being primarily responsible for bread flavor. This is probably due to several reasons. First, they have been consistently found in bread systems by numerous investigators. Second, the characteristic sensory properties are generally both potent and pleasing. Third, their presence, formation, and decomposition can be explained chemically as arising from a variety of reactions that take place during the bread making process. For example, they can arise from amino acids, as can be seen in Table 11.

Almost all amino acids, except perhaps proline, are quite reactive in the formation of aldehydes. Formation mechanisms will be discussed in more detail in a later section. At this stage it is sufficient to say that aldehydes are probably the best understood class of compounds associated with bread flavor.

A total of 11 aldehydes, with acetaldehyde being the most commonly reported, have been found in pre-ferments, thus suggesting the influence of fermentation on their formation. As would be expected, the vast majority (27) of the compounds outlined in Table 10 have been found in bread itself. The most commonly reported aldehydes in bread are in the formaldehyde to heptanal area and include saturated, as well as unsaturated, compounds.

Aldehydes have also been assumed to be one of the key flavor ingredients in rye products; a total of 27 aldehydes have been isolated in this area. In rye crispbread von Sydow and Anjou (1969) reported that *trans,trans*-2,4-decadienal was the main aldehyde (Table 12).

The authors also mentioned the influential role that fat can play in aldehyde formation since most of the aldehydes they found in rye crispbread can be considered characteristic of fat oxidation products. For example, they postulated that hexanal and 2,4-decadienal could have originated from linoleic acid and 2,4-heptadienal from linolenic acid.

Esters

One must assume that the primary pathway for ester formation in bread systems is through the interaction of alcohols and acids. Since ethanol is the predominant alcohol found in a bread system, one would also assume that most of the esters would be of the ethyl variety. Likewise, commonly occurring acids such as formic and acetic would be logical choices for ester formation. The esters reported in various bread systems are summarized in Table 13.

In pre-ferments ethyl acetate is the most common ester. A total of seven esters have been found in bread; two of these are furfuryl esters (Mulders et al., 1973), which are derived from furfuryl alcohol. For the most part only relatively simple short chain acid-based esters have been found in bread.

TABLE 10

Aldehydes Reported in Bread Systems

Aldehyde	Pre-ferments	Oven vapor	White bread	Rye products
Formaldehyde	Miller et al. (1961) Linko et al. (1962a)		Ng et al. (1960) Lindo et al. (1962b) Hrdlicka et al. (1963) Linko and Johnson (1963) Wick et al. (1964) Davidek et al. (1965) Rothe (1966) El-Dash and Johnson (1967) Salem et al. (1967) Lorenz and Maga (1972) Mulders and Dhont (1972)	Hampl et al. (1964) Hrdlicka and Honischova (1967)
Acetaldehyde	Smith and Coffman (1960) Kohn et al. (1961) Miller et al. (1961) Linko et al. (1962a) Borovikova and Roiter (1971a)	Baker et al. (1953) Wiseblatt (1960a)	Ng et al. (1960) Ocker (1961) Wiseblatt and Kohn (1960) Linko et al. (1962b) Hrdlicka et al. (1963) Linko and Johnson (1963) Rothe (1963a) Rothe (1963b) Wick et al. (1964) Ocker (1964) Rothe (1966) El-Dash and Johnson (1967) Salem et al. (1967) Korolkova and Rakhmankulova (1968) Johnson and El-Dash (1969) Markianova and Roiter (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971a,b,c) Borovikova et al. (1971) Markianova et al. (1971) Lorenz and Maga (1972) Mulders and Dhont (1972) Mulders et al. (1972) Roiter and Borovikova (1972) Rothe et al. (1972) Mulders (1973)	Rothe (1960) Hampl et al. (1964) Rothe (1966) Tokareva and Smirnova (1966) Hrdlicka and Honischova (1967) Rothe and Boehme (1967) Rothe (1971) Rothe et al. (1972)

TABLE 10 (Continued)

Aldehydes Reported in Bread Systems

Aldehyde	Pre-ferments	Oven vapor	White bread	Rye products
Propanal	Linko et al. (1962a) Borovikova and Roiter (1971a)	–	Linko et al. (1962b) Hrdlicka et al. (1963) Linko and Johnson (1963) Wick et al. (1964) El-Dash and Johnson (1967) Korolkova and Rakhmankulova (1968) Johnson and El-Dash (1969) Markianova and Roiter (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971a,b,c) Borovikova et al. (1971) Markianova et al. (1971) Lorenz and Maga (1972) Roiter and Borovikova (1972)	Hampl et al. (1964) Bratovanova (1965) Tokareva and Smirnova (1966) Hrdlicka and Honischova (1967)
2–Methylpropanal	Miller et al. (1961) Linko et al. (1962a) Borovikova and Roiter (1971a)	Ng et al. (1960)	Linko et al. (1962b) Hrdlicka et al. (1963) Linko and Johnson (1963) Rothe (1963a) Wick et al. (1964) El-Dash and Johnson (1967) Salem et al. (1967) Korolkova and Rakhmankulova (1968) Johnson and El-Dash (1969) Markianova and Roiter (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971a) Borovikova et al. (1971) Markianova et al. (1971) Mulders and Dhont (1972) Mulders et al. (1972) Roiter and Borovikova (1972) Rothe et al. (1972) Mulders (1973)	Rothe (1960) Hampl et al. (1964) Rothe (1966) Tokareva and Smirnova (1966) Hrdlicka and Honischova (1967) Rothe and Boehme (1967) von Sydow and Anjou (1969) Rothe (1971) Rothe et al. (1972)

TABLE 10 (Continued)

Aldehydes Reported in Bread Systems

Aldehyde	Pre-ferments	Oven vapor	White bread	Rye products
2–Oxopropanal	Kohn et al. (1961) Borovikova and Roiter (1971a) Kohn et al. (1961) Miller et al. (1961)	Baker et al. (1953)	Wiseblatt and Kohn (1960) Hrdlicka et al. (1963) Rothe (1963a) Borovikova and Roiter (1971a) Mulders and Dhont (1972) Roiter and Borovikova (1972) Rothe et al. (1972)	Hampl et al. (1964) Rothe (1966) Hrdlicka and Honischova (1967) Rothe and Boehme (1967) Rothe et al. (1972)
2–Propenal		–	Borovikova and Roiter (1971a) Borovikova et al. (1971) Markianova et al. (1971) Mulders and Dhont (1972)	Hampl et al. (1964) Hrdlicka and Honischova (1967)
2–Phenylpropenal			Korolkova and Rakhmankulova (1968)	–
Butanal	Kohn et al. (1961) Miller et al. (1961) Borovikova and Roiter (1971a)	–	Wick et al. (1964) El-Dash and Johnson (1967) Johnson and El-Dash (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971b) Borovikova et al. (1971) Markianova et al. (1971) Lorenz and Maga (1972) Mulders and Dhont (1972) Roiter and Borovikova (1972)	Hrdlicka and Honischova (1967)
2–Methylbutanal	Miller et al. (1961) Linko et al. (1962a)	–	Ng et al. (1960) Linko et al. (1962b) Hrdlicka et al. (1963) Linko and Johnson (1963) Rothe (1963a) Rothe (1963b) Rothe (1966) El-Dash and Johnson (1967) Korolkova and Rakhmankulova (1968) Johnson and El-Dash (1969)	Rothe (1960) Hampl et al. (1964) Rothe (1966) Tokareva and Smirnova (1966) Hrdlicka and Honischova (1967) Rothe and Boehme (1967) von Sydow and Anjou (1969) Rothe et al. (1972)

TABLE 10 (Continued)

Aldehydes Reported in Bread Systems

Aldehyde	Pre-ferments	Oven vapor	White bread	Rye products
2-Methylbutanal (continued)			El-Dash and Johnson (1970) Rothe et al. (1972) Mulders et al. (1973)	
3–Methylbutanal	Kohn et al. (1961) Miller et al. (1961) Linko et al. (1962a) Borovikova and Roiter (1971a,b,c)	–	Linko et al. (1962b) Hrdlicka et al. (1963) Linko and Johnson (1963) Wick et al. (1964) El-Dash and Johnson (1967) Salem et al. (1967) Johnson and El-Dash (1969) Markianova and Roiter (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971a,b,c) Borovikova et al. (1971) Markianova et al. (1971) Mulders and Dhont (1972) Roiter and Borovikova (1972) Rothe et al. (1972)	Rothe (1960) Hampl et al. (1964) Hrdlicka and Honischova (1967) von Sydow and Anjou (1969)
2–Butenal	–	–	Wiseblatt and Kohn (1960) Wick et al. (1964)	Hrdlicka and Honischova (1967)
Pentanal	Miller et al. (1961) Linko et al. (1962a) Borovikova and Roiter (1971a)	Ng et al. (1960)	Linko et al. (1962b) Linko and Johnson (1963) Wick et al. (1964) El-Dash and Johnson (1967) Johnson and El-Dash (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971a,b,c) Borovikova et al. (1971) Markianova et al. (1971) Mulders and Dhont (1972) Roiter and Borovikova (1972)	Hrdlicka and Honischova (1967) von Sydow and Anjou (1969)
2–Methylpentanal	–	–	El-Dash and Johnson (1967) Johnson and El-Dash (1969) El-Dash and Johnson (1970)	Hrdlicka and Honischova (1967)

TABLE 10 (Continued)

Aldehydes Reported in Bread Systems

Aldehyde	Pre-ferments	Oven vapor	White bread	Rye products
Hexanal	Kohn et al. (1961) Linko et al. (1962a) Borovikova and Roiter (1971a)		Ng et al. (1960) Linko et al. (1962b) Linko and Johnson (1963) El-Dash and Johnson (1967) Johnson and El-Dash (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971b) Borovikova et al. (1971) Markianova et al. (1971) Lorenz and Maga (1972) Mulders and Dhont (1972) Mulders et al. (1972) Rother and Borovikova (1972) Mulders et al. (1973)	Hrdlicka and Honischova (1967) von Sydow and Anjou (1969)
2-Ethylhexanal			Wiseblatt and Kohn (1960) Wick et al. (1964) El-Dash and Johnson (1967)	
Heptanal	–	–	El-Dash and Johnson (1967) Korolkova and Rakhmankulova (1968) Lorenz and Maga (1972) Mulders and Dhont (1972)	von Sydow and Anjou (1969)
Octanal		–	Mulders and Dhont (1972)	
2-Octenal	–	–	–	Hrdlicka and Honischova (1967) Von Sydow and Anjou (1969)
Nonanal	–	–	Lorenz and Maga (1972) Mulders and Dhont (1972)	Hrdlicka and Honischova (1967)
2-Nonenal		–	Mulders and Dhont (1972)	von Sydow and Anjou (1969)
Dodecanal	–	–	–	Hrdlicka and Honischova (1967)
2,4-Heptadienal	–	–	–	von Sydow and Anjou (1969)
Trans, cis-2,4-decadienal	–	–	Mulders et al. (1973)	von Sydow and Anjou (1969)
Trans, trans-2,4-decadienal	–	–		von Sydow and Anjou (1969)

TABLE 10 (Continued)

Aldehydes Reported in Bread Systems

Aldehyde	Pre-ferments	Oven vapor	White bread	Rye products
Benzaldehyde	Kohn et al. (1961) Borovikova and Roiter (1971a)	–	Borovikova and Roiter (1971b) Borovikova et al. (1971) Markianova et al. (1971) Mulders et al. (1972) Mulders et al. (1973)	von Sydow and Anjou (1969)
4–Hydroxybenzaldehyde	–	–	Mulders and Dhont (1972)	–
Phenylacetaldehyde	Borovikova and Roiter (1971a)	–	Borovikova and Roiter (1971a) Borovikova et al. (1971) Markianova et al. (1971) Mulders and Dhont (1972)	Rothe (1960) Hampl et al. (1964) Bratovanova (1965) Hrdlicka and Honischova (1967) von Sydow and Anjou (1969)
2–Furaldehyde	Borovikova and Roiter (1971a)	Baker et al. (1953)	Ng et al. (1960) Wiseblatt and Kohn (1960) Hrdlicka et al. (1963) Linko and Johnson (1963) Rothe (1963a) Wick et al. (1964) Salem et al. (1967) Korolkova and Rakhmankulova (1968) Markianova and Roiter (1969) Borovikova and Roiter (1971c) Borovikova et al. (1971) Markianova et al. (1971) Mulders and Dhont (1972) Mulders et al. (1972) Rothe et al. (1972) Mulders et al. (1973)	Rothe (1960) Hampl et al. (1964) Bratovanova (1965) Rothe (1966) Tokareva and Smirnova (1966) Hrdlicka and Honischova (1967) Rothe and Boehme (1967) Rothe (1971) Rothe et al. (1972)
3–Furaldehyde	–		Mulders et al. (1973)	
5–Methyl–2–furaldehyde	–	–	Mulders and Dhont (1972) Mulders et al. (1973)	

TABLE 10 (Continued)

Aldehydes Reported in Bread Systems

Aldehyde	Pre-ferments	Oven vapor	White bread	Rye products
5-Hydroxymethyl 2-furaldehyde	–	–	Kretovich and Takareva (1950) Hrdlicka et al. (1963) Linko and Johnson (1963) Salem et al. (1967) Daniels (1971) Mulders and Dhont (1972) Rothe et al. (1972)	Kretovich and Takareva (1950) Rothe (1960) Hampl et al. (1964) Hrdlicka and Honischova (1967) Rothe (1971) Rothe et al. (1972)
2-Furan-dialdehyde	–	Coffman (1966)	–	
4-Hydroxy-3-methoxy-benzaldehyde				von Sydow and Anjou (1969)

TABLE 11

Influence of Amino Acid Additions on the Formation of Various Aldehydes in Bread Crust

Amino acid added	Formaldehyde	Acetaldehyde	2-Methylpropanal	2-Methylbutanal
Control	0.49*	1.06	1.10	1.33
Glycine	1.88	1.73	1.56	1.41
Alanine	0.90	3.44	3.26	1.27
Valine	1.30	2.38	8.57	2.61
Leucine	0.51	1.18	1.22	2.78
Isoleucine	0.91	1.90	2.27	3.94
Glutamic acid	1.12	2.03	1.83	1.68
Histidine	1.43	3.59	2.72	2.62
Lysine	1.74	3.75	3.68	3.33
Phenylalanine	0.61	1.67	1.22	1.68
Proline	0.56	0.78	1.13	1.08
Arginine	0.36	1.31	0.97	1.96
Methionine	0.49	1.43	1.43	1.22

*Mg/100 g
From Salem et al. (1967).

TABLE 12

Aldehyde Distribution in Rye Crispbread

Aldehyde	Percent*
2-Methylpropanal	–
2-Methylbutanal	0.2
3-Methylbutanal	0.2
Pentanal	0.2
Hexanal	0.2
Heptanal	0.05
2-Octenal	0.05
2-Nonenal	0.09
2,4-Heptadienal	0.09
trans,cis-2,4-Decadienal	0.07
trans,trans-2,4-Decadienal	0.3

*Percent of total flavor fraction evaluated.
From von Sydow and Anjou (1969).

Von Sydow and Anjou (1969) found predominantly ethyl esters in rye crispbread. A notable exception was the occurrence of two β-phenylethanol alcohol-based esters. A total of ten esters have been reported for rye products. Von Sydow and Anjou (1969) also reported on the occurrence of a series of long chain acid-based esters (C:10-C:16), as can be seen in Table 14.

The main ester they found was ethyl palmitate; the total ester fraction amounted to approximately 3.5% of the total flavor fraction. This group felt that none of the esters they reported play an important role in rye crispbread flavor. However, in the case of white bread, one may speculate that since many simple esters have potent and pleasing aromas, they could influence bread odor and flavor.

Ether Derivatives

Only one ether derivative has been reported to be present in white bread. This compound is ethyl furfuryl ether and was found by Mulders et al. (1972, 1973). Difurfuryl ether has been reported by von Sydow and Anjou (1969) to be present in rye crispbread.

TABLE 13

Esters Reported in Bread Systems

Ester	Pre-ferments	White bread	Rye products
Ethyl formate	Smith and Coffman (1960)	Mulders et al. (1972) Mulders et al. (1973)	
Ethyl acetate	Johnson and Miller (1957) Johnson et al. (1958) Miller et al. (1961) Wick et al. (1964)	Mulders et al. (1972) Mulders (1973)	Tokareva and Smirnova (1966)
Ethyl lactate	Smith and Coffman (1960)		
Ethyl pyruvate		Ng et al. (1960) Wiseblatt and Kohn (1960)	–
Ethyl levulinate		Wiseblatt and Kohn (1960)	
1,3-Propanediol monoacetate	Smith and Coffman (1960)	–	
Furfuryl formate	–	Mulders et al. (1973)	
Furfuryl acetate		Mulders et al. (1973)	
Acetonyl acetate		Mulders et al. (1973)	–
Ethyl caprinate		–	von Sydow and Anjou (1969)
Ethyl laurate		–	von Sydow and Anjou (1969)
Ethyl myristinate			von Sydow and Anjou (1969)
Ethylpentadecanoate			von Sydow and Anjou (1969)
Ethyl palmitate		–	von Sydow and Anjou (1969)
Glycol diacetate			von Sydow and Anjou (1969)
Ethyl phenylacetate	–	–	von Sydow and Anjou (1969)
β-Phenylethyl formate			von Sydow and Anjou (1969)
β-Phenylethyl acetate		–	von Sydow and Anjou (1969)
Amyl bensoate			von Sydow and Anjou (1969)

TABLE 14

Esters Associated with Rye Crispbread

Ester	Percent*
Ethyl caprinate	0.2
Ethyl laurate	0.1
Ethyl myristinate	0.09
Ethyl pentadecanoate	0.02
Ethyl palmitate	2.7
Glycol diacetate	0.2
Ethyl phenylacetate	0.03
β-Phenylethyl formate	0.09
β-Phenylethyl acetate	0.1
Amylbensoate	

*Percent of total flavor fraction evaluated.
From von Sydow and Anjou (1969).

Furan Derivatives

It is generally agreed that most furan derivatives are probably thermally produced through carbohydrate breakdown. This can best be appreciated by viewing the data summarized in Table 15.

In the case of the crumb portion of bread, no 2-furaldehyde was found and the 5-hydroxymethyl-2-furaldehyde level remained essentially constant. However, in the crust 2-furaldehyde was detected, and the level of 5-hydroxymethyl-2-furaldehyde increased proportionally with increased sucrose content. These two compounds are also known to be reactive intermediates in the Maillard reaction (Hodge, 1953) and as such can undergo condensation with free amino acids. The influence of amino acids and also carbohydrate sources on 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde (HMF) production was evaluated by Salem et al. (1967). Their findings are summarized in Table 16.

The ability of amino acids to react with 2-furaldehyde and HMF varied, but essentially all amino acids except methionine reduced the levels of these two compounds. The most reactive amino acids were leucine

TABLE 15

Influence of Sucrose Concentration on 2-Furaldehyde and 5-Hydroxymethyl-2-furaldehyde (HMF) Levels in Bread

	Crust		Crumb	
Percent sucrose	2-Furaldehyde	HMF	2-Furaldehyde	HMF
4	0.325*	4.05	–	0.675
5	0.338	6.65	–	0.723
6	0.350	8.31	–	0.614
7	0.386	8.37	–	0.677
8	0.435	9.09	–	0.638

*Mg/100 g
From Linko et al. (1962b).

TABLE 16

Influence of Added Amino Acids and Carbohydrate Sources on 2-Furaldehyde and 5-Hydroxymethyl-2-Furaldehyde (HMF) Levels in Bread Crust

	Glucose		Xylose	
Amino acid	2-Furaldehyde	HMF	2-Furaldehyde	HMF
Control	0.08	1.11	0.45	1.05
Glycine	0.03	0.83	0.12	0.95
Alanine	0.10	0.80	0.06	0.99
Valine	0.02	0.95	0.08	1.09
Leucine	0.02	0.47	0.06	0.60
Isoleucine	0.01	0.46	0.10	0.64
Glutamic Acid	0.04	1.05	0.09	0.92
Histidine	0.04	1.09	0.07	0.66
Lysine	0.02	1.04	0.08	0.76
Phenylalanine	0.06	1.03	0.14	0.76
Proline	0.04	0.91	0.12	0.66
Arginine	0.15	0.79	ND	ND
Methionine	0.11	1.65	ND	ND

*Mg/100 g
ND: not determined.
From Salem et al. (1967).

and isoleucine. Apparently carbohydrate source was not an important factor since little difference between glucose and xylose was noted.

A complete listing of furan derivatives reported in bread systems can be found in Table 17. To date few reports have identified such derivatives in any unheated bread system. Two reports concern the presence of furan derivatives in oven vapors; Baker et al. (1953) found 2-furaldehyde and Coffman (1966) reported the presence of 2,5-furan dialdehyde.

Of the 24 furan derivatives reported in bread systems, 17 have been found in bread itself, with the most commonly reported ones being 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde. Numerous furan derivatives have been reported by Mulders and co-workers (Mulders and Dhont, 1972; Mulders et al., 1972; Mulders, 1973; Mulders et al., 1973) and include the parent compound furan. An interesting compound found by Mulders et al. (1973) was 2,5-dimethyl-2(2H)-furanone. This compound was earlier synthesized by Eugster et al. (1961), who claimed it possessed a strong odor of freshly baked bread. However, Mulders et al. (1973) did not find that this compound was typical of bread aroma. Perhaps concentration was a factor, or possibly an artifact was present in the original synthesis to explain this discrepancy. In addition, Mulders et al. (1973) reported that the above compound, and also 3-furaldehyde, were, to their knowledge, for the first time reported in the aroma of a food product.

With rye products von Sydow and Anjou (1969) were the first to report 14 furan derivatives in rye crispbread (see Table 18). The most predominant compound was furfuryl alcohol, which amounted to over 15% of the total volatile fraction.

Hydrocarbons

One report has appeared (Mulders et al. 1973) about the occurrence of the hydrocarbons toluene and limonene in white bread crust. Gas-liquid chromatography and mass spectral data were used to secure identification. However, no information about the relative or actual amounts detected, nor about the possible formation pathways for these compounds, was discussed. It should be noted that a seven-hour extraction using pentane and diethyl ether was used; there may be a possibility that the reported hydrocarbons were contaminants associated with the pentanes used. It is assumed that freshly redistilled solvents were employed, but this was not specifically indicated in the study.

Ketones

Maillard-type browning is the primary source of ketones, especially in bread crust. This is dramatized in the work reported by Salem et al. (1967), as shown in Table 19.

Essentially all amino acids except arginine were found to promote the production of 2-propanone (acetone) in bread crust. As can be seen, alanine and valine were highly reactive in the formation of acetone.

A total of 24 ketones, as outlined in Table 20, has been reported in various bread systems. Since a number of ketones have been found in pre-ferments, it is apparent that fermentation can also result in their formation. The most common ketones found in pre-ferments include acetone and methyl ethyl ketone (2-butanone). Baker et al. (1953) have also reported finding these two ketones along with 2,3-butanedione (diacetyl) in oven vapors.

Most of the ketones reported have been found in bread with almost every report dealing with ketones finding acetone to be present. Other commonly reported ketones in bread include methyl ethyl ketone, diacetyl and acetoin (3-hydroxy-2-butanone).

In rye products, acetone and diacetyl are the predominant ketones to be reported. In rye crispbread acetone was absent and acetoin represented the most abundant ketone (see Table 21).

Lactone Derivatives

Several groups have reported on the presence of lactone derivatives in bread products. In 1960 Smith and Coffman isolated butyrolactone from a bread pre-ferment system. This was followed by a report by Coffman (1966) who detected butyrolactone in oven gases. A report by von Sydow and Anjou (1969) identified five lactones associated with the aroma of rye crispbread. The compounds and relative amounts found are reported in Table 22.

TABLE 17

Furan Derivatives Reported in Bread Systems

Furan derivatives	Oven vapor	White bread	Rye products
2-Furaldehyde	Baker et al. (1953)	Ng et al. (1960) Wiseblatt and Kohn (1960) Linko et al. (1962b) Linko and Johnson (1963) Wick et al. (1964) Salem et al. (1967) El-Dash and Johnson (1970) Mulders and Dhont (1972) Mulders et al. (1972) Mulders et al. (1973)	Tokareva and Smirnova (1966) von Sydow and Anjou (1969)
3-Furaldehyde	–	Mulders et al. (1973)	–
5-Methyl-2-furaldehyde	–	Mulders and Dhont (1972) Mulders et al. (1973)	von Sydow and Anjou (1969)
5-Hydroxymethyl-2-furaldehyde	–	Kretovich and Tokareva (1950) Linko et al. (1962b) Linko and Johnson (1963) Salem et al. (1967) El-Dash and Johnson (1970) Daniels (1971) Mulders and Dhont (1972)	Kretovich and Tokareva (1950)
Furan	–	Mulders et al. (1972) Mulders (1973)	
2-Methylfuran	–	Mulders et al. (1972) Mulders (1973)	
2-Acetylfuran	–	Mulders et al. (1973)	von Sydow and Anjou (1969)
2-Acetyl-5-methylfuran			von Sydow and Anjou (1969)
2,5-Furan dialdehyde	Coffman (1966)	–	
2-Pentylfuran	–	Mulders et al. (1973)	von Sydow and Anjou (1969)
2-Propionylfuran			von Sydow and Anjou (1969)
1-(2-Furyl)-2-propanone	–	Mulders et al. (1973)	von Sydow and Anjou (1969)
1-(2-Furyl)-1,2-propanedione	–	Mulders et al. (1973)	–

TABLE 17 (Continued)

Furan Derivatives Reported in Bread Systems

Furan derivatives	Oven vapor	White bread	Rye products
1-(2-Furyl)-1,2-butanedione			von Sydow and Anjou (1969)
1-(5-Methyl-2-furyl)-1,2-propanedione			von Sydow and Anjou (1969)
Dihydro-2-methyl-3-(2H)-furanone		Mulders et al. (1973)	
2,5-Dimethyl-3-(2H)-furanone		Mulders et al. (1973)	
Ethyl furfuryl ether		Mulders et al. (1972)	
		Mulders et al. (1973)	
Difurfuryl ether			von Sydow and Anjou (1969)
Furfuryl alcohol		Mulders et al. (1972)	von Sydow and Anjou (1969)
		Mulders et al. (1973)	
Furfuryl formate		Mulders et al. (1973)	von Sydow and Anjou (1969)
Furfuryl acetate		Mulders et al. (1973)	von Sydow and Anjou (1969)
1-Furfuryl-2-formylpyrrole			von Sydow and Anjou (1969)
1-Furfurylpyrrole		Mulders et al. (1973)	

TABLE 18

Furan Derivatives Reported in Rye Crispbread

Furan derivative	Percent*
2-Pentylfuran	0.04
2-Furaldehyde	1.1
5-Methyl-2-furaldehyde	0.2
2-Acetylfuran	0.6
2-Acetyl-5- methylfuran	0.02
2-Propionylfuran	0.03
Furfuryl alcohol	15.2
Difurfuryl ether	–
Furfuryl formate	0.02
Furfuryl acetate	0.03
1-(2-Furyl)-1,2-propanedione	0.02
1-(2-Furyl)-1,2-butanedione	0.03
1-(5-Methyl-2-furyl)-1,2-propanedione	0.07
1-Furfuryl-2-formylpyrrole	0.07

*Percent of total flavor fraction evaluated.
From von Sydow and Anjou (1969).

TABLE 19

Influence of Amino Acid Additions on the Formation of 2-Propanone in Bread Crust

Amino acid added (0.02M)	Mg/100 g fresh crust weight 2-propanone found
Control	1.40
Glycine	3.62
Alanine	6.60
Valine	6.25
Leucine	2.10
Isoleucine	3.18
Glutamic acid	2.88
Histidine	5.40
Lysine	4.73
Phenylalanine	3.33
Proline	2.20
Arginine	1.44
Methionine	1.98

From Salem et al. (1967).

Even though the congregate amount of lactones found was approximately 1.5% of the total flavor fraction evaluated, the authors felt none of these compounds played a decisive role in bread flavor.

Two additional lactone derivatives were reported by Mulders et al. (1973) as present in white bread crust. The authors stated that they were not aware of any other report identifying 4-hydroxy-3-pentanoic acid lactone (β-angelica lactone) as being isolated from a food system. No amounts or possible flavor contribution of lactone derivatives were discussed in this report.

The lactones isolated in various bread systems are summarized in Table 23.

It should be noted that certain lactones have potent and characteristically unique flavor properties, and the occurrence of certain lactones in bread systems would be indicative that others may be present. In the future, the complete role of lactones in bread flavor may be elucidated.

Pyrazines

Pyrazines are heterocyclic nitrogen-containing compounds possessing unique flavor properties; they have been reported present in a wide variety of food products (Maga and Sizer, 1973a,b). To date, three investigative groups have reported on the presence of pyrazine derivatives in bread systems.

A report appeared in 1969 (von Sydow and Anjou) dealing with the aroma of rye crispbread. One of the aroma fractions investigated included the pyrazines, which were approximately 4.5% in volume of the total aroma mixture. The pyrazines found and their relative amounts in rye crispbread are summarized in Table 24.

Methylpyrazine was the most prevalent pyrazine derivative detected. In addition to the twelve compounds identified, the authors reported six related unidentified compounds, representing an additional 0.3%. Based on the characteristic odor of these compounds, the authors suggested that pyrazine derivatives were important to bread aroma. It was suggested that these products were the result of non-enzymatic sugar-amino acid reactions. However, it may be possible that certain pyrazines may actually be present in some of the original formulation materials, such as the flour or the dry skim milk.

Mulders et al. (1973) reported on the identification of 52 compounds isolated from the crust of white bread baked from flour, salt, yeast, and water only. Included in the compounds identified were methyl-, ethyl-, 2,3-dimethyl- and 2,5-dimethylpyrazine. Neither concentrations nor their possible flavor contribution was discussed. As mentioned previously, milk products may serve as a pyrazine source. Since in this study no milk product was used, the pyrazines were either naturally present or were formed during baking.

TABLE 20

Ketones Reported in Bread Systems

Ketone	Pre-ferments	Oven vapor	White bread	Rye products
2-Propanone	Smith and Coffman (1960) Kohn et al. (1961) Miller et al. (1961) Linko et al. (1962a) Linko et al. (1962b) Borovikova and Roiter (1971a)	Baker et al. (1953)	Ng et al. (1960) Ocker (1961) Wiseblatt and Kohn (1960) Hrdlicka et al. (1963) Linko and Johnson (1963) Rothe (1963a) Wick et al. (1964) Rothe (1966) El-Dash and Johnson (1967) Salem et al. (1967) Johnson and El-Dash (1969) Markianova and Roiter (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971a,b,c) Borovikova et al. (1971) Markianova et al. (1971) Lorenz and Maga (1972) Mulders and Dhont (1972) Roiter and Borovikova (1972) Rothe et al. (1972) Mulders (1973)	Hampl et al. (1964) Hrdlicka and Honischova (1967) Rothe et al. (1972)
2-Butanone	Miller et al. (1961) Linko et al. (1962a) Linko et al. (1962b) Borovikova and Roiter (1971a)	Baker et al. (1953)	Ng et al. (1960) Linko and Johnson (1963) Wick et al. (1964) El-Dash and Johnson (1967) Johnson and El-Dash (1969) El-Dash and Johnson (1970) Borovikova and Roiter (1971a,b,c) Borovikova et al. (1971) Markianova et al. (1971) Lorenz and Maga (1972) Mulders and Dhont (1972) Roiter and Borovikova (1972)	

TABLE 20 (Continued)

Ketones Reported in Bread Systems

Ketone	Pre-ferments	Oven vapor	White bread	Rye products
3-Hydroxy-2-butanone	Visser't Hooft and deLeeuw (1935) Smith and Coffman (1960)	–	Visser't Hooft and deLeeuw (1935) Hrdlicka et al. (1963) Rothe (1963a) Rothe (1963b) Wick et al. (1964) Rothe et al. (1972) Mulders et al. (1973)	von Sydow and Anjou (1969) Rothe et al. (1972)
2,3-Butanedione	Smith and Coffman (1960) Borovikova and Roiter (1971a)	Baker et al. (1953)	Wiseblatt and Kohn (1960) Rothe (1963a) Wick et al. (1964) Johnson and El-Dash (1969) Borovikova and Roiter (1971a,b,c) Borovikova et al. (1971) Markianova et al. (1971) Mulders and Dhont (1972) Mulders et al. (1972) Roiter and Borovikova (1972) Rothe et al. (1972) Mulders (1973)	Hampl et al. (1964) Rothe (1966) Hrdlicka and Honischova (1967) Rothe et al. (1972)
2-Pentanone	–	–	Wick et al. (1964) Mulders et al. (1973)	–
3-Penten-2-one	Borovikova and Roiter (1971a)	–	Wiseblatt and Kohn (1960) Borovikova and Roiter (1971c) Mulders et al. (1972) Mulders et al. (1973)	–
4-Methyl-3-penten-2-one	–	–		von Sydow and Anjou (1969)
2-Cyclopenten-1-one	–	–	Mulders et al. (1973)	–
2,3-Pentanedione	–	–	Mulders et al. (1973)	–
2-Hexanone	Kohn et al. (1961)	–	Wick et al. (1964) El-Dash and Johnson (1967) Lorenz and Maga (1972) Mulders and Dhont (1972)	Hrdlicka and Honischova (1967)

TABLE 20 (Continued)

Ketones Reported in Bread Systems

Ketone	Pre-ferments	Oven vapor	White bread	Rye products
3-Hexanone	-		Borovikova and Roiter (1971b,c) Borovikova et al. (1971)	–
2-Heptanone	-	-	Lorenz and Maga (1972) Mulders and Dhont (1972) Mulders et al. (1973)	Hrdlicka and Honischova (1967)
3-Heptanone	-		Wiseblatt and Kohn (1960)	–
3,4-Heptanone			El-Dash and Johnson (1967)	–
2-Octanone				von Sydow and Anjou (1969)
6,10,14,-Trimethyl-2-pentadecanone		–	–	von Sydow and Anjou (1969)
2-Heptadecanone	-	-		von Sydow and Anjou (1969)
Dihydro-2-methyl-3-(2H)-furanone			Mulders et al. (1973)	–
2,5-Dimethyl-3-(2H)-furanone			Mulders et at. (1973)	
2-Acetylfuran		–	Mulders et al. (1973)	–
1-(2-Furyl)-2-propanone	–		Mulders et al. (1973)	-
1-(2-Furyl)-1,2-propanedione	–	–	Mulders et al. (1973)	-
3-Hydroxy-2-methyl-4-pyrone	–	–	Mulders et al. (1973)	–
2-Methyl-3-oxolanone	–	–	–	von Sydow and Anjou (1969)

TABLE 21

Ketone Distribution in Rye Crispbread

Ketone	Percent*
3-Hydroxy-2-butanone	1.6
2-Octanone	0.04
2-Heptadecanone	0.08
6,10,14-Trimethyl-2-pentadecanone	0.2
4-Methyl-3-penten-2-one	0.08

*Percent of total flavor fraction evaluated.
From von Sydow and Anjou (1969).

TABLE 22

Lactone Derivatives Found in Rye Crispbread

Compound	Common name	Percent*
4-Hydroxybutanoic acid lactone	Butyrolactone	0.3
4-Hydroxypentanoic acid lactone	Valerolactone	0.1
4-Hydroxyhexanoic acid lactone	δ-Caprolactone	0.2
4-Hydroxynonanoic acid lactone	δ-Nonalactone	0.5
Dihydroactinidiolide	–	0.4
	Total:	1.5

*Percent of all flavor fractions evaluated.
From von Sydow and Anjou (1969).

TABLE 23

Lactone Derivatives Isolated from Bread Systems

Lactone derivative	Pre-ferments	Oven vapor	White Bread	Rye products
4-Hydroxybutanoic acid lactone	Smith and Coffman (1960)	Coffman (1966)	Mulders el al. (1973)	von Sydow and Anjou (1969)
4-Hydroxy-2-butenoic acid lactone	–	–	Mulders et al. (1973)	–
4-Hydroxypentanoic acid lactone	–	–	–	von Sydow and Anjou (1969)
4-Hydroxy-3-pentenoic acid lactone	–	–	Mulders et al. (1973)	–
4-Hydroxyhexanoic acid lactone	–	–	Mulders et al. (1973)	von Sydow and Anjou (1969)
4-Hydroxynonanoic acid lactone	–	–	–	von Sydow and Anjou (1969)
Dihydroactinidiolide	–	–	–	von Sydow and Anjou (1969)

TABLE 24

Pyrazine Derivatives Found in Rye Crispbread

Compound	Percent*
Pyrazine	0.01
Methylpyrazine	1.4
2,3-Dimethylpyrazine	0.5
2,5-Dimethylpyrazine	0.4
Ethylpyrazine	0.9
Trimethylpyrazine	0.6
2-Ethyl-3-methylpyrazine	0.2
2-Ethyl-6-methylpyrazine	0.2
3-Ethyl-2,5-dimethylpyrazine	0.3
Propylpyrazine	0.03
Vinylpyrazine	0.03
2-Vinyl-6-methylpyrazine	0.08
Total:	4.6

*Percent of all flavor fractions evaluated.
From von Sydow and Anjou (1969).

TABLE 25

Influence of Baking Time on Pyrazine Concentrations (ppm) in Bread Crust

Compound	Min. baking time at 218 °C				
	10	15	20	25	30
Methylpyrazine	23	7.6	6.0	3.1	2.3
Ethylpyrazine	0.20	0.46	0.21	0.35	0.45
2,3-Dimethylpyrazine	–	–	0.03	0.04	0.06
2-Ethyl-3-methylpyrazine	0.09	0.30	0.29	1.0	1.2
2-Methyl-6-propylpyrazine	0.30	0.33	0.26	0.24	0.23

From Sizer et al. (1973).

Sizer et al. (1973) reported on the influence of baking time on pyrazine concentration in the crust of white bread. A portion of their data is summarized in Table 25.

This group found methylpyrazine the main pyrazine derivative in white bread crust, just as von Sydow and Anjou (1969) found it most prevalent in rye crispbread. Baking time did influence pyrazine concentration. Compounds such as methylpyrazine dramatically decreased with increased baking time, while others, such as 2-ethyl-3-methylpyrazine, increased with baking time. The decrease of certain pyrazine compounds can be explained in several manners. Volatility may reduce the concentration of certain pyrazines with baking time, certain pyrazines may actually be destroyed, or they may serve as precursors for other pyrazine compounds. Based on the amounts found as compared to their odor thresholds reported in the literature, the authors concluded that pyrazines can significantly contribute to the sensory properties of bread.

Whether certain pyrazine compounds occur naturally in grains and flours is not known. With current pyrazine isolation and quantitation techniques, it would be a relatively easy task to answer this question.

The role of fermentation on pyrazine formation in bread has not been investigated. In other foods, such as cocoa beans and Natto, fermentation results in pyrazine compound formation.

A list summarizing the pyrazine compounds found to date in bread products can be found in Table 26.

TABLE 26

Pyrazine Compounds Isolated from Bread Products

Pyrazine	White bread	Rye Products
Unsubstituted pyrazine	–	von Sydow and Anjou (1969)
2-Methylpyrazine	Mulders et al. (1973) Sizer et al. (1973)	von Sydow and Anjou (1969)
2,3-Dimethylpyrazine	Mulders et al. (1973) Sizer et al. (1973)	von Sydow and Anjou (1969)
2,5-Dimethylpyrazine	Mulders et al. (1973)	von Sydow and Anjou (1969)
2-Ethylpyrazine	Mulders et al. (1973) Sizer et al. (1973)	von Sydow and Anjou (1969)
Trimethylpyrazine	–	von Sydow and Anjou (1969)
2-Ethyl-3-methylpyrazine	Sizer et al. (1973)	von Sydow and Anjou (1969)
2-Ethyl-6-methylpyrazine	–	von Sydow and Anjou (1969)
Propylpyrazine	–	von Sydow and Anjou (1969)
2-Methyl-6-propylpyrazine	Sizer et al. (1973)	–
3-Ethyl-2,5-dimethylpyrazine	–	von Sydow and Anjou (1969)
Vinylpyrazine	–	von Sydow and Anjou (1969)
2-Vinyl-6-methylpyrazine	–	von Sydow and Anjou (1969)

TABLE 27

Pyrrole Derivatives Found in Rye Crispbread

Compound	Percent*
Pyrrole	0.1
Acetylpyrrole	1.9
1-Methyl-2-formylpyrrole	0.05
1-Methyl-2-acetylpyrrole	0.07
5-Methyl-2-formylpyrrole	0.1
1-Furfuryl-2-formylpyrrole	0.07
Indole	0.2
Total:	2.5

*Percent of all flavor fractions evaluated.
From von Sydow and Anjou (1969).

Pyrrole Derivatives

A total of 7 pyrrole derivatives was reported by von Sydow and Anjou (1969) in rye crispbread. The compounds and the relative quantities found in the above study are summarized in Table 27.

Acetylpyrrole represented 80% of the total pyrrole fraction. It was suggested by the authors that due to their unique odors, pyrroles could be important to bread aroma. It was also postulated that they were derived from thermal reactions during baking involving non-enzymatic browning.

An additional three compounds were reported by Mulders et al. (1973) in white bread crust. This group also postulated that pyrroles are derived by non-enzymatic browning reactions or possibly by Maillard reactions. Mulders et al. (1973) also pointed out that other investigators have reported certain pyrrole derivatives possess cracker or bread-like odors. Such observations were reported by Kobayasi and Fujimaki (1965) for l-acetonylpyrroline; 2-acetyl-1-methylpyrrolidine and l-azabicyclo (3.3.0) octan-4-one by Hunter et al. (1966); and 2-acetyl-1,4,5,6-tetrahydropyridine by Hunter et al. (1969). However, none of these specific compounds were found in the current study (Mulders et al. 1973). Mulders and Dhont (1972) also reported the presence of the compound 3-hydroxy-2-methyl-4-pyrone in bread.

A summary of pyrrole derivatives found in bread products can be found in Table 28.

TABLE 28

Pyrrole Derivatives Isolated from Bread Products

Pyrrole derivative	White Bread	Rye Products
Pyrrole	Mulders et al. (1973)	von Sydow and Anjou (1969)
1-Methylpyrrole	Mulders et al. (1973)	–
2-Formylpyrrole	Mulders et al. (1973)	–
2-Acetylpyrrole	Mulders et al. (1973)	von Sydow and Anjou (1969)
1-Furfurylpyrrole	Mulders et al. (1973)	–
1-Methyl-2-formylpyrrole	–	von Sydow and Anjou (1969)
1-Methyl-2-acetylpyrrole	–	von Sydow and Anjou (1969)
5-Methyl-2-formylpyrrole	–	von Sydow and Anjou (1969)
1-Furfuryl-2-formylpyrrole	–	von Sydow and Anjou (1969)
Indole	–	von Sydow and Anjou (1969)
3-Hydroxy-2-methyl-4-pyrone	Mulders and Dhont (1972)	–

TABLE 29

Sulfur Compounds Isolated from Bread Products

Sulfur compound	White bread	Rye products
Dimethyl sulfide	Mulders et al. (1972) Mulders (1973)	–
Dimethyl disulfide	Mulders et al. (1972) Mulders (1973)	von Sydow and Anjou (1969)
3-Acetylthiophene	Mulders (1973)	–
2,3,4-Trithiapentane	–	von Sydow and Anjou (1969)
2-Formylthiophene	–	von Sydow and Anjou (1969)
Methane thiol	Ocker and Rotsch (1959)	Rotsch and Dorner (1957) Rotsch and Dorner (1958) Rothe and Thomas (1959)
Hydrogen sulfide	–	Rotsch and Dorner (1957) Rotsch and Dorner (1958)

Sulfur Compounds

In 1959 Ocker and Rotsch reported on the identification of methane thiol in white bread. The sulfur containing compounds dimethyl sulfide and dimethyl disulfide were detected in the vapors above white bread three hours after it was baked (Mulders et al., 1972). A nitrogen stripping technique was used to isolate the volatiles. In a later study, Mulders (1973) reported identifying the same two sulfur compounds using a different volatile vapor isolation technique with white bread. However, the quantities found in this later study were too small to even be calculated on the basis of relative amounts present. Another sulfur-based compound was identified by Mulders et al. (1973) as 3-acetylthiophene. It was found in a pentane-diethyl ether extract of bread crust. By viewing the published GLC scan, it is apparent that the relative proportion of 3-acetylthiophene detected was insignificant in quality. No postulations were made regarding the source of this latter sulfur-based compound.

With regard to rye bread, methane thiol has been reported present by Rotsch and Dorner (1957, 1958) and Rothe and Thomas (1959). Rotsch and Dorner (1957, 1958) also detected hydrogen sulfide in rye bread. Several sulfur-based compounds have been identified (von Sydow and Anjou, 1969) in rye crispbread that had been steam-distilled and ether-extracted. The sulfur compounds included dimethyl disulfide, 2,3,4-trithiapentane and 2-formylthiophene. The three compounds had a relative concentration to the other volatiles isolated of 0.16%, with 2-formylthiophene representing half this amount. Again, no formation pathways for these compounds were discussed, although one may assume that they originate from the thermal decomposition and rearrangement of sulfur-bearing amino acids. As can be seen in Table 29, sulfur compounds have only been reported in finished bread products.

TABLE 30

Miscellaneous Compounds Reported in Bread Products

Miscellaneous compounds	White bread	Rye products
Maltol	Bache (1910)	–
Isomaltol	Bache (1910)	–
1,1-Diethoxyethane	Mulders et al. (1972) Mulders (1973)	
Tetramethylbenzene	–	von Sydow and Anjou (1969)
Methylnaphthalene		von Sydow and Anjou (1969)
Dimethylnaphthalene	–	von Sydow and Anjou (1969)
Diphenylacetylene	–	von Sydow and Anjou (1969)
Phenol	–	von Sydow and Anjou (1969)
Cresol	–	von Sydow and Anjou (1969)
Ethylphenol	–	von Sydow and Anjou (1969)
2-Methoxyphenol	–	von Sydow and Anjou (1969)
4-Vinyl-2-methoxyphenol	–	von Sydow and Anjou (1969)
O-Hydroxydiphenyl	–	von Sydow and Anjou (1969)

Miscellaneous Compounds

Table 30 represents a compilation of reported volatile compounds that do not easily fit into any of the chemical classes just discussed.

The majority of these compounds are associated with rye crispbread. Von Sydow and Anjou (1969) cautioned that the first four compounds listed in Table 30 may possibly be artifacts, but they did not go into further detail. The compound 4-vinyl-2-methoxyphenol comprised 8.2% of the total volatile fraction in rye crispbread.

In conclusion, the complexity of bread flavor can be better appreciated by the fact that over thirteen chemical classes, comprised of over 100 compounds, have been reported present in various bread systems. It should also be noted that extensive and reliable quantitative data are painfully absent, which makes understanding bread flavor more difficult.

For the convenience of the reader all of the compounds that have been reported present in bread are summarized by compound class in Table 31.

FLAVOR ISOLATION TECHNIQUES

Introduction

If a major criticism has to be made of the isolation techniques used by bread flavor investigators, it is that few techniques were used by most investigative groups. Although some of the techniques had severe limitations, which were acknowledged by most groups, each succeeding investigator continued to use similar techniques. Admittedly, no one technique is adequate to extract the entire bread flavor spectrum, but the bread flavor chemists could have taken heed of the isolation techniques used by other food flavor chemists.

The results of numerous bread flavor investigations began to appear in the early 1960's; for the following decade similar procedures were used by all groups. However, recently innovative methods used by two groups in particular have resulted in the publication of more detailed and useful information about bread flavor than was produced by the previous reports combined.

This section will briefly outline the techniques used by choosing a representative report for each technique and pointing out some of the merits and limitations involved.

Volatile Reducing Substances

In 1949 Farber published a procedure to measure volatile organic substances. Baker et al. (1953) used this procedure for determining the volatile substances in bread crumb. Air at a flow rate of 1 liter per min for 10 min was passed through 2 g of bread crumb. The exit gases were passed through two test tubes in a

TABLE 31

Summary of Volatile Compounds Reported in Bread

Acids
Methanoic
Ethanoic
Propanoic
2–Methylpropanoic
2–Hydroxypropanoic
2–Oxopropanoic
Butanoic
3–Methylbutanoic
Pentanoic
4–Oxopentanoic
Hexanoic
Octanoic
Decanoic
Dodecanoic
Benzoic
*Tetrahydroxypentanoic
*Hydroxyethanolic
*2–Hydroxy–1,2,3–propantricarboxylic
*Butanedioic

Alcohols
Ethanol
1–Propanol
2–Propanol
2–Methyl–1 propanol
1–Butanol
2–Methyl–1–butanol
3–Methyl–1–butanol
1–Pentanol
2–Pentanol
3–Pentanol
1–Hexanol
*1–Octanol
2,3–Butanediol
*1 Penten 3 ol
Benzyl alcohol
Furfuryl alcohol
2–Phenylethanol
*4–Allylguaiacol

Aldehydes
Formaldehyde
Acetaldehyde
Propanal
2–Methylpropanal
2–Oxopropanal
2–Propenal
2–Phenylpropenal
Butanal
2–Methylbutanal
3–Methylbutanal
2–Butenal
Pentanal
2–Methylpentanal
Hexanal
2–Ethylhexanal
Heptanal
Octanal
*2 Octenal
Nonanal
2–Nonenal
*Dodecanal
*2,4–Heptadienal
Trans,cis 2,4 decadienal
**Trans,trans* 2,4 decadienal
Benzaldehyde
4–Hydroxybenzaldehyde
Phenylacetaldehyde
2–Furaldehyde
3–Furaldehyde
5 Methyl 2 furaldehyde
5 Hydroxymethyl–2–furaldehyde
2–Furan dialdehyde
4–Hydroxy–3–methoxybenzaldehyde

Esters
Ethyl formate
Ethyl acetate
Ethyl pyruvate
Ethyl levulinate
Furfuryl formate
Furfuryl acetate
Acetonyl acetate
*Ethyl caprinate
*Ethyl laurate
*Ethyl myristinate
*Ethyl pentadecanoate
*Ethyl palmitate
*Glycol diacetate
*Ethyl phenylacetate
*β–phenylethyl formate
*β–phenylethyl acetate
*Amyl bensoate

Ethers
Ethyl furfuryl ether
*Difurfuryl ether

Furan derivatives
2–Furaldehyde
3–Furaldehyde
5–Methyl–2–furaldehyde
5–Hydroxymethyl–2–furaldehyde
Furan
2–Methylfuran
2–Acetylfuran
*2–Acetyl–5–methylfuran
2–Pentylfuran
*2–Propionylfuran
1–(2–Furyl) 2 propanone
1–(2 Furyl) 1,2 propanedione
*1–(2 Furyl) 1,2 butanedione
*1–(5–Methyl–2–furyl)–1,2–propanedione
Dihydro–2–methyl–3–(2H)–furanone
2,5–Dimethyl–3–(2H)–furanone
Ethyl furfuryl ether
*Difurfuryl ether

TABLE 31 (Continued)

Summary of Volatile Compounds Reported in Bread

Furfuryl alcohol
Furfuryl formate
Furfuryl acetate
*1-Furfuryl-2-formylpyrrole
1-Furfurylpyrrole

Hydrocarbons
Limonene
Toluene

Ketones
2-Propanone
2-Butanone
3-Hydroxy-2-butanone
2,3-Butanedione
2-Pentanone
3-Penten-2-one
*4-Methyl 3-penten-2-one
2-Cyclopenten-1-one
2,3-Pentanedione
2-Hexanone
3-Hexanone
2-Heptanone
3-Heptanone
3,4 Heptanone
*2-Octanone
*6,10,14-Trimethyl-2-pentadecanone
*2-Heptadecanone
Dihydro-2-methyl-3-(2H)-furanone
2,5-Dimethyl-3-(2H)-furanone
2-Acetylfuran
1-(2-Furyl)-2-propanone
1-2(-Furtyl)-1,2-propanedione
3-Hydroxy-2-methyl-4 pyrone
*2-Methyl-3-oxolanone

Lactone derivatives
4-Hydroxybutanoic acid lactone
4-Hydroxy-2-butenoic acid lactone
*4-Hydroxypentanoic acid lactone
4-Hydroxy-3-pentenoic acid lactone
4-Hydroxyhexanoic acid lactone
*4-Hydroxynonanoic acid lactone
*Dihydroactinidiolide

Pyrazines
*Pyrazine
2-Methylpyrazine
2,3-Dimethylpyrazine
2,5-Dimethylpyrazine
2-Ethylpyrazine
*Trimethylpyrazine
2-Ethyl 3-Methylpyrazine
*2-Ethyl-6-methylpyrazine
*Propylpyrazine
2-Methyl-6-propylpyrazine
*3-Ethyl-2,5-dimethylpyrazine
*Vinylpyrazine
*2-Vinyl-6- methylpyrazine

Pyrrole derivatives
Pyrrole
1-Methylpyrrole
2-Formylpyrrole
2-Acetylpyrrole
1-Furfurylpyrrole
*1-Methyl-2-formylpyrrole
*1-Methyl-2-acetylpyrrole
*5 Methyl 2 formylpyrrole
*1-Furfuryl-2-formylpyrrole
*Indole
3 Hydroxy-2-methyl-4-pyrone

Sulfur compounds
*Hydrogen sulfide
Dimethyl sulfide
Dimethyl disulfide
Methane thiol
3-Acetylthiophene
2,3,4-Trithiapentane
2-Formylthiophene

Miscellaneous compounds
Maltol
Isomaltol
1,1-Diethoxyethane
*Tetramethylbenzene
*Methylnaphtalene
*Dimethylnaphtalene
*Diphenylacetylene
*Phenol
*Ethylphenol
*2-Methoxyphenol
*4-Vinyl-2-methoxyphenol
**O*-Hydroxydiphenyl
*Cresol

*Only in rye products.

TABLE 32

Influence of Baking Conditions on Measured Volatile Reducing Substances in Bread

Type of bake	Volatile reducing substances
Normal bake	420*
Overbake	365
Underbake	460
Quick bake	440
Slow bake	390

*Micro-oxidation equivalents.
From Baker et al. (1953).

TABLE 33

Influence of Post-baking Conditions on Measured Volatile Reducing Substances in Bread

Treatment	Volatile reducing substances
15 min after baking	440*
60 min after baking	420
Vacuum cooled, 7 min	310
Exposed to air, 1 day	13
Wrapped, 1 day	411
Wrapped, 3 days	315
Wrapped, 9 days	103
Wrapped and frozen, 7 days	414

*Micro-oxidation equivalents.
From Baker et al. (1953).

series, each containing 10 ml of 0.1*N* potassium permanganate in 1.0*N* sodium hydroxide. The amount of reduced permanganate was then measured iodimetrically and converted to micro-oxidation equivalents. Typical data obtained by this method are shown in Table 32.

If one looks quickly at these data, they appear logical; one could reason that overbaking will drive off more volatiles and the overbaked product has a lower value. However, if this were the case, the data presented comparing quick and slow baking would be difficult to explain. One might assume that prolonged baking increases bread flavor and the baking method is not a true indicator of residual bread flavor. The authors did concede that the method primarily measured ethanol. Another limitation of the method is the size (2 g) of crumb sample used: such a small sample could be influenced by its location within the loaf.

Even with these severe limitations, additional data presented by Baker et al. (1953) using the method in relation to post-baking conditions do appear logical (Table 33) in that with more adverse storage conditions, the amount of volatile substances decreased.

The only limitation not explained with the second set of data is, that upon cooling and storage, there is a migration of volatile compounds inward. Thus, sample location would be critical.

A somewhat similar procedure was proposed by Tokareva and Kretovich (1961), which they recommended as an index of bread quality. It involved extracting the sample with 0.1% solution of sodium bicarbonate, filtering, and adding an excess of sodium bicarbonate titrated with 0.1*N* and 0.01*N* iodine solution. The bound bisulfite was released with a standard solution of sodium carbonate, then titrated with 0.1*N* iodine. The bisulfite binding ability was expressed as ml of 0.01*N* iodine per 100 g of bread.

Oven Vapor Condensation

As discussed elsewhere in this review, the major limitation of this technique is that compounds no longer an active part of the baked product are being measured. Admittedly, the aroma of baking bread is quite pleasing and can be considered an important part of its sensory properties. However, in today's world the aroma of baking bread mass-produced at central points has little effect on consumer acceptance.

A typical example as outlined by Baker et al. (1953) will be discussed. The oven vent was connected by a glass tube to a series of Dry Ice® traps attached in turn to an aspirator. As baking proceeded, the gases formed condensed in the traps, and the condensates combined to be evaluated later.

DNPH Derivatives

Various groups have isolated carbonyl compounds through the formation of their 2,4-dinitrophenylhydrazone (DNPH) derivatives. For example, when working with pre-ferments, Linko et al. (1962a) prepared a 1% solution of 2,4-dinitrophenylhydrazine in 5*N* sulfuric acid. Then the fermentation gases evolved from the pre-ferment system were passed through the DNPH reagent: in the process, hydrazones of the volatile carbonyl compounds were formed. The resulting hydrazones were then extracted with several aliquots of chloroform and saved for future analysis.

This method is relatively specific for carbonyl compounds, and it can serve as a means of separating a complex mixture of volatile flavor compounds. However, since the reaction takes place in an acid state, the possibility exists that other compounds are being degraded, which can result in the formation of additional carbonyls.

Steam Distillation

A typical example of this method was reported by von Sydow and Anjou (1969). A representative sample of the product was suspended in water and steam distilled for 3.5 hr at atmospheric pressure. The severity of this treatment may be questioned because if any reactive materials were present in the baked product, they were given ample opportunity to form additional, or increased amounts, of compounds which are to be identified later. The distillate was then saturated with ammonium sulfate and extracted with three portions of distilled diethyl ether. Water present in the extract was removed by drying over sodium sulfate, and the solvent was removed by evaporation through Vigreux columns until a volume of 1.5 ml remained. The sample was further concentrated, by an unspecified procedure, to a volume of 0.1 ml and stored at −20°C until evaluated.

Vacuum steam distillation, with appropriate precautions for trapping excessively volatile compounds, or vacuum solvent distillation are recommended instead of atmospheric steam distillation. These methods would minimize the possibility of artifact formation.

Direct Solvent Extraction

In a portion of their study on pre-ferments Miller et al. (1961) used a direct solvent extraction method. Essentially, this involved the addition of the extracting solvent to the product. They extracted 200 ml portions of pre-ferments with 40 ml portions of diethyl ether in a separatory funnel and repeated the process until 1,200 ml of pre-ferment had been extracted. The ether extracts were then dried over sodium sulfate and analyzed as such since concentrating the extract was not mentioned. Thus, any losses due to volatilization during concentration were eliminated. In most cases some form of concentration is advised to facilitate detecting compounds that may be present in small quantities. Actually, solvent extraction, when performed using a freshly distilled and purified solvent, produces few artifacts, especially when compared to steam distillation.

A direct dual-solvent extraction technique was reported by Mulders et al. (1972). The first extraction was with water, thus assuming all bread flavor compounds are water soluble. The supernatant liquid was distilled using a climbing film evaporator and a liquid-vapor separator. Retention time in this system was estimated at 8 seconds at a maximum temperature of 32°C and a pressure of 30 mm of mercury. This reduced the original 17 liter volume to 1.7 liter which were then freeze concentrated to 150 ml. This concentrated product was then extracted with a 2:1 mixture of pentane-diethyl ether. The resulting extract was dried over sodium sulfate and the solvent removed using a Vigreux distillation column. The process itself is relatively gentle, but there are approximately five time-consuming steps which make the reliability of any quantitative data attempted questionable.

Direct Vapor Analysis

Another relatively rapid and simple technique is direct vapor analysis; a typical example would be that reported by Mulders (1973). A 50 g slice of bread was cut into small cubes and placed in a 360 ml flask which was then equilibrated in a 36°C water bath for 45 min. At that time vapor samples were removed by a preheated glass syringe and analyzed. The possibility of artifact formation using this procedure is minimal since neither excessive temperature nor other chemicals or solvents are employed. Also, losses due to extractions, transfers and concentrations are eliminated. The primary disadvantage of this method is that only the most volatile compounds are detected, and the complete flavor profile of the product may be lacking. There is also no guarantee that the volatile compounds found by this method are those specifically associated with the characteristic flavor being evaluated.

Nitrogen Flush and Precolumn Trapping

Undoubtedly the mildest isolation procedure was that reported by Mulders et al. (1972). A sample of bread was cut into small cubes and placed in a glass container through which prepurified nitrogen was

passed at a flow rate of 10 ml/min for 50 to 75 min. The exit gases were trapped in a Dry Ice cooled 30 cm by 3mm stainless steel column filed with uncoated glass beads 280 to 320 μm in diameter. The precolumn containing the stripped volatile was then removed and used for analysis. In this procedure no heat, solvents or other chemicals were used. One of its only limitations is that such a mild procedure probably does not remove all of the flavor compounds associated with bread flavor, and accordingly cannot be considered quantitative. Some investigators may also question cutting up the bread sample since compounds may escape in the process and increased exposure to air may have some consequences. A major advantage of the method is that it is relatively rapid to perform. Also, the efficiency of the system can be checked by sniffing the exit port of the precolumn to detect any volatiles not being trapped, and then smelling the stripped bread to determine if a characteristic odor still remains.

FLAVOR SEPARATION AND IDENTIFICATION TECHNIQUES

Introduction

For any flavor data to be meaningful, methods must be employed that simply and effectively separate the complex isolated mixtures into their individual components. Other prerequisites include the positive identification of the compounds and, ultimately, their quantitation. Some of today's advanced methods have assisted in separation and identification, but problems still face those investigators who are truly interested in determining concentrations. At this point some of the techniques employed will be discussed.

Traditional Methods

These procedures have been widely used for years by chemists; they supply information on the chemical characteristics of individual compounds which then can be used for identification purposes or quantitation.

An example would be the method used by Wiseblatt (1960a) to quantitate the amount of acetic acid present in the condensate obtained from oven vapors. Essentially the author used an acid-base type titration to arrive at an index of acidic compounds expressed as acetic acid. In reality other acids were probably also present, perhaps along with some compounds serving as buffering agents during the titration.

Another example would be the refractometer determination of ethanol from a pre-ferment mixture that probably contained other alcohols (Cole et al., 1962).

In the case of carbonyls several research groups have used a colorimetric procedure introduced by Lappin and Clark (1951). The problem with this procedure is that individual carbonyls give different colors and different color intensities; the more complex, the more unquantitative the procedure becomes.

Other traditional methods that have been used include specific gravity, melting point, and specific compound color reaction determinations.

Paper Chromatography

The use of paper chromatography has been reported in the separation of DNPH derivatives. However, the procedure is quite time-consuming and generally not all of the compounds present in a bread mixture are resolved through the use of only one solvent system. This is apparent from Figure 1. Thus, two solvent systems are required for more efficient separation.

Column Chromatography

This method has been used mainly to separate DNPH derivatives. For example, Ng et al. (1960) used a 2:1 silicic acid-celite column and various proportions of diethyl ether-Skellysolve-F mixtures. However, not all carbonyl derivatives present in the mixture were separated.

Thin-Layer Chromatography

Especially in the case of volatile compounds that have been derivatized, thin-layer chromatography has been used by numerous bread flavor investigators. If the mixtures are not too complex, it provides a relatively simple and inexpensive means of separating, identifying and roughly quantitating results. Attempts have been made to separate entire bread flavor mixtures, but, as can be seen in Figure 2, even with two-dimensional techniques complete separation was not achieved.

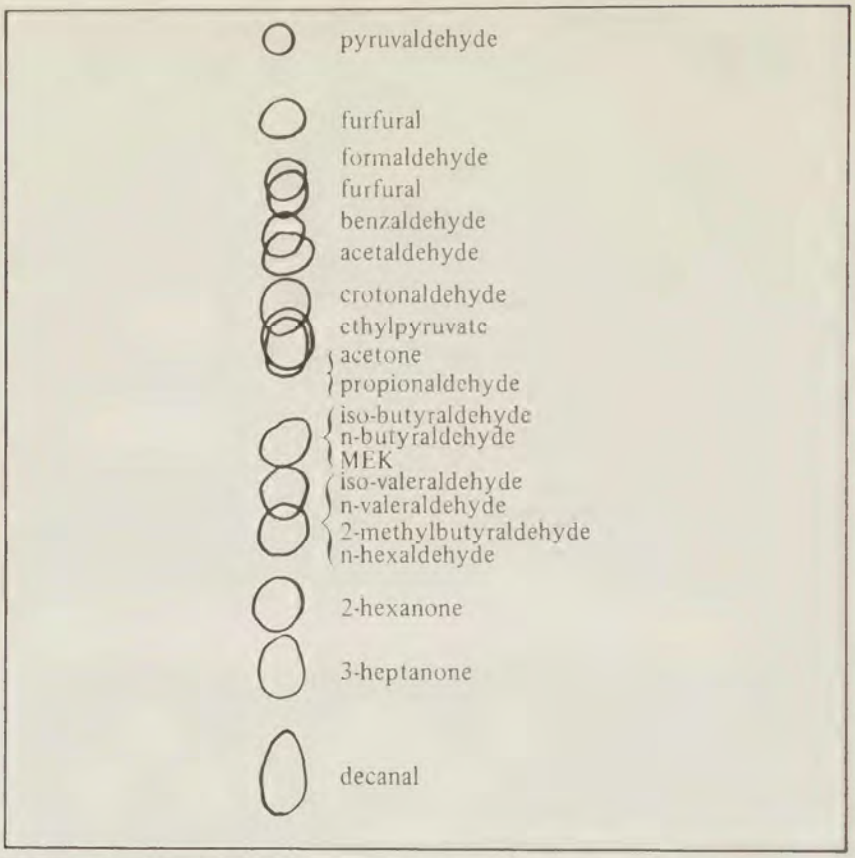


FIGURE 1. Typical paper chromatogram of pre-ferment carbonyl derivatives. (From Linko et al. (1962a)).

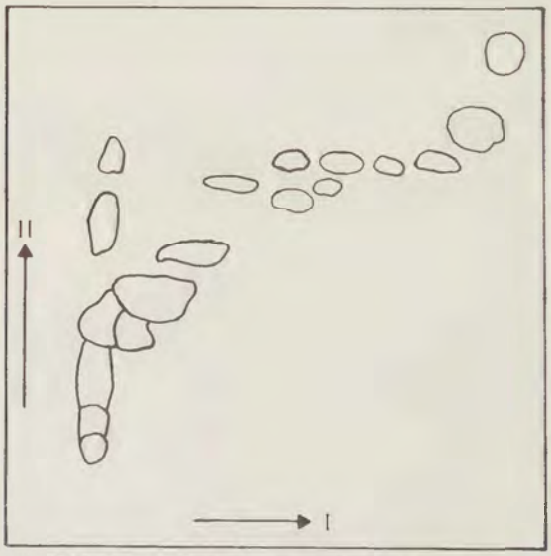


FIGURE 2. Typical two-dimensional thin-layer chromatogram. (From Daniels (1971)).

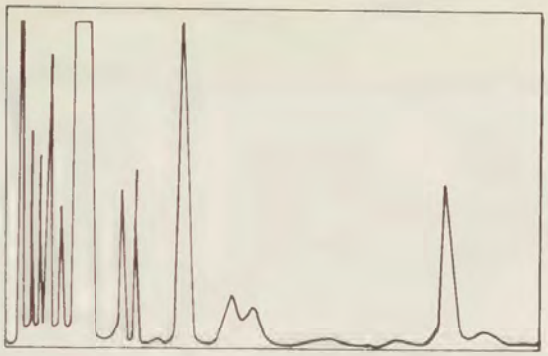


FIGURE 3. Typical gas-liquid direct vapor chromatogram. (From Mulders et al. (1972)).

Gas-Liquid Chromatography

The gas-liquid chromatograph has been a tremendous asset in the evaluation of bread flavor, especially since the introduction of temperature programming techniques. By selecting the appropriate separation conditions relative to temperature, flow rate, size of column and type of packing, a wide variety of classes of compounds can be effectively separated. Traditionally, compound identification using gas-liquid chromatography was based on matching retention times of authentic and unknown compounds separated under similar conditions on several types of columns. However, no definite identification can be made by this technique alone; time-consuming trapping techniques were introduced to obtain sufficient sample for verification identification by other analytical methods. The introduction of coupled gas-liquid chromatography – mass spectrometry analyses has been a tremendous asset, cost being the primary limiting factor of the technique. With the combined use of these two instruments, the structural identity of compounds incompletely separated by gas-liquid chromatography, or only appearing as minor peaks, can be resolved. Typical examples would be the works reported by von Sydow and Anjou (1969) and the Mulders group (1972). A typical scan using this technique is shown in Figure 3.

Most of the recent bread flavor works involving gas-liquid chromatography have attempted separations of total volatiles from bread systems. Perhaps more detailed separations could be obtained if the flavor concentrates obtained were first divided into at least acidic and basic fractions before gas-liquid chromatographic separation. This would simplify chromatograms which would be easier to interpret. Also, column packing materials specific for certain classes of compounds are currently available; work with these coatings would be informative.

A procedure introduced by Ralls (1960) and modified by Stephen and Teszler (1960) involving flash exchange gas-liquid chromatography was used by numerous groups in conjunction with the evaluation of DNPH derivatives of bread carbonyls. A typical example is that reported by Linko et al. (1962a). A mixture consisting of Celite and the derivative mixture was blended with alpha-ketoglutaric acid and placed in a capillary tube. The open end of the capillary tube was inserted in the septum of the gas chromatograph and the mixture was volatilized by the action of the alpha-ketoglutaric acid when an oil bath at 250°C was applied for 30 sec to the tube. Several limitations of the method include the possibility that complete regeneration is not achieved, especially of the longer chain carbonyls, and there may be product decomposition during the flashing process. Therefore, the procedure cannot be considered quantitative.

A summary of gas chromatographic conditions that have been applied to bread flavor systems is shown in Table 34.

TABLE 34

Gas-Liquid Chromatography Conditions Reported in Bread Flavor Investigations

Type of detector	Column size	Liquid phase	Solid phase	Reference
Thermal	10 ft × 1/4 in	Silicone-stearic acid	–	Wiseblatt (1960b)
–	5 ft × –	Carbowax® 400	Firebrick	Wiseblatt and Kohn (1960)
Thermal	6 ft × 1/4 in	20% Diisodecyl phthalate	Celite-545	Miller et al. (1961)
Thermal	6 ft × 1/4 in	30% Di(2–ethyl–hexyl) phthalate	Celite-545	Miller et al. (1961)
Thermal	6 ft × 1/4 in	25% Tetraethyleneglycol dimethyl ether	Firebrick	Miller et al. (1961)
–	10 ft × 1/4 in	Ucon® LB–1715	Chromosorb	Smith and Coffman (1961)
–	10 ft × 1/4 in	Ucon 50–HB–5100	Chromosorb	Smith and Coffman (1961)
–	10 ft × 1/4 in	Ucon 75–H–90,000	Chromosorb	Smith and Coffman (1961)
Thermal	6 ft × 1/4 in	Diisodecyl phthalate	Celite-545	Linko et al. (1962a)
Thermal	2m × 4mm	20% Quadrol®	Firebrick	Wick et al. (1964)
Thermal	2m × 8mm	20% Ucon–LB–1715	Chromosorb	Wick et al. (1964)
Thermal	2m × 8mm	20% DEGS	Chromosorb	Wick et al. (1964)
Flame	2m × 2mm	5% OPN	Gas Chrom A	Wick et al. (1964)
Flame	2m × 2mm	1% Ucon 50–HB–2,000	Gas Chrom A	Wick et al. (1964)
–	2m × 4mm	LAC–1–R–296®	Firebrick	Wick et al. (1964)
Flame	24 ft × 1/4 in	15% Ucon 75–H–90,000	Chromosorb-W	Coffman (1966)
–	46 ft × 1/4 in	15% Ucon 75–H–90,000	Chromosorb-W	Coffman (1967)
–	12 ft × 1/4 in	15% XE–60	Chromosorb-W	Coffman (1967)
Flame	10 ft × 1/8 in	20% Carbowax 20M	Chromosorb-P	Johnson and El-Dash (1969)
Flame	6 ft × 1/4 in	6% Apiezon	Anakrom-ABS	McWilliams and Mackey (1969
Flame	6 ft × 1/4 in	6% DEGS	Anakrom-ABS	McWilliams and Mackey (1969
Flame	6 ft × 1/4 in	3% Free fatty acid	Anakrom-ABS	McWilliams and Mackey (1969
Flame	5.6m × 3/8 in	12% SF–96 (50)	Chromosorb-W	von Sydow and Anjou (1969)
Flame	3.6m × 3/8 in	3% Carbowax 20M	Chromosorb-G	von Sydow and Anjou (1969)
Flame	10 ft × 1/8 in	20% Carbowax 20M	Chromosorb-P	El-Dash and Johnson (1970)
Flame	8 ft × 1/8 in	20% Carbowax 20M	Chromosorb-P	Lorenz and Maga (1972)
Flame	1.3m × 4mm	45% D6–550+5% acid stearic	Celite-545	Mulders and Dhont (1972)
Flame	2m × 3mm	5% EGA	Gas Chrom-Q®	Mulders and Dhont (1972)
Flame	3.75m × 4mm	15% LAC–1–R–296	Chromosorb-W	Mulders et al. (1972)
Flame	3.75m × 4mm	10% SF–96 (50)	Chromosorb-W	Mulders et al. (1972)
–	50m × 0.25 mm	Ucon 50–LB–550–X	–	Mulders et al. (1972)
Flame	4m × 4mm	15% LAC–1–R–296	Chromosorb-W	Mulders (1973)
Flame	4m × 4mm	15% Carbowax–400	Chromosorb-W	Mulders (1973)
Thermal	4m × 4mm	21% LAC–1–R–296	Chromosorb-W	Mulders et al. (1973)
Thermal	4m × 4mm	15% Apiezon–M	Chromosorb-W	Mulders et al. (1973)

FACTORS AFFECTING THE SENSORY PROPERTIES OF BREAD

Introduction

Various researchers have traditionally stressed that pleasing bread flavor arises from these three primary factors associated with the bread making process: ingredients, fermentation, and baking. When studying bread flavor, one quickly learns to appreicate the chemistry involved in changing a mixture of individual ingredients, through the mixing fermentation, and baking, into a unique product possessing little physical or sensory resemblance to the original starting materials.

Due to the extremely close interaction among the various steps involved, one cannot simply state which phase is the key to the entire area of bread flavor. This portion of the review will cite literature which demonstrates the influential role each step can contribute to the sensory properties of bread and related products. The term sensory properties includes aroma, taste and color since the acceptance or rejection of most food items can be highly correlated to their visual properties.

TABLE 35

Volatile Compound Species Differences in Various Cereal Grains

Grain species	Butanal (%)	Hexanal (%)
Wheat	7.8	10.0
Triticale	9.2	5.7
Rye	16.6	3.4

From Hougen et al. (1971).

TABLE 36

Differences in Free Amino Acids in Wheat and Rye Flour

Amino acid(s)	Wheat flour	Rye flour
Aspartic acid	9.4*	19.7
Glutamic acid	10.5	20.7
Serine	1.2	3.4
Glycine	2.3	4.5
Alanine	4.9	19.2
Glutamine	2.0	1.2
γ–Aminobutyric + tyrosine	3.3	8.3
Valine	2.0	8.2
Leucine + isoleucine	3.6	8.8
Phenylalanine	2.2	2.8
Threonine	2.4	5.8
Methionine	0	0.3

*Mg % of dry weight.
From Ketovich and Ponomareva (1961).

TABLE 37

Comparative Sensory Properties of Various Grain Flours and Protein Supplements

	Sensory properties		
Product	Powder odor	Liquid odor	Liquid flavor
Whole wheat flour	5.5*	4.9	4.6
Corn flour	4.0	5.6	6.5
Rice flour	5.5	7.5	5.5
Non-fat dry milk	7.3	8.3	7.0
Sodium caseinate	6.9	6.8	5.0
Buttermilk solids	5.8	7.2	5.2
Defatted soy flour	4.3	4.2	1.7
Full-fat soy flour	3.1	4.9	2.5
Isolated soy proteinate	7.0	7.0	3.0
Fish protein concentrate	1.9	1.0	1.7
Peanut flour	2.8	3.2	2.9
Cottonseed flour	7.6	6.1	4.5

*Mean score 1-strong; 10-mild.
From Maga and Lorenz (1973c).

Flour and its Components

Since flour is the main ingredient in bread, it makes a definite flavor contribution. The flavor of flour milled from sound wheat is mild; the starch and enzymes in flour, when combined with salivary amylase, account for a portion of the characteristic sweetness in bread (Otterbacker, 1959).

From a compositional standpoint, wheat contains many classes of flavor reactive compounds, some of which may be present only in trace amounts. However, from a grain variety standpoint, the volatile composition of various grains are quite similar (Hougen et al., 1971), but the components differ in quantity. This can be appreciated by viewing the data summarized in Table 35. Triticale, a cross of wheat and rye, had butanal and hexanal levels between the two parents.

As will be discussed in more detail in a later section, free amino acids can play an influential role in the development of bread flavor. It can be concluded from the data in Table 36 that some of the characteristic flavor difference between wheat and rye products is due to rye generally having significantly higher levels of free amino acids.

The relative odor and flavor properties associated with whole wheat flour are compared to other grain flours and protein supplements in Table 37.

In the powdered form the odor of whole wheat flour was rated approximately halfway between strong and mild. When the product was suspended at a 3% level in water, its odor and flavor intensity increased slightly; milder odors and flavors were noted for corn and rice flours in the reconstituted form.

TABLE 38

Influence of Wheat Class on Bread Sensory Properties

	Odor		Taste	
Wheat class	Best (%)	Poorest (%)	Best (%)	Poorest (%)
Soft red winter	17	59	24	56
Hard red winter	38	24	27	27
Hard red spring	45	17	49	17

From King et al. (1937).

TABLE 39

Influence of Flour Extraction Rate on Bread Sensory Properties

	Odor		Taste	
Extraction rate (%)	Best (%)	Poorest (%)	Best (%)	Poorest (%)
100	20	44	20	41
85	41	26	44	26
70	39	30	37	33

From King et al. (1937).

TABLE 40

Influence of Flour Bleaching on Bread Sensory Properties

	Odor		Taste	
Bleach treatment	Best (%)	Poorest (%)	Best (%)	Poorest (%)
Bleach no. 1	26	30	27	34
Bleach no. 2	37	35	41	32
Unbleached	37	35	32	32

From King et al. (1937).

An early study (Table 38) indicated that wheat class influenced the odor and flavor of bread.

These data demonstrated that the panel preferred the odor and flavor of bread made from hard red spring wheat over breads made from hard red winter or soft red winter wheat. These data were just reported as preferences and no comments were included as to the specific superior odor and flavor properties associated with bread baked from hard red spring wheat.

In this same study King et al. (1937) reported on the sensory properties of bread baked from flours varying in extraction rates. These data are summarized in Table 39.

This study was done in the late 1930's when an extraction rate of 85% was probably preferred from both an odor and flavor standpoint, which would probably not be the case today.

The influence of bleaching on bread sensory properties was also investigated (Table 40).

In the case of odor no clear-cut preference for bleached or unbleached flour was observed. However, in the case of flavor there was a clear preference for one of the bleached flours. These data were probably psychological in nature in that the panel associated a better flavor with the whiter bleached product. The low flavor acceptance of the other bleached flour was perhaps due to a residual flavor from the bleaching agent.

TABLE 41

Typical Wheat Flour Fatty Acid Composition

Fatty acid	Chain Length	Percent
Myristic	C–14:0	0.1
Palmitic	C–16:0	24.5
Palmitoleic	C–16:1	0.8
Stearic	C–18:0	1.0
Oleic	C–18:1	11.5
Linoleic	C–18:2	56.3
Linolenic	C–18:3	3.7
Arachidic	C–20:0	0.8
Other	–	1.1

From Nelson et al. (1963).

TABLE 42

Influence of Storage on Wheat Flour Fatty Acid Class Distribution

Lipid class	Control (–20°C)	25°C for 4 months	15°C for 6 months
Triglycerides	162*	94	89
Diglycerides	97	119	126
Monoglycerides	20	37	50
Free fatty acids	76	144	159

*Mg/100 g of flour.
From Clayton and Morrison (1972).

TABLE 43

Reactive Carbohydrates Reported in Wheat Flour

Carbohydrate	Percent carbohydrate
Glucose	0.04
Fructose	Trace
Maltose	Trace
Sucrose	0.27
Raffinose	0.17

From MacKenzie (1958).

At this point the role of specific chemical classes on flour flavor will be expanded. Lipids will be discussed first. As can be seen from Table 41, unsaturated fatty acids comprise approximately 70% of the total wheat flour lipids. From a flavor standpoint this is quite interesting since, due to their unsaturation, these lipids are less stable when stored and processed. The most common decomposition products of unsaturated fatty acids are carbonyls which possess their own characteristic flavors or serve as precursors for other flavor related compounds.

Free fatty acids are another important class of lipids. In Table 42 free fatty acids are shown naturally present in wheat lipids, their level increasing from the decomposition of triglycerides upon storage. There was an approximate doubling in the amount of free fatty acids present as the result of room temperature storage for four months. Thus, free fatty acids can also contribute to the flavor of wheat flour.

The role of carbohydrates on wheat flavor will now be discussed. Most of the carbohydrate material in wheat is in the form of starch and contributes little to overall flavor. However, a small portion of the carbohydrate material does occur in more reactive forms. These are represented in Table 43.

TABLE 44

Changes in Wheat Carbohydrates as Affected by Storage Conditions

Carbohydrate	Air	Nitrogen	Carbon dioxide
Glucose	7*	24	23
Fructose	5	18	16
Galactose	3	9	9
Maltose	1	4	3
Sucrose	21	39	36

*Mg/10 g dry weight.
From Lynch et al. (1962).

TABLE 45

Influence of Milling and Baking on Amino Acid Composition

Amino acid	Wheat	Flour	Bread
Alanine	3.3	2.8	2.9
Arginine	4.7	3.8	3.6
Aspartic acid	5.1	4.1	4.6
Cystine	2.0	2.1	1.9
Glutamic acid	28.5	34.5	31.7
Glycine	3.9	3.2	3.2
Histidine	1.9	1.9	1.9
Isoleucine	3.9	4.3	4.3
Leucine	6.5	7.0	7.1
Lysine	2.7	2.1	2.5
Methionine	1.8	1.7	1.9
Phenylalanine	4.4	4.9	4.8
Proline	9.9	11.7	11.1
Serine	5.1	5.4	5.5
Threonine	3.0	2.8	3.0
Tryptophan	1.1	1.0	1.0
Tyrosine	3.1	3.3	3.3
Valine	4.5	4.5	4.7

*G/16 g nitrogen.
From Hepburn et al. (1957).

Reducing sugars such as glucose and fructose are quite reactive from a bread flavor precursor standpoint; their roles will be discussed in a later section. Although reducing sugars or their precursors are generally added during bread making, some are naturally present in wheat.

Storage of flour can influence the amount of available reactive sugars, especially with regard to non-enzymatic browning reactions (Table 44).

Storage under nitrogen and/or carbon dioxide protected the reactive carbohydrates, whereas under atmospheric conditions the levels of all reactive sugars decreased, probably due to their interaction in the formation of non-enzymatic browning compounds.

Various segments of protein composition influence wheat's flavor properties. Table 45 shows that the total amino acid composition undergoes various changes from wheat to bread.

Certain nitrogenous compounds, specifically peptides and free amino acids, are highly reactive, primarily as precursors in the formation of numerous volatile compounds during fermentation and baking. Few free amino acids can be found in the crust of bread due to their participation in non-enzymatic browning reactions. This can best be appreciated by viewing the free amino acid composition as influenced by various phases of bread production (Table 46).

Free amino acids in the original flour can serve as an important source of bread flavor precursor material.

Few data exist on the amount and types of short-chained peptides present in wheat flour. Since most flavor chemists agree that peptides generally have a disagreeable, astringent flavor, an interesting study would be to isolate and quantitate peptides in flour as influenced by storage and processing.

Another class of compounds that until recently received little attention is the simple phenolics associated with wheat flour. The simple phenolic acids reported to date in various wheat fractions are summarized in Table 47. Aside from free phenolic acids, bound forms are also present in wheat flour; when released, the total amount present approaches 150 ppm (Table 48).

The role of milling on free phenolic acid distribution has also been investigated and a portion of the data obtained with triticale is summarized in Table 49.

The bran fraction contained the highest level of free phenolics. However, approximately 75% of the original amount present in grain was found in the flour fraction. Similar results were obtained for wheat samples.

TABLE 46

Free Amino Acid Distribution During Various Phases of Bread Production

Amino acid(s)	Fraction				
	Flour	Unfermented dough	Fermented dough	Crumb	Crust
Alanine	14.34[a]	86.98	22.94	29.05	2.12
Arginine	2.11	6.66	15.30	11.43	Trace
Aspartic acid	14.17	60.53	14.91	10.92	0.83
Cystine	0.56	3.25	1.16	1.01	Trace
Glutamic acid	8.85	71.85	46.83	51.39	1.13
Glycine	4.08	11.74	10.43	12.43	0.84
Histidine	0.95	–	–	–	–
Isoleucine	4.13	6.60	1.58	3.07	0.52
Leucine	5.54	8.66	1.73	4.79	0.27
Lysine	2.39	32.31	25.53	12.76	Trace
Methionine	0.69	2.11	0.95	1.83	Trace
Phenylalanine	3.31	5.86	0.18	1.95	1.64
Proline	4.66	21.65	17.11	11.21	0.44
Serine and threonine	27.50	68.14	19.22	22.88	1.24
Tyrosine	3.12	5.99	0.49	1.09	–
Valine	6.83	16.15	4.60	6.41	0.62

a: μmol/100 g dry basis.
From El-Dash, 1971.

TABLE 47

Simple Free Phenolic Acids Reported in Wheat Fractions

Phenolic acid	Grain	Germ	Flour
p–Hydroxybenzoic acid	–	–	Maga and Lorenz (1973b)
Salicylic acid	–	–	Maga and Lorenz (1973b)
Vanillic acid	–	–	Maga and Lorenz (1973b)
p–Coumaric acid	El-Basyouni and Towers (1964)	–	Maga and Lorenz (1973b)
o–Coumaric acid		–	Maga and Lorenz (1973b)
Gentisic acid	–	–	Maga and Lorenz (1973b)
Iso-ferulic acid	–	–	Maga and Lorenz (1973b)
Ferulic acid	El-Basyouni and Towers (1964)	King (1962)	Maga and Lorenz (1973b)
Caffeic acid	–	–	Maga and Lorenz (1973b)
Protocatechuic acid	–	–	Maga and Lorenz (1973b)
Sinapic acid	–	–	Maga and Lorenz (1973b)
Syringic acid	–	King (1962)	Maga and Lorenz (1973b)
Iso-chlorogenic acid	–	–	Maga and Lorenz (1973b)
Chlorogenic acid	–	–	Maga and Lorenz (1973b)

TABLE 48

Free and Total Phenolic Acid Distribution in Wheat Flour

Phenolic acid	Amount present (ppm)	
	Free	Total
ρ–Hydroxybenzoic acid	5	6
Salicylic acid	4	4
Vanillic acid	15	39
ρ–Coumaric acid	17	23
o–Coumaric acid	7	8
Gentisic acid	3	4
Iso-ferulic acid	1	4
Ferulic acid	18	32
Caffeic acid	–	3
Protocatechuic acid	3	6
Sinapic acid	–	15
Syringic acid	5	5
Iso-chlorogenic acid	–	1
Chlorogenic acid	–	5

From Maga and Lorenz (1973b).

TABLE 49

Influence of Milling on Free Phenolic Acid Distribution in Triticale

Phenolic acid	Amount present (ppm)			
	Grain	Bran	Shorts	Flour
ρ–Hydroxybenzoic acid	14	17	15	10
Salicylic acid	7	12	5	5
Vanillic acid	40	50	42	35
ρ–Coumaric acid	40	37	40	36
o–Coumaric acid	10	21	12	8
Gentisic acid	5	12	7	3
Iso-ferulic acid	5	7	7	4
Ferulic acid	34	43	35	30
Caffeic acid	5	10	7	3
Protocatechuic acid	4	8	7	2
Sinapic acid	14	16	15	12
Syringic acid	7	8	6	5
Iso-chlorogenic acid	2	4	2	1
Chlorogenic acid	7	10	7	5

From Maga and Lorenz (1973b).

TABLE 50

Possible Flavor Contribution of Free Phenolic Acids Found in Wheat Flour

Phenolic acid	Taste threshold (ppm)*	Possible flavor contribution**
p–Hydroxybenzoic acid	40	–
Salicylic acid	90	–
Vanillic acid	30	+
p–Coumaric acid	40	(+)
o–Coumaric acid	25	(+)
Gentisic acid	90	–
Ferulic acid	90	–
Caffeic acid	90	–
Protocatechuic acid	30	–
Syringic acid	240	–

*From Maga and Lorenz (1973a).
**–: Present in amounts significantly below reported threshold.
(+): Present in amounts near reported threshold.
+: Present in amounts at or above reported threshold.
From Maga and Lorenz (1973b).

Phenolic compounds possess strongly astringent organoleptic properties; in most food systems they would be considered objectionable. Therefore, the data presented in Table 50 demonstrates that, due to the amounts found, certain phenolic acids can contribute to the flavor properties of wheat.

It should also be noted that these data do not consider the possibility of synergistic effects among the phenolic compounds, which would further lower their taste threshold levels.

In the case of corn, heating increased the amount of simple phenolic acids (Steinke and Paulson, 1964). It would be interesting to measure phenolic composition as influenced by baking procedures to determine if the amount of simple phenolic acids actually increases. If this were so, perhaps phenolic compounds play an influential role in the somewhat drying and astringent sensation noted in bread.

Considering the role cereal grains play in the world food chain, relatively few studies have been published dealing with the volatile flavor compounds associated with these products. In the case of wheat flour, the data summarized in Table 51 are presented.

The majority of the volatile compounds reported in wheat flour have also been reported present in bread. Wheat itself is a direct source for many of the flavor compounds found in bread. Naturally the levels found in the two products may not be comparable; because of this, factors such as fermentation and baking have traditionally been identified as primary sources of bread flavor components.

Regarding the influence of storage on the flavor properties of wheat flour, Fellers and Bean (1970) found that storage for up to six months even at room temperature decreased bread acceptability. Their data are shown in Table 52.

Shortening

Shortening is responsible for crumb tenderization, improved texture, loaf volume, and flavor (Baker and Mize, 1939). A brief report by Baker and Mize (1939) mentioned that minor flavor differences were noted when breads were baked with no shortening, ordinary shortening, mineral oil, and ordinary shortening plus mineral oil. No specific data were presented.

Using levels of 0, 3, and 5% shortening, King et al. (1937) reported that a panel preferred the odor and taste of bread baked with the highest shortening level. In fact, bread odor and taste preferences increased with increasing shortening levels.

Shortening may also affect bread flavor by serving as a precursor for the formation of highly flavorful carbonyl compounds during thermal breakdown while baking. Kleinschmidt et al. (1963) have proposed the use of 0.5% peroxidized oil, based on flour weight, as a means of increasing bread flavor. The procedure involved the formation of peroxidized soybean oil by the action of soybean lipoxidase to obtain a peroxide

TABLE 51

Volatile Compounds Reported in Wheat Flour

Compound	Reference
*Methanol	Hougen et al. (1971)
*Ethanol	Hougen et al. (1971)
*3-Methyl-1-butanol	McWilliams and Mackey (1969)
*1-Pentanol	McWilliams and Mackey (1969)
*Acetaldehyde	McWilliams and Mackey (1969)
	Hougen et al. (1971)
*Propanal	Hougen et al. (1971)
*2-Methylpropanal	McWilliams and Mackey (1969)
	Hougen et al. (1971)
*Butanal	McWilliams and Mackey (1969)
	Hougen et al. (1971)
*2-Methylbutanal	McWilliams and Mackey (1969)
*Pentanal	McWilliams and Mackey (1969)
	Hougen et al. (1971)
*Hexanal	McWilliams and Mackey (1969)
	Hougen et al. (1971)
*Heptanal	McWilliams and Mackey (1969)
	Hougen et al. (1971)
*Octanal	McWilliams and Mackey (1969)
*2-Butenal	McWilliams and Mackey (1969)
*Phenylacetaldehyde	McWilliams and Mackey (1969)
*2-Propanone	Hougen et al. (1971)
*2-Butanone	McWilliams and Mackey (1969)
	Hougen et al. (1971)
3-Methyl-2-butanone	McWilliams and Mackey (1969)
2,2-Dimethyl-3-pentanone	McWilliams and Mackey (1969)
*2,3-Butanedione	McWilliams and Mackey (1969)
Cyclopentanone	McWilliams and Mackey (1969)
*Ethyl acetate	McWilliams and Mackey (1969)

*Also reported in bread

TABLE 52

Influence of Wheat Flour* Storage on Bread Acceptability

Storage temperature (°F)	Storage time (months)	Panel liking bread (%)
0	1	75
0	3	70
0	6	80
70	1	78
70	3	78
70	6	69
90	1	69
90	3	80
90	6	50
100	1	64
100	3	68
100	6	28

*70 parts flour, 30 parts wheat protein concentrate.
From Fellers and Bean (1970).

TABLE 53

Influences of Fat Content on Bread Sensory Preferences

	Odor		Taste	
Fat (%)	Best (%)	Poorest (%)	Best (%)	Poorest (%)
0	15	56	14	64
3	35	24	34	20
5	50	20	52	15

From King et al. (1937).

TABLE 54

Influence of the Addition of Peroxidized Oil* on Bread Flavor

Peroxide content (%)	Bread flavor
< 0.02	No flavor
0.02–0.03	Slight flavor
0.03–0.04	Definite flavor
0.05–0.06	Strong flavor

*0.5% Enzyme-peroxidized oil added.
From Kleinschmidt et al. (1963).

TABLE 55

Influence of Salt Level on Its Sensory Detection in Bread

Percent salt compared*	No. in panel	No. correct (triangle test)
0% vs. 1.25%	43	39**
0.25% vs. 1.25%	42	32**
0.50% vs. 1.25%	42	34**
0.75% vs. 1.25%	42	18
1.0% vs. 1.25%	43	14

*Percent on weight of finished bread.
**Significantly different at 5% level.
From Collyer (1966).

value of 0.03 to 0.04%. This material was then added to the formulation and the resulting bread flavor was evaluated.

Peroxide values of less than 0.03% did not impart enough flavor, while additives having peroxide values of more than 0.04% resulted in an objectionable flavor. Thus, the lipoxidase enzymatically breaks down the unsaturated fatty acids of the soybean oil substrate resulting in the formation of flavorful volatile compounds.

Salt

It has been reported by Dunn (1947) that salt serves three main functions in a bread formulation. These include stabilizing fermentation, strengthening the gluten, and developing flavor. He also stated that the proper function of salt in most foods is not to make the product taste salty, but to develop and bring out the natural flavors of the product. Thus, salt in bread system serves mainly in a flavor potentiation role.

Using sensory panel techniques Collyer (1966) determined panel sensitivity and salt level preferences in white bread. Some of these data are summarized in Table 55.

Although no data are presented to substantiate the fact, the author stated that there was a strong preference for the bread containing 1.25% salt based on the weight of the baked product. With this level serving as the control it was found that the untrained panel was able to significantly detect differences in salt levels of from 0 to 0.5% salt when compared to the control. However, no significant difference in flavor was detected when levels of 0.75 and 1.0% salt were compared to the 1.25% level. Therefore, it appears that when consumers are given a comparative choice, they prefer the higher salt level (1.25%). However, statistically no significant difference in flavor due to salt was detected when approximately half the control salt level was used.

An interesting project would be to analytically evaluate flavor extracts using gas-liquid chromatography of breads made from doughs having varying salt levels. It seems unlikely that salt could actively enter into a chemical reaction to form flavor compounds. However, salt may affect compound volatility by affecting the vapor of the product.

TABLE 56

Influence of Yeast on the Thermal Properties of Baking Bread

	Temperature (°F)	
Minutes of Baking	No yeast	Fermented
2	102	102
4	122	122
6	143	141
8	163	158
10	188	172
12	207	188
14	211	198
16	212	205
18	212	210
20	212	212

From Baker (1957).

Yeast

Yeast can influence bread flavor if excessively high levels are used: a characteristic yeast flavor will predominate in the final product. Numerous pure and mixed yeast cultures were obtained from commercial sources by Wardall (1910) and the resulting bread quality, including flavor, evaluated. No attempt was made to identify the yeasts present in the mixed cultures, but they generally produced bread of better flavor than pure strain yeasts.

Baker (1957) presented some interesting data which are summarized in Table 56.

He demonstrated that in an indirect manner yeast can influence bread flavor. The product containing no yeast culture achieved a higher temperature in a shorter period of time during baking as compared to bread containing yeast. For example, in the no-yeast product a temperature of 212°F was achieved in 16 min, whereas in the yeast containing bread, a temperature of 212°F was not obtained until after 20 min of baking. From a thermally induced flavor standpoint, yeast could tend to retard flavor formation. The difference in temperature between the two products was explained as follows: the gas formed from the yeast addition had an insulating effect, which caused the temperature to rise slower. Perhaps it would be interesting to study and evaluate the influence of various levels of yeast on thermally produced bread flavor in conjunction with the rate of temperature rise during baking. It is possible that from a total flavor standpoint, lower levels of yeast would result in greater amounts of thermally induced bread flavor components.

Markianova et al. (1971) prepared breads using a variety of hybrid yeasts, then compared the amount of volatile flavor compounds found against a compressed yeast control. Their data are summarized in Table 57.

All of the yeast hybrids they evaluated produced more total volatiles than the compressed yeast control. However, they concluded that all of the yeast hybrids produced bread of inferior sensory properties. The organoleptic properties of the bread made from the conventional yeast were described as pleasant, probably due to the presence of greater amounts of specific compounds such as valeraldehyde. Another possible explanation for this preference is that trace and measurable amounts of two unknown compounds were found in the hybrid yeast samples but not in the compressed yeast control. Also, perhaps the total volatile level was highly concentrated enough to make the aroma objectionable.

Bacterial Additions

The possible application of specific bacterial cultures in modifying or improving bread flavor was proposed by Fornet (1951) and investigated by Robinson et al. (1958a). They postulated that the proper amount of bacteria capable of producing short-chain organic acids would enhance bread flavor. Various pre-ferments were prepared and the total and individual bacterial populations determined. Total bacterial

TABLE 57

Influence of Yeast Hybrids on Bread Carbonyl Composition

	Mg/100 g of product				
	Yeast hybrid				Compressed
Compound	203	196/6	202	14	yeast
Methylglyoxal	0.008	0.003	0.002	0.008	0.008
Glyoxal	0.021	0.025	0.007	0.012	0.031
Acetaldehyde	0.063	0.027	0.025	0.009	0.016
Propionaldehyde	0.001	0.001	0.001	0.002	0.004
Isobutyraldehyde	0.009	0.009	0.003	0.004	0.007
Acrolein	0.012	0.032	0.014	0.013	0.021
Acetone	0.017	0.036	0.024	0.018	0.027
Butyraldehyde	0.041	0.027	0.019	0.008	0.013
Isovaleraldehyde	0.005	0.006	0.003	0.003	0.002
Methyl ethyl ketone + diacetyl	0.015	0.021	0.015	0.003	0.012
Valeraldehyde	0.051	0.043	0.041	0.029	0.091
Caproaldehyde	0.043	0.036	0.030	0.023	0.047
Ethyl propyl ketone	0.004	0.011	0.009	0.007	0.011
Unknown	Trace	Trace	0.003	0.005	–
Unknown	Trace	Trace	0.003	0.001	–
Benzaldehyde	3.518	2.973	3.922	3.519	2.960
Oxybenzaldehyde	1.914	1.641	1.441	1.620	1.627
Phenylacetylaldehyde	0.148	0.206	0.209	0.124	0.166
Furfural	2.235	2.105	2.178	2.037	1.627
Total	8.10	7.20	7.95	7.45	6.67

From Markianova et al. (1971).

populations in pre-ferments were found to increase slightly for up to two hours of incubation; to decrease with 2 to 6 hr of incubation; and again to increase after 6 hr. This study also demonstrated that the majority of the 65 different aerobic microorganisms originated from the yeast, both in number and quantity, and that the microflora present in the flour was vastly different in the pre-ferment. The most common genera isolated from the pre-ferments included *Micrococcus, Aerobacter, Proteus, Bacillus* and *Lactobacillus*. Some of the typical odor descriptions of breads baked with specific microorganisms are summarized in Table 58.

They concluded that the best flavored product resulted from the use of *Lactobacillus bulgaricus 09* or *L. Bulgaricus 09*, plus a buttermilk culture. The use of certain microorganisms evaluated in this study may have application in the production of novelty bread items such as cheese-flavored bread.

To explain the bacterial population decrease noted by Robinson et al. (1958a) during incubation of pre-ferments, Robinson et al. (1958b) measured variables such as acid and alcohol production. During this study they isolated two inhibitory substances that they postulated were elaborated by the yeast during fermentation. No positive identifications of these inhibitory substances were made.

The possible role that bacteria play on the formation of carbonyl compounds in dough fermentation was investigated by Kohn et al. (1961). they used dough containing a normal bacterial load and a specially treated low-bacteria dough. Their data are summarized in Table 59.

Data indicated that bacterial count has no effect on carbonyl composition of dough. It would have been interesting to compare carbonyl levels as influenced by dough bacterial levels after baking. As Robinson et al. (1958a) pointed out, bacteria can act as a good source of organic acids which when baked interact to form carbonyls.

The relatively nonsignificant role of added bacteria on bread flavor was also demonstrated by Linko et al. (1962a). They measured the amounts of certain carbonyls found in both the resulting pre-ferments and fermentation gases (Table 60).

They concluded that the addition of *Pediococcus cerevisiae* resulted in the formation of vast amounts of acetone.

TABLE 58

Odor Descriptions of Bread Baked With Added Microorganisms

Microorganism added	Odor description of fresh bread
Standard loaf pre-ferments:	
Aerobacter aerogenes	Similar to standard
Bacillus coagulans	Stronger than standard
Bacillus laterosporus	Slightly stronger than standard
Lactobacillus plantarum	Strong, like fermentation
Micrococcus caseolyticus	Strong, like fermentation
Lactobacillus leichmannii	Mild, like fermentation
Lactobacillus casei	Mild, like fermentation
Aged sponge dough:	
Lactobacillus fermenti	Mild, like standard
Lactobacillus casei	Mild, like standard
Lactobacillus brevis	Cheese-like
Lactobacillus bulgaricus	Cheese-like
Lactobacillus plantarum	Cheese-like
Lactobacillus lactis	Strong, not acceptable

From Robinson et al. (1958a).

TABLE 59

Influence of Dough Bacterial Count on Carbonyl Concentration

Carbonyl (s)	Normal dough*	Low-bacteria dough**
2-hexanone and hexanal	246 ppm	263 ppm
Acetaldehyde	33	15
Butyraldehyde	22	25
Isovaleraldehyde	24	22
Acetone	70	49

*52×10^6 bacteria/g of dough.
**1,200 bacteria/g of dough.
From Kohn et al. (1961).

TABLE 60

Influence of Added Bacteria on Carbonyl Production in Bread Fermentation Gases

Species added	Formaldehyde	Acetaldehyde	Propanal+ 2-propanone	Butanol+ 2-methylpropanal	Pentanal + 3-methylbutanal+ 2-methylbutanal
Control	21*	460	41	63	39
P. *cerevisiae*	36	490	1010	94	84
L. *bulgaricus*	27	510	51	63	39
S. *thermophilus*	27	500	41	49	29
A. *aerogenes*	27	490	41	49	29
S. *diacetilactic*	36	490	41	57	32
B. *brevis*	Trace	430	39	54	49
L. *plantarum*	Trace	560	41	60	36

*Mg/100 ml of pre-ferment.
From Linko et al. (1962a).

TABLE 61

Influence of Added Protease Enzyme Levels on Total Carbonyl Compound Production in Bread Crust

	Mg carbonyl/100 g bread crust	
Protease level (H.U.) /700 g flour	Papain	Rhozyme J-25
0	17.92	17.99
75	22.25	19.81
150	35.10	20.52
300	32.37	23.96
500	35.15	23.94
700	18.49	23.38
1,000	14.35	23.49

From El-Dash and Johnson (1967).

Enzyme Additions

El-Dash and Johnson (1967) postulated that induced proteolysis of wheat proteins during sponge fermentation would provide additional free amino groups, which could react in turn with reducing sugars to form a more flavorful bread product. Levels of 0 to 1,000 hemoglobin units (H.U.)/700 g of flour of papain and Rhozyme® J-25 were used, and various flavor related parameters measured. For example, the levels of water-soluble nitrogen in fermented doughs were measured and it was found that papain was quite effective in forming water-soluble compounds. In fact, it was so effective that at the higher levels of incorporation, the dough turned to a liquid mass. Thus, they were able to demonstrate that protease enzymes can increase the amount of reactive amino groups in a fermentation system.

Another variable measured was the effect of enzyme addition on crust color. To a certain enzyme addition level, crust color did darken, indicating a more reactive flavor system. However, at higher levels, especially with papain, crust color actually lightened. This happened because at the higher papain levels, loaf volume decreased to the point that the crusts were below the top edge of the baking pans. The total carbonyl levels in the bread crust were measured and these data are summarized in Table 61.

Papain at a level up to 500 H.U./700 g of flour increased total crust carbonyl content to approximately twice that of the non-enzyme control, and then the carbonyl level dramatically decreased. Rhozyme J-25 increased total crust carbonyl levels to a lesser degree, but the carbonyl level was maintained even at the highest levels of addition.

Protease type was also found to influence the levels of specific carbonyls formed. The predominant carbonyl produced from papain addition was propanal, while in the case of Rhozyme J-25, heptanal was predominant. Neither enzyme influenced the amount of formaldehyde formed. Limited sensory data are presented reporting that neither enzyme affected the taste of bread, yet the aroma of the bread containing 150 H.U./700 g of flour was significantly different from the nonenzyme control. El-Dash and Johnson concluded that the carbonyl concentration affected the aroma of bread, but not its taste. Throughout the study no data were presented concerning possible crumb flavor differences.

Roiter and Borovikova (1972) evaluated the volatile compounds of bread crumb and crust prepared with the addition of 0.001% of the enzyme preparation Amylorisin Pox to the dough. they concluded that bread prepared with this enzyme additive had better aroma and flavor properties than a control bread prepared without the enzyme addition. In Table 62 no qualitative differences were apparent.

They found that enzyme application increased volatile carbonyl compound concentration 2.3-fold in the crumb and 3.2-fold in the crust. Aliphatic compounds associated with the enzyme treated product increased 9 and 15 times in the crumb and crust, respectively.

Sugars

Sugar amount and source can affect the sensory properties of bread in several ways. For example, as shown in Table 63, sugar amounts can influence the formation rate of specific flavor related compounds

TABLE 62

Influence of Enzyme Addition to Dough on Carbonyl Compounds in Bread

	Mg/100 g of specific volume			
	With enzyme		No enzyme	
Compound	Crumb	Crust	Crumb	Crust
Methylglyoxal	0.16	0.28	0.06	0.06
Glyoxal	0.16	0.14	0.01	0.01
Acetaldehyde	0.17	0.47	0.04	0.06
Propionaldehyde	0.01	0.07	Trace	Trace
Isobutyraldehyde	0.01	0.13	0.01	0.01
Acrolein	0.04	0.07	0.01	0.04
Acetone	0.09	0.23	0.01	0.09
Butyraldehyde	0.01	0.18	0.01	0.01
Isovaleraldehyde	0.01	0.08	Trace	Trace
Unknown	0.04	0.36	Trace	Trace
Methyl ethyl ketone	0.02	0.04	Trace	Trace
Diacetyl	0.04	0.05	Trace	Trace
Valeraldehyde	0.25	0.46	0.02	0.03
Caproaldehyde	0.22	0.24	0.01	0.01
Ethyl propyl ketone	0.07	0.20	Trace	Trace
Furfural	6.35	18.30	2.62	4.70
Benzaldehyde	0.65	0.94	0.29	0.50
Oxybenzaldehyde	5.20	3.50	2.95	2.75
Phenylacetylaldehyde	0.90	1.66	0.14	0.30
Total	14.40	27.40	6.15	8.45

From Roiter and Borovikova (1972).

TABLE 63

Influence of Sugar Level and Fermentation Time on Acetoin Formation in Bread Dough

	Mg acetoin/150 g dough Hours			
Sugar (%)	1	2	3	4
0	1.9	0.8	0.2	0.1
2	2.0	2.5	1.9	1.1
5	2.1	3.9	3.5	2.6

From Visser't Hooft and de Leeuw (1935).

during fermentation by providing an energy source for yeast activity, which is influential in flavor compound formation.

Sugar sources vary in their ability to form thermally induced flavor compounds as demonstrated in Table 64.

Certain disaccharides such as sucrose, if not completely hydrolyzed and utilized during fermentation, are capable of forming relatively high levels of flavor compounds.

Aside from flavor contributions, sugars can also influence crumb and crust color. Ponte et al. (1963) demonstrated that adding pentosans had a detrimental effect on bread color, even though they were substituted at levels equivalent to more commonly used sugars. An approximate doubling in crust thickness was also noted when pentosans such as arabinose and xylose were included (Table 65).

To better understand the role of sugars in fermentation and bread flavor (Table 66), the levels of sugars as influenced by fermentation have been studied by Lee et al. (1959).

TABLE 64

Influence of Sugar Types on Carbonyl Composition in Bread Crust

Carbonyl (s)	Fructose	Galactose	Glucose	Lactose	Maltose	Raffinose	Sucrose	Xylose
Formaldehyde	1.3*	1.4	1.1	1.1	1.1	1.2	1.2	2.1
Acetaldehyde	2.1	3.5	2.3	2.2	2.2	2.0	2.1	2.0
Acetone + Propanal	15.1	15.9	8.4	10.8	19.4	18.9	20.9	7.4
Isobutyraldehyde + Methyl ethylketone	0.3	0.7	0.4	0.4	0.3	0.2	0.2	0.2
Isovaleraldehyde + valeraldehyde + 2-methylbutanal + hexanal	2.8	3.3	2.7	2.7	2.4	2.6	2.8	3.2

*mg/100 g dry matter
From Linko and Johnson (1963).

TABLE 65

Influence of Added Pentosans on Bread Color and Crust Thickness

Carbohydrates added	Crumb color	Crust color	Crust thickness (mm)
5.5% Glucose	Creamy white	Golden brown	2
3.0% Glucose + 2.5% arabinose	Dull	Chestnut	5
3.0% Glucose + 2.5% xylose	Dull	Chestnut	5.5
8.0% Glucose	Greamy white	Chestnut	2.5
3.0% Glucose + 5% arabinose	Dull	Dark chestnut	5
3.0% Glucose + 5% xylose	Dull	Dark chestnut	5.5

From Ponte et al. (1963).

TABLE 66

Changes in Sugar Concentrations in Sponges, Doughs and Breads as Influenced by Fermentation Time*

System	Fermentation time (min.)	Glucose (%)	Fructose (%)	Maltose (%)
Sponge	4	0.30	0.46	1.11
	90	0.11	0.32	1.24
	180	0.00	0.00	0.24
	235	0.00	0.00	0.05
Dough	6	0.12	0.14	0.28
	30	0.09	0.10	0.25
	90	0.00	0.00	0.14
Bread	–	0.00	0.00	0.28

*No sugar added in formulation.
From Lee et al. (1959).

TABLE 67

Influence of Added Sugars on Sugar Concentrations as Influenced by Fermentation Time in Doughs and Breads

System	Sugar added (5%)	Fementation time	Percentage found		
			Glucose	Fructose	Maltose
Dough	Glucose	6	2.70	0.10	0.38
		30	2.60	0.14	0.36
		90	1.75	0.12	0.20
Bread		–	1.53	0.10	0.15
Dough	Fructose	6	0.19	2.74	0.45
		30	0.17	2.45	0.34
		90	0.11	2.20	0.16
Bread		–	0.10	1.66	0.10
Dough	Sucrose	6	1.55	1.52	0.47
		30	1.46	1.45	0.40
		90	1.18	1.37	0.19
Bread		–	0.98	1.21	0.18
Dough	Maltose	6	0.08	0.12	2.56
		30	0.08	0.13	2.22
		90	0.00	0.00	2.08
Bread		–	0.00	0.00	1.79

From Lee et al. (1959).

When no sugar was added to the formulation, they found that glucose and fructose were absent in bread. These monosaccharides were not present in dough after approximately 90 min of fermentation, probably because they were utilized by yeast. Maltose was still present in the dough after 90 min of fermentation and its level actually increased during baking. Based on these data, no glucose or fructose were available for thermal reaction.

When five percent of various sugars were added, they found that approximately half of the sugar remained after only 6 min of fermentation. Added residual sugars were also found in the bread (Table 67).

Since carbohydrates and amino acids react readily to form a wide variety of compounds, some highly pigmented, Rubenthaller et al. (1963) measured their reactivity based on their ability to darken bread crust (Table 68).

They added equimolar concentrations of either glycine, lysine or glutamic acid to breads, along with carbohydrates representative of pentosans, hexoses, disaccharides and trisaccharides. Of the three amino acids, glutamic acid was found to be the least active.

In a similar study Linko and Johnson (1963) added various amino acids to bread and measured the resulting amino acid composition of both crumb and crust (Table 69).

As expected, crust amino acid levels, independent of sugar incorporated, were quite low when compared to the crumb portions.

Protein Additions

The methods and merits of fortifying bread with protein are not the subject of this review; it should be sufficient to say that the majority of proposed additives have certain detrimental sensory effects on bread quality. Flour substitution levels above 15% are not common. The data reported by Kim and de Ruiter (1968), as shown in Table 70, explain the situation (Table 70).

TABLE 68

Influence of Equimolar Concentrations* of Carbohydrates and Amino Acids on Bread Crust Color

Carbohydrate	Amino Acid			
	None	Glycine	Lysine	Glutamic Acid
None	41.0**	27.0	34.5	44.5
Pentoses				
Arabinose	15.5	13.0	11.5	14.0
Ribose	15.0	11.0	10.5	12.5
Xylose	15.5	11.0	10.0	13.0
Hexoses				
Galactose	17.5	10.5	11.5	13.0
Glucose	21.5	14.5	15.0	23.0
Levulose	20.0	14.0	14.0	21.0
Mannose	19.5	14.5	14.5	19.5
Sorbose	16.0	11.0	11.0	14.0
Rhaminose	23.0	15.0	14.0	18.5
Disaccharides				
Cellobiose	20.0	14.0	10.5	17.0
Lactose	17.0	11.0	10.5	15.5
Melibiose	15.5	11.0	10.0	15.0
Sucrose	21.5	15.5	14.0	17.0
Maltose	25.0	18.0	16.0	21.0
Trehalose	31.0	22.5	25.5	35.0
Trisaccharides				
Melezitose	26.0	20.5	18.0	21.0
Raffinose	21.5	10.0	9.0	10.5

*Glycine 0.2 g and hexoses 2 g.
**The higher the number, the lighter the color.
From Rubenthaller et al. (1963).

TABLE 69

Influence of Sugar Type on Selected Amino Acid Composition in Bread Crumb and Crust

Sugar	Aspartic Acid		Glutamic Acid		Alanine		Isoleucine + leucine	
	Crumb	Crust	Crumb	Crust	Crumb	Crust	Crumb	Crust
Arabinose	3.0*	0.7	2.8	0.8	1.8	0.9	0.7	0.3
Cellubiose	3.0	0.2	4.0	1.0	1.5	0.6	0.3	0.1
Fructose	3.4	0.2	4.4	0.9	1.2	0.4	0.2	0.1
Galactose	3.6	1.4	3.6	1.2	1.4	0.8	0.3	0.1
Glucose	3.6	0.8	5.2	1.6	1.4	0.6	0.4	0.1
Lactose	3.6	0.6	2.8	0.7	1.6	0.8	0.4	0.1
Maltose	4.6	0.8	2.8	0.5	1.6	0.6	0.4	0.1
Mannose	4.2	0.6	4.0	1.2	1.4	0.5	0.3	0.1
Melibiose	3.4	0.5	2.8	0.4	1.5	0.8	0.2	0.1
Raffinose	4.2	0.4	4.0	0.9	1.5	0.5	0.2	0.1
Rhamnose	4.4	1.0	3.0	0.6	2.0	1.2	0.4	0.1
Sorbose	5.8	0.6	2.8	0.4	1.7	0.5	0.4	0.1
Sucrose	3.8	0.4	4.4	0.9	1.5	0.5	0.2	0.1
Xylose	7.0	0.6	3.2	0.2	2.8	0.8	0.8	0.1

*Mg/100 g dry matter.
From Linko and Johnson (1963).

TABLE 70

Sensory Properties of Protein Supplemented Non-wheat-based Breads*

Protein additive	Crumb color	Taste description
Low-fat peanut	Rather white	Good, fairly neutral
Whole fish	Gray-green	Somewhat fishy
Torula	Ochre yellow	Spoiled fish
Cottonseed	Greenish yellow	Fairly good
Lipoprotein	Light gray	Fairly good
Peanut proteinate	Light gray	Fairly good
Defatted peanut	Grayish brown	Good, malt-like
Full-fat soy	Lemon yellow	Fairly good, neutral
Enzymatic soy	Grayish cream	Salty, fairly good
Defatted soy	Grayish cream	Fairly neutral, good
Soy proteinate	Rather white	Good, neutral
Flaked sesame	Rather white	Fairly good
Defatted coconut	Gray	Bad
Coconut concentrate	Light gray	Coconut Taste
Low-fat sesame	Light gray	Good
Low-fat safflower	Dirty gray	Spicy

*Yam flour base.
From Kim and de Ruiter (1968).

TABLE 71

Effect of Casein and Gliadin Additions on Bread Odor and Taste

Additive*	Sample location	Sensory property	Triangle test level of significance**	Panel preference
Casein	Crumb	Odor	0.05	6 Control, 3 casein
Gliadin	Crumb	Odor	0.01	9 Control, 1 gliadin
Gliadin	Crumb	Taste	0.01	7 Control, 2 gliadin
Gliadin	Crust	Taste	0.05	5 Control, 4 gliadin

*Level was 1.22g/100 g of dough.
**Compared to no-additive control.
From Wick et al. (1964).

These data are for non-wheat-based products, and the color imparted by most additives detracts from their use. The other major sensory limitation is the resulting flavor; some protein additives can be highly detrimental from a flavor standpoint.

Most common bread formulations have a protein additive incorporated. Usually this additive is dry milk solids; traditionally, the use of dry milk solids has been promoted because of their functional and sensory contributions. Specifically, the use of dry milk solids results in a finished product with better flavor and color.

Wick et al. (1964) reported on the odor and taste of bread to which 1.22 g of either casein (milk protein) or gliadin (corn protein) was added to 100 g of dough (Table 71).

In all cases the panel preferred the sensory properties of the controls baked without additives. Although protein additions were at a level closely approximating the protein level if dry milk solids were used, significant differences in preferences were noted. In the case of dry milk solids the lactose present can significantly contribute to flavor properties associated with bread.

Amino Acid Additions

Some nutritionists have suggested that the fortifying of bread with certain amino acids, especially lysine,

would be a significant advance in improving the nutritional value of bread products. In 1959 Ehle et al. reported on the taste properties of white bread, cake, and donuts to which varying amounts of lysine monohydrochloride were added. They reported the taste threshold concentration of the lysine additive in white bread was 0.5 g/100 g of flour. This concentration was approximately double the level recommended from a nutritional improvement standpoint. In the case of donuts, which had ingredients such as vanilla, cinnamon, and nutmeg added, taste threshold levels approached 1.5 g/100 g of flour. At concentrations above taste threshold panel members described the product as tasting salty, bitter or having a peculiar aftertaste. The characteristic lysine taste was most pronounced in the crust. At the recommended supplementation level this group reported no significant difference in taste between lysine fortified and unfortified breads, either in the crust or crumb.

A major disadvantage of adding lysine was that it had a dramatic crust-browning effect which would certainly influence acceptability of the product. The authors suggested longer baking time at a lower temperature to overcome this problem. However, a slowdown in the baking process might be resisted because of economic considerations. A minor reservation about this study is that the amount of lysine remaining in the product was not measured. If baking losses are considered, perhaps higher levels of lysine would be required to satisfy nutritional requirements; the higher levels might more closely approximate taste threshold levels in the product. For example, Rosenberg and Rohdenburg (1951) reported that lysine losses in white bread ranged from 9.5 to 23.8%, the average loss as a direct result of baking being approximately 15%. They reported that toasting resulted in another 10 to 15% loss of lysine and staling brought about another 5 to 10% loss. Similar results on lysine destruction due to baking were obtained by McDermott and Pace (1957); they found minimal lysine losses in the crumb, whereas lysine loss in the crust approximated 15%. Pomeranz (1962) found minimal lysine losses in bread crumb ranging from 2 to 10% depending on the type of flour utilized. Lysine destruction in bread crust can be critical, especially in bread products that have a large crust area to crumb area, such as rolls. The problem is also complicated since if additional lysine is added to compensate for baking losses, objectionable flavors and colors may result.

Zentner (1961) reported on using lysine to improve the crust color of certain flour types normally producing bread with pale, greyish crust. In this study lysine was not added for nutritional considerations, but because it would react with reducing sugars to form desirable pigment products.

In addition to their nutritional value, free amino acids can also influence bread flavor and color. The possibility that certain amino acids may be useful as bread flavor enhancers was appreciated by various groups investigating bread flavor. For example, Wiseblatt and Zoumut (1963) reported on the aroma properties from the interaction of numerous amino acids with dihydroxyacetone (Table 72).

They concluded that the reaction of the amino acids proline, isoleucine and serine resulted in bread related aromas.

A similar approach to bread flavor was reported by Morimoto and Johnson (1966); they reacted various amino acids with glucose. Their observations are shown in Table 73.

They likewise observed a bread-like aroma from the reaction of proline. Other amino acids judged to possess bread-like aromas included aspartic acid, alanine, leucine, isoleucine and valine.

Earlier, Wick et al. (1964) had evaluated bread odor and taste properties after the direct addition of 100 mg of certain amino acids to 100 g of dough. In most cases, the panel preferred the sensory properties of the control breads containing no amino acid additions. One exception was proline; the panel statistically preferred the odor of the proline additive product. No difference in flavor preference was noted between the proline product and a control with no amino acid added (Table 74).

The use of amino acids as bread flavor precursors will be discussed in a later section.

Rooney et al. (1967) expanded earlier reports on the role of amino acids in bread flavor by measuring levels of carbonyl compounds formed in a model system through the interaction of amino acids and glucose (Table 75).

Proline reacted to form relatively low levels of volatile carbonyls in relation to some of the more reactive amino acids. Thus, degree of reactivity may not be critical, but proper individual, as well as total, concentrations could be the key to desirable bread flavor.

Their model system work was expanded (Table 76) to include a starch paste system.

The most significant difference between this table and the previous one was that quantities detected

TABLE 72

Aromas Resulting from the Action of Amino Acids and Dihydroxyacetone

Amino acid	Resulting aroma
Proline	Very strong, crackers, crust, toast
Lysine	Strong, dark corn syrup
Valine	Strong, yeasty, protein hydrolysate
Alanine	Weak, caramel
Glutamic acid	Moderate, chicken broth
Aspartic acid	Very weak
Arginine	Very weak
Cysteine	Mercaptan, hydrogen sulfide
Hydroxyproline	Weak, like proline
Phenylalanine	Very strong, hyacinth
Leucine	Strong, cheesy, baked potato
Isoleucine	Moderate crust
Serine	Weak, vaguely like bread
Threonine	Very weak
Methionine	Baked potato
Glycine	Baked potato
Histidine	Very weak

From Wiseblatt and Zoumut (1963).

TABLE 73

Aroma Properties Resulting from the Reaction of Glucose and Amino Acids

Amino acid reacted	Resulting aroma
Serine	Moderate
Glutamic acid	Moderate
Hydroxyproline	Weak
Aspartic acid	Strong, breadcrust
Tyrosine	Weak
Alanine	Moderate, breadcrust
Arginine	Weak
Isoleucine	Moderate, breadcrust
Valine	Moderate, breadcrust
Tryptophan	Strong
Histidine	Moderate
Proline	Strong, breadcrust, cracker
Threonine	Weak
Cystine	Strong, hydrogen sulfide
Methionine	Strong, baked potato
Glycine	Moderate
Phenylalanine	Strong, flower
Lysine	Weak
Leucine	Moderate, breadcrust

From Morimoto and Johnson (1966).

TABLE 74

Effect of Amino Acid Additions on Bread Odor and Taste

Additive – level	Location	Property	Level of Significance*	Preference
Alanine 100 mg/100 g dough	Crust	Odor	< 0.001	18 Control, 8 alanine
Alanine 100 mg/100 g dough	Crust	Taste	< 0.001	16 Control, 9 alanine
Arginine 100 mg/100 g dough	Crumb	Odor	0.01	11 Control, 10 arginine
Histidine 100 mg/100 g dough	Crumb	Taste	0.05	8 Control, 5 histidine
Proline 100 mg/100 g dough	Crumb	Odor	0.05	4 Control, 13 proline
Proline 100 mg/100 g dough	Crust	Odor	0.001	7 Control, 15 proline
Proline 100 mg/100 g dough	Crust	Taste	0.001	12 Control, 11 proline
Leucine 50 mg/100 g dough	Crumb	Odor	0.03	2 Control, 1 leucine
Valine 100 mg/100 g dough	Crust	Odor	0.01	16 Control, 3 valine
Valine 100 mg/100 g dough	Crust	Taste	0.03	15 Control, 2 valine

*Compared to no-additive control.
From Wick et al. (1964).

were dramatically reduced in the latter system. The variation in volatile compounds produced among all amino acids evaluated was quite small in the starch paste system.

Because free amino acids are flavor reactive, estimates of free amino acid levels as influenced by the baking process have been made. As seen in Table 77, and discussed previously, flour can serve as a free amino acid source.

Adding yeast and mixing resulted in a 300% increase in the amount of free amino acids. However, as fermentation progressed the level was approximately halved. Thermal reactions account for the low amount of free amino acids remaining in bread crust.

The same general trend was reported by El-Dash (1971) for specific free amino acids (Table 78).

TABLE 75

Carbonyl Formation from Glucose-Amino Acid Interactions in a Model System

Amino acid	Mg compound formed				
	Formaldehyde	Acetaldehyde	2-Propanone	2-Methylpropanal	3-Methyl butanal
None	0.40	0.16	0.08	–	–
Glycine	0.60	2.06	0.56	0.34	0.30
Alanine	0.48	13.72	0.95	1.26	0.29
Valine	0.82	3.16	4.93	40.1	4.08
Leucine	0.79	2.13	2.00	1.32	82.3
Isoleucine	0.73	2.64	1.75	2.64	79.0**
Glutamic acid	0.15	1.41	0.45	0.37	–
Histidine	0.18	0.59	0.47	0.29	–
Lysine	0.30	1.88	0.98	0.51	0.40
Arginine	0.30	0.88	1.24	0.36	–
Phenylalanine	0.56	2.19	0.85	–	6.28***
Tryptophan	0.39	2.11	6.08	1.32	0.30
Proline	0.09	0.68	0.34	0.23	–
Methionine	0.59	7.60*	2.09	0.63	0.59

*Includes methional.
**2-Methylbutanal.
***Includes Phenylacetaldehyde.
From Rooney et al. (1967).

TABLE 76

Carbonyl Formation from Glucose and Amino Acid Interactions in a Starch Paste System

Amino acid	Formaldehyde	Acetaldehyde	2-Propanone	2-Methylpropanal	3-Methylbutanal
None	0.03	0.01	0.05	0.09	–
Glycine	0.06	0.33	0.14	0.28	0.16
Alanine	0.06	0.87	0.25	0.34	0.23
Valine	0.08	0.45	0.26	3.15	0.32
Leucine	0.07	0.27	0.18	0.43	1.36
Isoleucine	0.04	0.32	0.14	0.26	5.29***
Glutamic acid	0.06	0.28	0.16	0.24	0.29
Histidine	0.06	0.29	0.12	0.26	0.06
Lysine	0.05	0.44	0.15	0.31	0.21
Phenylalanine	0.06	0.43*	0.18	0.14	0.15
Proline	0.03	0.33	0.14	0.25	0.16
Arginine	0.04	0.29	0.14	0.26	0.10
Methionine	0.09	0.06**	0.21	0.27	0.19

*Includes phenylacetaldehyde.
**Includes methional.
***2-Methylbutanal.
From Rooney et al. (1967).

Measurable amounts of the free amino acid lysine were lacking in bread crust.

As mentioned previously, free amino acids can also influence crust color. This is apparent from data in Table 79.

Adding any amino acid darkened crust color. Certain amino acids, such as methionine and arginine, were highly reactive in the presence of glucose. The range of darkening with xylose as the carbohydrate source was smaller than with glucose, but xylose alone initially produced a darker crusted product than did glucose used alone.

TABLE 77

Total Free Amino Acid Content in Various Bread Systems

System	Free amino acids (mg/100 g)
Flour	13
Unfermented dough	52
Fermented dough	23
Unfermented bread crumb	37
Fermented bread crumb	22
Unfermented bread crust	13
Fermented bread crust	2

From El-Dash and Johnson (1970).

TABLE 78

Influence of the Baking Process on the Free Amino Acid Content

Amino acid (s)	Flour	Unfermented dough	Fermented dough	Bread crumb	Bread crust
Alanine	14.3*	87.0	23.0	29.1	2.1
Arginine	2.1	6.7	15.3	11.4	Trace
Aspartic acid	14.2	60.5	14.9	10.9	0.8
Cystine	0.6	3.3	1.2	1.0	Trace
Glutamic acid	8.9	71.9	46.8	51.4	1.1
Glycine	4.1	11.7	10.4	12.4	0.8
Histidine	1.0	–	–	–	–
Isoleucine	4.1	6.6	1.6	3.1	0.5
Leucine	5.5	8.7	1.7	4.8	0.3
Lysine	2.4	32.3	25.5	12.8	Trace
Methionine	0.7	2.1	1.0	1.8	Trace
Phenylalanine	3.3	5.9	0.2	2.0	1.6
Proline	4.7	21.7	17.1	11.2	0.4
Serine and threonine	27.5	68.1	19.2	22.9	1.2
Tyrosine	3.1	6.0	0.5	1.1	–
Valine	6.8	16.2	4.6	6.4	0.6

*μmol/100 g dry basis.
From El-Dash (1971).

TABLE 79

Influence of Amino Acid and Sugar Additions on Crust Color (% Reflectance)

Amino acid	Glucose	Xylose
None	30.3*	21.8
Glycine	18.5	12.2
Alanine	19.5	14.5
Valine	22.2	15.0
Leucine	20.0	13.8
Isoleucine	21.8	18.0
Glutamic acid	19.0	17.5
Histidine	17.0	10.6
Lysine	17.6	12.2
Phenylalanine	18.3	12.0
Proline	23.5	18.5
Arginine	8.5	–
Methionine	7.0	–

*The smaller the number, the darker the color.
From Salem et al. (1967).

TABLE 80

Influence of Dough Absorption on Bread Preferences

Dough absorption	% Water	% Preference*	% Preference*	% Preference**
Stiff	56	39	72	59
Normal	62	31		
Slack	68	30	28	41

*Tested 24 hr after baking.
**Tested 72 hr after baking.
From Cathcart (1937).

TABLE 81

Effect of Dough Mixing Time on Crust Color and Flavor

Mixing time	Crust color	Flavor
Slightly mixed	Light, gray	Raw dough, flour
Mixed to optimum	Brown	–
Overmixed	Full, deep brown	Full, rich

From Baker et al. (1953).

Absorption

One could reason that the percent of water absorption in bread dough could affect final bread flavor by influencing the crumb and crust temperature of the baking bread. For example, a dough having a low absorption would heat more rapidly, attaining a higher crust temperature since there would be less water to evaporate from the system. Likewise, a dough with high absorption would heat more slowly, and the amount of thermally induced flavor compounds would be lower.

In Cathcart's (1937) report, a sensory panel studied the influence of absorption on baked bread (Table 80).

In one series of this study the percent of water added created stiff, normal and slack doughs that were evaluated for bread preference. Thirty-nine percent of the panel preferred the bread made from the stiff dough. When only stiff and slack doughs were compared, the majority of the panel (72%) preferred the stiff dough product. The influence of storage time was also evaluated with regard to degree of absorption; after 72 hr of storage, 59% of the panel still preferred the lower absorption product. The water absorption of dough had a definite effect on bread flavor; the panel selected the product with the least absorption which should have been the most flavorful.

Mixing

Baker et al. (1953) reported that mixing time can influence the crust color and flavor of bread (Table 81).

They observed that undermixing resulted in a light gray crust and raw dough flavor, whereas overmixing produced a full, deep, brown color and a full, rich flavor. With undermixing, the ingredients are not fully dispersed and conditions are not optimum for color and flavor formation. The opposite is true for an overmixed dough; more chemical breakdown has occurred, which enhances the flavor.

Mixing is a critical function in bread production and much research has been devoted to evaluating mixing techniques. For example, Fortmann (1959) evaluated various mixing techniques and their effects on the amount of carbonyls found in bread crumb. His data are summarized in Table 82.

This was the era when much controversy existed concerning the flavor quality of conventional vs continuous mix bread. Fortmann (1959) found that the continuous mix product had approximately half the crumb carbonyl level as conventional mix bread. No data were presented comparing the crust carbonyl

TABLE 82

Influence of Type of Mixing on Carbonyl Content in Bread Crumb

Mixing – additive	mg/g crumb
Conventional bread	0.096
Continuous mix	0.041
Continuous mix + oxidized lard	0.244
Laboratory bread – open mixer	0.044
Laboratory bread – oxygen mix	0.084
Laboratory bread – oxygen mix + lipoxidase	0.120

From Fortmann (1959).

TABLE 83

Influence of Fermentation Technique and Time on Acetoin Production in Bread Dough

Mg acetoin/150 g flour

Fermentation technique	Hour				
	1	2	3	4	5
Straight-dough	2.5	1.5	0.6	0.3	–
Sponge-dough	0.0	0.0	0.0	1.1	3.2

From Visser't Hooft and de Leeuw (1935).

TABLE 84

Influence of Fermentation Temperature and Time on Acetoin Formation in Bread Dough

Mg acetoin/150 g dough

Fermentation temperature (°F)	Hours			
	1	2	3	4
77	0.2	1.3	3.4	2.5
86	2.0	2.5	2.2	1.1
96	2.0	0.0	0.1	0.2

From Visser't Hooft and de Leeuw (1935).

levels in the two products. He demonstrated quite dramatically that crumb carbonyl level could be greatly changed by the type of mixing employed. The use of oxygen and lipoxidase during mixing resulted in the highest crumb carbonyl level.

Fermentation Procedures

Until recently fermentation was considered one of the key stages in the proper development of desirable bread flavor. However, there are indications that fermentation can be minimized, or even eliminated. Historically, the straight- and sponge-dough methods of fermentation have been used for the batch production of bread. An early study demonstrated that the levels of certain bread flavor related compounds could be influenced by the fermentation method employed (Table 83).

For example, if the straight-dough process were used, acetoin levels gradually decreased as fermentation time increased; in sponge-doughs acetoin did not appear until after four hours of fermentation. The same study also pointed out the importance of fermentation temperature and time on acetoin production (Table 84).

With a temperature of 77°F, acetoin production was slow, peaking after three hours of fermentation. With an intermediate fermentation temperature of 86°F, acetoin production reached its maximum after two hours. At a temperature of 96°F, peak production was achieved in one hour.

King et al. (1937) also evaluated the sensory properties of bread as influenced by fermentation temperature (Table 85).

They found that both the odor and taste of bread fermented at 86°F was preferred to bread fermented at 78°F. Presumably, the higher fermentation temperature resulted in more characteristic bread flavor.

The role of fermentation time on total organic acid and carbonyl levels was investigated by Cole et al. (1962) (Table 86).

No organic acids were detected at the beginning of fermentation, but their level dramatically increased after one to two hours. The level of organic acids continued to rise gradually through the remaining time. In

TABLE 85

Influence of Fermentation Temperature on Bread Sensory Properties

Fermentation temperature (°F)	Odor		Taste	
	Best (%)	Poorest (%)	Best (%)	Poorest (%)
86	58	42	57	43
78	42	58	43	57

From King et al. (1937).

TABLE 86

Influence of Fermentation Time on Total Acid and Carbonyl Concentration

Fermentation time (hr)	Total organic acids*	Total carbonyl compounds**
0	0.00	2.8
1	0.04	11.0
2	0.69	20.0
3	0.91	24.0
4	0.91	23.0
5	1.10	21.7
6	1.25	19.3

*Meq sodium hydroxide to neutralize acids in 50 ml pre-ferment.
**μmol acetophenone/l pre-ferment.
From Cole et al. (1962).

TABLE 87

Influence of Fermentation Method on the Odor and Taste of Bread

Test	Method of mixing	Odor		Taste	
		Best (%)	Poorest (%)	Best (%)	Poorest (%)
1	Straight dough	51	49	42	57
2	Straight dough	37	62	27	72
1	Sponge	49	51	57	42
2	Sponge	62	37	72	27

From King et al. (1937).

the case of carbonyls, there was a gradual rise in concentration through three hours of fermentation and then the level gradually dropped for the remaining time.

King et al. (1937) evaluated the odor and taste preferences of bread made from the straight- and sponge-dough procedures (Table 87).

They presented data from two separate tests. In the case of odor, no clear-cut preference was noted in one test, whereas in the other series, the odor of bread prepared by the sponge process was preferred. In both taste tests a definite preference for the sponge process product resulted.

Slightly different results (Table 88) were obtained in a much later study by Jackel and Ersoy (1961).

When straight- and sponge-dough processes were compared, the fermentation aromatics and acids resulting from the straight-dough procedure were judged more intense than those observed from the sponge-dough process.

TABLE 88

Influence of Fermentation Method on the Sensory Properties of Bread

	Sensory property		
Fermentation method	Fermentation aromatics	Fermentation acids	Yeasty taste
Straight dough	4*	4	4
Sponge dough	3	3	4

*Intensity scale from 0 to 4.
From Jackel and Ersoy (1961).

TABLE 89

Influence of Fermentation Time on Acid Production in Pre-ferments

Fermentation time (hr)	Lactic acid	Acetic acid
2	65*	15
4	70	35
8	80	40
16	100	50
24	130	50

*Mg/100 ml of pre-ferment.
From Johnson et al. (1958).

Johnson et al. (1958) also found that acid production (lactic and acetic) increased as fermentation time increased. Over the rather extended fermentation times studied, lactic acid concentration increased approximately twofold and that of acetic acid threefold (Table 89).

Linko et al. (1962b) compared the carbonyl composition in the crust and crumb of bread prepared by four different fermentation methods (Table 90).

In the crust portion, the total carbonyl level was highest in bread produced by the sponge method (29.8 mg/100 g) and lowest in the no-time fermentation method (21.7 mg/100 g). In the crumb portion the highest total carbonyl levels was found using the pre-ferment method, while the lowest level was associated with the straight-dough fermentation method.

The interaction of fermentation time on free amino acid distribution is summarized by the work of Morimoto (1966) in Table 91.

For most free amino acids there was a decrease, or actual disappearance, after six hours of fermentation. However, the free glycine level was found to increase.

The exact role of fermentation in relation to certain volatile carbonyls (Table 92) was measured by El-Dash and Johnson (1970).

Varied results were obtained, dependent on individual compounds. In most cases concentrations increased, but the concentrations of several major compounds decreased. These data were complicated because crust was evaluated and losses due to volatility may not have been considered (Table 93).

A similar study was performed by Roiter and Borovikova (1971), except fewer compounds were evaluated and only the exact influence of fermentation was measured. Again, the concentration of most compounds measured increased.

The importance of fermentation on final bread flavor has been seriously questioned by numerous researchers. Their main argument is that although the concentration of a compound has been found to develop or increase due to fermentation, there is no definite evidence that its presence in bread can be directly related to bread flavor. This philosophy is especially common among proponents of shortened or

TABLE 90

Influence of Fermentation Technique on Carbonyl Production

Carbonyl(s)	Fermentation Method							
	Straight		Sponge		No-time		Pre-ferment	
	Crust	Crumb	Crust	Crumb	Crust	Crumb	Crust	Crumb
Formaldehyde	0.99*	0.20	0.98	0.20	0.86	0.17	1.02	0.14
Acetaldehyde	2.20	0.32	2.17	0.35	1.65	0.29	1.82	0.35
Acetone + propionaldehyde	12.8	0.75	17.1	0.85	10.7	0.81	15.6	2.11
Iso-butyraldehyde + methyl ethyl ketone	0.82	0.14	0.97	0.15	1.47	–	0.70	0.23
Iso-valeraldehyde + valeraldehyde + 2-methylbutanal + hexaldehyde	2.02	0.51	1.60	0.76	1.18	0.86	3.23	0.62
Furfural	0.16	–	0.34	–	0.31	–	0.04	–
Hydroxymethylfurfural	3.19	0.65	6.65	0.72	5.43	0.59	3.29	0.56
Total carbonyl compounds	22.2	2.6	29.8	3.0	21.7	2.8	25.7	4.0

*Mg/100 g.
From Linko et al. (1962b).

TABLE 91

Influence of Fermentation Time and Baking on Free Amino Acid Content

Free amino acid(s)	Dough		French-type bread	
	0 Hour	6 Hour	Crumb	Crust
Aspartic acid	0.55*	0.05	0.07	0.03
Threonine and serine	1.08	0.13	0.18	0.07
Glutamic acid	0.58	0.11	0.28	0.10
Proline	0.08	0.10	0.13	0.08
Glycine	0.17	0.26	0.32	0.14
Alanine	1.08	0.07	0.18	0.08
Valine	0.21		0.05	0.02
Methionine	0.04	0.01	0.01	0.002
Isoleucine	0.10		0.03	0.01
Leucine	0.14	0.04	0.05	0.02
Tyrosine	0.08		0.02	0.005
Phenylalanine	0.09		0.02	0.008
Tryptophan	0.30	0.05	0.03	0.02
Lysine	0.13	0.11	0.18	0.08
Arginine	0.14	0.10	0.06	0.05

*μm/g (dry basis).
From Morimoto (1966).

no-time fermentation methods. The author feels that this attitude is somewhat unrealistic because if this assumption were expanded to include the flavor properties of other food systems, few data would be valid today.

Sensory data have shown that acceptable bread products can be made using abbreviated mixing and fermentation techniques. For example, Butterworth (1935) reported that unless cut drastically, fermentation time had little influence on the resulting odor and flavor of bread. It should be noted that his data represented the totaled scores of five judges.

TABLE 92

Influence of Fermentation on Carbonyl Content of Bread Crust

Compound(s)	Unfermented crust	Fermented crust
Ethanal	37.4*	27.0
Propanal	21.6	21.6
2-Propanone + 2-methylpropanal	26.9	30.0
Unknown	15.6	17.4
Butanal	Trace	0.5
2-Butanone	53.2	29.1
2-Methylbutanal + 3 methylbutanal	1.4	1.1
Unknown	1.1	1.3
Pentanal	0.7	0.8
2-Methylpentanal	8.4	9.9
Hexanal	4.6	4.8
Furfural + hydroxymethylfurfural	14.2	16.1

*mol/100 g.
From El-Dash and Johnson (1970).

TABLE 93

Influence of Fermentation on the Levels of Certain Carbonyls

Compound	Mg/100 g of specific volume	
	Before fermentation	After fermentation
Furfural	1.12	1.70
Benzaldehyde	2.28	4.80
Oxybenzaldehyde	0.80	1.07
Phenylacetylaldehyde	0.15	0.06

From Roiter and Borovikova (1971).

Cornford (1962), using duo-trio sensory methods, reported no statistical difference in flavor intensities between breads fermented for 3 or 18 hr using bulk fermentation, as these breads were compared to breads made by the Chorleywood process, which utilizes intense mechanical mixing in place of bulk fermentation. He also reported that bread made from conventionally mixed dough undergoing no fermentation had the same flavor intensity as normally fermented bread. However, flavor was judged only on the basis of intensity; possible differences in overall flavor impression or perception were not mentioned.

Collyer (1966) also reported on the sensory properties of breads made by using various fermentation techniques. For example, she evaluated crumb flavor differences in brew-bread and conventional bulk-fermented bread as influenced by storage. These data are summarized in Table 94.

She reported a significant difference in flavor between the two fermentation methods. She also concluded that freshness had no significant effect on preference influenced by fermentation method.

The same fermentation methods were used to evaluate the crumb and crust portions of bread stored for 16 hr. When crumb and crust portions were evaluated independently, no significant differences in flavor were noted. However, it was pointed out that a trend toward preference for the bulk-fermented bread was noted (Table 95).

The odor properties of freshly baked laboratory bread fermented by the bulk and Chorleywood processes were compared, and in four out of five triangle tests performed no significant flavor difference was noted.

A further flavor evaluation regarding storage influence was performed comparing three hour commercially bulk-fermented bread with Chorleywood process bread (Table 96).

TABLE 94

Influence of Fermentation Method and Time on Bread Preference

Bread age (hr)	Triangle test significance	Preference		
		Brew bread	Control	No preference
4	Significant 5% level	7	10	5
28	Significant 5% level	9	12	0

From Collyer (1966).

TABLE 95

Influence of Fermentation Method on Crumb and Crust Bread Preferences

Portion – fermentation methods compared	Triangle test significance	Preference		
		Brew bread	Bulk	No preference
Crumb-brew vs. bulk	Not significant at 5% level	3	10	2
Crust-brew vs. bulk	Not significant at 5% level	4	7	1

From Collyer (1966).

TABLE 96

Flavor Comparisons of Breads Prepared by Various Fermentation Methods

Fermentation method compared	Storage time (hr)	Triangle test significance	Preference		
			Bulk	Chorleywood	No preference
Bulk vs. Chorleywood	6	Not significant at 5%	4	0	5
Bulk vs. Chorleywood	30	Not significant at 5%	7	10	2

From Collyer (1966).

These data indicated that no significant difference in flavor was detected; it was concluded that the chemical products of yeast fermentation are not of prime importance in dictating bread flavor.

A Canadian group has also reported similar results, i.e. mechanically developed bread was not significantly distinguishable in aroma and taste from bread fermented by the traditional sponge-dough method (Table 97).

However, it should be noted that the formulations used incorporated high protein flours (12.8 to 16.0%). This factor would tend to minimize any flavor differences.

Proofing

The amount of time permitted for a product to proof could influence its flavor since proofing can be considered an extension of fermentation. An early study by Cathcart (1937) bears out this assumption (Table 98).

TABLE 97

Aroma and Flavor Comparisons of Bread as Influenced by Fermentation Method

Sensory property	Age of bread	Triangle test significance	Preference		
			Sponge-and dough	Mechanical development	No preference
Aroma	2	Not significant at 5%	11	4	1
Aroma	20	Not significant at 5%	5	5	6
Taste	20	Not significant at 5%	11	3	4

From Kilborn and Tipples (1968).

TABLE 98

Influence of Proof Time on Bread Preference

Proof time	% Preference
25 min underproofed	40
Normal proof time	60
25 min overproofed	38
Normal proof time	62

From Cathcart (1937).

TABLE 99

Influence of Proofing on Organic Acid Content in Dough and Bread

System	Meq. total acids
Dough, not proofed	10.1
Dough, proofed	11.8
Bread	13.1

From Cole et al. (1963).

TABLE 100

Influence of Proofing on Volatile Alcohol Content in Dough and Bread

System	Ml. volatile alcohols
Dough, not fermented	1.74
Dough, fermented	2.80
Bread	1.00

From Cole et al. (1963).

TABLE 101

Influence of Proofing on Total Carbonyl Content in Dough and Bread

System	Mmol. total carbonyls
Dough, not proofed	2.3
Dough, proofed	2.8
Bread	3.8

From Cole et al. (1963).

The panel expressed a strong preference for products that were proofed for a normal period of time over products that were either over- or underproofed. With overproofing, harsh flavors develop; with underproofing, a full bread flavor is lacking.

Cole et al. (1963) attempted to demonstrate the changes influenced by proofing in specific classes of bread flavor compounds. In addition, they measured these same compound classes after baking. In this way the relative importance of bread flavor formation up to the proofing step in bread production was shown in relation to the actual baking step.

In the case of organic acids (Table 99), they reported that proofing increased the level by approximately 17% over that of a no-proof control.

However, baking was found to increase the total organic acid level 30% over a no-proof control. Although proofing increased organic acid levels, the effect of the actual baking process was more influential.

When the volatile alcohol content was measured (Table 100), again proofing was found to increase the overall concentration, in this case by approximately 60% over that of the no-proof control. However, as would be expected, the baking process resulted in a significant decrease in the amount of alcohols, probably due to volatility.

Proofing resulted in an approximate increase of 20% in the total amount of carbonyls measured (Table 101).

TABLE 102

Influence of Proofing on the Levels of Certain Carbonyls

Compound	Mg carbonyl 100 g of product	
	Before proofing	After proofing
Furfural	1.70	1.76
Benzaldehyde	4.80	4.88
Oxybenzaldehyde	1.07	4.25
Phenylacetylaldehyde	0.06	0.13

From Roiter and Borovikova (1971).

However, carbonyl content increased 65% due to baking when compared to the no-proof control. It can be appreciated that proper proofing can be important to the overall flavor of bread.

In a later study, Roiter and Borovikova (1971) followed the change in concentration of four specific flavor compounds as influenced by proofing. This information is summarized in Table 102.

There was an increase in concentration for all compounds. In some cases the increase was four fold (oxybenzaldehyde). The exact reasoning following changes in composition of such compounds as furfural and benzaldehyde, predominantly formed under thermal conditions, was not discussed.

Loaf Size

It is well established that the temperature rise within a dough mass during baking is a direct function of oven temperature and the size of dough mass (Bailey and Munz, 1938). It is also known that the interior temperature of a dough mass will not exceed the boiling point of water, but within the crust, much higher temperatures are attained. This is especially true after most of the evaporation cooling effect has subsided. For thermal flavor formation the conditions are ideal, especially in the crust. The importance of dough size on its thermal properties is explained in Figure 4.

Dough from the same batch was made into three different size loaves (regular 510 g; pup 200 g; micro 40 g) and proofed to height before baking under the same conditions. Just before baking, thermocouples were carefully inserted into the center and immediately below the surface of the loaves. The temperature rise was obtained for five different bakes with a recording potentiometer. These values were averaged to form Figure 4. The temperature rise was most rapid with the micro loaves and least rapid with the regular sized product. For example, it took 5 min for the micro loaf crumb to reach 180°F, while the pup loaf required 12 min and the regular loaf 18 min to reach the same temperature. The smaller dough masses underwent more extensive thermal treatments, which theoretically could result in increased flavor formation.

In this same study crust weights were averaged; for the regular, pup and micro loaves the weights were 17.4, 20.6 and 29.1%, respectively. From this standpoint the smaller loaf sizes could also be expected to contain more flavor compounds.

Rothe (1971) evaluated the influence of loafsize on the levels of certain compounds present in the crumb and crust of rye bread (Table 103).

Significantly higher levels of ethanol were found in the crumb than in the crust. This was expected due to its volatility. The opposite was found for furfural and hydroxymethylfurfural, which would verify their thermally induced formation. Regarding loaf size, conflicting data are presented. For example, although one would expect the smaller loaf to contain higher levels of the heat induced compounds, the opposite was reported. No explanation was offered for this apparent discrepancy.

Type of Oven

Another factor that could influence bread flavor is the type of oven used. Presumably this is due to the efficiency differences in the heating and heat retention rates of various ovens. If bread were baked in two different ovens for the same amount of time, sensory differences could be apparent. In a study appearing in

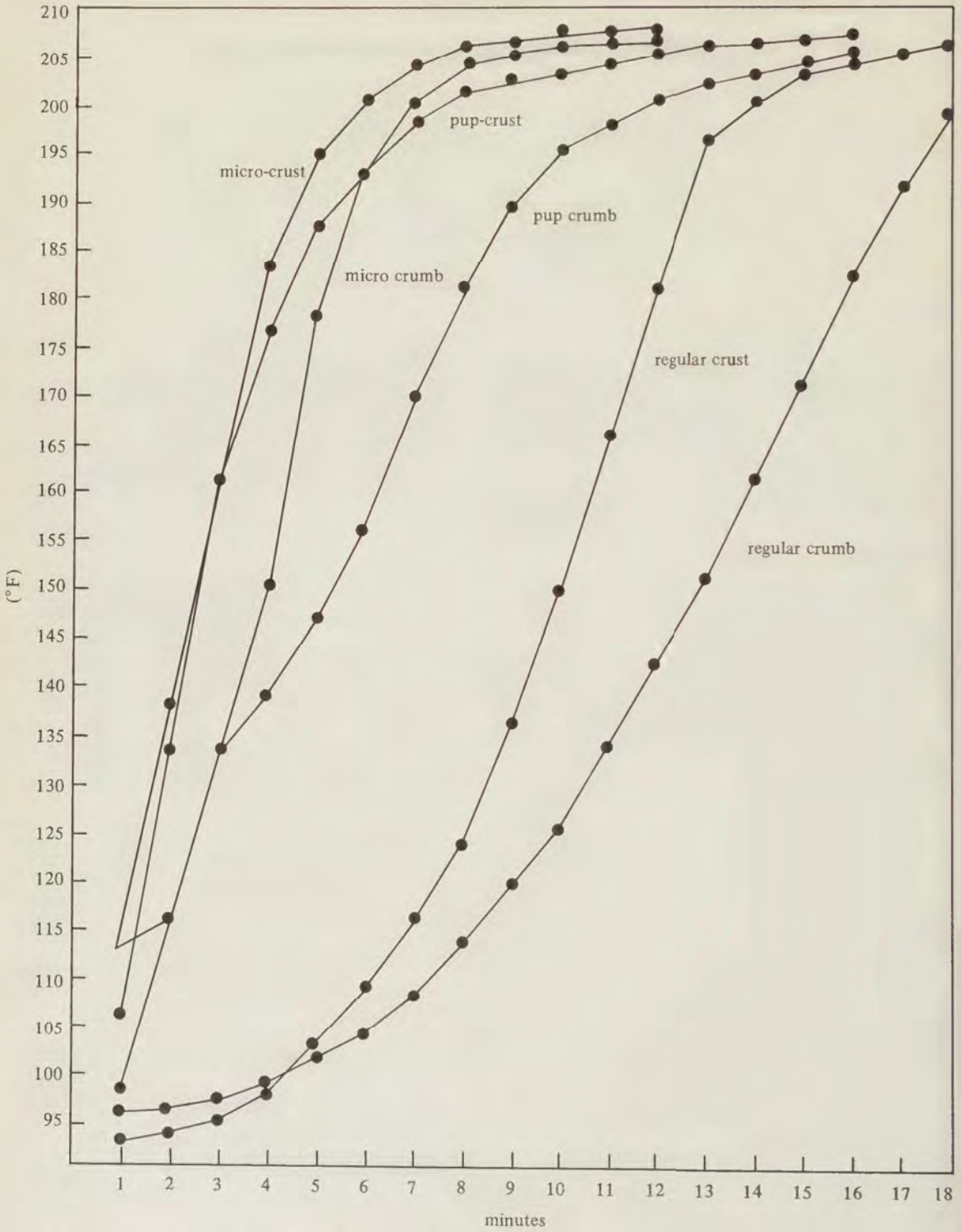


FIGURE 4. Influence of loaf size on the thermal properties of baking bread. (From Maga (unpublished data)).

TABLE 103

Influence of Loaf Size on the Flavor Compound Composition (ppm) in Rye Bread

Compound	Crust		Crumb	
	3.0 kg loaf	1.5 kg loaf	3.0 kg loaf	1.5 kg loaf
Furfural	25	12	0.7	0.3
Hydroxymethyl furfural	660	370	18	18
Isopentanal	27	20	1.6	1.1
Ethanol	890	630	3870	3350

From Rothe (1971).

TABLE 104

Effect of Oven type, Temperature, Baking and Time on Relative Carbonyl Composition

Compound	Type of oven-time-temperature			
	Grate (150-200 °C)		Steam-tube drawplate (180 °C)	Traveling tray (230-270 °C)
	60 min	80 min	56-60 min	48 min
Methylglyoxal	1*	1	1	1
Hydroxymethylfurfural	1	1	1	1
Furfural	2	3	3	2
Not identified		1	1	1
Formaldehyde	2	3	3	2
Diacetyl	1	1	1	1
Methional	3	2	3	2
Acetaldehyde	3	2	3	2
Phenylacetaldehyde	1	1	1	1
Propenal	1	1	1	1
Butenal	1	1	1	1
Acetone + propanal	3	2	3	2
Butanal	1	1	2	2
Methylpropanal	1	1	1	1
2-Methylbutanal	3	2	3	3
3-Methylbutanal	3	2	3	3
Pentanal	3	3	3	2
Methylpentanal	3	2	3	2
Hexanal	3	1	3	2
2-Hexanone	2	1	2	2
2-Heptanone	2	1	2	1
Octanal	2	1	2	1
Decanal	2	1	1	1
Dodecanal	2	1	1	1

*1: Small; 2: medium; 3: large.
From Hrdlicka and Honischova (1967).

the foreign literature (Hrdlicka and Honischova, 1967) blends of wheat and rye flour (60/40) were used for bread baked in three different types of ovens operated at various temperatures. The resulting breads were analyzed for volatile carbonyl compounds and for their sensory properties. The relative intensities of the compounds found are summarized in Table 104.

The same compounds are identified in all breads but ratios of individual compounds varied. The authors'

TABLE 105

Odor and Flavor Properties of Bread as Influenced by Oven Type and Time of Baking

Oven type	Baking time (min)	Oven temp. (°C)	Odor rating	Flavor rating	Odor of crumb
Grate	60	203	3*	3	Acid-aromatic
Grate	80	106	3	3	Acid-aromatic
Grate	60	215	4	3	Acid-aromatic
Grate	80	172	3	3	Acid-aromatic
Steam-tube drawplate	56	180	3	3	Slightly acid-agreeable
Traveling tray	48	230-270	2	3	Slightly acid

*0: Disagreeable; 5: excellent.
From Hrdlicka and Honischova (1967).

TABLE 106

Influence of Baking Temperature on Bread Sensory Properties

	Odor		Taste	
Baking temperature (°F)	Best (%)	Poorest (%)	Best (%)	Poorest (%)
450	31	69	35	65
425	69	31	65	35

From King et al. (1937).

interpretation of these data was that bread baked in the grate-type oven had a well-balanced composition of volatile compounds. As expected, baking in the grate-type oven for longer periods of time decreased the relative amounts of certain volatile compounds. The steam-tube draw-plate oven, which is similar in construction to the grate-type oven, produced similar results. In the case of the traveling-tray oven, an inferior product, one with an unbalanced ratio of volatile compounds, resulted. They concluded that ovens with lower heat favored more desirable bread flavor.

The odor and flavor properties of these breads were also judged on a six point scale ranging from zero, for strong and disagreeable, to five for excellent. Some of these data are summarized in Table 105.

These data indicate that no differences in the flavor rating were detected. The grate-type oven, in one instance, produced bread with a superior odor, while the traveling-tray oven's product had an inferior odor. Perhaps an expert panel would be able to detect minor sensory property differences due to oven type, which is purely academic. In a normal commercial operation the manufacturer has control over baking time and temperature, which are probably more important to final bread flavor than the oven used.

Baking Time and Temperature

Knowledge of heat's influence on bread flavor has established that baking time and temperature can definitely influence the sensory properties of bread. However, as shown by King et al. (1937) in Table 106, higher baking temperatures are not always preferable.

They found that 69% of the panel preferred the odor, and 65% preferred the taste, of the bread baked at the lower temperature. Actually, the lower temperature used in this study was close to a normal baking temperature; the panel may have been influenced by this factor. Perhaps higher baking temperatures than normal can result in excessive loss of pleasing volatile compounds and in the formation of bitter flavor complexes.

The influential role of baking time can be appreciated by viewing data obtained by Rothe (1966) with rye bread crust and summarized in Table 107.

TABLE 107

Influence of Baking Time on Carbonyl Composition (mg%) and Crust Properties in Rye Bread Crust

	Baking time (min)		
Crust thickness (mm)	30 / 1	50 / 3	70 / 4.5
Sensory properties	mild, pleasing	slightly bitter	very bitter
Compound			
Acetaldehyde	0.95	1.56	1.89
2-Methylpropanal	0.02	0.19	0.70
2-Oxypropanal	0.60	1.00	1.30
2-Methylbutanal	0.50	2.03	3.60
2-Furaldehyde	0.33	0.74	1.67

From Rothe (1966).

TABLE 108

Influence of Baking Time on the Composition of Flavor Components in Rye Bread

Baking time (min)	Crust thickness (mm)	Crust furfural (ppm)	Crust acetaldehyde (ppm)	Crumb ethanol (ppm)
30	2.7	5.4	16.3	2900
40	3.2	9.8	18.5	2600
50	3.7	15.2	21.0	2350
60	4.1	18.5	22.7	2300
70	4.6	21.7	26.2	2300

From Rothe (1971).

The overall sensory properties became more objectionable as baking time increased from 30 to 70 min. Levels of the five compounds evaluated also increased with additional baking time. In the case of 2-methylpropanal, the level increased 35 times when baking time was extended from 30 to 70 min. A compound that can have pleasing sensory properties at low concentrations can become quite objectionable at higher concentrations. Another point brought out in this study was the dramatic increase in crust size because of increased baking time.

Similar data were presented by Rothe (1971); his study dealt with the influence of baking time on the composition of certain compounds in the crust and crumb of rye bread (Table 108).

Increasing baking time from 30 to 70 min resulted in approximately four times the furfural in the crust. As expected the amount of ethanol in the crumb decreased, due to volatility.

A detailed study dealing with the changes baking time caused in carbonyl composition was reported by Borovikova and Roiter (1971d). As can be seen from Table 109, no qualitative changes were observed.

Quantitative changes, however, were quite dramatic. For example, the total carbonyl concentration in the crumb dropped from a high of 13.4 mg/100 g of product to approximately half this amount after 55 min of baking. From this it would appear that the thermal production of carbonyls is not prevalent in the formation of bread crumb flavor. Data presented for individual crumb compounds indicated that most compounds were being volatilized, or destroyed, as baking time increased. For bread crust they reported a gradual increase in total carbonyl content as baking time increased, primarily due to the thermal formation of compounds. It is somewhat surprising that more dramatic differences were not found in the crust considering the wide range in baking times evaluated. Perhaps volatility was quite important; after a certain amount of time of the volatiles were lost to the atmosphere.

TABLE 109

Influence of Baking Time on Carbonyl Content of Crumbs and Crust

	Mg carbonyl 100 g of product							
	Crumb Baking time				Crust Baking time			
Compound	15	30	45	55	15	30	45	55
Methylglyoxal	0.05	0.02	0.09	0.05	0.08	0.12	0.11	0.04
Glyoxal	0.17	0.07	0.33	0.39	0.85	0.72	0.86	0.46
Acetaldehyde	5.25	1.93	1.98	0.65	1.43	0.93	0.07	0.07
Propionaldehyde	0.03	0.03	0.02	0.01	0.01	0.01	0.01	0.01
Isobutyraldehyde	0.11	0.04	0.04	0.02	0.12	0.04	0.04	0.02
Acrolein	0.07	0.04	0.13	0.05	0.23	0.16	0.18	0.09
Acetone	0.14	0.07	0.17	0.08	0.17	0.21	0.10	0.09
Butyraldehyde	0.08	0.06	0.15	0.06	0.16	0.15	0.09	0.05
Isovaleraldehyde	0.06	0.02	0.01	0.01	0.06	0.04	0.04	0.01
Unknown	–	0.01	0.06	0.01	0.01	0.03	0.01	0.06
Methyl ethyl ketone	0.02	0.01	0.03	0.02	0.04	0.01	0.01	0.05
Diacetyl	0.05	0.01	0.06	0.02	0.05	0.70	0.01	0.05
Valeraldehyde	0.29	0.08	0.06	0.02	0.87	0.77	0.68	0.39
Caproaldehyde	0.24	0.08	0.49	0.14	0.43	0.49	0.41	0.16
Ethyl propyl ketone	0.04	0.04	0.04	0.02	0.11	0.12	0.09	0.03
Furfural	1.80	0.55	0.43	0.82	1.42	1.90	2.16	5.30
Benzaldehyde	0.89	0.44	0.29	0.82	0.90	1.55	4.50	5.60
Oxybenzaldehyde	4.00	4.60	3.46	2.68	6.92	7.80	6.80	4.55
Phenylacetylaldehyde	0.10	0.08	0.05	0.14	0.20	0.80	1.26	1.35
Approx. Total	13.4	8.17	8.43	6.21	14.04	16.55	17.42	18.30

From Borovikova and Roiter (1971c).

TABLE 110

Influence of Freshness on Bread Preference

Age (hr)	% Preference
4	40
12	60
4	43
24	57
4	62
48	38
12	81
24	19
12	68
48	32

From Cathcart (1937).

Storage Conditions

The aroma and flavor of bread changes rapidly after baking. Both manufacturer and consumer continually search for bread products that have a lasting, desirable fresh-baked flavor.

Several early investigators demonstrated that storage has a detrimental effect on the sensory properties of bread. In the five sets of data reported by Cathcart (1937), three sets clearly demonstrated the harmful effect of storage on bread acceptance (Table 110).

TABLE 111

Influence of Bread Freshness on Bread Sensory Preferences

	Odor		Taste	
Age in hr	Best (%)	Poorest (%)	Best (%)	Poorest (%)
12	47	22	44	20
24	22	38	30	34
48	31	40	25	46

From King et al. (1937).

TABLE 112

Influence of Storage on Volatile Content in Breads

	V.R.S.* meq	
Product	Fresh	24 Hours
Rye bread	114	4.6
White bread A	179	6.3
White bread B	275	4.4

*Volatile reducing substances.
From Farber (1949).

TABLE 113

Influence of Storage on the Sensory Properties of Bread*

	Sensory properties		
Hours after baking	Fermentation aromatics	Fermentation acids	Yeasty taste
1	4.0**	4.0	4.0
12	2.0	3.5	4.0
24	0.5	3.1	4.0
48	0.25	3.0	4.0

*Made by the straight-dough procedure
**Intensity scale from 0 to 4.
From Jackel and Ersoy (1961).

In the case of 4-hour-old bread vs 12-and 14-hour bread, the older breads were preferred. Since the panel was asked to judge overall preference, the fresh bread may have been judged too moist and, as such, downgraded.

King et al. (1937) also evaluated the influence of storage time on the odor and taste properties of bread. However, their freshest product was already 12 hr old when evaluated; by then the majority of flavor changes had probably already occurred. From the standpoint of odor and taste, the freshest product was judged best (Table 111).

A later study by Farber (1949) demonstrated that there was a dramatic change within a 24-hr period in the amount of volatile reducing substances in various bread products (Table 112).

The same general trend was reported by Jackel and Ersoy (1961), who used a rather limited five point intensity scale to rate the fermentation aromatics, fermentation acids and yeasty taste detected with bread storage (Table 113).

The aromatic level was most dramatically affected by storage; after 12 hr only half of the original amount was considered present. The acid intensity dropped slightly, and after 48 hr of storage, 75% of the original level was still present. No change in yeasty taste was noted throughout the storage period.

Borovikova and Roiter (1971c) provided detailed volatile flavor compound analyses of the crumbs and crusts of breads that were stored for varying periods of time, with and without wrappers (Table 114).

Initial readings were taken after three hours, and the total volatile compound levels were 19.2 mg/100 g of specific volume in the crust, and 3.2 mg/100 g in the crumb. In the case of unwrapped bread, carbonyl content decreased with storage by 85% in the crust and 22% in the crumb. With wrapped bread the aliphatic carbonyl levels in both crust and crumb increased for the first 12 hr and then decreased; the aromatic carbonyls increased in the crumb and decreased in the crust. These results were attributed to the slower cooling rate of the wrapped product.

With the Flavor Profile Analysis method of sensory evaluation, Caul and Vaden (1972) attempted to follow the sensory changes associated with bread storage. Data they obtained in the analysis of crust aroma, crumb aroma, crust flavor and crumb flavor are summarized in Tables 115-118.

A possible criticism of this study is that the first analyses were performed when the product was already 24 hr old. Most of the dramatic changes in odor and flavor had probably already occurred. However, the initial sampling schedule closely approximated consumer consumption patterns. From these data the authors concluded that the degree of flavor blending and complexity decreased as bread aged. With storage they observed that some flavor characteristics disappeared and others appeared.

Lorenz and Maga (1972) also reported on the influence of storage on the sensory preferences of bread (Table 119).

The fresh bread received the highest acceptability rating; after four days of storage an average ranking of "dislike slightly" was recorded. In addition, the changes in relative concentrations of certain volatile carbonyls were followed (Table 120).

In the carbonyl mixture, aldehydes accounted for approximately 73% of the total in fresh bread, but after five days of room temperature storage, their composite level had decreased to 15%.

BREAD FLAVOR APPLICATIONS

Introduction

Gross chemical composition and ingredients of bread are well-defined by law. Consequently, manufacturers rely primarily on sensory factors as promotional selling points for their product. Thus the modification, improvement and retention of desirable bread flavor is vital to sales. In the area of flavor research most basic research has some degree of application and most of the information previously discussed has been used in modern bread production. Perhaps the true value of any knowledge about the chemistry of bread flavor can be measured by the patent literature generated in the area. However, one problem is that the relative importance of the flavor claims made in a majority of patents can be difficult to evaluate because of descriptive terms used. Examples of such terms include "an improvement in bread flavor" and "a bread-like flavor resulted."

Selected Bread Flavor Patents

Based on his early observations on the composition of oven vapor condensates, Wiseblatt (1960a) formulated a synthetic mixture which, when added to warm water (1 ml/150 ml), produced a pleasant aroma similar to the original oven gases isolated (Table 121).

From a practical standpoint this approach, when applied to bread flavor enhancement, is of little value. The compounds in question are quite volatile and, if added to a dough system, would be volatilized during baking.

Considerable effort has been devoted to bread flavoring materials suitable for addition to chemically leavened breads since these products normally lack characteristic bread aroma and flavor. For example, Moriarty and Newlin (1962) patented the addition of flavor-enhancing agents formed as condensation products resulting from the reaction among certain amino acids and sugars. They claimed that leucine and sugars formed typical flavors and aromas described as toasty and bread-like, associated with fresh

TABLE 114

Influence of Storage Conditions on the Carbonyl Composition of Bread Mg Carbonyl Compounds/100 g of Product

	Unwrapped								Wrapped in polyethylene							
	Crumb Hours				Crust Hours				Crumb Hours				Crust Hours			
Compound	3	12	24	48	3	12	24	48	3	12	24	48	3	12	24	48
Methylglyoxal	0.08	0.07	0.03	0.01	0.06	0.06	0.06	0.05	0.08	0.08	0.03	0.02	0.06	0.20	0.35	0.06
Glyoxal	0.10	0.19	0.11	0.01	0.28	0.10	0.20	0.19	0.10	0.07	0.19	0.12	0.28	0.73	0.72	0.20
Acetaldehyde	0.30	0.30	0.03	0.01	0.14	0.08	0.03	0.02	0.30	1.87	0.50	0.30	0.14	0.60	0.26	0.07
Propionaldehyde	0.01	0.01	0.01	0.01	0.01	0.04	0.01	0.01	0.01	Tr.	Tr.	Tr.	0.01	0.01	0.01	0.05
Isobutyraldehyde	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.08	0.03	0.02	0.02	0.10	0.08	0.03
Acrolein	0.06	0.04	0.02	0.01	0.05	0.04	0.06	0.02	0.06	0.07	0.04	0.04	0.05	0.65	0.21	0.06
Acetone	0.08	0.06	0.03	0.09	0.08	0.10	0.04	0.07	0.08	0.05	0.03	0.03	0.08	0.47	0.21	0.10
Butyraldehyde	0.08	0.04	0.04	0.01	0.04	0.06	0.06	0.04	0.08	0.05	0.04	0.03	0.04	0.24	0.19	0.05
Isovaleraldehyde	0.08	0.04	0.01	0.01	0.01	0.02	0.02	0.02	0.08	0.11	0.03	0.03	0.01	0.12	0.03	0.01
Unknown	0.04	0.01	0.01	0.01	0.01	Tr.	Tr.	0.01	0.04	0.01	Tr.	Tr.	0.01	0.19	Tr.	Tr.
Methyl ethyl ketone	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.02	0.01	0.01	0.01	0.04	0.02	0.02
Diacetyl	0.04	0.02	0.01	0.01	0.03	0.03	0.02	0.01	0.04	0.01	0.01	0.01	0.03	0.04	0.01	0.01
Valeraldehyde	0.36	0.24	0.14	0.04	0.28	0.22	0.29	0.21	0.36	0.17	0.15	0.05	0.28	1.01	0.97	0.30
Caproaldehyde	0.18	0.09	0.06	0.01	0.05	0.19	0.14	0.09	0.18	0.06	0.11	0.02	0.05	0.87	0.59	0.12
Ethyl propyl ketone	0.04	0.02	0.01	0.01	0.03	0.03	0.16	0.02	0.04	0.07	0.03	0.02	0.03	0.11	0.10	0.02
Furfural	0.43	0.34	0.23	0.25	8.40	2.59	1.62	0.76	0.43	0.42	0.48	0.97	8.40	2.16	1.63	1.46
Benzaldehyde	0.27	0.21	0.20	0.14	4.80	0.17	1.24	0.56	0.27	0.40	0.46	0.67	4.80	4.70	4.34	3.67
Oxybenzaldehyde	0.96	0.93	0.90	0.82	4.80	1.78	1.48	1.30	0.96	1.20	1.32	1.50	4.80	5.40	3.44	3.36
Phenylacetylaldehyde	0.05	0.03	0.03	0.02	0.08	0.10	0.09	0.11	0.05	0.21	0.55	1.06	0.08	0.11	0.06	0.06
Approx. total	3.22	2.67	1.89	1.49	19.20	5.64	5.54	3.51	3.22	4.69	4.00	4.88	19.20	17.75	13.22	9.65

From Borovikova and Rotter (1971b).

TABLE 115

Flavor Profile Analysis of Bread Crust Aroma as Influenced by Storage

24 Hr (Intensity 1½)		48 Hr (Intensity 1)		72 Hr (Intensity 1)		96 Hr (Intensity 1)	
Note	Level	Note	Level	Note	Level	Note	Level
Caramel	1	Caramel	1	Browned Flour	1	Browned Flour	1
Sweet	)(	Browned Flour	1	Caramel	)(	Caramel	)(
Browned Flour	1	Wheaty	)(				
Wheaty	)(						

)(: Threshold.
1: Slight.
From Caul and Vaden (1972).

TABLE 116

Flavor Profile Analysis of Bread Crumb Aroma as Influenced by Storage

24 Hr (Intensity 1)		48 Hr (Intensity 1)		72 Hr (Intensity 1)		96 Hr (Intensity 1)	
Note	Level	Note	Level	Note	Level	Note	Level
Sweet	)(	Sweet	)(	Yeasty (old)	1	Sour	½
Yeasty	1	Yeasty	1	Sour	)(	Yeasty	1
Ethanol	½	Wheaty	)(	Wheaty	)(	Wheaty-starchy	1
Wheaty	½	Doughy	)(	Starchy (old)	1		

)(: Threshold.
½: Threshold-slight.
1: Slight.
From Caul and Vaden (1972).

TABLE 117

Flavor Profile Analysis of Bread Crust Flavor as Influenced by Storage

24 Hr (Intensity 1)		48 Hr (Intensity 1)		72 Hr (Intensity 1)		96 Hr (Intensity 1)	
Note	Level	Note	Level	Note	Level	Note	Level
Browned flour	1	Browned flour	1	Browned flour	1	Papery-browned flour	1
Caramel	½	Caramel	)(	Papery	)(	Bitter	)(
Bitter	)(	Bitter	)(	Bitter	)(		

)(: Threshold.
½: Threshold-slight.
1: Moderate.
From Caul and Vaden (1972).

TABLE 118

Flavor Profile Analysis of Bread Crumb Flavor as Influenced by Storage

24 Hr (Intensity 1)		48 Hr (Intensity 1)		72 Hr (Intensity 1)		96 Hr (Intensity 1)	
Salty	)(	Sweet	)(	Starchy	1	Starchy	1
Doughy	½	Doughy	½	Sour	½	Salty	)(
Yeasty	1	Yeasty	1	Yeasty (old)	1	Yeasty (old)	1
Starchy	)(	Sour	)(			Sour	1

)(: Threshold.
½: Threshold-slight.
1: Slight.
From Caul and Vaden (1972).

TABLE 119

Influence of Bread Age on Panel Acceptability

Storage time	Average panel score*
2 hr	1.95
2 days	3.55
4 days	4.50

*Eight point scale – 1: like extremely; 8: dislike extremely
From Lorenz and Maga (1972).

TABLE 120

Influence of Storage on Relative Carbonyl Composition in Bread

Compound	Freshly baked	5-Day-old
Formaldehyde	2.5*	0.2
Acetaldehyde	4.0	0.9
Acetone	4.5	1.7
Propanal	13.8	1.3
Butanal	22.7	0.8
2-Butanone	11.0	14.7
2-Hexanone	8.2	67.4
Hexanal	8.9	2.4
2-Heptanone	3.4	1.1
Heptanal	1.3	–
Nonanal	14.2	9.5
Unknown	5.5	–

*Relative %
From Lorenz and Maga (1972).

TABLE 121

Synthetic Bread Aroma Formulations

Compound	Amount (mg)*	Amount (ml)**
Ethanol	4	100
Acetaldehyde	10	0.1
Acetic acid	40	–
Furfural	20	0.5
Acetylmethylcarbinol	6	–
Pyruvic acid	–	2.0
2-Ethylhexanal	–	0.2
Diacetyl	–	0.015
2-Butenal	–	0.2
Methylglyoxal		0.8

*From Wiseblatt (1960a).
**From Wiseblatt and Kohn (1960).

TABLE 122

Sensory Properties of Non-fermented Breads

Leavening system	Sensory properties: Fermentation aromatics	Fermentation acids	Yeasty taste
Yeast (control)	4*	4	4
Glucono-delta-lactone (GDL)	0	0.5	0
GDL + inactive dry yeast	0	0.5	4
GDL + yeast extracts	0	0.5	1-4
GDL + protein hydrolysates	0	0.5	0-2
GDL + carbohydrates	0	0.5	0
GDL + organic acids	0	2-4	0
GDL + amino acids	0	0.5	2-4

*Intenstiy scale from 0 to 4.
From Jackel and Ersoy (1961).

TABLE 123

Influence of the Addition of a Dry Fermentation Flavor Additive (DFF) on the Sensory Properties of Straight Dough Breads

Conditions	Sensory properties: Fermentation aromatics	Fermentation acids	Yeasty taste
3 Rises, no DFF	4*	4	4
3 Rises + 0.375% DFF	4+	4+	4+
2 Rises, no DFF	3	3.5	4
2 Rises + 0.375%	3.8	4	4+
1 Rise, no DFF	1.5	2.5	4
1 Rise + 0.375% DFF	2.9	3.7	4+

*Intensity scale from 0 to 4+.
From Jackel and Ersoy (1961).

yeast-raised bread. The amino acids arginine and histidine formed buttery notes. Their patent covered the formation of flavor compounds either prior to incorporation into the bread dough, or the addition of the precursors to the dry mix, resulting in flavor compound formation during the baking process. They acknowledged that the cost of certain pure amino acids would make the process prohibitive, and they proposed proteinaceous material as the amino acid source. Products such as cottonseed flour and soybean meal were either hydrolyzed with hydrochloric acid or with enzymes. They reported that the optimum amount of total free amino acids needed to form the flavor enhancing agents ranged from 0.2 to 0.4% dry weight.

The approach used by Jackel (1963) was to form a flavor concentrate suitable for addition to a chemically leavened product by preparing a fermentation brew. The brew was composed of 15 to 25% yeast solids, 4 to 8% of a fermentable carbohydrate source, preferably dextrose, and 4 to 6% of non-fat dry milk solids. Under anaerobic conditions at 86°F, the fermentation was carried out for 4 to 16 hr. Optimum development of the flavor compounds was monitored by measuring the titratable acidity. Jackel claimed that a titratable acidity within the range of 0.48 to 0.58 produced optimum flavor. If the acidity fell much lower, a cheese-like off-flavor was noted. The fermentation process was halted by pasteurization at 150°F for 15 min and the resulting product was dried and used as a bread flavoring agent.

The information required for the granting of the above patent was reported by Jackel and Ersoy in 1961. Their preliminary data with the use of glucono-delta-lactone in place of fermentation demonstrated that common bread flavor characteristics were lacking (Table 122).

The use of glucono-delta-lactone and other classes of common bread ingredients also resulted in inferior sensory properties. Next they added dry fermentation flavor extract. As seen in Table 123, they

TABLE 124

Influence of the Addition of a Dry Fermentation Flavor (DFF) Additive Levels on the Sensory Properties of Non-fermented Breads

Leavening – % additive	Sensory property: Fermentation aromatics	Fermentation acids	Yeasty taste
Yeast	4*	4	4
Glucono-delta-lactone (GDL)	0	0.5	0
GDL + 0.5% dry fermentation flavor (DFF)	0.5	0.9	1.0
GDL + 1.0% DFF	0.9	1.5	1.9
GDL + 1.5% DFF	1.5	3.1	3.4
GDL + 2.0% DFF	2.2	3.9	3.9
GDL + 2.5% DFF	2.8	4.2	4.3
GDL + 3.0% DFF	3.5	4.7	5
GDL + 3.5% DFF	3.9	5	5

*Intensity scale from 0 to 5.
From Jackel and Ersoy (1961).

TABLE 125

Influence of Storage and Leavening System on the Sensory Properties of Non-fermented Bread

Leavening	Hours after baking	Sensory properties: Fermentation aromatics	Fermentation acids	Yeasty taste
Yeast	1	4*	4	4
GDL + 2% DFF	1	2.3	4	4
Yeast	12	2	3.5	4
GDL + 2% DFF	12	1.2	3.5	4
Yeast	24	0.5	3	4
GDL + 2% DFF	24	0.5	3	4
Yeast	48	–	3	4
GDL + 2% DFF	48	0.4	3	4

GLD: Glucono-delta-lactone.
DFF: Dry fermentation flavor.
*Intensity scale from 0 to 4.
From Jackel and Ersoy (1961).

demonstrated that the addition of 0.375% of the dry extract significantly increased the sensory properties of bread made by the straight-dough procedure.

When they evaluated the effect of adding glucono-delta-lactone and the dry fermentation flavor material to nonfermented bread as shown in Table 124, flavor intensity was quite strong.

It should be noted that a level of at least 2.0% of the flavor extract was required. The influence of storage on nonfermented breads containing glucono-delta-lactone and 2% flavor extract is summarized in Table 125.

No significant difference in flavor intensity was noted with storage time; both samples lost flavor intensity quite readily.

A yeast-levened flavor resulted from a mixture of yeast autolyzate and maltol (Lendvay, 1970), which could be incorporated into chemically leavened products. Essentially a mixture of yeast, powdered sugar and maltol was fermented at room temperature until the volume increased 35%. Then additional sugar and maltol were added and the temperature raised to 55°C for 16 hr to permit autolysis. The final step involved heating the mixture to 90°C and holding for two hours before packaging. The resulting brown liquid was then added to dough and baked, or dried and incorporated into the product.

TABLE 126

Sensory Properties of 0.1% Maltol in Yeast Rolls

Panel of 36 flavor descriptions	Control	Maltol
Odor:		
Fresh bread	13	18
Yeasty, doughy, sour	16	11
Stale, musty, moldy	6	4
Sweet	0	5
Taste:		
Fresh bread	15	21
Sweet	5	5
Sour, fermented	7	2
Stale, musty	3	0
Flat, bland	3	4
Bitter	3	3
Preference (two with no preference)	12	22

From Hodge and Moser (1961).

TABLE 127

Sensory Properties of 0.1% Isomaltol in Yeast Rolls

Panel of 34 flavor descriptions	Control	Isomaltol
Odor:		
Fresh bread	12	21
Yeasty, doughy	15	6
Stale, musty, moldy	2	4
Sweet	0	3
Taste:		
Fresh bread	12	16
Sweet	3	5
Sour	3	2
Stale, musty	5	2
Salty	2	0
Cucumber	0	1
Preference (four with no preference)	13	17

From Hodge and Moser (1961).

The incorporation of maltol and related products as bread flavor enhancers was evaluated by Hodge and Moser (1961). They added 0.1% maltol or 0.1% isomaltol to yeast-roll formulations and, according to Tables 126 and 127, samples containing the additives were preferred in both odor and flavor over controls baked without additives.

The formulation of a synthetic bread flavor derived from the pretreatment of whey followed by yeast and bacterial fermentations was patented by Bundus and Luksas (1969 a,b,c,d). A mixture of bakers yeast and nontoxic bacteria of the coccus family was inoculated into a whey medium and held at 86°F for 14 to 18 hr with air bubbled through the system during the growth period. The resulting product was dried and used as a bread-flavoring additive at ranges from 0.5 to 15% of the flour weight. A level of 6% was found to be optimum. Their 1969b patent provided means of pretreating the whey. A high-heat treatment of the

whey resulted in better flavor development since low-heat treatment resulted in slow yeast growth. Also, high-heat treatment of the whey probably induced the formation of additional flavor compounds. They also disclosed the use of enzymatically treated whey, created by lactase action and the direct addition of lactic acid, to improve the resulting flavoring material. The 1969c disclosure used a whey substrate low in lactose by simply diluting the whey with water. Their last patent (1969d) provided another method of pretreating whey to remove a portion of the lactose.

Earlier observations prompted Hunter and Walden (1969) to obtain a bread flavor patent based on the reaction products formed from heating a proline and glycerol to 100 to 150°C range in the ratio of 1 to 10 parts of glycerol per part of proline. While heating for 5 to 30 min the volatiles formed were flushed from the reaction with nitrogen and trapped in an acid trap, thus forming the nonvolatile salts. The flavor material was then added at levels of 0.1 to 1%, based on flavor weight. It was noted that other alkaline polyols were equally as effective as glycerol and that the reaction was promoted by alkaline conditions maintained by the addition of sodium hydroxide or carbonate. The flavor compounds formed supposedly provided a richer, longer-lasting fresh bread aroma in day-old bread, as compared to a day-old control containing no additive, and they did not alter bread color and textural properties.

The above patent resulted from preliminary data reported by Wiseblatt and Zoumut (1963) and Hunter et al. (1966, 1969). Wiseblatt and Zoumut (1963) noted a cracker-like aroma when proline and dihydroxyacetone were heated. Hunter et al. (1966) prepared bread flavor-like additives by heating a mixture of proline, glycerol and dihydroxyacetone. They then added the resulting product to dough at various levels. At levels near 0.2% of the flour weight, the additive reinforced the normal crust aroma of baked bread. Likewise, an improvement in crumb aroma and flavor was noted. However, when added at levels near 2 to 3%, an objectionable, peanut-like aroma and flavor resulted.

Later, Hunter et al (1969) described the preparation and identification of the compound they thought was responsible for the observed cracker odor. The compound was identified as 1,4,5,6-tetrahydro-2-acetopyridine. They stressed that similar compounds in the mixture also had cracker-like characteristics. It was reported that when one part of the synthetic compound was added to 100,000 parts of fresh bread extract, the crusty aroma was enhanced. They also sprayed a solution containing 6 ppm of the compound on week-old bread and, after air-drying, noted that fresh bread odor was restored to the crust.

Later Buchi and Wuest (1971) reported on the synthesis of the compound in question. They confirmed that the compound had sensory properties similar to bread. Another point mentioned was the compound was highly sensitive to air and precautions had to be taken in its preparation and storage.

The early bread flavor work of Wiseblatt also led to several patents. In 1966, Wiseblatt was granted a patent for forming bread flavor related compounds by the thermal interaction of aliphatic ketols with acids or certain amino acid decarboxylation products. The example given reported the reaction of proline with 1,3-dihydroxyacetone. Flavor application in chemically leavened instant bread mix resulted in acceptable flavor. It was also noted that the flavor improvement was even more pronounced when the bread was toasted. Several additional claims were granted to Wiseblatt in a 1967 patent.

A patent was granted to Cort (1970) for forming a bread flavor enhancer by heating a mixture of proline, glycine, valine, glutamine and glycerol. It was claimed that, by varying the ingredient ratios, either a cracker-like, biscuit-like or bread-like flavor and aroma resulted.

Several patents have been granted in the area of incorporating flavored shortening products to enhance bread flavor. For example, Nakel (1967) claimed that the use of a flavored fat or oil containing pyroline could impart an enhanced crusty flavor to bread. It was pointed out that both concentration and pH influenced the resulting flavor. In the case of bakery products, levels of 1 to 6 ppm based on flour weight, and a pH range of 5 to 6.5, was suggested.

A flavor-based shortening patent was also granted to Dirks and Nakel (1967). The resulting crusty flavor was formed by the reaction of piperidine, proline and dextrose by various methods. Final levels of the unspecified reaction product in baked bread ranged from 700 to 1,300 ppm based on flour weight.

The production of flavored shortening was also the basis of a patent granted to Dirks and Nakel (1968). The process involved fermenting yeast and sugar to develop typical fermentation flavor; then vegetable oil was added to the mixture and heated. During the heating process the oil absorbed the fermentation flavor. The mixture was then decanted, resulting in a fermentation-flavored oil which could then be used in a normal bakery operation.

TABLE 128

Influence of Added Organic Acids on the Flavor of Non-fermented Bread

Product	Moles organic acids /700 g flour	Flavor rank*
Fermented	0	+++
Non-fermented	0	
Non-fermented	1.0×10^{-5}	+
Non-fermented	2.0×10^{-5}	++
Non-fermented	3.0×10^{-5}	+++
Non-fermented	4.0×10^{-5}	++++

*Exact definition not given.
From Johnson and Sanchez (1972).

TABLE 129

Influence of Added Organic Acids* and Free Amino Acids on the Flavor of Non-fermented Bread

Product	% Added amino acids**	Flavor rank***
Fermented	0	+++
Non-fermented	0	–
Non-fermented	0.1	++
Non-fermented	0.2	+++
Non-fermented	0.4	++++

*3.0×10^{-5} mol/700 g flour added to non-fermented products.
**Mixture of 20 amino acids in unspecified ratios.
***Exact definition not given.
From Johnson and Sanchez (1972).

The addition of an edible, enzyme-peroxidizable fatty material and enzyme source was the basis for a patent granted to Higashiuchi et al. (1963). The mixture resulted in the formation of peroxidized fatty material for which claims of product flavor improvement were made. Later Ferrari (1965) was granted a patent for the addition of enzyme-peroxidized oils which performed the same flavor function.

Recently, another bread flavor researcher has applied for a patent based on the data presented in Tables 128 and 129.

The proposed additive is a mixture of 20 amino acids obtained by the hydrolysis of wheat gluten and salts of the monocarboxylic acids found in normally fermented dough. As seen in Table 128, organic acids at a level of 3.0×10^{-5} moles/700 g of flour were judged to result in the same flavor intensity as normally fermented bread. In Table 129 an amino acid level of 0.2% based on flour weight was required to achieve the same flavor intensity as the control. This additive is being proposed for use with a no-time fermentation method.

CONCLUSION

The information summarized in this review represents only a portion of that published on the flavor properties of bread. Flavor chemistry is quite complex, in the case of bread flavor. The mechanisms involved in the formation and retention of bread flavor are far from completely understood.

Perhaps the work reported by Mulders (1973), a portion of which is summarized in Table 130, can be cited as an example of the basic information that is still needed to more completely understand the complexity of bread flavor.

TABLE 130

Composition, Odor Threshold Values and Odor Values of a Synthetic Bread Flavor

Compound	Concentration (ppm)	Odor threshold (ppm)	Odor value*
Ethanol	10^4	900	11.1
1-Propanol	9	40	0.2
2-Methyl-1-propanol	7	3.2	2.2
3-Methyl-1-butanol	7.5	0.77	9.7
Acetaldehyde	6.8	0.12	57
2-Methylpropanal	0.1	0.01	10
3-Methylbutanal	0.02	0.007	2.9
2-Propanone	1.4	300	< 1
2,3-Butanedione	0.005	0.0065	0.8
Ethylformate	0.6	17	< 1
Ethyl acetate	0.25	6.2	< 1
1,1-Diethoxyethane	0.15	0.042	3.6
Furan	0.016	4.5	< 1
2-Methylfuran	0.013	3.5	< 1
Dimethyl sulfide	0.005	0.001	5
Dimethyl disulfide	0.0025	0.00016	15.6
Total mixture	10,032.8615	80	125.4

*Concentration divided by odor thresholds.
From Mulders (1973).

Based on quantitative data obtained from bread volatiles, he formulated a synthetic mixture which resulted in a gas-liquid chromatogram identical to an authentic bread head-space sample. However, the odor of the synthetic mixture more closely resembled that of dough than that of bread; he concluded that neither the components detected in the original bread, nor their ratios, are completely characteristic of the odor of bread. However, he did not say that they are not important contributors to bread flavor. Based on their odor values, certain compounds could definitely contribute to a major portion of overall bread flavor.

Another conclusion reached by Mulders is that a particular component, due to its extremely low concentration but potent characteristic, was not detected by the analytical method used. Perhaps a sample larger than the 50 g used would have been advisable. The above conclusion was supported by the facts that there were areas in the scan where no apparent peak was observed, but odor sensations described as "golden brown crust," "bread" and "smell of bakery" were noted. Work is currently underway to identify these extremely potent and elusive compounds. Perhaps when identified, they will be the missing piece in providing the complete bread flavor profile.

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CONFECTIONS

Hard Candies

Hard candies are solid solutions containing a minimum amount of water and forming hard, glassy masses. Alternatively they can be defined as solidified sugar syrup with or without the addition of carbohydrates having a solids content of 98 98.3% dissolved in 0.3–2% water with optionally added flavors and colorants. Hard candies are made in countless varieties. Their composition varies from pure sucrose to a mixture of carbohydrates with the addition of acid flavors and colorants. Depending on the method of preparation, they can be classified as transparent, granular, or satinate (silky look). Candy can be shaped by cylinders, cutters, or molds.

In the production of hard candy, care must be taken to avoid caramelization and the inversion of the sugar. Suitable raw materials and adequate manufacturing techniques must be accurately selected for each type of candy. Even the small amount of water employed can play an important role; alkaline water favors degradation of sucrose, whereas acid water favors sugar inversion. The commonly used acidulants (citric, malic, and tartaric) that are a complementary and indispensable addition to the flavor ingredients must be properly dosed as not to negatively interfere with the preparation of the mix. Too large amounts of reducing sugars cause candy to be sticky, while low levels hinder the formation of granules. A suitable addition of reducing sugars regulates moisture gain; excessive moisture gains or losses by candy are the most decisive factors causing deterioration of the finished product. The optimum percentage of reducing sugar based on the anhydrous product varies between 13–17% depending on climatic conditions.

The old method of cooking sugar under atmospheric pressure in the presence or absence of preheaters has been replaced by vacuum, high-vacuum, or semi-continuous vacuum techniques. The sucrose-glucose ratio governing the baking temperature can vary from 80:20, 70:30, 65:35, and 60:40 to more exceptional ratios, depending on particular requirements or specific formulations.

Once the candy mix is prepared, flavor ingredients and colorants are added. Flavoring also includes the addition of acidulants. The dispersion of the required ingredients must be made at the lowest possible temperature and effected by hand or mechanical mixing. When satinate candies are desired, "stretching" of the mix is effected by allowing air to be drawn into the mixture. The mix is finally pulled into strands that are passed through a molding machine.

From an examination of the various operations connected with the manufacture of hard candy, it is apparent that the commercial value of hard candy (as well as the products based on sugar alone, such as filled and gum candies, fondants, and tablets) is based primarily on adequate flavoring. Candy and similar products with a slow melting process flavor saliva and thus extend the pleasant taste sensation. The choice of flavors and the dosage of acids represent the most delicate stage of the manufacturing process; a suitable choice of the above ingredients justifies by itself the production of candy. Candy flavors should not be too aggressive as to cause violent flavor sensations; the flavor should be released slowly and uniformly to further the desire for a continuing flavor sensation. Obviously the preference for a variety of flavors and the relative flavor intensity may determine the manufacture of candy products having particular flavor characteristics.

Candy flavors are countless; only a few (such as orange, lemon, and mandarin) account for the largest segment of candy production. Mint-flavored candy is prepared using trirectified peppermint essential oil, since the use of menthol is not advisable. A small amount of menthol together with trirectified oil can be used to strengthen the flavor of certain candy types. Anethol or Chinese anise (m.p., 21–22°C) is preferred for use in anise-flavored candies; the essential oils and citric acid are used in citrus-flavored candy. The compounded essential oil and citric acid are used for citron flavors. Compounded essential oils are used for fruit or fantasia flavors, since concentrated juices interfere with candy manufacture because of their contribution of residual moisture. The optimum yield of flavors for hard candy is 1 kg per ton (1 × 1,000). Dilution of the more concentrated compounded flavors must be carried out beforehand using high-boiling and anhydrous solvents. Propylene glycol, ethylene glycol ethyl ester, and carbitols are preferred to 95% alcohol.

Filled Candies

Filled candy consists of two basic parts—the shell and the filling. This candy type can be considered derived from Neapolitan candies—hard candies poured into molds containing a piece of candied fruit or a coffee bean in the center. However, filled candies have a much thinner, more fragile shell and a more fluid filling.

Filled candy must provide a pleasant total flavor sensation when the shell is crushed in the mouth and the filling is exposed. Manufacturing of filled candies follows to a certain extent the basic techniques for the manufacturing of hard candies (preparation of the mix, baking of the shell, and final molding). The types vary widely because of filling formulations, formation of the strand, etc. The shell can be neutral or slightly flavored with a flavor compatible with that of the filling; it may or may not contain colorants and, if flavored, proportional amounts of acids. It can be transparent or satinate. The filling may vary in consistency; it can be gelatinous (fruit jellies or fondants), thick and syrupy (concentrated fruit juices or pastes containing suitable amounts of glucose syrup), or fluid (liqueurs or corresponding flavor imitations).

A description of the operative techniques for the preparation of the above products goes beyond the scope of the book: therefore, only the importance of the flavoring techniques is underlined. The flavoring of the shell follows the same guidelines set forth as in hard candy; the flavoring of the filling follows the criteria used for syrups and liqueurs in the choice of the most suitable flavors.

Taffy

This type of soft candy contains approximately 4–5% moisture and is prepared by a controlled Maillard reaction between sugar and milk proteins. Small scale production of taffy calls for boiling sugar, glucose, fresh milk or cream, butter, and only a complementary flavor together with a little vanillin. Flavoring is developed essentially by the caramelization of sugar in the mix. The industrial production of taffy, although based in general on the above principle, uses various basic mixes that are flavored with suitable compound flavors prior to molding. The formulation of the compounded flavors (usually having a 1 × 1,000 to 1 × 2,000 yield) falls in the category of cream and butter flavor imitations, which blend extremely well in the candy mix.

More complex and functional flavors are those that not only exhibit the butter note but also caramel and, sometimes, coffee notes. These flavors are often available in a powdered form having a 1 × 500 yield.

Fondants

Fondants represent a very important category among those products manufactured with cooked sugar (hard candy, taffy, etc.). The French name indicates the characteristic melting property that is primarily a function of the moisture content (10–12%) in the product. Moisture content alone, however, does not govern the candy consistency; this is determined by several other factors. Fondants are essentially semi-worked products very useful in the manufacture of confections, *e.g.*, as a filling for pralines, dragées, and other candies; as a frosting for pastries, cakes, and cookies; and as a special flavor ingredient in taffy. Classic fondants consist of molded or powdered boiled sugar covered with chocolate, adequately flavored, colored, and garnished.

The manufacturing technique is rather simple but follows strict basic rules. The consistency of the mass is dependent on the cooking temperature and the sucrose to glucose ratio, which should be kept at a 10:1 minimum. First the sugar is heated and completely dissolved in water; then glucose is added to the syrup in the required amount. The mixture is boiled to about 110 °C, yielding a supersaturated solution in which the excess sucrose crystallizes on rapid cooling. The cooling mass is stirred to cause crystallization of sucrose into very thin (less then 10 mm) crystals.

Whenever the fondant is to be used as candy rather than an ingredient in other products, it is flavored at this stage, colored with suitable dyes, thoroughly mixed, and poured into molds. Flavoring is extremely important to fondants; good results are achieved when the same flavor ingredients employed in hard candies are utilized. The flavor yields, however, are almost double in strength, using the

same flavor ingredients, since there is no thermal or vacuum treatment involved. The flavor sensation also is perceived more rapidly because of the softness of fondants. The basic flavors are very similar to those employed for hard candies with the exception of anise, which is not used; the acid content is usually about 50% less than that used in hard candy. Good flavor results may also be obtained using fruit-juice-based flavors or fruit pastes by formulating the fondants to a suitable consistency. The flavoring of fondants to be used in other products should be chosen according to the end-use and should follow the guidelines indicated for typical fondants.

Gum Drops

Gum drops, gums, and gelatins are three classic candy types often designated by several other names causing a great deal of confusion. These products are prepared with natural gums (*e.g.*, gum arabic), mixtures of gum and gelatin, or gelatin alone, together with sucrose, glucose, glycerol, and water. Colorants, flavors, and acids complement the basic formulation. The sugar content or the degree of sweetness, the acid content, and the flavor intensity in such products vary somewhat from country to country. The products are characterized by their consistency: gum drops exhibit a rather hard consistency, gums are somewhat softer, and gelatins are quite plastic. All such products exhibit a transparent mass (foaming should be avoided during stirring to prevent opalescence) and are shaped by pouring the fluid mass into powdered (starch) molds. The product surface can be shiny, or it can be covered with crystalline sugar. The operative techniques and the mixtures of various ingredients are specific for each product; they are usually prepared not only for confections but also for pharmaceutical purposes (cough drops, laxatives, etc.).

A typical preparation consists of heating the sugar and the gum solutions separately, mixing the two solutions together with the desired colorants, acids, and flavors, pouring the mixture into powdered molds, cooling, drying, and finally polishing. The inversion of sugar must be controlled and dosed according to the desired characteristics of the final product; this is especially true in the preparation of gelatins. Because of their intrinsic composition, these products may be flavored with a wide variety of ingredients, such as fruit juice and pulp, essential oils, isolates, and compounded oils. Flavor components are limited only by a suitable choice of the gum mix. Also wine (Bordeaux, Marsala, Madeira, port, Malaga, etc.) and liqueurs (curaçao, kirsch) are used to flavor gelatins. Fruit juices most frequently employed include apple, strawberry, raspberry, orange, red and black currant, cherry, blueberry, grape, and licorice. The last juice, with added menthol, anethol, eucalyptol, or mixtures thereof, is extensively used to flavor gum drops and gums. Citrus essential oils are very suitable for flavoring gelatins; the corresponding imitation fruit flavors may also be used when fruit juices cannot be added because of technical and/or economic limitations. The flavors used for hard candies are considered generally suitable, except that the yield is almost doubled, *i.e.*, a hard candy flavor having a yield of 1 × 1,000 will exhibit an approximately 1 × 2,000 yield in gelatins.

Tablets

Flavored tablets and disks of various shapes and sizes for use as is and as pharmaceutical bases are obtained by compressing powdered mixes in the presence of agglutinating ingredients. To improve the compactness and the tablet consistency, the ingredients are prepared in granules with or without the addition of water and small amounts of gum (arabic, tragacanth) or starch. Flavoring is usually carried out with spray-dried flavor ingredients.

Confetti (Hard, Sugar-coated Candies)

Confetti consists of cores of varying shapes and sizes coated with sugar frosting. The candies are processed in special rotating drums to obtain a uniform, smooth sugar coating. The core usually consists of one of the following ingredients: almond, hazelnut, pistachio; spice fragments (clove, cinnamon); flavored and molded fondant; molded, minced almond paste; flavored gum-based gels and tablets; and candied fruit. An enormous variety of confections (and also pharmaceutical products) can be prepared by the above manufacturing technique, together with special operative techniques required by specific products. Usually the core is coated with natural gums to favor the adhesion of the

sugar coating: the sugar is introduced into the rotating equipment partially as syrup and partially as finely granulated sugar. The sugar coating may be colored by adding dye dissolved in syrup toward the end of the coating operation. Vanilla or other suitable flavor ingredients can be added to the sugar syrup. The coating for certain products may consist also of chocolate, syrup, and sugar. Cores consisting of candied fruit, spices, and almond paste require no additional flavoring; tablet or fondant cores are flavored in the manufacturing process.

Cocoa and Chocolate Candies

The seeds of *Theobroma cacao*, a plant native to Central America, were carried to Europe about the sixteenth century. The industrial use of cocoa seeds is, therefore, over 400 years old. Although chocolate, as known today, was first produced toward the beginning of the nineteenth century, it has become one of the basic food ingredients and flavors. Cocoa derivatives include cocoa powder (sweet or bitter, with varying degrees of solubility), chocolate drink (obtained by dissolving cocoa powder in milk or water with or without the addition of sugar), chocolate bars (bitter and milk chocolate), and cocoa butter. All the above products exhibit different characteristics directly related to the fabrication methods, type, origin, and pretreatment of the seeds. The commercial qualities are, therefore, dependent on many variables.

Briefly, cocoa seeds are treated according to the following operations: fermentation (which influences the aromatic characteristics; the length and the method of fermentation vary depending on the growing site), drying, roasting, peeling, and crushing. The seeds are partially defatted (removal of cocoa butter) by hot pressing. Grinding and specific additional treatments follow to prepare the final cocoa powder. To prepare chocolate bars, the powder is mixed with other ingredients (sugar, milk, nougat, vanilla flavor); the mixture is refined and freed from lumps; it is then ripened at different temperatures and for various lengths of time depending on the quality, tempered, and finally molded.

Basic flavoring is introduced by mixing the flavor ingredients into the chocolate mixtures. Vanilla flavor is the most common and is obtained by using vanillin (also ethyl vanillin and propenylguaethol). Several other complementary flavors are employed; however, their addition is dependent on the use of chocolate in combination with other products. Chocolate bars and candy can be filled with flavored fondants, liqueur-soaked fruit, dry, roasted, or candied fruit, liqueurs, etc. The function of chocolate as a frosting and a flavoring for various filling ingredients follows the specific guidelines previously indicated for individual products.

Nougat

Nougat is a confection consisting mainly of honey, sugar, egg white, peeled sweet almonds (sometimes combined with pistachio, nougat, and roasted almond), candied fruit, glucose, and chocolate (for the so-called brown nougat). It is prepared by mixing the ingredients under heat using special techniques and is formed by pouring the mixture into wafer-coated molds. Typical hard nougat is usually vanilla-flavored, but other flavors are also used, such as lemon, orange, mint, cinnamon, clove, and coffee. The flavor ingredients are added toward the end of the mixing operation, immediately after the addition of the nougat, almond, pistachio, and similar products.

DAIRY PRODUCTS

Introduction

Countless pastry and food products require flavors similar to milk or its more important derivatives. These flavors must be sufficiently concentrated and stable when added to semi-finished or finished food products in place of the less stable natural dairy flavors, from which it is almost impossible to extract the active flavor principles in a form suitable for use.

Milk

Imitation milk flavors can be prepared using cream-flavor imitations in those food products containing powdered milk. Some flavor results are readily obtained in this manner, although the duplication is far from satisfactory. More recently the demand for specific milk flavors for use with liquid and powered products in which the above flavoring technique cannot be employed has increased steadily. Natural milk flavor is rather unstable and varies widely, depending not only on the animal's feeding habits but also on the animal itself (cow, sheep, goat). Generally, milk flavor is defined as the flavor of fresh cow's milk.

To prepare a milk flavor imitation, the following notes are usually blended: vanilla (vanillin, veratric aldehyde, ethyl vanillin), coumarin, melilotus, liatris, dihydrocoumarin (where use is permitted), diacetyl, and trace amounts of butyric acid and esters (ethyl capronate, cinnamyl butyrate, etc.). Methyl acetyl carbinol may also yield a positive contribution to the flavor as a total or partial replacement for diacetyl.

The resulting flavor imitations should be used with great care; when properly dosed, they may satisfy the odor requirements but are somewhat lacking in taste. The unavailability of the basic flavor principles present in natural milk (which also determine the characteristic flavor in a food product through primary or secondary reactions with the food substrate) makes a perfect imitation of the natural flavor somewhat problematic.

In order to better define the flavorist's search for milk flavor imitations, it is extremely helpful to know the exact composition of natural milk flavor. The studies of milk-flavor constituents conducted from 1938 to present allow the following observations:

1. The sweet taste of milk is attributable to lactose; the salty taste, to sodium chloride.
2. Fresh cow's milk flavor can be defined as *normal* and *abnormal*. A *normal* flavor is the flavor characteristic of freshly recovered milk formed through regular physiological processes. An *abnormal* milk flavor is caused by extraneous factors, such as the composition of the animal's feed and chemical degradations following milking.

Keeping in mind that feeding affects milk flavor, the milk flavor produced by cows fed with odorless and purified feed (cellulose, starches, sucrose, urea, inorganic ammonium salts, A and D vitamins, corn oil) has been taken as a reference standard. The following components present at low concentration have been identified in normal milk flavor: acetone, 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, formaldehyde, acetaldehyde, saturated straight chain C_3 to C_{12} aldehydes, saturated straight and branched chain C_{13} to C_{16} aldehydes, butyric and other low-molecular-weight fatty acids, and methylmercaptan.

A few components identified in other fresh dairy products may also be considered as probably occurring in milk flavor: diacetyl (in fresh butter), isovaleric aldehyde (in fresh cream), *cis*-4-heptenal (in the cream flavor of fresh butter), and δ-lactones (in butter, cream, and pasteurized milk).

The study of *abnormal* milk flavor can be defined according to the following scheme:

- Abnormal milk flavor caused by extraneous factors
  - 1. Feed components
  - 2. Chemical degradations following milking
    - Souring
    - Oxidation
    - Photo-oxidation
    - Heating
    - Concentration
    - Drying

Abnormal milk flavors may be classified into two types: flavors similar to, and flavors different from

the flavor of the feed. This is a somewhat thin-lined classification, since strongly aromatic herbs (artemisia, hops, etc.) may be present occasionally in the feed; other products may also form in the feed during storage. This may determine the additional presence in normal milk flavor of alcohols, aldehydes, low-molecular-weight esters, and ketones. Operations subsequent to milking together with storage conditions may also affect the resulting milk flavor.

Souring (Rancid Flavor)

The souring of milk with the formation of the characteristic sour flavor is usually determined by an enzymatic (lipase) scission of the fatty acids present in milk. Lipolysis may occur spontaneously, or it may be induced by excessive agitation (pumping, homogenizing, etc.), separation and clarification, heating to 30 C with subsequent recooling, freezing with subsequent thawing, and adding small quantities of raw milk to pasteurized milk. All such conditions or manipulations can cause the formation of low-molecular-weight free fatty acids, chiefly butyric acid.

Oxidation

The so-called oxidized flavor of milk is believed to be caused by enzymatic and non-enzymatic conditions. The following components have been identified in oxidized milk flavor: saturated C_5 to C_{16} aldehydes, hexenal, 2-hepten-1-al, 2-octen-1-al, 2-nonen-1-al, 2-decen-1-al, 2-undecen-1-al, 2,4-nonadien-1-al, 2,4-decadien-1-al, 2,4-undecadien-1-al, and 2,4-dodecadien-1-al. A comparison of the analytical findings of an oxidized and a non-oxidized milk flavor indicates that the two flavors have a very similar qualitative composition (2-hexen-1-al, 2-hepten-1-al, 2,4-decadien-1-al, 2,4-undecadien-1-al, and 2,4-dodecadien-1-al are present only in the oxidized flavor) but a very different quantitative composition. In fact, a remarkable increase (almost double) of the flavor component ratios and a five-fold increase of the hexenal content (together with a few insignificant decreases of other components) is observed in the oxidized milk flavor. Trace metals such as copper and iron can accelerate non-enzymatic oxidation.

Photo-oxidation

The oxidative action of light on milk flavor is twofold: (1) it causes the oxidation of lipids with consequential formation of the oxidized flavor having a composition similar to the spontaneously formed (or copper-induced) oxidized flavor, and (2) it causes the formation of the so-called activated flavor caused primarily by proteolytic degradation of methionine (and probably of other sulfur-containing amino acids). This brings about the much disputed presence of methional (β-methylmercapto propionaldehyde), methyl mercaptan, dimethyl sulfide, and acrolein.

Heating

Heating normally applied during pasteurization may cause a more or less pronounced cooked flavor, depending on the length and the intensity of the heat cycle. This operation causes a decrease of the redox potential, which is reflected by the formation in the flavor of hydrogen sulfide and other volatile sulfides formed by the liberation of SH groups present in lactoglobulins. When milk undergoes unusually high heat cycles, it develops a pronounced caramelized flavor from the presence of fermentation products and the dehydration of sugars.

Concentration and Drying

Milk undergoes more or less extensive heat cycles during concentration and drying operations. Therefore, cooked and caramelized off-flavors may develop in a manner similar to those discussed above.

Analysis of concentrated and dried milk having off-flavors confirm the presence of the following:

1. **Sugar derivatives** (by Maillard reaction): furfural, hydroxymethylfurfural, diacetyl, and maltol.
2. **Decomposition products from amino acids** (Strecker's degradation): methylpropanal, and 3-methylbutanal.
3. **Derivatives formed by autoxidation**: formaldehyde, acetaldehyde, propionaldehyde, *n*-valeraldehyde, hexyl aldehyde, heptyl aldehyde, nonyl aldehyde, decyl aldehyde,

dodecyl aldehyde, and tetradecyl aldehyde (aldehydes are also present in untreated milk at different concentration levels, however).

4. **Derivatives formed by hydrolysis**: capronic, caprilic, capric, lauric, myristic, and palmitic acids.
5. **Derivatives formed by unknown processes**: acetone, 2-butanone, 2-pentanone, 2-hexanone, 2-heptanone, 2-nonanone, 2-undecanone, 2-tridecanone, 2-pentadecanone, δ-decalactone, δ-dodecalactone, δ-tetradecalactone, γ-dodecalactone. The presence of *p*-aminoacetophenone derived from indican present in milk is also probable.

Some authors have reported the presence of additional flavor components in milk flavor; the presence of benzaldehyde is traced to the type of feed, whereas vanillin (reported in pasteurized milk) may be traced to the heat treatment of the lignin eventually present in milk. In conclusion it is apparent that not one but several milk flavors occur naturally.

Cream

Most of the considerations concerning milk flavor are also applicable to fresh cream flavor. Cream is mechanically separated from milk and may contain from 18–48% butter fats.

Skimming, *i.e.*, the separation of fat from the aqueous layer of milk, determines flavor concentration together with the total or partial removal of the sour note. Cream flavor is sweeter and mellower than milk flavor. To prepare cream flavor imitations, the same ingredients listed for milk flavor imitations are usually applicable with the frequent addition of citrus notes (orange, lemon, citron, mandarin), floral notes (heliotropin, clove, rose), and undernotes based on sulfur-containing compounds (methyl sulfide, etc.). By the proper compounding of the ingredients and by using more modern techniques, it is possible to avoid the massive use of coumarin (or similar products), once a basic flavor component for cream flavor imitations. The use of coumarin (where permitted), in addition to yielding an excellent cream flavor, makes these products quite acceptable; the total coumarin content in the finished product usually does not exceed 20–22 ppm. Similar considerations are also applicable to those formulations strictly related to the use of cream flavor (taffy, Dutch cream, etc.). A guideline formulation for cream flavor imitations consists of the following:

Cream Flavor

Approximate Yield: 1 × 2,000

Ingredient	Parts
Glyceryl tributyrate	200
Melilotus tincture (15% in 65% alcohol)	170
Methyl acetyl carbinol	115
Ethyl vanillin	50
Woodruff tincture (15% in 65% alcohol)	35
Diacetyl	30
Heliotropin	30
Ethyl butyrate	20
Butyric acid (10% aqueous solution)	11
Ethyl capronate	9
Mandarin essential oil (10% solution in alcohol)	4
Lemon essential oil (10% solution in alcohol)	3
γ-Undecalactone (1.0% solution in alcohol)	3
Citronellol (10% solution in alcohol)	1
Neroli essential oil (10% solution in alcohol)	1
γ-Nonalactone (1.0% solution in alcohol)	1
Solvent	9,317
Total	10,000

Ice Cream and Sherbet

Typically, ice cream is a dairy product congealed and prepared from cream, milk, skim milk, condensed milk, butter, or a combination of these ingredients with the addition of sugar, various

flavors, stabilizers, and colorants (optional). Air is drawn into the mixture during the congealing process. The product, originated in Europe by famous Sicilian and Neapolitan pastry masters, today is industrially produced throughout the world. The production of creamless or butterless ice cream dates back to the fifteenth century and was discovered probably by accident. The first production of a cream-based ice cream is mentioned in *The Experienced English Housekeeper*, published in 1769. In 1800 the homogenizer was invented in France. It was only between 1940 and 1945 that the production of ice cream packages suitable for maintenance at very low temperatures were developed and therefore suitable for delayed consumption of the product.

Classification

A standard classification for ice cream, sherbets, and frozen cream (cream gelats) is not yet possible because of the countless variations in the composition, ingredients, and production methods. The U.S. manufacturers have grouped products into classes, such as regular or Philadelphia ice cream, French or Neapolitan ice cream, sherbets, ices, and more recently ice milk. Keeping in mind the fundamental difference between true ice cream containing cream or its derivatives in addition to the regular ingredients of sherbets (sugar, fruit juices, flavors, and sometimes milk), all other specialities could be included in one of the above categories, depending on their basic formulation. Taking into account also the possible use of milk in sherbets, three fundamental categories should suffice to group all of the various ice-cream products:

1. Ice cream, containing cream or its derivatives
2. Milk sherbets, containing whole, powdered, or condensed milk
3. Ices, formulated without milk or milk derivatives.

Ingredients

The generic term *ice cream* is commonly used to define a congealed product consisting of a mixture of dairy products, sugar, flavors or liqueurs, colorants, and, if required, stabilizers. The finished product may or may not contain eggs, fresh, preserved, or dried fruit, fruit juices, etc.; it is thoroughly homogenized by pounding or mixing during the congealing process. Regular ice cream generally contains no more than 5% colorants (where permitted) and flavors calculated on the volume of the ice-cream mixture prior to congealing.

Ice sherbets are prepared with fruit juices, sugar, stabilizers, with or without fruit, acids, colorants, flavors, and water. Usually they contain approximately 28–30% sugar and no milk or dairy products.

Milk sherbets (ice milks) are prepared using fruit juices, sugar, stabilizers, and dairy products (whole, skim, condensed, or powdered milk) that totally or partially replace the water used in ice sherbets.

The use of stabilizers is governed by regulatory agencies in the various countries. Among the stabilizers employed are agar-agar, sodium alginate, calcium sulfate, gelatin, carob seed gum, guar gum, oatmeal gum, gum tragacanth, Irish moss and extracts, lecithin, carboxymethyl cellulose, and a few others. Emulsifiers consist usually of mono- and diglycerides obtained by glycerolysis of edible fats. The use of emulsifiers is also subject to specific regulations in various countries.

Ice-cream composition consists of the uncongealed mixture of all ingredients with the exception of air and flavors. The composition is usually expressed as a per cent of the various ingredients, *e.g.*, per cent milk fats, per cent non-fat milk solids, per cent sugar, per cent egg yolk solids, per cent stabilizers, and per cent total solids. The per cent of milk fats varies more than all other constituents, ranging from 8–24%. When the per cent of milk fats is increased, the per cent of non-fat milk solids must decrease accordingly. Usually a well balanced commercial ice cream formulation contains 36–42% total solids and 20–26% total milk solids.

Flavor is considered one of the most important features of ice cream; the taste includes the almost tactile sensations caused by the consistency of the product as well as the true flavor. Ice-cream flavor results from all of the ingredients; some ingredients do not exhibit a very pronounced and detectable flavor per se but contribute to the overall flavor sensation. Delicate and bland flavors may be used quite freely, since they do not put too much stress on the consumer's acceptance; strong, definite notes tend to wear out a consumer's acceptance faster even at rather low levels.

Vanilla is, without any doubt, the most accepted and popular ice-cream flavor. Statistics show that 75% of the total ice-cream production contains vanilla flavor. Ideal flavor ingredients would be the extracts of vanilla pods, but the demand for more concentrated products is increasing very rapidly. Vanillan together with vanilla in suitable mixture can be employed for ice-cream flavoring. Cocoa and chocolate flavors follow vanilla in popularity. For chocolate ice-cream flavoring approximately 2 kg cocoa or 3 kg chocolate per 50 kg of ice-cream mixture is employed with an equal weight of sugar. Cocoa or chocolate together with sugar must be added with the other dry ingredients prior to pasteurization.

Other types of flavor ingredients employed are almost exclusively geared toward fruit flavors—raspberry, strawberry, banana, lemon, orange, mandarin, pistachio, apricot, peach, etc. A few fantasia flavors, such as nougat and liqueur flavors, have also found remarkable acceptance. To obtain good flavor formulations, it is advisable, whenever feasible, to use the best available fruit juices. In a few cases (if permitted by local regulations on the manufacture of ice cream), it might prove useful to employ natural or synthetic flavors formulated according to the guidelines for the flavoring of syrups (see p. 707). Excessive amounts of volatile esters or pronounced coumarin-type notes should be avoided in ice-cream flavor formulations.

Production

Both in batch and continuous ice-cream production, the ingredients are added approximately in the same order. The liquid ingredients are placed together in the container, agitated, and heated. The dry ingredients, including powdered milk and egg, cocoa, sugar, and stabilizers, are added while stirring prior to heating at temperatures exceeding 49 C. Butter, frozen cream, and other frozen products are crushed in small pieces prior to pasteurization, allowing sufficient time to melt. Subsequently, pasteurization is carried out at high temperatures (109–117 C); this favors the kill of bacteria, imparts improved body and better flavor, and protects the product from oxidation. The mixture is then transferred to a homogenizer; homogenization consists of passing the mixture through a small orifice at high speed with pressure exerted by means of a piston pump forcing the liquid through tiny valves. A permanent and uniform suspension of fat is thus obtained by reducing the droplet size to less than 2 microns. The resulting ice cream is extremely uniform and smooth. The homogenizing temperature varies between 63–77 C. After homogenization, the mixture is immediately cooled to 0–4 C and allowed to "set" in suitable containers until ready for use. The *setting*, or ripening process, has been practiced since the very beginning of ice-cream production. The fat solidifies during setting, while the stabilizer swells (if gelatinous) and combines with water.

Proteins in the mixture may alter slightly, and the viscosity increases because of this. Undoubtedly the consistency of the products improves, as does its resistance to melting. Until not too long ago, ripening lasted a minimum of 24 hours; more recently 3–4 hours has been established as sufficient for ice-cream ripening. During setting the temperature must be kept around +2 C and sometimes as low as −2°C to −1°C.

At this stage, ice cream is congealed as quickly as possible, since the ice crystals that form during quick freezing are much finer than those obtained in a slow-freezing cycle. Therefore, congealing and withdrawal from the freezer must be effected very rapidly. In a continuous freezer the operation takes only a few seconds; in a batch freezer congealing takes approximately 6–10 minutes. Ice cream is finally transferred to freezers to harden; the crystals formed during this congealing stage are much larger.

The flavoring of so-called ice-cream flavor compositions follows the same guidelines mentioned above for ice cream and sherbets. Liquid flavors are not usually employed in the preparation of such products; good powders are usually available commercially. Individual and compounded spray-dried fruit flavors and lyophilized fruit juices are important flavor forms for ice-cream products.

Yogurt

There are numerous techniques for the preparation of yogurt, ranging from home to industrial production. To obtain products of consistent quality, cow's milk concentrated to about two-thirds of the original volume or regular cow's milk containing a little powdered milk is employed. The milk is

coagulated directly in the distribution containers by inoculating with *Thermobacterium bulgaricum* cultivated in symbiosis with *Streptococcus thermophilus*. Coagulation is completed after 3–5 hours at 40–45°C. After this operation, yogurt is ready and must be cooled to low temperature to stop the fermentation of lactic acid, whose content in the finished product should be kept around 1%.

Yogurt prepared as described is white, does not separate serum, and has a pleasant, cheese-like appearance with a slightly sour flavor. Yogurt, consumed as is or with the addition of a little sugar, has won growing acceptance throughout the world and owes its widespread acceptance to complementary flavors. The acid yogurt flavor blends well with fruit flavors. Fruit-flavored yogurts are obtained by adding a suitable amount of flavored syrup (raspberry, strawberry, whortleberry, apricot, mandarin) to the yogurt immediately after coagulation. The best production employs syrups based on natural fruit juices or, simply, concentrated juices when sweetening is not required. Syrups flavored with strengthened fruit juices or with compounded flavors of the same type used in syrups may also be employed. Preliminary trials using lyophilized juices have given excellent results from a technical viewpoint.

Butter

Once established that the cream flavor is highly appreciated in milk and that cream is used to make butter, it is logical that the same cream flavor imitations with only slight modifications are the basis for most simple butter flavor formulations. The same ingredients are therefore used in the traditional formulations in slightly different proportions. These usually contain larger amounts of butyric, valeric, acetic, and lactic acids; esters (cinnamyl and ethyl butyrate, ethyl capronate, butyl butyryl lactate); trace amounts of additional products (cinnamaldehyde, benzylideneacetone, benzaldehyde, tributyrin, triacetin); various light notes of essential oils and extracts (nutmeg, civet, and fenugreek); and acetyl propionyl in products of the butterscotch type. All of the above ingredients are rather simple and intended primarily for pastry flavoring. Should more complex and more functional formulations be required (kept within the limitations imposed by government regulations and toxicological considerations), the study of the composition of natural butter flavor and the use of products with a long-established record of safety may very well supply interesting leads. It must be kept in mind that butter flavor has various notes and varying compositions depending on the following types: fresh butter, melted butter, roasted butter, or butter cooked in the presence of fats, sugar, flour, and other ingredients used in pastry and food products.

An inquiry into butter flavor formulations by the user must clearly specify the desired type; it is the flavorist's task to prepare formulations suitable for the various applications. Ultimately and ideally, a fresh butter flavor imitation should be capable of duplicating the natural product following the specific manufacturing treatment. The most important constituents of fresh butter are given below:

Components of Fresh Butter

Ingredient	Parts, ppm
Acetaldehyde	<0.1
Acetone	<0.1
Acetonin (acetyl methyl carbinol)	19
Bovolide (2,3-dimethyl-2,4-nonadien-4-olide)	0.45
Diacetyl	4.5
Formaldehyde	<0.1
2-Heptanone	<0.1
n-Hexyl aldehyde	<0.1
Isobutyraldehyde	<0.1
Isovaleral	1
2-Nonanone	<0.1
n-Nonyl aldehyde	<0.1
Phenylacetic aldehyde	<0.1

The aldehydes may be considered derivatives of the oxidative enzymatic decarboxylation of amino acids; the ketones, as probable derivatives from the decarboxylation of β-ketoacids; acetyl methyl carbinol, as a precursor rather than a derivative of diacetyl; bovolide, present in all butter types, could be dependent on the feed. Additional products, already encountered in heated milk, have also been identified in butter, *e.g.*, aldehydes, ketones, alcohols, aliphatic methyl and ethyl esters, lactones, and dimethyl sulfide.

Carbonyl compounds appear to play only a secondary role in the constitution of fresh butter flavor; δ-lactones appear to have been identified only in melted butter. They impart a well accepted flavor to melted or cooked butter, but their presence is totally objectionable in fresh butter flavor. A few formulations useful for the preparation of butter flavors are simply based on lactic and acetic acid, acetaldehyde, dimethyl sulfide, and diacetyl. A few authors have suggested the use of α- or γ-carboxy lactones (odorless C_6 to C_{12}) as precursors of the lactones present in melted butter flavor.[19]

Margarine

The discovery of margarine is commonly attributed to the French chemist Hippolyte Mege-Mouries, who patented the product in France and England in July, 1869. Mege-Mouries had observed that starving cows, although losing weight and giving less milk, still secreted fats in their milk. He came to the conclusion that cows consume their own body fat and that the *oleomargarine* in the cow's body is transformed into butter by enzymatic action of pepsin. A further deduction was that the odorous volatile coloring matter becoming rancid was not originally present in natural (white) fat, but it developed by action on organized tissues by fermentation, heat, and chemical agents. Mege-Mouries concluded that milk fats (so-called butter) were derived from modified fats in the body of the animal. By applying the above theories, the inventor first prepared a virgin tasteless and odorless fat and then a kind of true butter.

Margarine was originally produced in France and shortly thereafter in Holland, Denmark, Austria, Hungary, Germany, Great Britain, and the United States. Margarine production was conditioned by the availability of inexpensive fats suitable for the purpose. Therefore, the perfecting of the hydrogenation process of oils gave great impetus to the industrial production of margarine.

Fats Used in Margarine

Through the process of hydrogenation, the liquid glycerides (fats) are transformed into a solid fat at room temperature. The process allows the use of almost all vegetable fats for margarine production; this fact started the refining of coconut, linseed, soybean, safflower, palm, and whale oils. Today the margarine industry, taking advantage of both the hydrogenation and deodorizing processes as well as other oil-refining techniques, may use almost any edible oil or raw material. The largest portion of the raw materials consists of vegetable oils (and whale oil for the balance) in the English production of margarine. Vegetable oils are used as the starting material in 98.5% of U.S. margarine, the balance consisting of animal fats.

While in the United States the fats employed consist almost exclusively of linseed and soybean oils, at least four different fatty raw materials are used in English production. These include coconut oil, palm seed oil, peanut oil, palm oil, and small percentages of cottonseed, sesame, and safflower oils. Margarine production requires the use of fresh and fairly pure fatty raw materials. The fat must be physiologically and hygienically suitable and free of toxic constituents. For instance, castor oil is not suitable.

With the exception of cold-expressed olive oil and safflower seed oil, the extracted fats exhibit an unpleasant taste from the presence of non-glyceride impurities and the formation of acids by glyceride decomposition. Raw fats, therefore, require refining prior to use. The fats also must be non-nutritive. Normally natural fats are readily digested as long as their melting points are not far above the human body temperature. Their chemical composition must be suitable for the purpose for which they are intended. A few fats, such as hardened palm oil, confer remarkable plastic properties to the finished product, *i.e.*, they render the product readily spreadable. Others, such as coconut oil, enhance the

friability of the product. The fat must be free of oxidizable products, and the physical properties must be correspondent to the end-use for which the product is intended.

Natural fats are mostly liquid and must be hydrogenated to reach the optimum melting point. These requirements are never met by raw fats, which usually contain impurities responsible for the dark color, turbidity, and disagreeable odors. Fats must undergo various refining processes prior to being transformed into suitable raw materials for margarine production. Only freshly extracted and refined fats should be employed in the production of margarine, since raw and paste fats (even the refined and hardened types) tend to deteriorate during storage and transport.

Production of Margarine

Margarine is an emulsion consisting of fat and water. Although the amount of dispersed water varies from country to country, it is usually about 16%. Margarine is a stable solid emulsion at room temperature with a consistency, plasticity, appearance, color, and flavor resembling butter. Colorants and flavors are added during the manufacturing process.

The production cycle can be outlined as follows:

1. Preparation of the aqueous phase
2. Preparation of the fatty phase
3. Emulsification of the two phases
4. Cooling
5. Plastification
6. Packaging

The aqueous phase may consist of pure sterilized water, aqueous lactose, lactic acid, or solutions of other ingredients. Most of the producing countries employ milk ripened by a bacteriological process similar to that employed for the production of butter. In this way margarine acquires a bland butter flavor. The synthetic flavor ingredients normally added to margarine do not impart the same agreeable taste as ripened milk.

Milk also contains emulsifying substances that help the formation of margarine emulsion. It is common practice, however, to add emulsion stabilizers when milk is used. Four different milk products can be used in the aqueous phase: cream (34–45% fats), whole milk (3–5% fats), skim milk (almost fat-free), and powdered skim milk reconstituted with water. The first two products are almost never used because of their high cost. Pasteurized and cooled milk is inoculated with a strain of bacteria to induce the ripening process, during which lactic acid is formed from lactose as well as flavor substances from fermented citric acid accompanying the lactic fermentation. These two fermentations are necessary for the formation of butter flavor. When ripening is complete, the acid content ranges between 0.75–0.80%.

With regard to the fatty phase, countless combinations of different fats may be used. Usually hydrogenated fats with a high melting point are mixed with soft fats. Deodorized fats are kept in aluminum containers just above their melting point. The ingredients are subsequently pumped into containers, placed over scales, and then mixed with suitable equipment.

From here the mixture is transferred into an emulsifying tank. The aluminum container, the scale-controlled mixer, and the emulsifying tank must be connected in such a way as to render the process almost continuous. At this stage the aqueous phase is at a temperature of 10°C, and the fatty phase, at 50°C maximum; higher temperatures might cause oxidation. First, the fatty phase is introduced, and ground ice is added to yield the required water ratio in the finished product and to allow a faster hardening of fats. At this point sodium chloride, sodium benzoate, EDTA, other stabilizers, and the eventual water-soluble emulsifiers are added. The dispersion of water into the fatty phase should not be too fine in order to avoid an excessive oily appearance in the finished product.

Cooling was at one time a separate operation. More recent techniques permit emulsification and cooling operations to be performed simultaneously in a single piece of equipment. In the last 20 years a method of cooling in pipes has been perfected. The machine emulsifies, cools, and mixes so that the product comes out of the pipes with a consistency suitable for direct molding and packaging.

The main additives, in addition to the above mentioned ones, are emulsifiers, anti-spattering agents, chelating agents, vitamins, flavor ingredients, colorants, antioxidants, and preservatives.

Flavor is an extremely important factor to the margarine consumer. The objective of margarine producers is to duplicate a butter flavor, which does not exist as a definite form since it varies enormously. The butter flavor in margarine is introduced mainly with the ripening process of milk added during the manufacturing process. It is well known that the main component influencing butter flavor is diacetyl, which is formed by bacteriological action on milk. Chemically, diacetyl is 2,3-butandione ($CH_3—CO—CO—CH_3$); it can be prepared by oxidation of acetyl methyl carbinol. Diacetyl is also produced synthetically by oxidation of methyl ethyl ketone with nitric acid and subsequent decomposition of the resulting isonitroso compound.

Whenever ripened milk is not added during the production of margarine for specific technical or economic reasons, the addition of butter flavors or compounded margarine flavors is definitely advisable. The formulation of such products may be realized in two versions, *i.e.*, hydrosoluble or liposoluble types. However, this is complicated by patents tending to limit the use of the potential flavor components. The formulation makes use of diacetyl and acetyl methyl carbinol as basic materials; substitutes for diacetyl could be the homologous ketones, *e.g.*, acetyl propionyl and dipropionyl. It has been definitely ascertained that margarine flavor is significantly improved by the addition of 0.2% monosodium glutamate, which is another flavor potentiator for margarine active at ppm levels.

Cheese

Each cheese type exhibits a peculiar and characteristic flavor dependent on the flavor of the milk used, the various curdling and manufacturing methods (salting, heat cycle, etc.), the type of fermentation, aging, and even the climatic conditions prevalent on the production site. In order to tackle a problem that presents an enormous number of variables, it is necessary first to classify the several hundred cheese products according to basic criteria (independent of the cheese flavor and palatability but based only on the industrial method of preparation); then the most representative examples from each category will be discussed. The following classification may be adopted:

1. Cheese made of whey plus curd (ricotta, mysost)
2. Cheese made of curd alone

These two classes may be further subdivided as follows:

1.	Fermented cheese	Hard, grating cheese (Romano, Parmesan, etc.)
	Ripened, aged	Hard (Cheddar, Swiss, Gruyere, Provolone, etc.)
		Semi-soft (Roquefort, Blue, Gorgonzola)
		Soft texture (Camembert, Brie, etc.)
2.	Non-fermented cheese	High fat (cream, Neufchâtel)
	Unripened	Low fat (cottage, baker's)
3.	Melted cheese	

Cheese may also be classified as cooked, semi-cooked, and raw.

The imitation of cheese flavors is extremely problematic because there are so many varieties, especially when complete flavor (odor and taste) results are required. Flavor imitations in the majority of cases attempt to duplicate odor only; the following products find application for this purpose: butyl butyryl lactate, isovaleric and capronic acids, ethyl butyrate, and methyl *n*-amyl ketone. In certain cases (*e.g.*, Roquefort cheese), the use of ammonium isovalerate may be of interest, whereas trace amounts of the most important cream flavor components may be usefully employed in the formulation of melted cheese flavors. For more complex and functional flavor formulations, the study of the components of natural cheese flavors may prompt valuable information. Although there are no available analyses of the constitution of non-fermented cheese flavors, it appears likely that the latter must best be closely related to (1) milk flavor, (2) thermally degraded milk flavor, or (3) microbiologically degraded milk flavor.

A discussion of fermented cheese flavors becomes even more complex. While components of milk flavor "as is" may be considered as playing only a secondary role, products derived from the degradation of proteins, fats, and carbohydrates must be considered responsible for the characteristic flavor.

Proteins serve as a substrate for microorganisms. A few peptides are also responsible for the bitter taste. Amino acids formed by proteolysis are not responsible for the typical cheese flavor but provide a background note and probably function as flavor enhancers. A positive cheese-flavoring action is exerted by the decomposition products of amino acids.

Fats play a primary role as modifiers and solvents for aromatic compounds. However, the precursors of lactones, methyl ketones, esters, alcohols, and fatty acids formed by enzymatic (lipase) hydrolysis are directly implicated and have been identified among the components of the characteristic cheese flavor. Carbohydrates and lactose are a source of energy for lactic acid bacteria. The unused carbohydrate portions end up in whey, and only slight traces are left in the curd; traces may be very important flavor precursors, however.[20]

The following ingredients are present in cheese flavor:

Components of Cheese Flavor

Ingredient	Parts, ppm
Acetaldehyde	1.40
Acetone	1.60
1-Butanol	0.70
2-Butanol	0.30
Butanone	0.30
Diacetyl	0.80
Dimethyl sulfide	0.11
Ethanol	16.30
Ethyl butyrate	0.60
2-Heptanone	0.45
2-Methylbutyraldehyde	0.42
Methyl caproate	1.50
2-Pentanone	0.98
1-Propanol	2.90

The characteristic flavor of blue cheese has been the subject of intense research.[21-24] To formulate blue-cheese flavor imitations, the following products may be found useful:

1. Acids: acetic, benzoic, butyric, caproic, caprylic, hydroxybenzoic, *p*-hydroxyphenylacetic
2. Ketones: acetone, 2-heptanone, 2-nonanone, 2-pentanone, 2-undecanone
3. Alcohols: 2-heptanol, 2-nonanol, 2-pentanol, 2-phenylethanol
4. Esters and aldehydes: ethyl butyrate, methyl caproate, methyl caprylate, and a few aliphatic aldehydes

Acids must be employed in amounts equal to more than 80% of the total mixture.

THE ROLE OF ENZYMES IN FOOD FLAVORS

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INTRODUCTION

Proteins, carbohydrates, and lipids are the three main sources of food flavors. Some minor flavor precursors such as polyphenols, nucleotides, and the pigments of carotenoid series also contribute to a certain extent in flavor development.[1] Naturally occurring food enzymes and enzymes involved in the metabolic process of microorganisms used in ripened and fermented foods play a major role in the development of food flavors from these precursors.

Hewitt and co-workers[2,3] reported that the typical flavor of a number of food products, such as milk, celery, spinach, tomatoes, oranges, strawberries, etc., lost in food processing may be restored by the addition of the right enzyme preparation. In a typical experiment, Hewitt et al.[2] prepared a blanched and dehydrated product from fresh watercress. The dehydrated material was quite flavorless. Reconstitution of dried watercress did not improve the flavor and it tasted and smelled like hay. However, when a tasteless and odorless enzyme preparation from white mustard (white mustard and watercress both belong to the *Bressica* family) was added to the reconstituted product, the typical odor and taste of watercress was restored within a few minutes. The dramatic effect of mustard enzymes in restoring watercress flavor as proposed by Hewitt et al.[3] is reproduced in Figures 1 and 2.

The work of Hewitt et al.[2,3] amply demonstrates the importance of enzymes in the flavor development of food products. Unfortunately, comparatively little work has been done along this line to provide better insight of the various steps involved in flavor development by enzymatic action. Such information could be of great advantage in designing process details in the commercial processing of foods. Severe flavor losses during processing may be compensated by preserving the precursors and restoring the original flavor of processed food by enzymatic action. Additional research and developmental work are required on the structure of various flavor precursors, the nature of enzymes which act on these flavor precursors, and the reactions which take place. Some information on the nature of enzymes involved in the development of important flavor compounds is known. However, in order to study the enzymatic reactions and

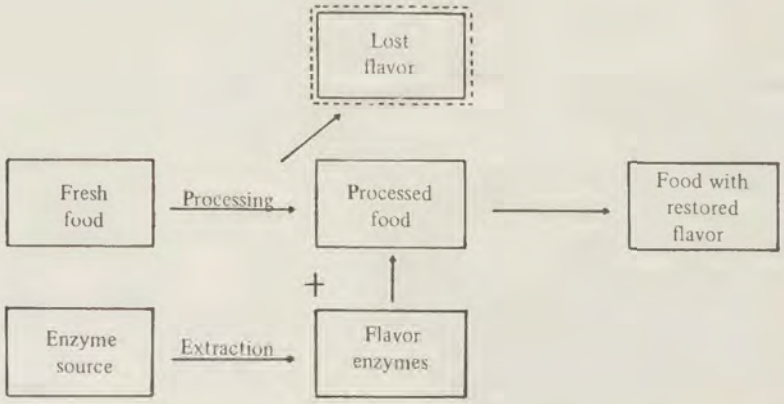


FIGURE 1. Restoration of natural flavor to processed foods. (From Hewitt, E. J. et al., in *Chemistry of Natural Food Flavors*, Mitchell, J. H., Jr., Leinen, N. L., Mrak, E. M., and Bailey, S. D., Eds., Chicago Quartermaster Food and Container Institute, Chicago, 1957, 88. With permission.)

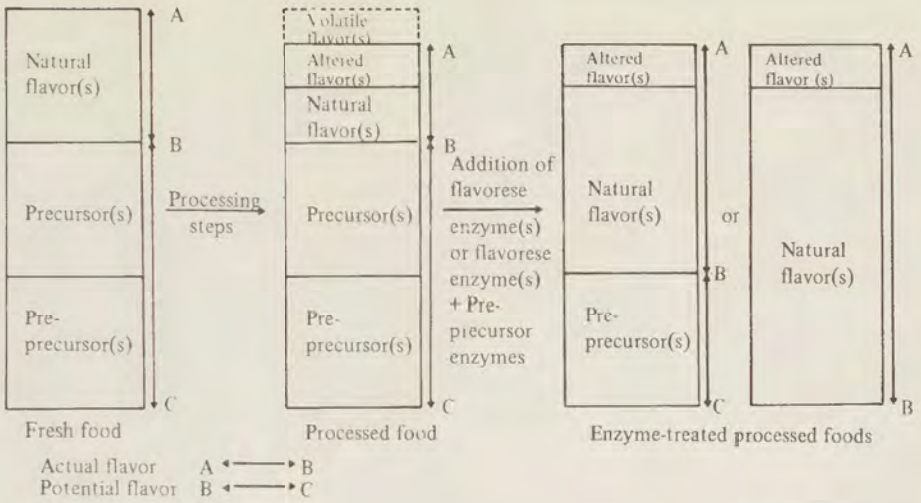


FIGURE 2. Barographs illustrating survival of flavor precursors and pre-precursors in conventional heat processing and action of enzymes on flavor precursors and pre-precursors in processed foods. (From Hewitt, E. J. et al., in *Chemistry of Natural Food Flavors*, Mitchell, J. H., Jr., Leinen, N. L., Mrak, E. M., and Bailey, S. D., Eds., Chicago Quartermaster Food and Container Institute, Chicago, 1957, 90. With permission.)

intermediate steps precisely and to adopt the information in preserving food flavors during processing, purified enzyme extracts would be required. The purified enzymes may be studied for their specificities and concentrations using model systems. The information obtained from these studies may then be applied to food systems and the influence of other enzymes and ingredients present in the food on the basic enzymatic reaction can be followed. In addition, as suggested by Hewitt et al.,[2,3] it would be desirable to study the flavor precursors and perhaps the flavor pre-precursors. These relatively nonvolatile compounds may be separated from the bulk of the food products by appropriate methods, such as column and ion-exchange chromatography, and identified by using a combination of infrared, nuclear magnetic resonance, pyrolytic gas chromatography, and mass spectrometry. Finally, the action of enzymes, believed to be involved in flavor development, on the isolated precursors could be studied and the liberated flavor examined by the sensory panel and instrumental techniques.

The climatic conditions, method and the time of harvesting, geographic location, and the species of plants are known to influence the flavor of foods, especially fresh foods. The flavor enzyme and precursor study would give us some information on the nature of enzymes and precursors in the plants that are influenced by these factors. The day can be foreseen when foodstuffs may be processed according to their flavor precursor content, rather than for their flavor.[4]

The processed foods are stabilized by substantially destroying or inactivating all the enzymes present. This inactivation, often done by blanching, is specifically aimed at enzymes which induce off-flavor development during storage of processed foods. One such enzyme is peroxidase. Thus, when blanching is carried out to the point where peroxidase activity is substantially destroyed, most of the other enzymes present in foodstuffs are also destroyed or inactivated. In other words, in inactivating the enzymes that are deleterious to food stability, the enzymes involved in flavor formation are also affected. The fresh flavor of the food is altered or partially destroyed by processing because many flavor compounds are volatile or heat-labile. Flavor precursors seem to survive processing, thereby representing a potential or latent source of fresh flavor.[2,3] The precursor and enzyme study may also provide information for selective destruction or control of enzymes and/or precursors responsible for undesirable flavors produced during storage of food products.

MILK AND MILK PRODUCTS

Milk produced from normal healthy cows contains a wide variety of enzymes. In their report on the Enzyme Nomenclature, to the Manufacturing Section of the American Dairy Science Association, Shahani et al.[5] compiled the available information on the bovine milk enzymes. All the major data concerning these enzymes were consolidated in a tabular form by these workers and can be conveniently referred to. They also attempted to discuss the physiological as well as technological significance of these enzymes. Milk enzymes are believed to originate in the secretory epithelial cells of the mammary gland and their presence may be regarded as the "spilling over" from these cells and serum during the milk secretion process.[6,7] It is surprising that there are few readily observed changes in milk directly attributed to enzymes other than lipase,[8] which causes lipolysis of milk fat, and possibly xanthine oxidase,[9] implicated with oxidative deterioration of milk. Zittle[10] believes that the pasteurization of milk as a common practice may be one of the reasons. Many milk enzymes are heat-sensitive and loose their catalytic activity when heated. Second, the enzymatic changes which do occur may not be obvious if the physical stability and flavor of milk are not altered. On the other hand, some heat-inactivated enzymes regain their activity during storage and may continue to act for a long time if a suitable substrate is available, as in the case of protease.[11] The reaction products in such cases continue to build up and may bring about spoilage or other detectable changes even though the concentration of residual or reactivated enzyme may be negligibly small. It is, however, difficult to distinguish between changes brought about by enzymes inherent in milk and the ones produced by microorganisms during prolonged storage.[10]

Some of the milk enzymes and their approximate concentrations in fresh cow milk that may have some role in the development of desirable or undesirable flavors are given in Table 1. It may be noted from this table that milk contains significant amounts of amylase, lipase, xanthine oxidase, and peroxidase.

TABLE 1

Partial List of Bovine Milk Enzymes[6,12]

Enzyme	Concentration in milk[a]			Specificity, substrate	Optimum pH	Optimum temp. °C
	Fresh	Pasteurized[b]	Sterilized[c]			
Aldolase (4.1.2.13)				Ketose mono- and diphosphate, fructose 1,6-diphosphate	Assayed at pH 7.0	35
α-amylase (E.C.3.2.1.1)	11,800	950	620	α-1,4-D Glucan linkages in polysaccharides, starch glycogen, polysaccharides, and oligosaccharides	7.4	34
A-esterase (3.1.1.2)				Aryl esters	8.0	37
B-esterase (3.1.1.1)				*n*-Methyl esters of fatty acids, triglycerides	8.0	37
C-esterase (3.1.1.8)				Choline esters, tributyrin	8.0	37
Lipase (3.1.1.3)	109	–	–	Glycerol esters in emulsion	9.0 to 9.2	37
Peroxidase (1.11.1.7)	22,100	5,400	0	H_2O_2 and some organic peroxides	6.0 to 7.0	20
Protease (3.4.4.-)				Tryptic and/or chymotryptic specificity	8.0 6.5	37
Xanthine oxidase (1.2.3.2)	175	145	0	Aldehydes, oxypurines, pterin, DPN, xanthine	6 to 9 6 to 9	37

[a]All enzyme units are expressed in international units (IU)
One IU = moles of substrate transformed per minute per 1,000 ml milk
[b]15 sec at 74°C
[c]15 min at 115°C

Esterase

This enzyme catalyzes the hydrolysis of esters. Forster et al.[13] reported the presence of three esterases, A, B, and C, in milk. A-esterase hydrolyzes aromatic esters such as phenyl acetate. B-esterase hydrolyzes aliphatic and aromatic esters but not choline esters, whereas C-esterase splits choline esters more rapidly than aliphatic or aromatic esters.[14] Unlike milk lipases, very little work has been done on milk esterases for a possible role in the development of desirable or undesirable flavors in dairy products. Jensen[15] has reported that B-esterase behaves identically to the lipase in whole milk and contains glycerol hydrolase activity. Recently Kitchen[16] provided some insight into the nature and distribution of milk esterases. An important property in relation to the presence of milk esterases in Cheddar cheese is that the esterases are soluble at pH 4.6. It is unlikely, therefore, that any high proportion of milk esterases would be present in the curd, although, as some mechanical occlusion of whey proteins occurs during cheese making, some enzyme would be present in the final pressed cheese. Over the lengthy period of ripening, this small amount of enzyme might still be significant in relation to flavor development. The concentration of these enzymes in Cheddar cheese is so small that is is not possible to determine it experimentally and provide evidence for any contribution by these enzymes in flavor development. The contribution of these enzymes in the flavor of other dairy products is not known.

Lipase

Bovine milk contains lipases which hydrolyze milk fat and liberate fatty acids. Milk fat is especially rich in short chain fatty acids such as butyric acid. Liberation of these fatty acids from milk fat by the action of milk lipases imparts undesirable flavor, termed "rancid," to dairy products. Milk products such as cream and butter prepared from raw milk often develop rancidity on storage. An important use of milk lipases is in the manufacture of blue and Roquefort cheeses. "Peppery taste" of blue cheese has been attributed to short chain fatty acids and their hydrolyzable salts which are produced by the action of native milk lipases and lipases produced by microorganisms during cheese ripening.

It is believed that milk contains at least two different lipases, one irreversibly adsorbed on the fat globule membrane when milk is cooled, and the other associated with the casein of milk plasma.[17] Purified slime lipase shows an apparent specificity for short chain fatty acid-containing glycerides.[18] This enzyme shows no intramolecular specificity and hydrolyzes both short and long chain fatty acids at the same rate provided the fatty acids occupy the 1- and 3-positions in the same molecule.[19] However, it exhibits positional specificity, i.e., fatty acids in the 1- and 3-positions are hydrolyzed at a faster rate compared to fatty acids in the 2-position. The slime lipase that exists in association with casein is the major lipase in milk. Chandan and Shahani[20] isolated this enzyme in pure form and studied its properties (Table 2).[18,21,22]

Milk from some cows (up to 22%) in a herd is known to become rancid quickly.[23] The term "spontaneous" milk has been coined for such milks. The "spontaneous" milk does not require any treatment other than cooling when drawn or shortly after milking to 15 to 20°C to hasten lipolysis.[24] On the other hand, cooling and aging do not accelerate the lipolysis significantly in nonspontaneous or normal milk. Lipases from normal milk may be activated by homogenization of raw milk between 37.7 and 54.4°C for a short time. Other forms of agitation, such as shaking raw milk, churning raw milk or cream, and pumping, accelerate lipolysis. Increase in surface area of the substrate is the most important reason for the increase in lipolytic activity.[25] Thermal manipulations and certain chemicals, i.e., $CaCl_2$, $MgCl_2$, pseudoglobin, euglobin, lactalbumin, etc., also activate milk lipases. The spontaneous rancidity can be prevented or reduced by mixing with four to five times its volume of nonspontaneous milk.[27] Since only one out of five cows in a herd produces spontaneous milk, this defect is automatically eliminated in market milk. The mechanism involved in the inhibition of lipolysis in spontaneous milk by dilution with nonspontaneous milk is not known. In his review on the deterioration of milk lipids, Schwartz[26] speculated the presence in nonspontaneous milk of a labile inhibitor of spontaneous milk lipase.

TABLE 2

Properties of Purified Slime Lipase (Milk)[18,21,22]

		Reference
Optimum pH	9.0	18
Optimum temperature	37°C	18
Optimum substrate concentration	10%	18
Effect of		
Oxygen	Inhibitory	18
Light	Inhibitory	18
Heat	Inhibitory	18
Certain salts	Inhibitory	21
Glutathione	Stabilizing	21
p-Chloromercurobenzoate	Inhibitory	21
N-Ethylmaleimide	Inhibitory	21
Iodoacetate	Inhibitory	21
H_2O_2	Inhibitory	21
Substrate specificity		
Milk fat	Lipolyzed	22
Vegetable oils	Lipolyzed	22
Triglycerides	Lipolyzed	22
Simple esters	Not lipolyzed	18
Positional specificity	1,3 position	22

Peroxidase

Peroxidases are defined as enzymes catalyzing the following reaction:

$$ROOH + AH_2 = H_2O + ROH + A$$

The compound ROOH may be HOOH or some other organic peroxide. Milk peroxidase, often referred to as lactoperoxidase, has been isolated in pure form.[28,29] It appears to be associated with the albumin or whey protein components of milk. It constitutes about 1% of the total serum protein content and is fairly heat stable compared to other milk enzymes.[30] The number and nature of organic compounds that can serve as hydrogen acceptors for lactoperoxidase have not been fully investigated. Peroxidases, in general, use hydrogen peroxide, methyl hydrogen peroxide, ethyl hydrogen peroxide, and similar compounds as hydrogen acceptors. The hydrogen donors may be phenols, amines, or other organic compounds. The reaction mechanism seems to be based on the formation of enzyme-hydrogen donor complexes and two univalent oxidation steps, as shown below, where AH_2 stands for hydrogen donor and A for oxidized acceptor.

Lactoperoxidase + H_2O_2 = Complex I;
Complex I + AH_2 = Complex II + AH;
Complex II + AH = Lactoperoxidase + A

The last step in this chain seems to be rate limiting. Milk peroxidase may be involved in oxidative deterioration of milk lipids. This enzyme should be thoroughly investigated for its physicochemical properties and its role, if any, in off-flavor development in dairy products.

Protease

Proteases hydrolyze the peptide linkages of proteins. Some of the peptides and amino acids released by the action of protease serve as precursors of flavoring compounds. Milk contains a very small amount of protease. Kaminogawa et al.[31] reported that milk protease has a sharp pH optimum at 8.0 with an accompanying shoulder at 6.5, shows tryptic and chymotryptic substrate specificity, and is most effectively inhibited by diisopropylfluorophosphate. They also found that when the protein was in more purified state, it could be destroyed by heating to 80°C for 10 min; however, when present in aseptically canned milk, considerable proteolysis occurred after storage for 30 days at 30°C. Among different casein fractions, β-casein has been found most susceptible to proteolysis followed by α- and k-casein.[31,32] Raw milk under normal conditions does not undergo spontaneous proteolysis, although protease exists in association with k-casein in milk. Murthy et al.[11] observed proteolysis in stored sterilized milk and attributed it to reactivation of protease. The presence of residual enzyme in pasteurized and evaporated milk has not been established. It is quite possible that upon long storages the residual or reactivated enzyme may initiate flavor and texture defects.[33]

Xanthine Oxidase

Xanthine oxidase is a nonspecific enzyme since it catalyzes the oxidation of purines, pyrimidines, and aldehydes. It oxidizes aldehydes to acids with the hydrated aldehyde as the intermediate step.[26,30,34] A similar hydration occurs at a carbon-nitrogen double bond in xanthine and on subsequent transfer of hydrogens, uric acid is formed. Thus, the action of xanthine oxidase on purines and aldehydes is more similar than one would anticipate from a quick look at the formulas. The hydrogens, when activated on the enzyme, can be transferred to other molecules such as redox dyes and to oxygen.[10] The term dehydrogenase is often used for this enzyme. The presence of xanthine oxidase in microsomal particles has been reported.[35] Xanthine oxidase is a metallo-protein, containing molybdenum and iron. It has a molecular weight of about 300,000 to 400,000 and pI 5.3 to 5.4. It is fairly stable to heat and, in contrast to other enzymes, its activity in milk increases with several heat treatments, homogenization, and by protease and lipase action.[5] The variation in xanthine oxidase content of milk produced in different localities apparently is related to the molybdenum content of the forage consumed by the cow.[37]

Xanthine oxidase, because of its broad range of activities, has been considered as perhaps responsible for some of the oxidative deterioration in the flavor of milk. The evidence, however, has been conflicting. Studies of Rajan et al.[38] and Smith and Dunkley[39] could not establish a correlation between xanthine oxidase content and oxidative flavor, based on chemical test or taste panel scores. Aurand and co-workers,[40-42] on the other hand, observed that the spontaneously oxidized flavor could be prevented either by the use of heat or an enzyme inhibitor. Subsequently they showed that the occurrence of spontaneously oxidized flavor could be correlated with a high level of xanthine oxidase activity and that specific inhibitors for xanthine oxidase were effective in preventing off-flavor development. They concluded that (1) high xanthin oxidase activity can be correlated with spontaneously oxidized flavor and (2) lability of the unsaturated fatty acids toward enzymatic oxidation was related to degree of unsaturation, i.e., linolenic acid was oxidized rapidly, linoleic acid at a very slow rate, and oleic acid unoxidized.

In contrast, other workers[39,43-45] have reported that ascorbic acid and copper were the essential reactants for the spontaneous flavor development and they were unable to obtain results consistent with xanthine oxidase theory.

Kiermeier and Grassmann[9] studied the relationship between xanthine oxidase and oxidized flavor in milk and reported that the milk containing active xanthine oxidase and buffered linoleic acid oxidized xanthine 1.5 to 2 times and adenine about 10% faster than normal milk. Various aldehydes tested could not act as substrate for xanthine oxidase.

Other milk enzymes that may have some role in flavor development of dairy products include aldolase and amylase. However, no information to this effect about these enzymes is available.

CULTURED DAIRY PRODUCTS

The contribution of microorganisms in the development of "typical" flavor of cultured dairy products is

well known. However, detailed studies to provide deeper insight into the genesis of these flavors are still needed. Microorganisms naturally present or added during manufacture of cultured dairy products and cheeses metabolize carbohydrates, lipids, and proteins for energy and growth. The volatile flavor compounds are produced as by-products of these metabolic processes, catalyzed by microbial enzymes.

Several excellent reviews on the flavor of cultured dairy products have appeared in recent years.[46-49] A number of species of *Lactobacilli, Streptococci,* and *Leuconostoc* are used in starters for the manufacture of cultured dairy products. These aroma-producing lactic acid bacteria belong to the *Lactobacillaceae* family and may be homofermentative or heterofermentative. A thorough treatment of lactic acid bacteria may be found elsewhere.[50,51] These organisms are Gram-positive, nonsporulating cocci or rods. *Leuconostoc citrovorum, Leuconostoc dextranicum,* and *Streptococcus diacetilactis* are the main species used for aroma production in starter cultures. Diacetyl is the most important flavor compound in these products. Other compounds, such as acetaldehyde, acetylmethylcarbinol, 2,3-butanediol, acetic, and propionic acids, are also produced.

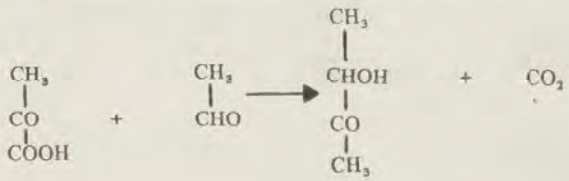
Homofermentative

Lactic acid bacteria belonging to this group produce as much as 1.8 mol of lactic acid per mol of glucose with minor amounts of acetic acid, ethanol, and carbon dioxide.

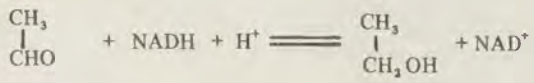
Embden-Meyerhof-Parnas (EMP) pathway is the main metabolic pathway for carbohydrate metabolism[52] (Figure 3). The factors affecting the nature of end products of fermentation of homofermentative lactic acid bacteria have not been studied thoroughly. In the case of *Streptococcus faecalis,* the end products depend very much on culture conditions, i.e., at pH 5.0 to 6.0 pyruvate is reduced by lactate dehydrogenase to D-, L-, or D,L-lactic acid. At neutral or slightly alkaline pH, however, pyruvate metabolism leads to the production of formic and acetic acid and ethanol in the ratio 2:1:1.[53]

Homofermentative lactic acid bacteria also use fructose, mannose, galactose, and disaccharides such as lactose, maltose, and sucrose as substrates. These sugars are converted into intermediates of EMP pathway by inducible enzymes.[50]

Lees and Jago,[54] quoted by Doelle,[50] have found a new pathway in certain *Streptococci,* i.e., *Streptococcus diacetilactis, Streptococcus lactis,* and *Streptococcus cremoris.* These bacteria utilize lactose and threonine from casein hydrolysate with the formation of glycine and acetaldehyde (Figure 4). The enzyme catalyzing the utilization of threonine is aldolase (L-threonine acetaldehydelyase, E.C. 4.1.2.5), which require pyridoxal phosphate as a cofactor. Acetaldehyde itself can be metabolized further via three different pathways, depending upon the availability of three enzymes as well as the utilization of lactose via the EMP pathway:[50] (1) Acetaldehyde and glyceraldehyde 3-phosphate are joined under the catalytic action of deoxyriboaldolase to form deoxyribose phosphate. (2) These bacteria also possess an enzyme which combines pyruvate with acetaldehyde with the formation of acetoin:



The action of this enzyme has been called a synthetase reaction by Lees and Jago, who gave the name "acetoin synthetase." (3) The third possible acetaldehyde metabolism is directed by an active alcohol dehydrogenase (alcohol:NAD oxidoreductase, E.C. 1.1.1.1) which converts acetaldehyde to ethanol:



There may be, of course, a number of *Streptococci* which do not follow this metabolism, as was shown with the glycine requiring *Streptococcus cremoris* Z8. The strain lacks the threonine aldolase.[50]

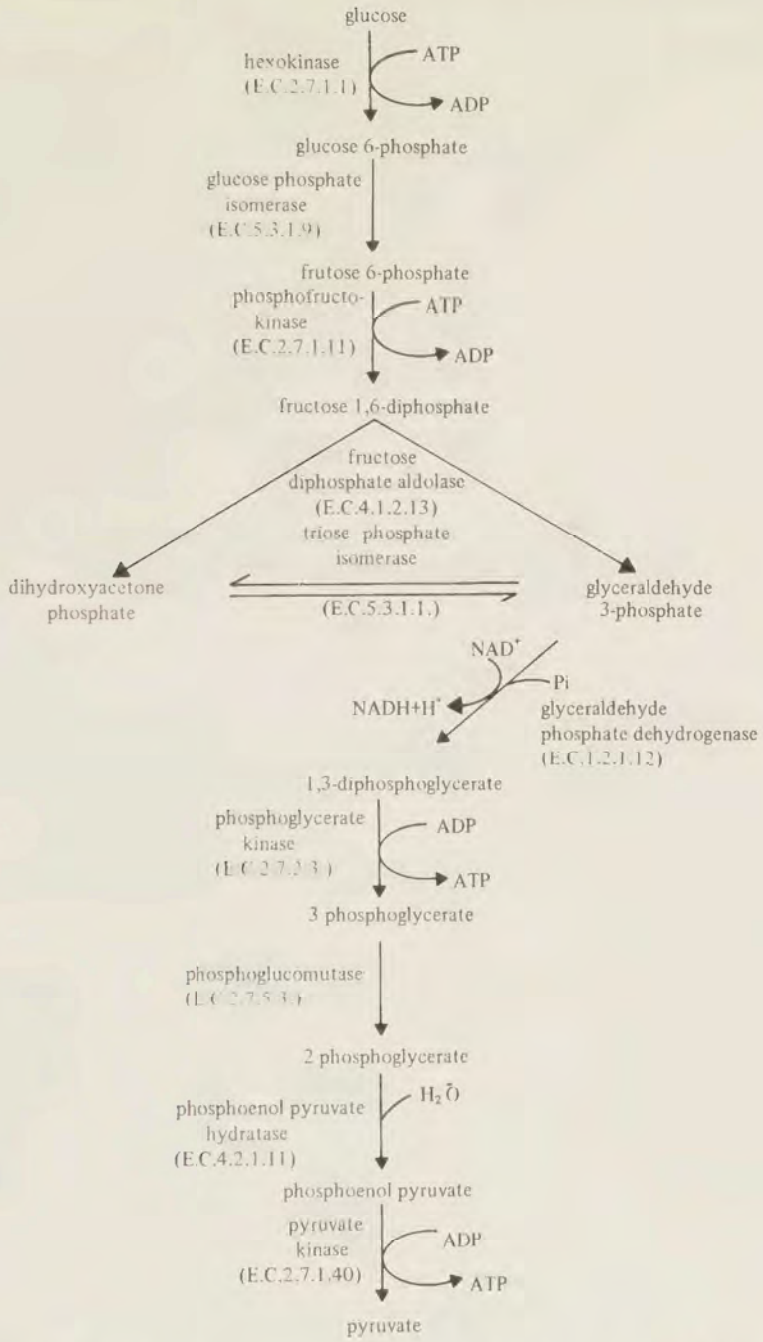


FIGURE 3. Embden-Meyerhof-Parnas (EMP) pathway of carbohydrate metabolism.

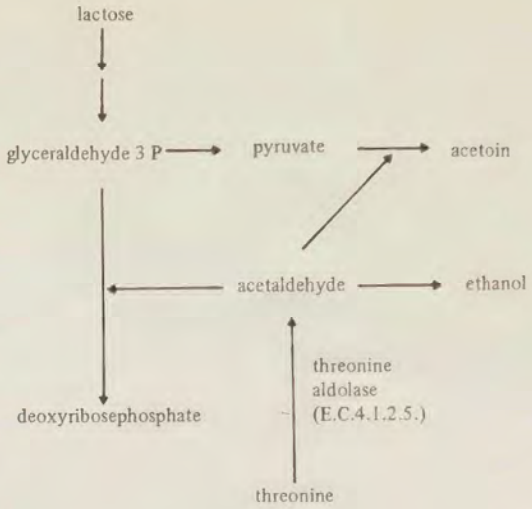


FIGURE 4. Utilization of threonine and lactose by certain *Streptococci.*[53]

Heterofermentative

Organisms that ferment hexoses with the formation of less than 1.8 mol of lactic acid per mol of glucose and in addition ethanol, acetate, glycerol, mannitol, and carbon dioxide are called "heterofermentative." The main group of organisms are strains of *Leuconostoc*, some strains of *Lactobacilli* and others.[52]

Leuconostoc-type heterofermentation results in the formation of 0.8 mol of lactic acid, 0.1 to 0.2 mol of acetate, 0.9 mol of CO_2, 0.8 mol of ethanol, and 0.2 to 0.4 mol of glycerol.

Leuconostoc species possess phosphoketolase pathway (Figure 5). All three other pathways, Embden-Meyerhof-Parnas pathway, hexose monophosphate pathway, and Entner-Doudoroff pathway are found to be absent.[50]

Investigations into the presence of enzymes in heterofermentative microorganisms have revealed the presence of hexokinase (ATP:D-hexose 6-phosphotransferase, E.C. 2.7.1.1), phosphoglycerate kinase (ATP:3-phospho-D-glycerate 1-phosphotransferase, E.C. 2.7.2.3), glycerophosphate dehydrogenase (L-glycerol-3-phosphate: (acceptor) oxidoreductase, E.C. 1.1.99.5), D-lactate dehydrogenase (D-lactate:NAD oxidoreductase, E.C. 1.1.1.28), ethanol dehydrogenase (alcohol:NAD oxidoreductase, E.C. 1.1.1.1),[55] acetaldehyde dehydrogenase, and acetoin dehydrogenase (acetoin:NAD oxidoreductase, E.C. 1.1.1.5). Fructose diphosphate aldolase (E.C. 4.1.2.13) and triose phosphate isomerase (D-glyceraldehyde 3-phosphate ketol isomerase, E.C.5.3.1.1) are absent.[50] The lack of the latter two enzymes makes it impossible for the EMP pathway to function. Enzymes of the HMP pathway present are a glucose 6-phosphate dehydrogenase (E.C. 1.1.1.49) and 6-phosphogluconate dehydrogenase (E.C. 1.1.1.43).[56,57]

Two mechanisms have been proposed for the synthesis of diacetyl by lactic acid bacteria.[58-60] The mechanism proposed by Speckman and Collins[58] involves the condensation of active acetaldehyde and acetyl CoA (Figure 6). Using cell-free extracts of *Streptococcus diacetilactis* and *Leuconostoc*, these workers reported that only acetoin was formed from pyruvate in the absence of coenzyme A. Thiamine pyrophosphate (TPP) and Mg^{++} or Mn^{++} were required for acetoin synthesis. Addition of acetyl CoA to these solutions restored the ability to produced diacetyl. The second mechanism proposed by Seitz et al.[59] involves the oxidative decarboxylation of α-acetolactic acid (Figure 7). The latter mechanism of diacetyl synthesis has also been detected in yeast.[60] Citric acid fermentation and biosynthesis of diacetyl, acetoin, and 2,3-butanediol have been discussed in detail by Lindsay[46] and Collins.[48] In their study on the role of citrate and acetoin in the metabolism of *Streptococcus diacetilactis*, Harvey and Collins[61] noticed that this organism does not produce diacetyl and acetoin when grown in broth, on glucose, or lactose with no citrate or substitute of citrate. On the other hand, addition of citrate to milk enhances the production of acetoin and diacetyl. Based on these observations, these workers concluded that acetoin and diacetyl are produced only as a result of overproduction of pyruvate from citrate, which in turn is a consequence of the fact that

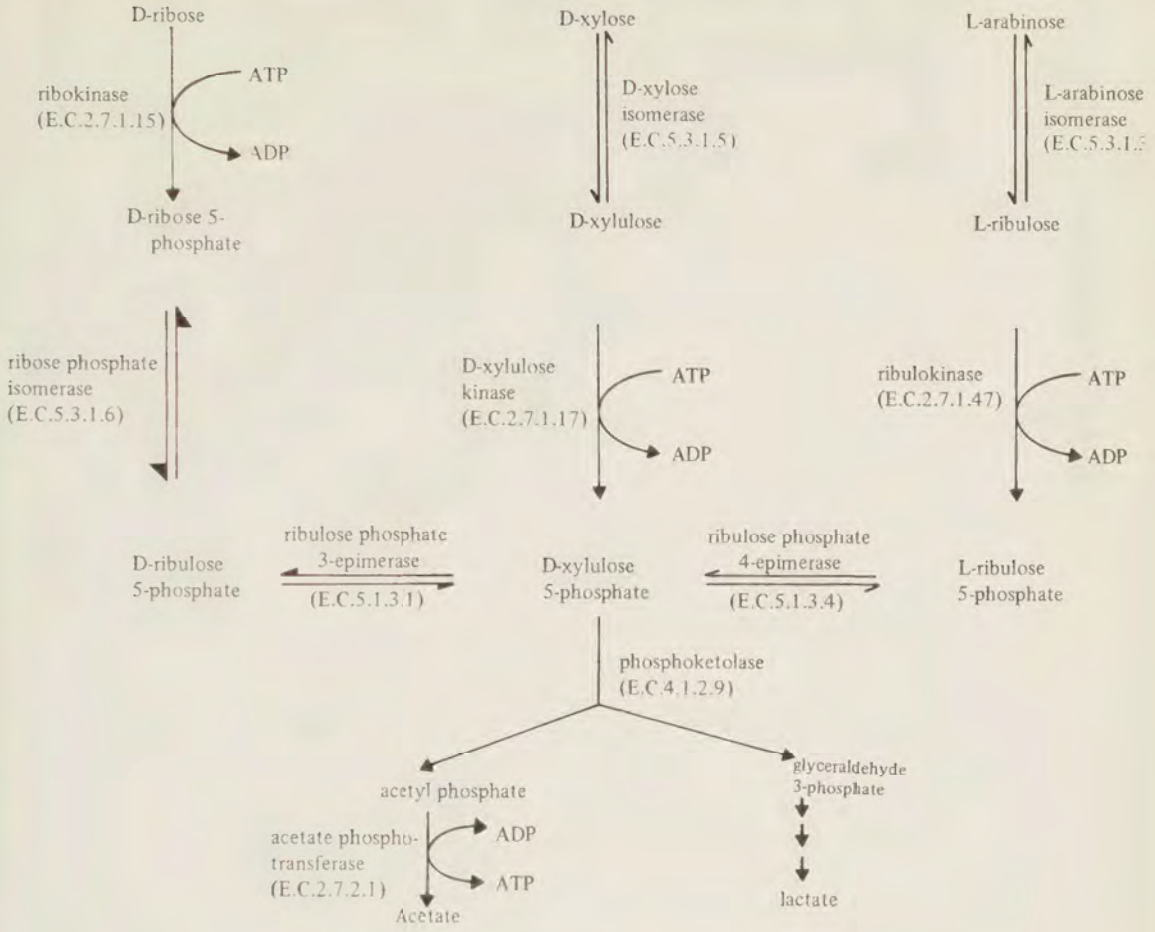
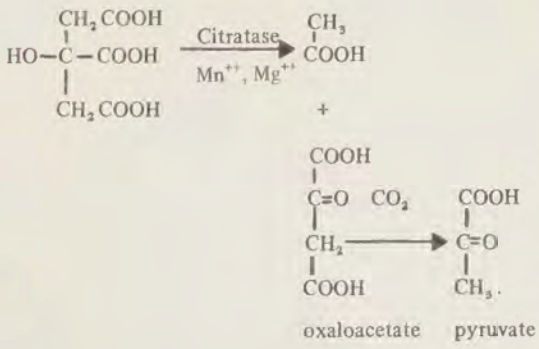


FIGURE 5. Pentose phosphoketolase pathway.

the entry of citrate into cells is uncontrolled. The absence of acetoin and diacetyl in citrate-devoid medium has been explained on the basis that in the normal carbohydrate metabolism 1 mol of glucose produces 2 mol of pyruvic acid and 2 mol of NAD (nicotinamide adenine dinucleotide) are reduced. This reduced NAD needs to be oxidized back to NAD for glucose metabolism to continue, and lactic acid bacteria use pyruvate as hydrogen acceptor to reoxidize NAD and convert it to lactic acid. However, these microorganisms do not need NAD for converting citrate to pyruvate:



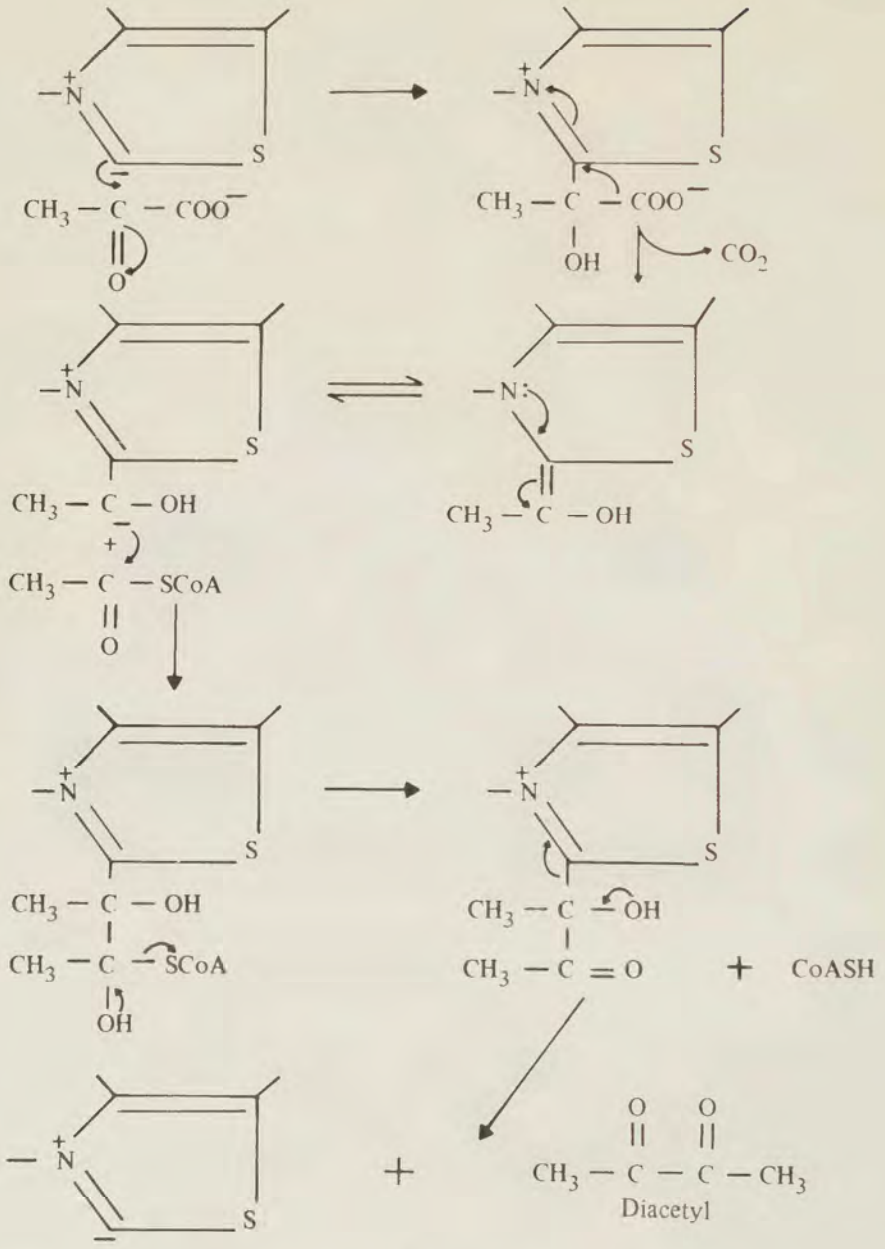


FIGURE 6. Mechanism for diacetyl biosynthesis by *Streptococcus diacetilactis* and *Leuconostoc citrovorum.*[57]

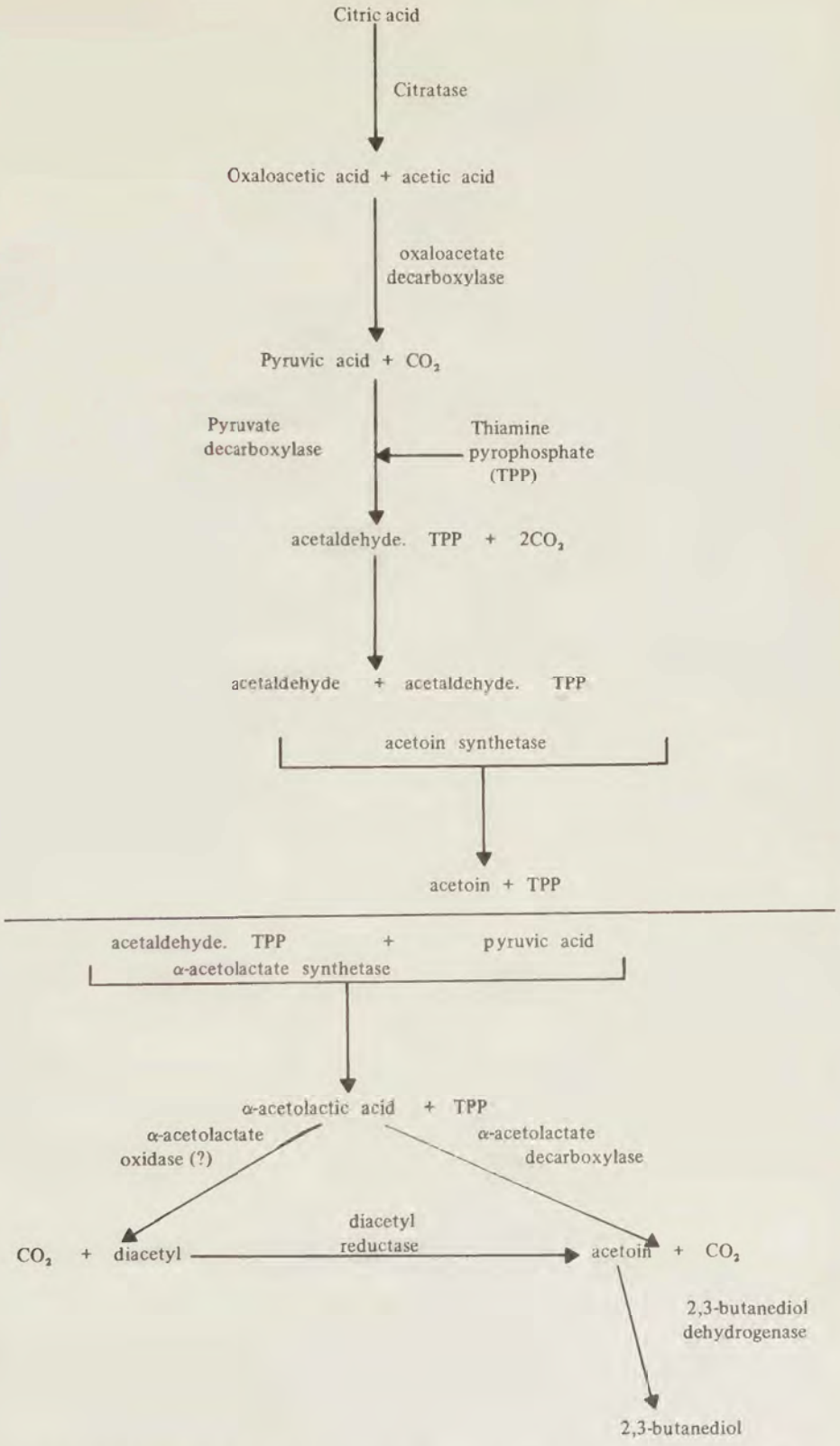


FIGURE 7. Pathways for conversion of citric acid by *Streptococcus diacetilactis*. (From Speckman, R. A. and Collins, E. B., *J. Bacteriol.*, 95, 174, 1968. With permission.)

It is believed that these microorganisms produce diacetyl and acetoin primarily as means of converting excess pyruvate into nontoxic neutral compounds.[61] These compounds are also involved in the reoxidation of NAD.[48] In the cultured dairy products diacetyl concentration increases for some time, as the bacterial cells multiply and produce diacetyl. However, after prolonged incubation diacetyl is converted to acetoin by diacetyl reductase present in *Streptococcus diacetilactis* and other starter organisms[59] by the following mechanism:

$$CH_3.CO.CO.CH_3 + NADH + H^+ \rightarrow CH_3.CO.CHOH.CH_3 + NAD^+$$

Since the presence of diacetyl causes serious flavor defects in citrus juices, beer, and distilled liquors, advantage may be taken of the irreversibility of diacetyl reductase reaction to eliminate buttermilk flavor in these products.[47] The enzyme has an optimum pH of 7.0, which makes it unsuitable for use in citrus juices with pH level around 4.0. However, a method of protecting the enzyme and regenerating reduced NAD has been developed so that commercial use of enzymes, especially in beer, seems likely.[62]

Diacetyl production is pH dependent. Above pH 5.5 little diacetyl is produced. At low pH diacetyl reductase activity is slight[63] and at the same time citrate permease required for the active transport of citrate into the cell is much more active.[64] As discussed earlier, lactic cultures normally require a source of pyruvate in addition to carbohydrate for the production of considerable amounts of diacetyl, acetoin, and 2,3-butanediol. Consequently, sparing effect exerted by $NADH_2$ oxidase on the pyruvate produced from carbohydrate may not be of great importance. It is probably limited because the oxidases of *Streptococcus diacetilactis* and other organisms that have been studied, function optimally near neutrality.[64] However, $NADH_2$ oxidase undoubtedly has an important influence on the ratio of diacetyl to acetoin since diacetyl, acetoin, and 2,3-butanediol are structurally related and represent three levels of oxidation of same four-carbon skeleton. A limitation on the accumulation of diacetyl in cultures is the reduction of diacetyl to acetoin and acetoin to 2,3-butanediol. Since each of these reductions requires $NADH_2$ and a donor of electrons, oxidation of $NADH_2$ by oxidase results in larger accumulation of diacetyl.[64]

Aeration of cultures also increases diacetyl production. *Streptococcus diacetilactis* possesses an enzyme that oxidizes reduced NAD in the presence of oxygen.[64] Aeration stimulates the production of this enzyme and results in the decrease of pyruvate that must be converted to lactic acid; thus, more pyruvate becomes available for diacetyl production. Also with the oxidation of reduced NAD, there is less need for conversion of diacetyl to acetoin.[48]

Another importance of oxygen has to do more directly with the synthesis of diacetyl. The synthesis of diacetyl requires acetyl-CoA.[58] Lipoic acid is involved in the formation of acetyl-CoA from hydroxyethyl-thiamine pyrophosphate and coenzyme A.[65] In this mechanism the lipoic acid is reduced. NAD is necessary for reoxidation of lipoic acid, and in turn oxygen and $NADH_2$ oxidase are required for the reoxidation of NAD.[64] Thus oxygen influences the formation of diacetyl by influencing the formation of acetyl-CoA.

Based on the available information on diacetyl synthesis, Gilliland[66] developed a process for preparing concentrated cultures using *Leuconostoc citrovorum* for flavor intensification in dairy products like buttermilk and cottage cheese. In this method, a culture is grown in a broth medium. When the culture reaches maximum population, cells are harvested by centrifugation and resuspended in small volume of 10% nonfat milk solids (NFMS). The culture concentrate so prepared is dispensed in 1-g quantities and stored under liquid nitrogen (196°C). This concentrate is inoculated into 10% NFMS to yield a population equal to an 18-hr milk culture. The inoculated milk is adjusted to pH 4.5 (optimum for diacetyl production) with citric acid. At various intervals samples are removed and assayed for diacetyl. When diacetyl concentration reaches a desirable level, it may be added to buttermilk or to cream used for cottage cheese dressing. Taste panel studies indicated preference for concentrated cultures over conventional milk culture because of high diacetyl concentration. The author argues that the use of concentrated cultures from a culture supplier to directly inoculate acidified milk eliminates 20 to 24 hr required to grow *Leuconostoc* culture in dairy plant. Because flavor concentrates can be produced under closely controlled conditions and their activity checked before sale, more uniformity in flavor and aroma of creamed cottage cheese should result from their use in preparing the cream dressing.

In his review on the cultured dairy products, Lindsay[46] has given a good account of flavor compounds

which give a typical flavor character to cultured dairy products. Among carboxylic acids produced by lactic acid bacteria, acetic acid, being the major volatile acid in cultured products, is important in the flavor. The acidic taste of these products is largely due to lactic acid. Lactic acid being nonvolatile does not influence the aroma of these products. Very little attention, from a flavor standpoint, has been paid to other volatile acids such as formic, propionic, butyric, and valeric acids found in very small amounts in cultured dairy products. These acids may have some contribution in overall flavor balance of these products.

A small concentration of acetaldehyde is considered desirable in cultured dairy products.[46] The flavor balance of butter cultures was reported to be closely related to the diacetyl:acetaldehyde ratio. Desirable full-flavored cultures exhibit ratios from 3:1 to about 5:1, and a green flavor if the ratio drops below 3:1, and when the ratio exceeds 5:1, a harsh diacetyl flavor becomes apparent:

$$\underset{\text{harsh}}{13:1} \longleftrightarrow \underset{\text{good}}{5:1} \longleftrightarrow \underset{\text{green}}{3:1} \longleftrightarrow 0.4:1$$

All *Streptococci* used in starter cultures produce acetaldehyde[67] and give a green flavor defect when overgrowth of *Streptococci* takes place. Bills and Day[68] showed that the concentration of ethanol varies from 0.2 to 36.8 ppm among starter strains and lower ethanol concentrations were accompanied by high acetaldehyde concentrations, consistent with the following reaction:

$$CH_3\text{-}CHO \xrightarrow[NADH + H^+ \quad NAD^+]{} CH_3CH_2OH$$

Following this, Keenan et al.[69] showed that *Leuconostoc* strains utilized acetaldehyde and that the green flavor defect could be overcome by incorporating 25 to 50% *Leuconostoc* in lactic starter cultures.

Culture-related flavor defects have been reviewed by Sandine et al.[70] Work done in this area indicates that the lack of diacetyl flavor in cottage cheese, cultured buttermilk, and sour cream is a major problem. Starter cultures and other contaminants contain diacetyl reductase which destroys diacetyl. This reaction proceeds more rapidly at higher temperature[71] and so proper refrigeration in retail stores becomes important. Use of hydrogen peroxide and catalase in buttermilk and sour cream improves the diacetyl production and its stabilization.[72] The possible role of oxygen in this connection has been discussed earlier. Morgan et al.[73] studied the malty defect of milk cultures. 3-Methylbutanol, 2-methylpropanol, 3-methylbutanal, and 2-methylpropanal were identified from the milk culture of *Streptococcus lactis* var. *maltigenes*. These compounds were absent in the cultures of nonmalty strains of *Streptococcus lactis*. Although the volatiles of milk cultures with malty defect contained more of the branched chain alcohols than the corresponding aldehydes, organoleptic comparison of the aroma of the untreated culture with that in which the aldehydes had been removed by treatment with hydroxylamine indicated that the typical malty aroma was principally due to aldehydes. Morgan[74] recently reported that the malty defect of milk cultures could be simulated by adding 0.34 ppm 3-methylbutanal to good quality homogenized pasteurized milk and used as a standard for judging this defect by an expert flavor panel. Similarly, the fruity defect caused by *Pseudomonas fragi* could be simulated in milk by the additon of a mixture of pure ethyl butyrate and ethyl hexanoate in 1,2-propanediol to give concentration of 0.35 and 0.50 ppm of the respective esters.[75]

CHEESE FLAVOR

During cheese ripening a number of chemical reactions proceed simultaneously, representing a dynamic system. Many of the reactions are mediated by microbial and native milk enzymes. During cheese ripening, protein, fat, and carbohydrate are degraded to varying degrees to yield a complex mixture of compounds, some of which contribute to the characteristic cheese flavor.[72] The microflora of cheese is complex and variable because different types of microorganisms predominate at different stages of cheese ripening. A list of microorganisms and enzymes used in cheese making is given in Table 3.[73]

TABLE 3

Microorganisms and Enzymes Used in Cheese Making[77]

Streptococcus lactis
Streptococcus cremoris
Streptococcus citrovorum
Streptococcus faecalis
Streptococcus zymogenes

Streptococcus durans
Streptococcus liquefaciens
Streptococcus thermophilus
Streptococcus diacetilactis
Leuconostoc cremoris

Lactobacillus caseii
Lactobacillus lactis
Lactobacillus bulgaricus
Bacterium lineus

Micrococcus caseolyticus
Pseudomonas fragi
Propionibacterium shermanii
Trametes sanguinae
Penicillium roqueforti

Penicillium camemberti
Penicillium frequentans
Calf lipase
Lactase
Enzymes from filbert nuts and *Saccharomyces cerevisiae*
Extracted enzymes from selected milk and cheese bacteria

Cheddar Cheese

A large number of compounds have been identified from Cheddar cheese. Amino acids and peptides, produced primarily by proteases of cheese microflora during cheese ripening, provide the brothy background to cheese flavor and as such play an important role in the taste of Cheddar cheese. Various amines such as tyramine, cadavarine, putrescine, and histamine have also been identified from normal Cheddar cheese.[76] Amino acids and amines produced from proteins also act as precursors of a number of aldehydes reported in Cheddar cheese and are produced probably by transamination and decarboxylation reactions. The Strecker degradation of various amino acids to corresponding aldehyde of one less carbon atom also contributes to cheese flavor. Although the reaction is nonenzymatic, the proteolytic activity of cheese would influence it.

$$R.CO.CO.R + R'.CHNH_2.COOH =$$

$$R'.CHO + CO_2 + R.CHNH_2.CO.R$$

Keeney and Day[78] studied individual amino acids for the character of odor yielded on Strecker degradation that would be of significance in "toasted" or "heated" cheese products. Glycine, tryptophane, arginine, histidine, lysine, aspartic acid, serine, threonine, and thyrosine yielded no odor. The following amino acids yielded the indicated odors:

alanine	–	malty
valine	–	apple
leucine	–	malty
isoleucine	–	malty-apple
proline	–	mushroom
phenylalanine	–	violets
cystine	–	H_2S
methionine	–	cheesy-brothy
glutamic acid	–	bacterial agar

The degradation products of lipids are essential for Cheddar flavor, as Cheddar cheese made from skim milk is practically devoid of Cheddar character.[79] Patton[80] reported that the 2:0, 4:0, 6:0, and 8:0 fatty acids are of primary importance in Cheddar cheese aroma. He suggested that acetic acid is of special importance in the unique aroma of cheese. In the absence of acetic acid, the volatile fatty acids found in cheese would promote hydrolytic rancid character. Bills and Day[81] determined the free-fatty acid concentrations of several cheese samples (Table 4) and concluded that in view of the variation in individual free-fatty acid concentrations and lack of direct relationship of free-fatty acids with the flavor of good quality Cheddar cheese, the balance between free-fatty acids and other flavor constituents is more important to Cheddar flavor than the concentration of free-fatty acids alone. Recently, Ohren and Tuckey[82] reported that the typical flavor of Cheddar cheese was related to the balance between free-fatty acids and acetate (Table 5). According to these workers, the microbial content of milk has a significant influence on the acetic and free-fatty acid content of cheese (Table 6).

Day et al.[83] identified several methyl ketones containing odd-numbered carbon atoms from Cheddar cheese and suggested that these may be the products of the normal curing process. The concentrations of these ketones are quite small and may also be formed by the degradation of β-keto esters normally found in milk fat.[84] Butanone, which is found in relatively large concentration in Cheddar cheese, may be produced from reduction of acetoin to 2,3-butylene glycol, which is in turn dehydrated to the ketone.[85] Citrate-fermenting bacteria produce a small amount of diacetyl in Cheddar cheese. The mechanisms of diacetyl production by these organisms have been discussed under cultured dairy products section.

Ethanol and 2-butanol are the two major alcohols in Cheddar cheese.[85] Day and Libbey[86] identified traces of secondary alcohols corresponding to the methyl ketone analogs. According to Day,[76] apparently some of the bacteria associated with ripening possess alcohol dehydrogenase capable of reducing the ketone and aldehyde analogs. Ethanol is probably produced as the end product of EMP or Entner-Doudoroff

TABLE 4

Summary of the Analysis of Free-fatty Acids in 14 Samples of Cheddar Cheese[81]

Fatty acid	Average concentration in mg/kg cheese	Concentration range in mg/kg cheese	Analytical precision (percent ±)
2:0	865	275–1,325	1.79
4:0	115	71–207	2.16
6:0	38	18–79	0.99
8:0	41	21–74	1.86
10:0	49	40–80	1.64
12:0	81	55–123	1.54
14:0	218	134–315	0.90
16:0	503	300–689	0.81
18:0	172	104–246	1.05
18:1	467	312–630	0.85
18:2	69	37–125	1.07
18:3	40	21–62	1.36

TABLE 5

Relationship Between Free-fatty Acids + Acetic Acid in Determining the Flavor of Cheddar Cheese

Flavor	Free-fatty acid + acetate (μmol)	Moles free-fatty acids/μmol acetate
Fine, Cheddar	12 to 28	0.55 to 1.0
Fermented, rancid, fruity, unclean	28	1.0
Flat	12	0.55

(From Sandine, W. E. and Elliker, P. R., *J. Agric. Food Chem.*, 18, 557, 1970. With permission.)

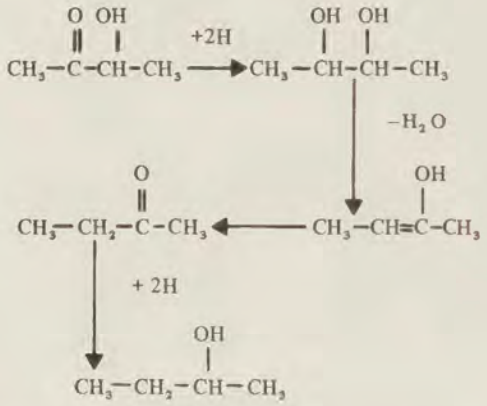
TABLE 6

Relationship of Standard Plate Count (SPC) of Milk to the Level of Free-fatty Acids + Acetic Acid Found in Cheddar Cheese Analyzed after 3 Months

SPC/ml		Free-fatty acids + acetate (μmol/g)	
Raw	H_2O_2	Raw	H_2O_2
1,000	300	18	11
7,000	150	21	17
20,000	9,000	20	18
20,000,000	50,000	45	24
21,000,000	16,000,000	59	53
32,000,000	10,000,000	80	26

(From Sandine, W. E. and Elliker, P. R., *J. Agric. Food Chem.*, 18, 557, 1970. With permission.)

pathway, depending upon the bacteria used.[57] Scarpellino and Kosikowski[85] postulated that 2-butanol was a terminal product in the breakdown of acetoin and proposed the following mechanism for its formation:



Bills et al.[87] reported ethyl butyrate and ethyl hexanoate as compounds primarily responsible for the fruity flavor defect of Cheddar cheese. Fruity samples contained two to ten times greater concentrations of ethyl butyrate and ethyl hexanoate compared to normal Cheddar cheese. Levels of ethanol were 6 to 16 times greater in fruity cheeses. It was suggested that the extensive production of ethanol may be responsible for the accentuated esterification of free fatty acids, thus resulting in higher levels of ethyl esters.

Mold-ripened Cheeses

The chemistry of flavor developments in mold-ripened cheeses is very complex. In addition to the processes leading to the formation of normally ripened cheeses, the metabolism of mold developing on or within such cheeses contributes to the characteristic flavor. In some of the mold-ripened cheeses, such as Roquefort, Gorgonzola, blue, and Stilton, the enzymes produced by *Penicillium roqueforti* play an important part in flavor development, in addition to the softening of the curd and the formation of various breakdown products. *Penicillium roqueforti* shows a very high lipase activity which leads to the rapid production and accumulation of a number of fatty acids, mainly caprylic acid but also capric and caproic acids.[49] These fatty acids are involved in the formation of methyl ketones which impart characteristic flavor to these cheese varieties.

In the ripening of Camembert cheese besides *Penicillium camemberti*, various film yeasts and *Geotrichum* species play an important role in flavor development by reducing the acidity of the cheese surface before

the main mold becomes established. Information on the chemical compounds involved in Camembert maturation and the specific contribution of each group of organism to the development of the characteristic Camembert flavor is still very meager.[47]

The Embden-Meyerhof-Parnas (EMP) scheme (Figure 3) represents a pathway whereby many molds metabolize sugars. Several enzymes of the EMP pathway have been reported to occur in *Penicillium chrysogenum.*[88] The pentose phosphate pathway (Figure 4) is also an important pathway in the dissimilation of sugars. Heath and Koffler[89] estimated that two thirds of glucose metabolized by *Penicillium chrysogenum* was through the oxidative pathway. The Entner-Doudoroff pathway, which is so important in the metabolism of some bacteria, seems to have little place in fungal metabolism.[90]

Little information is available on the role of proteolysis and its effects on blue cheese flavor. *Penicillium roqueforti* has active proteolytic enzyme(s). Imamura and Tsugo[91] studied the changes of milk proteins by *Penicillium roqueforti* and found that although albumin was most readily decomposed of all the milk proteins, the changes in casein were of greater significance. The large quantities of amino acids released by proteolytic enzymes impart a "brothy" taste which constitutes an important background on which the typical flavor is superimposed.[76]

Several investigators have studied the lipase(s) of *Penicillium roqueforti.*[92-94] Eitenmiller et al.[92] partially purified the lipase of *Penicillium roqueforti* and reported that this enzyme had an optimum pH of 8.0 and an optimum temperature of 37°C. Maximum lipolytic activity occurred with 5% butter oil emulsion as the substrate. $MnCl_2$ and $MgCl_2$ stimulated the enzyme activity. The lipase was thermolabile, being inactivated completely within 10 min at 50°C. It hydrolyzed tributyrin, tricaprylin, tricaprin, tripropionin, and triolein in decreasing order. The fatty acids released by the action of *Penicillium roqueforti* and milk lipases have long been recognized as important components of blue cheese flavor. The short chain fatty acids, i.e., 4:0, 6:0, and 8:0, impart the characteristic "peppery" taste and act as methyl ketone precursors.

The methyl ketones, especially 2-heptanone and 2-nonanone, are generally considered the key flavor components of blue cheese.[76] The formation and metabolism of methyl ketones by fungi during the ripening process in mold-ripened cheeses appear to involve four main enzymic mechanisms:[95]

a. the liberation of free-fatty acids from the triglycerides of milk fat by lipases;
b. oxidation of the free-fatty acids to β-keto acids;
c. decarboxylation of β-keto acids to methyl ketones; and
d. reduction of methyl ketones to secondary alcohols.

The pathway of fatty-acid oxidation and methyl ketone formation is given in Figure 8.[95] *Penicillium roqueforti* spores[96] as well as mycelium[97,98] are capable of producing methyl ketones from fatty acids. Studies on the fatty acid metabolism[99] by the spores of *Penicillium roqueforti* indicate that both short chain as well as long chain fatty acids are metabolized into homologous series of methyl ketones and CO_2.

A large number of primary and secondary alcohols have been isolated from blue cheese.[100,101] Of the primary alcohols identified, methanol and ethanol appear to be important in flavor formation.[76] The secondary alcohol analogs of methyl ketones found in blue cheese result from reduction of corresponding ketone by mold mycelium by the following mechanism:[102]

$$RCOCH_3 \underset{DPN+}{\overset{DPNH + H^+}{\rightleftharpoons}} RCHOHCH_3$$

In recent years several attempts have been made to reduce the time needed for maturation of cheese by adding flavors produced by microorganisms and changing various parameters of cheese manufacture. Cort and Riggs[103] claim that cheese of the Roquefort or Camembert type may be produced by adding enzymes extracted from *Penicillium roqueforti* and *Penicillium camemberti* to the milk or to the curd, respectively, during manufacture. The method is claimed to be applicable to other cheese varieties, e.g., Cheddar, where the enzyme extract is prepared from a mature Cheddar cheese. Hedrick et al.[104] recently patented a process of blue cheese preparation by adding a blue cheese mold to the cheese and ripening the curd in a

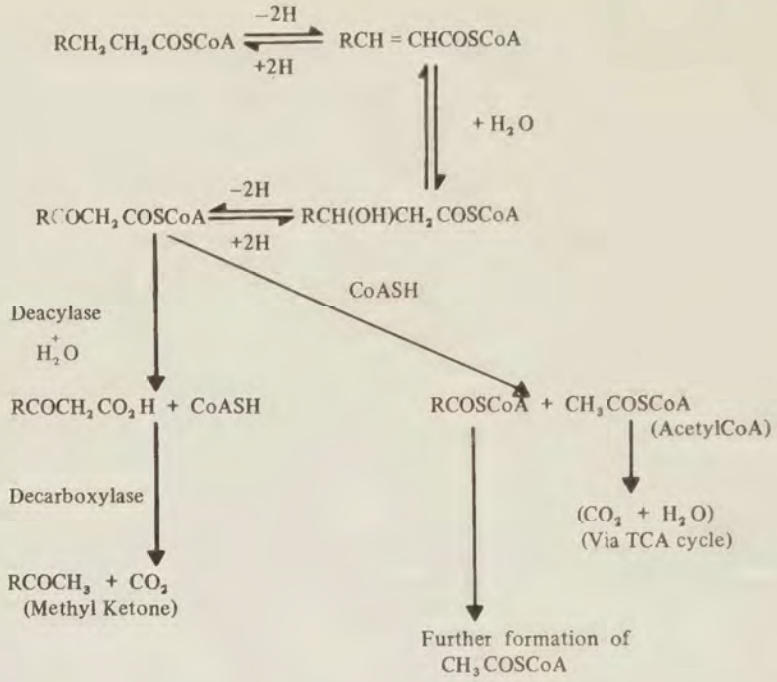


FIGURE 8. Mechanism of methyl ketone formation from fatty acids. (From Heath, E. C. and Koffler, H., *J. Bacteriol.*, 71, 174, 1956. With permission.)

divided condition. Ripening is said to be accelerated and slime formation minimized. A Dutch patent[105] on cheese flavor makes use of microorganisms that metabolize fat and produce volatile compounds closely simulating cheese flavor. A medium high in animal or plant fat (40 to 60%) and low in protein (not more than 3%) is used for flavor production. The medium is also fortified with carbohydrates, minerals, trace elements, vitamins, and other growth substances. The pH is preferably held at 4.5 and the incubation period is 48 hr at temperature 20 to 40°C. *Pencillium* (especially *P. roqueforti*), *Candida lipolytica*, *Oidium lactis*, *Cladosporium*, *Micrococcus*, and *Lipomyces* are recommended.

Processes have also been developed for preparing cheese flavorings. Knight[106] patented a process for producing blue cheese flavor by treating milk or cream with lipase to convert milk fat to fatty acids and fermenting the resulting milk-fatty acid mixture with *Penicillium requeforti* under submerged aerobic conditions. In this process free-fatty acids are converted to methyl ketones and the composition smells like blue cheese. Watts and Nelson[107] patented a similar process for blue cheese flavor manufacture. Recently, Dwivedi and Kinsella[108] developed a continuous process for blue cheese flavor manufacture by submerged fermentation of lipolyzed milk fat with the mycelium of *Penicillium roqueforti*.

MISCELLANEOUS ENZYMES

Enzymes such as lipases and proteases from sources other than milk and bacterial starter cultures are finding greater use in the modified dairy flavors. Nelson,[109] in his review on enzymatically produced flavors from fatty systems, has given an interesting account of the use of lipolyzed milk in chocolate. Rancidity, although considered a highly undesirable character in most dairy products, is finding use as a flavor enhancer and is used in developing desirable flavor notes. Anti[110] has produced a variety of tastes ranging from cream to butter from lipolyzed flavors formed by the action of lipase on butter fat emulsions. Recipes are given for their use in butterscotch, caramel, and butterscotch kisses. These confections are said to have improved flavor characteristics. Tanabe Seiyaku C. Ltd. of Japan has recently patented a process[111] of manufacturing highly flavorful yogurt by the addition of lipase at the start of the process.
start of the process.

Major applications for enzyme modified milk fat include:[109]

a. chocolate products, including milk chocolate, compound coatings, and chocolate flavor syrups and beverages;

b. butter flavors, including margarine, butter creams, and butter sauces;

c. milk and cream flavors, including coffee whiteners, imitation sour cream, and imitation milks;

d. cheese flavor, particularly when the flavor profile of Italian-type cheese is desired. Neelakatan et al.[112] reported that the type and amount of lipase used in Italian cheeses play an important role in flavor development and provide some of the better means of flavor control. In a similar study Langler and Day[113] investigated major free-fatty acids in Swiss cheese and discussed their importance.

Flavor profiles from lipolyzed milk fat can exert a considerable range of effects on food flavor. At very low addition levels, a sensation of richness is imparted without any detectable free-fatty acid flavor character. As addition levels are increased, the flavors imparted resemble cream or butter. When addition levels are relatively high, the flavor imparted suggests cheese.[109] Lipases from different sources give different free-fatty acid profile in lipase-treated milk fat. This property or lipases may help in simulating flavors precisely.

Proteolytic activity during the ripening of cheeses in also extensive. Apart from the participation of starter cultures, it depends in part on the coagulating enzyme system which is used in the formation of curd. The extent of proteolytic breakdown in cheeses can be judged from the production of free-amino acids which contribute to the flavor of the cheese. The extent of hydrolysis varies with the nature of the coagulating enzyme. Vegetable rennets and pancreatin show a high rate of proteolysis and frequently produce a bitter taste in cheese. Deaminases, decarboxylases, aminases, transaminases, and other enzymes are active in cheese and lead to the production of a variety of amino acids, amines, keto acids, aldehydes, ammonia, and other derivatives. Although very little information is available, it is quite possible to influence the flavor of cheese by changing the concentration and the source of proteolytic enzyme used for clotting the milk.

Richardson and Nelson[114] developed a screening method for rapidly indicating the sensitivity of various cheese ripening agents. Freshly ground mild cheese curd was inoculated with high levels of enzyme preparations, incubated at 21°C for 3 days and evaluated organoleptically. This method could be used in evaluating the role of various microorganisms and their enzyme systems in cheese ripening. Similar methods could be developed for cultured dairy products.

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SAUCES, DRESSINGS, CONDIMENTS, AND POWDERED FLAVORS

Introduction

Sauces, dressings, condiments, and powdered flavors represent technological difficulties in classifying because of the countless flavor ingredients employed and the manner in which they are combined. These products are really new flavors developed through the centuries to impart characteristic flavor to traditional cuisines. Generally, this category of flavor ingredients includes products specifically designed for flavoring fried, boiled, broiled, or roasted meat and fish, cooked or raw vegetables, and pasta and cereal products.

Taste, tradition, availability of certain products, and dietary requirements have all been influential factors in the choice of flavor ingredients and their relative ratio in the flavoring mixtures. Sometimes these can be very simple, such as oil and vinegar dressings, or much more complex, such as vinegar sauces, tomato sauces (tomato ketchup, tomato chutney), Worcestershire sauce, the countless fondue sauces, and mixed spice powders (*e.g.*, curry).

The topic is too complex for an extensive discussion and goes beyond the scope of the book. The following is, therefore, a limited presentation of information concerning the flavoring of the most important products.

Sauces and Salad Dressings

Tables 9 and 10 list some traditional dressings, sauces, butters, etc. and indicate the *base* ingredients together with additional flavor ingredients used to augment the product. It is important to note that in almost all instances, the *base* contributes not only form, texture, mouth-feel, etc., but also a flavor background. In commercial products shelf-life requirements necessitate using emulsifiers, thickeners, antioxidants, and preservatives; these have not been included in the ingredients list, since they rarely contribute flavor to the finished product.

Mayonnaise

The Duc de Richelieu is credited with introducing mayonnaise into France in 1757. Although the original sauce, native to Minorca, was heavily dosed with garlic, legend tells that the Duc separated the garlic flavor before introducing the sauce into France.

Modern mayonnaise formulations are based on egg yolk, olive or light salad oils, lemon juice or wine vinegar, and salt; they are spiced with mustard, white pepper, cayenne pepper, and sometimes ginger and paprika. Other ingredients employed in mayonnaise include stabilizers, chelating agents, and preservatives to improve shelf-life; in the United States mayonnaise has standards of identity that specify the product. Essential oils may also be employed in flavoring mayonnaise. A characteristic formulation consists of the essential oils of mustard (4 parts), lemon (3 parts), celery (1 part), nutmeg (1 part), and black pepper (1 part).

TABLE 9

Salad Dressings

Name	Base	Flavor ingredients
Avocado	Mashed ripe avocado, salt, sugar, whipped heavy cream	Lemon juice, lemon peel
Celery seed	Salad oil, lemon juice, vinegar, salt, sugar	Onion (grated), honey, celery seed, paprika, dry mustard
Chili mayonnaise	Mayonnaise	Chili sauce
Citrus	Beaten egg, whipped heavy cream, sugar	Orange peel, lemon peel, lemon juice
Cooked dressing	Enriched flour, beaten egg yolk, milk, butter, vinegar, salt, sugar	Dry mustard, cayenne
Creamy mayonnaise	Mayonnaise, heavy cream	
French, clear	Salad oil, vinegar, lemon juice, salt, sugar	Dry mustard, paprika, cayenne

TABLE 9 (continued)

Salad Dressings

Name	Base	Flavor ingredients
French, creamy	Salad oil, egg, vinegar, salt, sugar	Paprika, cayenne
French, fruit	Salad oil, lemon juice, vinegar, sugar, salt	Orange juice, paprika, onion (grated)
French, garlic	Salad oil, vinegar, salt, sugar	Dry mustard, garlic (crushed)
French, snowy	Salad oil, white vinegar, blue cheese, salt, sugar	Onion juice, dry mustard, white pepper
Italian, classic	Olive oil, wine vinegar (also distilled), lemon juice	
Italian, spiced	Olive oil, white vinegar, salt	White pepper, celery salt, cayenne, dry mustard, garlic (minced), Tabasco sauce
Lemon-honey	Honey, salt	Lemon juice
Lime-honey	Honey, salt	Lime juice
Marshmallow	Mayonnaise, marshmallow creme	Orange juice, lemon juice
Pineapple	Unsweetened pineapple juice, corn starch, beaten eggs, cream cheese, salt, sugar	Orange juice, lemon juice
Pink fruit	Mayonnaise, salt	Cranberry juice, almond (toasted)
Russian	Cooked sugar and water, tomato ketchup, vinegar, salt, salad oil	Celery seed, paprika, lemon juice, Worcestershire sauce, onion
Shawano	Salad oil, tomato ketchup, sugar, vinegar, salt	Paprika, dry mustard, onion, garlic, steak sauce
Thousand island	Mayonnaise, chopped and sieved hard-boiled egg, salt	Chili sauce, green pepper, celery, onion, paprika
Tomato	Salad oil, condensed tomato soup, vinegar, sugar, salt	Worcestershire sauce, dry mustard, paprika, garlic (minced), onion
Vinaigrette	Clear French dressing, minced hard-boiled egg, chopped green olive	Chives, pimento
Yogurt	Mayonnaise, yogurt, sugar, salt	Lemon juice, lime juice

TABLE 10

Sauces

Name	Base	Flavor ingredients
Aioli, classic	Egg yolk, olive oil, salt	Garlic, lemon juice
Aioli (Greek Skordalia)	Egg yolk, olive oil, salt, bread crumbs	Garlic, lemon juice, blanched ground almonds, walnuts, or pine nuts
Ali-oli, Spanish	Olive oil, crumbled crustless white bread, salt	Garlic, lemon juice
Allemande	Hot veal, chicken, or fish broth, flour, butter, egg yolk, heavy cream, salt	Mushroom, white pepper, powdered nutmeg, lemon juice
Avgolemono	Hot lamb, chicken, or vegetable broth, salt, egg yolk	White pepper, lemon juice
Bagna Cauda	Olive oil, butter	Garlic, anchovy (minced)
Barbecue (Gaucho)	Tomato ketchup, water, sugar, salt, vinegar	Worcestershire sauce, Tabasco, celery seed
Barbecue (for meats)	Tomato ketchup, vinegar, honey, salt	Prepared mustard, Tabasco
Barbecue (for poultry)	Salad oil, Worcestershire sauce	Lemon juice, garlic
Bâtarde	Butter, flour, boiling water, egg yolk, heavy cream, salt	Black pepper, white pepper, lemon juice
Béarnaise	Shallots (minced), tarragon wine vinegar, egg yolk, butter, salt	Tarragon (chopped), chervil, cayenne pepper

TABLE 10 (continued)

Sauces

Name	Base	Flavor ingredients
Béchamel	Butter, flour, milk, salt	Onion, cayenne pepper
Bercy	Butter, hot fish broth, flour, heavy cream	Onion, dry white wine, parsley
Beurre Manie	Soft butter, flour, cream	
Beurre Meuniére	Clarified butter (browned)	Lemon juice
Beurre Montpellier	Yolks of hard-boiled egg, soft butter, mayonnaise, salt	Minced watercress, parsley, tarragon, chives, chervil, shallots, sour gherkin, garlic, anchovy, cayenne pepper
Beurre Nair	Clarified butter (browned)	Red wine vinegar, parsley, capers
Blueberry	Cooked blueberries, cornstarch	Lemon juice
Bordelaise, classic	Dry red wine, sauce Espagnole, meat glaze, sliced marrow (cooked), butter, salt	Shallots, pepper, parsley, lemon juice, bay, thyme
Bordelaise, sweet	Sherry, brown sauce, diced beef marrow (cooked), salt	Green onion, parsley
Brown, classic	Beef broth, butter, flour, salt	Tomato puree, pepper
Brown, spiced	Beef broth, butter, flour, salt	Tomato puree, pepper, browned onion, minced carrot, celery
Butters (*also see* Beurre)		
Anchovy	Butter (soft)	Anchovy paste (or fillets)
Bercy	Butter (soft), poached beef marrow, dry white wine, salt	Lemon juice, pepper, shallots, parsley
Chivry	Butter (soft)	Chives, parsley, chervil, tarragon, shallots
Garlic	Butter (soft)	Blanched, mashed garlic
Indian ghee	Melted butter separated from oil and white residue	
Lemon	Butter (soft), salt	Lemon juice, parsley, pepper
Lobster	Butter (soft), cooked lobster, roe, and strained lobster meat	
Maitre d'hôtel	Butter (soft), prepared mustard, salt	Pepper, parsley, tarragon, lemon juice
Most daintie	Butter (soft)	Cinnamon (or paprika), nutmeg (or mace)
Russian nutmeg	Butter (soft)	Cinnamon, nutmeg, chives, white pepper, lemon juice
Snail	Butter (soft), finely minced shallots (sauteed), salt	Garlic, parsley, pepper, nutmeg, thyme
Caper	Mayonnaise, sour pickles, capers	Chopped capers, prepared mustard, parsley
Chaud-froid	Chicken broth, flour, heavy cream, egg yolk, gelatin, aspic, salt, butter	Dry white port, onion, diced carrot, celery, pepper, tarragon leaves, bouquet garni (parsley sprigs, parsley root, bay leaves, dried thyme)
Chili	Tomatoes, brown sugar, cider vinegar, green peppers, salt	Celery, onion, cloves, dry mustard, cinnamon
Chinese mustard	Water (boiling), dry English mustard, salad oil, salt	
Chocolate, regal	Unsweetened chocolate, corn syrup, sugar, water, evaporated milk	Vanilla
Cocktail	Mayonnaise, chili sauce	Lemon juice, Worcestershire sauce, Tabasco, horseradish, paprika
Coney	Ground beef (browned), water, tomato sauce, salt, monosodium glutamate	Onion, garlic, chili powder
Cranberry	Cooked cranberries, sugar, water	
Cranberry, spiced	Jellied cranberry sauce, steak sauce, brown sugar, salad oil	Prepared mustard

TABLE 10 (continued)

Sauces

Name	Base	Flavor ingredients
Cumberland	Melted currant jelly, port wine	Orange juice, lemon juice, orange and lemon rind (simmered), shallots, prepared mustard, powdered ginger, cayenne pepper
Creole	Seasoned tomato sauce, broiled mushrooms, green pepper	
Custard sauce	Egg yolk, sugar, salt, scalded milk	Vanilla
Dal	Lentils, butter, light beef broth, salt	Onion, hot chili pepper (green), dried chili pepper (red), turmeric (or curry powder), mustard seed, coriander
Demi-glace	Sauce Espagnole, meat glaze, madeira or tawny port	
Diable	Brown sauce, Worcestershire sauce	Onion, sauterne, peppercorns (crushed)
Dill	Flour, butter, chicken broth, sugar, vinegar, egg yolk	Dill, dill weed
Duxelles	Sauce Espagnole, tomato puree, olive oil, butter, salt	Mushroom, shallots, onion, pepper, white wine, parsley
Espagnole	Butter, brown sauce, dry white wine, beef broth, salt, pepper	Tomato paste, onion, carrot, bouquet garni (bay, thyme, peppercorns, parsley)
Fossen Flodepeberrod (Danish frozen horseradish cream)	Whipped heavy cream, sugar, salt, white pepper	Lemon juice, horseradish
Hollandaise	Egg yolk, cold water, butter, salt	Lemon juice, cayenne pepper
Hummer Sao (Norwegian lobster sauce)	Allemande sauce of fish stock, lobster meat (diced), butter, salt	Pepper, cognac (or sherry)
Jalapena (Mexican hot sauce)	Plum tomato (drained), olive oil, beef broth, sugar	Jalapena chili peppers, thyme, garlic, onion
Maltaise	Egg yolk, butter, salt	Orange juice, cayenne pepper
Mint, classic	Mint leaves, salt, sugar	Vinegar
Mint, popular	Mint jelly, salt	Vinegar
Mornay	Béchamel sauce	Gruyere and Parmesan cheese
Mousseline	Hollandaise sauce, heavy cream	
Nantua (French lobster sauce)	Béchamel sauce made with fish stock, milk, heavy cream (scalded), lobster butter, diced lobster, salt	Pepper
Orange	Butter, sugar, orange juice	Orange peel and oils
Pesto	Basil leaves, olive oil, Parmesan cheese, salt	Garlic, pine nuts, pepper
Pomme d'amour	Tomato, olive oil, butter, salt	Bouquet garni, wine vinegar, garlic, basil, sugar, pepper
Raisin	Beef broth, brown sugar, salt, cornstarch	Red wine vinegar, currant jelly, madeira wine, seedless white or black raisins, bouquet garni
Ravigote	Vinaigrette dressing	Shallots, onions, capers, chives, chervil, parsley, tarragon
Rémoulade	Mayonnaise, minced capers, minced sour pickles, onions	Dijon mustard, parsley, tarragon, chives, chervil, anchovy paste
Rémoulade, hot	Olive oil, onion, brown sauce, dry white wine, lemon, salt	Garlic, tarragon, chervil, basil, parsley, cloves, capers, Dijon mustard
Robert	Butter, onion, sauce Espagnole, salt, pepper	White wine, sugar, Dijon mustard

TABLE 10 (continued)

Sauces

Name	Base	Flavor Ingredients
Rouille de Marseille	Pimento, egg yolk, olive oil, hot fish broth	Chili pepper sauce, garlic
Salsa verde (Italian green sauce)	Parsley, olive oil, salt	Garlic, black pepper, capers, lemon juice
Soubise	Onions, butter, béchamel sauce, salt, pepper, heavy cream	Nutmeg, sugar
Suprême	Velouté (chicken), strong chicken broth, butter, heavy cream, salt	Mushroom, pepper
Sweet and sour, Chinese	Peanut oil, soy sauce, cornstarch, chicken broth, sugar	Garlic, scallions, mushrooms, carrot, bamboo shoots, ginger, vinegar
Tartare	Mayonnaise, sweet gherkins, Dijon mustard	Scallions, chives, capers, olive
Velouté	Butter, hot veal, chicken or fish broth, flour	Onion
Verte (green French sauce)	White bread crumbs, dry white wine, sorrel or spinach, parsley, heavy cream, salt	Tarragon, sage

Mustard

Mustard is probably the most widespread among table sauces. Several countries boast the production of specialty products, among which French, English, and German types are the best known. The various mustard types differ mainly in sharp or aromatic flavor. French mustard (Dijon) has a sharp taste and contains vinegar, white mustard, flour, salt, turmeric, cayenne pepper, clove buds, and pimento. English mustard sauce contains, in addition to the above ingredients, sugar, tapioca, black mustard, and white pepper. German mustard sauce is made with approximately the same ingredients with the addition of wine.

In England Piccalilli type sauces are widely used. These consist of mustard sauces containing chopped vegetables (*e.g.*, cauliflower, cucumber, onion) and flavored with additional ingredients, such as cinnamon, cumin, fenugreek, nutmeg, and ginger.

Cremones mustard, frequently used in northern Italy but otherwise little known, is a condiment for boiled meat. The product originated and is manufactured in Cremona, a town well known for its gastronomic and pastry specialties. It consists of a fruit-based mustard prepared as follows: whole or chopped fruits are initially steeped in sucrose syrup; the syruped fruit then is transferred into mustard-flavored syrup in containers suitable for distribution. The flavoring consists of the addition of natural or synthetic mustard essential oil to sugar syrup. The mustard essential oil distributes uniformly in the fruit during a ripening period prior to sale. The final product contains approximately 35% syrup (by weight of the syruped fruit) and is flavored by approximately 0.01% mustard essential oil. The use of black mustard flour has been practically abandoned.

Ketchups and Chutneys

Ketchups and chutneys consist chiefly of fruit concentrates or pulp or flavored vegetables. The most important products in the category are tomato ketchup and tomato chutney. Aside from the type of fruit pulp or fruit concentrate used, specific flavor formulations based on essential oils that yield the characteristic spice note in the finished product have become quite popular. These formulations usually contain approximately 50% clove essential oil; the balance is made up of suitable blends of cinnamon, nutmeg, pimento, mace, mustard, and celery.

There is only a very slight difference in the flavoring of tomato ketchup and chutney. However, they differ quite substantially in consistency due to the use of thickening agents (*e.g.*, tragacanth gum) and to the use of more or less concentrated tomato bases. Although countless flavor variations are

possible, they are all confined within specific formulation guidelines. Tomato ketchup is prepared with tomato concentrate, sugar, water, vinegar, onion, salt, tragacanth gum, and spices such as nutmeg, cardamom, cinnamon, clove buds, and coriander. Ingredients of tomato chutney include tomato concentrate and pulp, sugar, water, vinegar, onion, salt, spices (coriander, cayenne pepper, cinnamon, cardamom, pimento, celery), reinforced by the addition of essential oils (garlic, clove bud, etc.).

Mushroom ketchup is vinegar-free and contains hydrolyzed proteins, soy sauce, and water. Clove buds, pimento, black pepper, ginger, and cardamom are used for flavoring. Mushroom ketchup is used also as a flavor ingredient in thin-sauce formulations, such as Worcestershire.

Walnut ketchup is made basically with vinegar, soy sauce, onion, anchovies, and hydrolyzed proteins. Clove buds, ginger, mace, and black pepper are used as flavor ingredients. Walnut ketchup also is used as a flavor ingredient in Worcestershire sauce.

Apricot and onion chutneys (of Anglo-Saxon origin) contain similar flavor ingredients, such as ginger, cinnamon, paprika, cayenne pepper, pimento, and coriander. Apricot chutney calls for the use of a 6:1 ratio of onion to apricot; the onion-apricot mixture is pickled in vinegar, sweetened with sugar, and thickened with tragacanth gum and tapioca. Onion chutney is prepared with onion, tomato, grape, tamarind, and dates in a 7:2:1:1 ratio, respectively; small levels of other flavor ingredients are added (sometimes a lemon note is also added).

Thick Sauces

These sauces exhibit a fairly thick consistency; they are based mainly on fruits (date, apple, mango, tamarind, lemon, and grape), tomato, molasses or sugar syrup, tapioca and similar flours, vinegar, salt, hydrolyzed proteins, anchovies, tragacanth gum, and a large variety of spices. Countless formulation blends are possible; mushroom ketchup is added to several formulations. A popular thick sauce available in the United States lists the following ingredients: tomato paste, distilled vinegar, corn syrup, raisins, salt, orange base, orange peel, caramel, dehydrated garlic, dehydrated onions, gum tragacanth, herbs, spices, and water.

Thin Sauces

Among the more fluid sauces Worcestershire is undoubtedly the best known and most widely imitated product. The formulation of Worcestershire sauce is complicated by the presence of finished products, such as mushroom and walnut ketchups and soy sauce. (For the preparation of mushroom and walnut ketchups, see the preceding discussion of Ketchups and Chutney.) Soy sauce, also used in the preparation of these ketchups, consists of a liquid brown sauce of Japanese (Soyu) or Chinese (Chiang Yu) origin prepared by prolonged fermentation of soy followed by salt-pickling. Worcestershire sauce also contains vinegar, sherry and brandy, cane sugar, salt, tamarind pulp, pork liver, and minced spices (mace, coriander, pimento, black or cayenne pepper). The cooking of pork liver (8–10 hours), the partial boiling of the various ingredients, and the mixing and final refining of the sauce represent only a few among several complicated steps. The complex preparatory technique makes the imitation of Worcestershire sauce extremely difficult. In some recipes for Worcestershire-type sauces, lemon pulp, mushroom powder, anchovies, hydrolyzed proteins, garlic, and caramel are used.

Anchovy Sauce and Paste

Regular anchovy paste is made without the addition of flavor ingredients. It is prepared by grinding cleaned and boned anchovy fillets and then adding a sufficient amount of salt to the fish paste. Anchovy sauce of Anglo-Saxon production has a much more complex formulation. Depending on the type, it contains vinegar (together with acetic acid), water, salt, tragacanth gum, cayenne pepper, mace, apple pulp, tamarind, tomato, ginger syrup, caramel, dates, raisins, garlic, lemon, citric acid, clove buds, bay, and scallions.

Tomato Sauces

In addition to the countless types of tomato-based sauces that do not require warming and are used for flavoring meats and vegetables, there are also tomato sauces that are served hot with macaroni,

spaghetti, rice, etc. Tomato sauces served hot with pasta products and featuring typical recipes of the Italian cuisine have been available commercially for many years. The best known types follow:

1. Neapolitan-style tomato sauce containing, in addition to both precooked tomato paste and peeled tomatoes, fats, salt, a little sugar, celery, carrot, pepper, and onion.
2. Bolognese-style tomato sauce (ragout) that, in addition to containing the above ingredients, contains cooked ground meat flavored with the same ingredients used in the sauce.

Flavored Vinegars

The use of flavored vinegars is still quite prevalent in various countries; they are used either as a complementary condiment or as an alternate for salad vinegar or in other food products. In the past flavored vinegars were homemade by careful infusion of herbs and spices in pure wine vinegar. Formulations of such condiments were developed from gourmet preferences in various regions and are countless in number. The following recipe for truffle-flavored vinegar is mentioned as an example.

Truffle-flavored Vinegar

Ingredients:

White truffles	20 g
Garlic	5 g
Paprika	5 g
Geranium leaves	3 g
Wine vinegar	1 l

Preparation:

1. Crush the first four ingredients in a mortar containing a few drops of the wine vinegar.
2. Transfer the mixture into a bottle filled with the remainder of the vinegar.
3. Keep the mixture in a sealed bottle for at least one month, agitating periodically, until ready for use.

Truffle-flavored vinegar is also prepared by other recipes employing different doses, preparation methods, and ingredients (black truffles, black pepper).

Following are a few interesting blends of flavored vinegars:

1. Vinegar, capers, rosemary, sage, basil, garlic, and elder flowers.
2. Vinegar, lemon, garlic, onion, tarragon, and celery root.
3. Vinegar, tarragon, basil, elder flowers, mint, thyme, bay leaf, rosemary, garlic, paprika, clove, cinnamon, pepper, and capers.
4. Vinegar, tarragon, bay leaf, musk yarrow, clove, and nutmeg.

The last formulation above represents an imitation of true tarragon-flavored vinegar and has found widespread acceptance.

Those relatively few flavored vinegars that are manufactured are usually prepared according to the following methods:

1. Tarragon-flavored vinegar by an infusion of tarragon in vinegar.
2. Capsicum-flavored vinegar by an infusion of cayenne pepper in vinegar.
3. Spice-flavored vinegar by an infusion of cayenne pepper, clove buds, pimento, ginger, coriander, black mustard, and black pepper in vinegar.
4. Rosemary-flavored vinegar by infusion of rosemary, peppermint, and angelica root in wine vinegar.
5. French-type flavored vinegar by infusion of tarragon, basil, elder, thyme, rosemary, scallions, lemon peel, white pepper, pimento, bay leaf, and radish in wine vinegar with the addition of salt and sucrose.

In the industrial preparation of flavored vinegars, it is more convenient to use alcoholic tinctures, essential oils, oleoresins or fluid extracts of the various herbs or spices. The much higher flavor yields of these flavor ingredients, together with their degree of solubility in vinegar, must be taken into account. For insoluble products it may be convenient to use alcoholic extracts of the various flavor ingredients.

Compounded Table and Cooking Spices

Ground spices frequently are used for flavoring freshly cooked food immediately prior to consumption. The most frequently used spices include white and black peppers, paprika, and celery-flavored salt, all of which are fairly simple products. Compounded ground spices are also employed. Typical formulations call for the use of a blend of the following finely comminuted spices:

1. Paprika (6 parts), ginger (30 parts), pimento (30 parts), mustard (60 parts), black pepper (60 parts), fenugreek (90 parts), turmeric (130 parts), coumarin (60 parts), coriander (720 parts), salt (12 parts), vinegar (30 parts).
2. Black pepper (38 parts), ginger (7.5 parts), turmeric (7.5 parts), black mustard (4 parts), cumin (40 parts), nutmeg (3 parts), clove (4 parts), anise (1.8 parts), sugar (4 parts), dried and ground sweet almond (45 parts); the minced spices are mixed with tartaric acid (4 parts).
3. Coriander (1 part), paprika (1 part), cumin (2 parts), mustard (1 part), grape (3 parts), ginger (3 parts), white pepper (6 parts), turmeric (16 parts).
4. Mustard (40 parts), cinnamon (5 parts), cardamom (1 part), ginger (10 parts), paprika (3 parts), fenugreek (5 parts).
5. Marjoram (15 parts), parsley (21 parts), thyme (25 parts), lemon peel (12 parts), celery (4 parts), basil (12 parts), bay leaf (5 parts).

Curry is a compounded spice of Oriental origin. Its composition varies depending on its origin—India, Red Sea countries, Indonesia, Hong Kong, etc. A typical simplified curry formulation includes the following: cinnamon (1 part), clove buds (1 part), ginger (1 part), fenugreek (1 part), mustard (1 part), chili (1 part), coriander (1 part), turmeric (1 part), cumin (1 part), cardamom (1 part); approximately 30 ingredients are present in a true curry formulation.

SOUPS AND BROTHS

Bouillons for Broths and Condiments

The preparation of bouillons has had a decisive growth following World War II. At one time they were considered auxiliary culinary products or surrogate products of only limited interest. Today bouillons are considered indispensable ingredients in food preparation both at home and in restaurants because of their twofold function –the imparting of and the enhancing of food flavors. The reasons for the increased acceptance of these products are numerous, the most important of which is probably the substantial changes in manufacturing practice from empiric to scientific on an industrial scale. This has in turn offered guarantees of high quality required by products of large consumption.

Early bouillon preparations consisted mainly of animal or vegetable proteins hydrolyzed by hydrochloric acid and subsequently neutralized with sodium carbonate to form sodium chloride. Yeast residues from distilleries, dextrin, and vegetable and animal broth concentrates complemented the protein mixture. True meat extracts represented only a minor portion of such products with the exception of a few high-quality preparations. The transition to current products has occurred gradually. Parallel to the increasing demand for such products, formulations have been improved through continuing experience; today they are perfectly matched to specific end-use requirements. To arrive at these results, however, old formulations based on chemical reactions have been abandoned; the new bouillon formulations consist mainly of blends. Today's bouillon production is based on the following basic types:

1. Bouillons with strong, aromatic, vegetable flavor, also used in condiments.
2. Lean beef bouillons with meat and vegetable flavor.
3. Fat beef bouillons with meat and vegetable flavor.
4. Mixed flavor bouillons, spiced and seasoned for use with condiments in the presence and/or absence of tomatoes.
5. Chicken bouillons.

Basic raw materials in the preparation of bouillons include monosodium glutamate and other flavor enhancers, hydrogenated fats, concentrated meat and vegetable extracts, soybean and other flour types, powdered milk, lactose, yeast extract, sodium chloride, and flavors. The relative doses in the blends are important and directly related to the technological skill of the manufacturer. Flavoring must be compatible with the blend, but it is usually geared toward a few specific trends. In bouillons a typical flavor base is celery, onion, and carrot. Turmeric is often added, especially to fatty-type products. Flavors may be added as powdered, dried vegetables, concentrated extract, essential oil, oleoresin, or oleoresin plated over a salt carrier. Nutmeg also yields good flavoring results when added at suitable levels to vegetable-flavored bouillons (No. 1 above).

In bouillons for condiments, the inventiveness of the formulator finds extensive room for implementation with the limitation that pepper, ginger, capsicum, and similar products must be used only as minor ingredients and not as basic flavors. Rosemary and laurel flavors also may be used to characterize the product, but their presence limits the number of end-use applications.

Finished Soup Products

The demand for products suitable for the quick preparation of finished soups has increased remarkably in recent years, not only in quantity but also in variety. The quality of such products has been continuously perfected, justifying their widespread acceptance at all social levels as basic components of daily food. Products have been formulated to satisfy the taste of a very large majority of consumers, and formulations have been patterned after reknowned culinary recipes.

Technically these products (containing all the necessary ingredients) are formulated so as to reduce the cooking time to a minimum. It is sufficient to open the package, disperse the product in the required amount of water, then heat to boiling; the resulting product is ready for consumption. To arrive at such results, all ingredients normally requiring prolonged cooking must be precooked and then dehydrated to permit extended storage and packaging in a minimum amount of space. As in all soups, including homemade varieties, various flavor ingredients characteristic of each type of product are usually added.

Since most products consist of coarsely ground ingredients, powdered anhydrous flavors are usually employed. Dispersions of liquid flavors on suitable carriers are normally employed. When the direct use of dried, powdered herbs is not feasible or convenient, oleoresins plated on a salt carrier or similar flavor blends may be more functional. Monosodium glutamate and other flavor potentiators, yeast extracts, and similar products are almost exclusively utilized together with salt to complete and enhance the flavor. The precooked ingredients generally consist of farinas, cereal products, and vegetables. Spray-dried, dried, and dehydrated vegetables prepared by methods most suitable for the individual ingredients are used; to these are added hydrogenated fats, dry skim milk, various inorganic salts, and sometimes sugar. Flavor ingredients are used following the same criteria employed in the preparation of specific homemade products. It should be remembered that neutral blends require a larger number of flavor ingredients. It may be necessary at times to mask the specific flavor of certain ingredients or to reinforce the corresponding notes of certain dried vegetables. Since prolonged cooking of the finished, ready-to-eat soup is not required, precooked food flavors should be considered; for example, the flavor of roasted onion is entirely different from that of fresh onion.

DESSERTS

Puddings and Gelatins

In the past the preparation of dessert products such as puddings and gelatins were almost exclusively left to the extemporaneous expertise of home cooking. However, prepared gelatins and puddings have attained a remarkable importance in recent years by entering the category of industrial food products; their consumption has been increasing constantly. Reasons for their increased popularity include ease of preparation, mouth-feel, and storage stability; most important is the variety and ease of flavoring.

Generally, pudding and gelatin formulations should be prepared with flavor materials suitable for prolonged storage. The ingredients, depending on local government regulations, are chosen in general from among the following: rice or corn starches, roasted flours, milk powders, sugars, thickeners (alginate, agar, pectins), colorants, and flavors. Pudding powders can be added to milk or water, while gelatin-based powders are used only with water. Sometimes dry powdered milk is blended in the pudding formulation, in which case the addition of water is necessary. As to the flavor ingredients, pudding powders are most frequently flavored with vanilla, chocolate, Dutch custard, almond, pistachio, mandarin, and zabaglione; fruit flavors, such as strawberry, raspberry, apricot, banana, pineapple, pear, plum, apple, red currant, peach, together with citrus, rose, and pistachio flavors, are usually used in gelatin powders.

Pudding and gelatin flavors must be in powder form for better dispensibility with the other powders in the blend. Vanillin or natural vanilla extract may be used for vanilla flavors. Cocoa powder and a little vanilla may be used directly for chocolate flavors, whereas compound spray-dried or plated flavor ingredients may be used to impart other flavors. The use of lyophilized fruit juices may also give excellent results in the preparation of certain flavors for gelatin products.

Honey

Honey flavor, although it follows certain basic guidelines, often exhibits characteristic floral notes, depending on the flowers on which the bees feed. A few honey types are distinguished by their specific floral note, such as lavender, rose, genet, linden, etc. These various honey types are originally from areas where flowers of the corresponding type are cultivated or grow wild in the proximity of the hive. Honey flavor imitations do not take into account these particular flavor notes and attempt to duplicate only the basic honey note formulated with a more or less pronounced and generic floral note.

Considering that honey may find use not only as a sweetener but also as a flavor ingredient in pastry products and in candy, honey flavor imitations are prepared to exhibit characteristically high flavor yields. This permits the replacement of natural honey in formulations such as powdered products where natural honey cannot be employed because of technical reasons. In addition to pastry, natural and imitation honey flavors are popularly employed in tobacco and drugs.

The basic component on which honey flavor imitations are based is phenylacetic acid. A minute addition of formic acid is generally advisable. In addition to phenylacetic acid, the addition of esters to the formulation is important. Ethyl pelargonate, amyl acetate, ethyl acetate, and amyl valerate also may be added. However, flavor imitations based on these esters only (even with the addition of methyl acetophenone) exhibit a particular note of very limited use. The use of acetates, such as phenyl, ethyl, phenethyl, isobutyl, allyl, *p*-cresyl, cyclohexyl, and guayl, imparts more specific notes. Phenethyl acetate, benzyl cinnamate, phenethyl propionate, linalyl butyrate, and cinnamyl butyrate are also excellent auxiliary flavor ingredients when used with carvacryl acetate, *p*-cresyl acetate, *p*-cresyl ethyl ether, ethyl phenoxyacetate, and traces of amyl acetate.

Once the exact ratio between phenylacetic acid and the esters has been chosen, it is necessary to add vanillin, sometimes heliotropin, and a generic floral note that is normally introduced with essential oils. The most functional oils for this type of formulation include rose, clary sage, celery, jasmine, lavender, camomile, neroli, cardamom, together with genet and mimosa absolute. To better define the use of essential oils, it is important to point out that excellent flavor effects are already obtained by using only rose and clary sage essential oils, provided vanillin is also present in sufficient amounts. A guideline formulation for imitation honey can be represented by the following:

Imitation Honey Flavor

Ingredients	Parts
Phenylacetic acid	555
Amyl valerate	230
Amyl acetate	170
Ethyl acetate	100
Ethyl phenylacetate	90
Rum ether	25
Vanillin	25
Methyl phenylacetate	15
Ethyl formate	7
Lemon balm essential oil	3
Maltol (1% solution in alcohol)	3
Clary sage essential oil	2
Formic acid	2
Orange essential oil	2
Rose absolute	1
Solvent (ethylene glycol ethyl ester)	770
Total	2,000

For tobacco a rather simple honey formulation consists of phenylacetic acid, ethyl vanillin, methyl phenylacetate, methyl acetophenone, and geranium essential oil. It is not advisable in this instance to add heliotropin or hydroxycitronellal to strengthen the floral note.

Fruit Preserves

Marmalades (*confettura*), jellies, jams, and preserves are prepared by blending concentrated fruit pulp and/or juice with sugar and sometimes thickeners, such as pectin. The resulting product must be a gel sufficiently thick for easy spreading.

Preparation is usually performed by cooking and concentrating in either open or vacuum concentrators sometimes equipped with automatic devices for determining dry residue. In general, the dry residue of fruit preserves is about 60%. The initial method of preparation of the pulp or juice is normally used to classify various products. For example, marmalade is prepared from mashed pulp after removal of the peel, seeds, residual leaves, and stems by compressing the cooked fruit through a sieve. Preserves are prepared from peeled and de-seeded fruit cut into pieces. Jellies are prepared from fruit juice; jellies usually do not contain water insoluble substances.

Specific technological procedures are employed for the preparation of these products. However, the basic concept governing the preparation of gelatins and the addition and choice of sugars should be considered perfectly valid. Sucrose tends to invert because of heat and the presence of acid, while thickeners are more active at low pH values. In the preparation of marmalades, two-thirds of the required sugar is added prior to cooking, while the remainder is added toward the end; the thickener (pectin) is then added and finally acidulants as required. By this method an excessive inversion of sucrose to dextrose with subsequent potential crystallization of the dextrose is avoided, while a partial inversion of sucrose is effective to prevent the crystallization of sucrose. The optimum ratio in the resulting product should be two-thirds sucrose and one-third inverted sugar. The amount of sugar usually varies between 60-65%, based on the weight of the pulp and depending on the content of natural acids and pectin. In addition to beet (alkaline) and cane (acid) sugars, corn syrup, malt extracts, and glucose are also used in mixture with the sugar. The use of sorbitol in place of sugar is conditioned by the specific dietary requirements of consumers.

Preserves usually do not require additional flavoring; in several countries flavoring of preserves is not permitted. Marmalades, preserves, and jellies are used as flavor ingredients in confections and pastry. Very interesting flavor effects are obtained by blending these products (particularly fluid preserves) with yogurt or whipped cream.