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THE CHEMISTRY OF THE ODOUR OF FOODSTUFFS

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I. INTRODUCTION

The last few years have seen the introduction and vigorous development of a new field of chemistry — the chemistry of the odour of foodstuffs. This review considers the main lines of investigation from 1956 to 1961 on the chemistry of the odour of meat, fish†, bread, milk and milk products, cocoa, and coffee.

At present the primary task of the chemistry of odour is to investigate the connection between odour and the physicochemical nature of the material, and on this basis to construct a theory to explain the mechanism of the interaction of substances with the olfactory organs. A theory of odour will enable a directed "synthesis" of the aroma of food products to be achieved and an objective odour analyser to be created; such an analyser will find wide application not only in the food and perfumery industries, but also in chemistry as an improved method for the analysis of volatile compounds. In medicine it may be used as a sensitive diagnostic apparatus for various diseases associated with the disturbance of metabolism.

Investigations of the chemistry of odour should also help in solving many of the most important problems of the food industry, in the first place retention of the original odour of commercial food products, avoidance of undesired flavours, shortening of ripening periods, and prevention of aging processes. Of particular significance for the food industry is the creation of aromatic mixtures to reproduce the odours of foodstuffs. In the future, synthetic compositions of food aromas will have particular value in connection with the production of artificial food. Solution of the above problems requires the combined efforts of chemists, physiologists, microbiologists, and food technologists.

The rapid development of the chemistry of odour has been held back by the absence of proper methods of analysis. Our olfactory organs are unsurpassed as analytical devices, and the best methods of analysis cannot as yet compete with them. A man can, for example, distinguish vanillin at a concentration of 10^{-14}. Additional difficulties in studying the odour of food products arise because the odour and the taste of food are extremely closely related, and can be separated only with difficulty, especially in the case of products having little taste and aroma, the latter being perceived only during actual consumption. Analysis of the odour of food products is also made difficult by the fact that odour is associated with the presence of minute quantities of a mixture of volatile substances: for example, 1 kg of cheese contains 1–2 mg of the material responsible for its aroma. Moreover, the aromatic mixture which provides the odour of food products is a multicomponent composition, containing sometimes up to 70 volatile substances. It is not surprising therefore, that the main advances in the chemistry of odour have been made in the last five years, and are principally associated with the use of various types of chromatography, particularly gas chromatography. Investigation of the odour of food products has required specific methods for the isolation and identification of the volatile substances responsible for the odour.

II. METHODS OF ISOLATION AND IDENTIFICATION

Methods of Isolation

Steam distillation in a current of nitrogen at 1–2 mmHg and 35–40° is generally used to separate the odoriferous principles from the mass of foodstuff [1-5]. The aromatic substances are sometimes distilled under a high vacuum (10^{-5}–10^{-6} mmHg) in a film evaporator over the same temperature range; the distillate is collected in a series of traps cooled to temperatures of -10° to -180°. [6-10] When these methods of concentration are used, there is the possibility of a change in the composition of the aromatic material when the foodstuff is heated.

The aromatic substances are sometimes separated by centrifuging [11] or by repeated extraction with solvents [12]; with the latter method, possible losses of readily volatile substances must be borne in mind, as well as the danger of contamination by trace impurities present in the solvent.

† Section VI has been written by S. D. Sokolov.

The oil carrying the aroma of the food product, obtained by this concentration, is then separated into the various classes of compound, and the individual components are identified.

Methods of Identification

The substances responsible for the aroma of foodstuffs can be identified by any physical or chemical method which can detect small amounts of a material in a complex mixture. The methods most widely employed in recent years are the various forms of chromatography. For example, the carbonyl compounds present in the odour of all foodstuffs can be separated by paper chromatography of their 2,4-dinitrophenylhydrazones[5,6,13-15], by thin-layer chromatography[16], or on columns of various adsorbents[17-19]. The carbonyl compounds are regenerated from the 2,4-dinitrophenylhydrazones by boiling with γ-oxovaleric or α-oxoglutaric acid[20,21].

Gas chromatography is the most frequently used for the analysis of components of odours, mainly because of its high sensitivity: modern chromatographs can determine 10^{-13} mole of a substance. Because of this high sensitivity, preliminary concentration of the odour can in some cases be omitted[22,23]. Moreover, the high resolving power of gas chromatographs (up to several 10^4 theoretical plates) and the use of stationary phases of varying selectivity enable the components of the odour to be analysed without preliminary separation into different chemical classes, and their proportions to be determined. Recently analysis by gas chromatography has often been combined with mass spectrometry and spectrographic methods of analysis[9,22-26]. The presence of a compound in a mixture is considered proved, even without isolation, if the same retention time, infrared spectrum, and mass spectrum are obtained as for the known compound itself.

The analysis of odours by gas chromatography requires a knowledge of the possibilities and limitations of the different types of detector which may be employed.

Recently Buttery and Teranishi[22] made a special study of the efficiency of the various types of detector in the analysis of the odours of foodstuffs without preliminary concentration, using for analysis the vapour taken from above the surface of the food product. They found that the sensitivity of thermal-conductivity detectors was much reduced by the presence of water vapour in the sample. Moisture does not lower the sensitivity of flame-ionisation detectors, but these have the disadvantage of insensitivity to hydrogen sulphide and low sensitivity to other sulphur compounds[8]. Moreover, the effectiveness of most standard chromatographs with flame-ionisation detectors is reduced because the products are identified only by their retention times, and combination with mass-spectrometric and spectroscopic methods of analysis is impossible because of combustion of the material in the detector.

According to Buttery and Teranishi, the best results in the analysis of anhydrous mixtures are given by argon ionisation detectors with ^{90}Sr as β source[27,28]; detectors with ^{147}Pm [29] or RaD as β source or with ^{226}Ra [30] as α source are only one-half to one-third as sensitive. Although the sensitivity of an argon β-ionisation detector is reduced in the presence of water vapour, it can be successfully employed for the analysis of sulphur compounds; it was so used in 1961 for the analysis, without preliminary concentration, of the sulphur-containing compounds in the odour of cabbage[9].

Clearly, the most promising device for the analysis of an odour would be a chromatograph of semipreparative type fitted with a means for temperature programming containing a β-ionisation detector through which only a part (about 5%) of the flow of gas is passed. Automatic temperature programming would considerably simplify the analysis, because the substances responsible for the aroma boil over a wide temperature range. Such a chromatograph could provide for simultaneous analysis of the components of the odour by mass-spectrometric and spectroscopic methods.

A more complete separation and identification of the compounds in aromatic mixtures by gas chromatography is generally carried out by using several columns with stationary phases of different polarity. Apiezon and silicone vacuum greases are used as non-polar phases, and polyglycols and their esters as polar phases.

Gas chromatography has provided rich new possibilities for the study of the chemical composition of food odours, but nevertheless the experience of recent years shows that the sensitivity of even the best chromatographs is still insufficient for the qualitative and quantitative determination of the composition of aromatic mixtures.

There is as yet not a single food product for which the composition of the materials responsible for its aroma has been fully determined. Further improvement in the analytical methods is required for the successful development of the chemistry of food odours.

III. THE ODOUR OF MILK AND MILK PRODUCTS

1. Milk, Cream, Butter

Flavours. The study of the aroma of milk and milk products has been stimulated primarily by the need to understand the reasons for the presence in them of tainted flavours, so that the latter may be avoided. There has been much study of the most frequently met taint in milk products, the "oxidised" flavour[4,31-37]. The "oxidised" flavour of milk, cream, and butter is due to autoxidation of the milk fat, the flavours at different stages of the oxidation being named separately. The first stages of oxidation are generally characterised by "cardboard", "oily", "drying oil", and "cucumber" flavours, and the later stages give rise to "mushroom", "tallowy", "fishy", and finally "metallic" flavours in the milk or milk product. These tastes appear particularly rapidly when the milk product is illuminated. The presence of copper‡ also greatly increases the rate of oxidation[38]. The mechanism of the catalysis of the oxidation of fats by metals of variable valency has been investigated in detail[40].

Investigations have shown that carbonyl compounds are the main causes of the oxidised flavour of milk and milk products. The reproduction of this flavour requires a whole complex of the saturated and unsaturated carbonyl compounds produced in the oxidation. The various shades of flavour are produced by an excess of one or more of the carbonyl compounds.

‡ The copper content of milk varies from 0 to 128 μg litre^{-1}.[39]

Day and Lillard[4,41] have compared the compositions of the carbonyl compounds in fresh and oxidised milk fat (Table 1). It is seen that the aroma of milk fat is produced by at least 27 carbonyl compounds — the C_1-C_{10} normal aldehydes, C_3-C_{11} α-unsaturated aldehydes, C_3-C_{15} methyl ketones, and hepta-2,4-dienal. The quantity of unsaturated carbonyl compounds increases with the degree of oxidation; for example, milk fat having a fishy taste, which appears at a later stage in the oxidation, contains more of the unsaturated aldehydes, especially hepta-2,4--dienal.

Table 2 gives the various flavours of oxidised milk fat arising because of the presence of an excess of one or more carbonyl compounds over the general level of carbonyl compounds present in the aroma of fresh milk fat.

El Negoumy *et al.*[40] synthesised the C_5-C_{10} alka-2,4--dienals, and determined the odour which they give to milk.

TABLE 1. Percentage content of carbonyl compounds in the odour of fresh and oxidised milk fat*.

Carbonyl compound	Fat with tallowy flavour	Fat with fishy flavour	Fresh fat	Carbonyl compound	Fat with tallowy flavour	Fat with fishy flavour	Fresh fat
C_1+C_2-al	32.47		0.7	C_{11}-one			0.13
C_3-al	5.04		0.07	C_{13}-one	4.01		
C_4-al	1.41			C_{15}-one			
C_5-al	9.96	4.0		C_3-enal			
C_6-al	9.23	25.0	0.14	C_4-enal	0.42		
C_7-al	18.80	20.0	0.16	C_5-enal	1.46	3.0	0.07
C_8-al	3.28	1.0		C_6-enal	0.38	4.0	
C_9-al	2.70	5.0	0.07	C_7-enal	1.91	3.0	
C_{10}-al	1.82	1.0	0.18	C_8-enal	0.66	2.0	
C_3-one				C_9-enal	4.18	5.0	0.06
C_5-one				C_{10}-enal	1.28		
C_7-one				C_{11}-enal			
C_9-one				C_7-2,4-dienal		8.0	

* The content of some of the compounds listed has not been determined.

TABLE 2. Substances producing various flavours in milk and milk products.

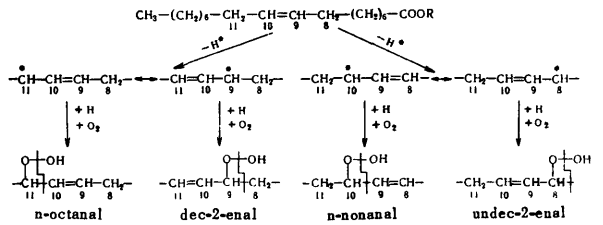
No.	Flavour*	Substances causing the flavour	Ref.
1	Cardboard and tallowy	n-octanol, oct-2-enal, n-nonanal, hepta--2,4-dienal, non-2-enal, undecanal**	34, 35, 40
2	Oily	n-pentanal, n-hexanal, n-heptanal, hex--2-enal, penta-2,4-dienal, deca-2,4--dienal	42–44
3	Drying oil	n-butanal, n-pentanal, pent-2-enal	45, 46
4	Mushroom	oct-1-en-3-one, heptan-2-ol	47
5	Cucumber	non-2-enal	48
6	Metallic	oct-1-en-3-one	47
7	Sunlight	methional	12, 49–52
8	Cereal	5-hydroxymethylfurfural, furfural, isobutanal, isopentanal, 5-methyl-furfural	53, 54
9	Acetone	acetone, acetoacetic acid, β-hydroxy-butyric acid	55, 56
10	Malty	isovaleraldehyde	37, 57–60
11	Coconut	δ-decanolactone, δ-dodecanolactone	12, 61–63
12	Bitter	monobutyrin, dibutyrin	64

* 1–6 are flavours arising by autoxidation of milk fat, milk, and milk products; 7–12 are flavours not associated with autoxidation of milk fat.

** Undecanal alone imparts a "grassy" odour to milk.

The C_7-C_{10} alkadienals produced an oily flavour, not immediately, but after a certain time, sometimes 5 min. A similar effect was observed by Patton[42], who produced an oily flavour in milk by adding 10^{-6} part of deca-2,4-dienal. The appearance of this flavour may be due to reaction of dienals with some constituents of the milk, since water does not acquire an oily flavour when C_7-C_{10} dienals are added to it. According to Hoffman[65] the oily flavour may depend also on the distribution of the dienal in the various phases of the milk. It is also possible that the stereochemical structure of the dienal has some significance. Synthetic dienals are in the *trans–trans* form, while the dienals isolated from milk fat contain also some *cis–trans* form. Recently Stark and Forss have shown[47] that the addition of 10^{-8} part of oct-1-en-3-one to milk produces a metallic flavour, confirmed by a tasting test. Addition of this ketone in amount close to the threshold of odour produces a mushroom flavour in milk and a flavour close to the cardboard flavour in skimmed milk. The threshold for oil and water was also shown to be 10^{-9} and 10^{-10} part of oct-1-en-3-one respectively.

It is now firmly established that unsaturated acids (oleic, linoleic, linolenic, etc.) present in milk fat may be the precursors of saturated and unsaturated carbonyl compounds. It has recently been confirmed experimentally that oxidation products of linoleate and linolenate impart an oxidised taste to milk[66]. The formation of carbonyl compounds by the oxidation of an oleate may be represented:



The oxidation of fats has been considered in terms of the chain theory in a recent monography by Emanuel' and Lyaskovskaya[67], which also considered the inhibition of the autoxidation of fats and gave a list of the antioxidants used in different countries for the preservation of fat-containing food products. The use of sodium gentisate (2,5-dihydroxybenzoate) has recently been proposed for preventing the oxidised flavour in milk and cream and increasing their storage life[68]. With the addition of 0.004% of sodium gentisate, cream and milk can be kept at -23° for six months, even if they contain copper. Table 2 shows the compounds responsible for the flavours not associated with autoxidation of milk fat.

Prolonged boiling of milk produces a "cereal" odour (the odour of "toasted cereal"). This odour is generally inherent in dried milk. Bassette and Keeney[53,54] investigated the odour of milk having a cereal flavour, identified a number of volatile carbonyl compounds, and determined the content of some of them (Table 3).

It is seen from Table 3 that, compared with fresh milk fat, fat-free dried milk contains additionally isobutyraldehyde, isovaleraldehyde, furfural, 5-methylfurfural, and 5-hydroxymethylfurfural, the last apparently having the most significance.

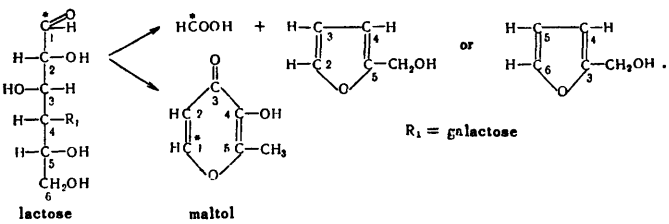
Keeney was able to reproduce the cereal odour by adding 5 micromoles of 5-hydroxymethylfurfural per litre of milk[54],

TABLE 3. Carbonyl compounds isolated from fat-free dry milk with "cereal" flavour.

Carbonyl compound	Content in milk, μg litre^{-1}	Carbonyl compound	Content in milk, μg litre^{-1}
Isobutyraldehyde	0.33	Formaldehyde	1.92
Isovaleraldehyde	0.17	Acetaldehyde	11.90
Hexanal	0.38	Acetone	7.20
Heptanal	0.23	Furfural	*cis*-2.38 *trans*-1.20
Octanal	0.17	Butanone	0.21
Nonanal	0.46	5-Methylfurfural	
Dodecanal	2.82	5-Hydroxymethylfurfural	

and he made the very likely suggestion that 5-hydroxymethylfurfural, furfural, and methylfurfural are formed by the Maillard reaction between lactose and the milk amino-acids.

Patton[69-72] was the first to obtain information on the part played by the Maillard reaction in the chemical reactions of the organic constituents of milk under the influence of heat. He showed that when milk is heated, [1-^{14}C]lactose produces, in the presence of milk proteins, labelled maltol [3-hydroxy-2-methylpyran-2-one] and formic acid and unlabelled furfuryl alcohol. Patton suggested the following process for the formation of these compounds:



Patton showed[49] that the "sunlight" flavour is due to the accumulation of methional [β-methylthiopropionaldehyde] in the milk. This is the flavour acquired by milk on exposure to sunlight. The methional is produced by oxidation of the methionine present in the milk casein:

$$CH_3S-CH_2-CH_2-CH(NH_2)-COOH \xrightarrow{O} CH_3S-CH_2-CH_2-C(=O)H + NH_3 + CO_2.$$

The presence of riboflavin in the milk promotes the formation of methional. The addition of 5×10^{-8} part of methional to milk gives the typical sunlight odour.

An excess of compounds producing the "acetone" flavour in milk (see Table 2) is due to the activity of intestinal microorganisms (*Bact. cloacae*) and also to ketosis in the cow[53,54].

A "malty" flavour in milk and milk products is produced by isovaleraldehyde[37,57-60], which is assumed to be formed by the microbiological fermentation of leucine:

$$(CH_3)_2CH-CH_2-CH(NH_2)-COOH \xrightarrow{O} (CH_3)_2CH-CH_2-C(=O)H + NH_3 + CO_2.$$

A common taint in milk and milk products is a bitter taste. An investigation into the causes of this taste showed that bitter fat contains 4–5 times as many free hydroxy-groups as does fresh fat. Ljunggren and Storgards consider that the bitter taste is imparted to milk and milk products by monobutyrin and dibutyrin, which they were able to isolate[64].

A "coconut oil" flavour is met with in milk, cream, and especially butter. Patton and his coworkers established[49-51] that it arises when the milk or milk product contains an excessive amount of δ-decanolactone or δ-dodecanolactone, the odour threshold of the former in milk being 10^{-6} part. Patton notes that unboiled fresh milk does not contain these lactones, which appear only when milk or cream is heated.

Patton also showed[12] that the bad odour of γ-irradiated milk is due to acetaldehyde, methanethiol, methyl sulphide, and methyl disulphide.

On the basis of the investigations reviewed, it may be considered established that the flavour of milk and milk products is most often due not to one, but to several compounds, the odour being greatly dependent on their concentration and on the properties of the medium to which they are added. Some confirmation of this is found in the interesting results obtained by Patton and Josephson[73] in their determination of the odour thresholds of certain volatile compounds present in the aroma of milk and milk products (Table 4).

It is seen, for example, that 0.05 mg of methional per litre gives skimmed milk a brothlike odour. As already indicated above, addition of this amount of methional to whole milk produces a sunlight flavour. Methional itself smells of raw pumpkin. Unfortunately, the absence of reliable objective evaluation of odour in many cases makes analysis of published data difficult.

Odours. The investigation of taints in the taste of milk and milk products has accumulated a large amount of information on the composition of the volatile substances which impart the aroma to fresh milk and milk products. The odoriferous components of milk and milk products include aldehydes, alkyl methyl ketones, acids, lactones, amines, and sulphur compounds. Currently there is vigorous activity on the quantitative determination of each component. Table 5 contains data on the qualitative composition of the aroma of milk and milk products, obtained by various workers in recent years.

It is seen that this aroma contains all the saturated straight-chain aldehydes, except butyraldehyde, from C_1 to C_{10}, and in addition isobutyraldehyde, isovaleraldehyde, hepta-2,4-dienal, pent-2-enal, non-2-enal, furfural, and benzaldehyde.

Unbranched methyl ketones with an odd number of carbon atoms, from acetone to pentadecanone, make up a substantial part of the aroma of milk and milk products, and there are present only two ketones — butanone and hexanone — with an even number of carbon atoms. The quantitative content of various aldehydes and ketones in milk fat[4] has already been given in Table 1.

TABLE 4. Odour threshold for some compounds in various media.

Compound	Medium	Threshold, mg litre^{-1}	Odour
Butyric acid	milk	25	rancid milk
Hexanoic acid	milk	14	rancid milk
Acetaldehyde	skim milk	1.3	burnt, malty
Acetone	ditto	500	chemical, medicinal
Butanone	»	50	fermented, sour milk
Methional	»	0.05	brothlike
Methyl disulphide	»	0.021	putrid, burnt
Dimethyl sulphide	water	0.012	malty, "cowy"
Methanethiol	water	0.002	boiled cabbage

TABLE 5. Compounds found in the aromas of milk and milk products.

Class of compound	Compound			Ref.
Aldehydes	formaldehyde acetaldehyde propionaldehyde valeraldehyde hexanal	octanal nonanal decanal* isobutyraldehyde isovaleraldehyde	pent-2-enal non-2-enal hepta-2,4-dienal furfural benzaldehyde	74–79
Alkan-2-ones	acetone butanone pentanone	hexanone nonanone undecanone	tridecanone pentadecanone	4, 78, 80–82
Acids	formic acetic propionic butyric hexanoic	octanoic decanoic lauric tridecanoic* myristic	pentadecanoic* palmitic margaric stearic	74, 83, 84
Amines	ammonia methylamine	ethylamine butylamine	diethylamine pyrrolidine*	85–87
Sulphur compounds	methanethiol methyl sulphide	methyl disulphide hydrogen sulphide	methional	12, 81, 88
Lactones	δ-decanolactone	δ-dodecanolactone		12, 89
Multifunctional compounds	biacetyl	acetoin		87, 90–96

* The presence of these compounds is not yet firmly established.

In 1962 Patton and his coworkers determined the amounts of various carbonyl compounds found in the aroma of heated cream and milk[79] (Table 6).

Patton has also shown[78] that the content of carbonyl compounds increases with the time of heating milk and cream; the heptanone content, for example, increased several hundredfold on heating.

The aroma of milk and milk products contains all the unbranched saturated acids from formic to myristic, with the exception of valeric, heptanoic, and nonanoic (Table 5). Formic, acetic, propionic, butyric, and hexanoic acids are present as such in milk. A litre of milk can contain up to 35 mg of butyric acid and 27.5 mg of hexanoic acid[84]. Acids containing an even number of carbon atoms from C_8 to C_{18} are found as the triglycerides, which are volatile in steam[74,83]. Aliphatic acids with an odd number of carbon atoms (C_5, C_7, C_9) have been found in oxidised milk fat[83].

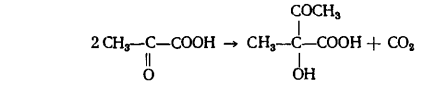
Other acids which affect the taste and possibly the aroma of milk and milk products include lactic and pyruvic acids[84,97,98], α-oxoglutaric, acetoacetic, oxaloacetic, and oxalosuccinic acids[98,99], and citric acid[100,101]. The content of free acids increases when milk and milk products are heated.

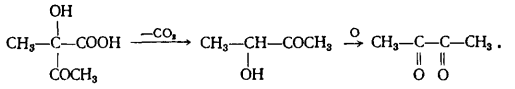
δ-Decanolactone and δ-dodecanolactone have been detected in pasteurised milk, and in cream and butter[12,89]. Lactones apparently make up a substantial part of the aroma of fresh butter, and the use of various δ- and ε-lactones for flavouring margarine has been patented in England, the U. S. A., Germany, and Australia[102–105].

Although present in minute amounts, sulphur compounds play a substantial part in forming the aroma of milk. In 1956 Patton and coworkers[106] isolated methyl sulphide from the volatile components of milk, and they later found methanethiol, methyl disulphide, methional, and hydrogen sulphide[12,81,88].

Recently ammonia, methylamine, ethylamine, and butylamine have been detected among the volatile components of milk and milk products[85–87]. Pyrrolidine may also be present, but this has not yet been definitely established[85].

Biacetyl is also a substantial component of the aroma of cream and fresh butter, being produced by the lactic acid bacterium *Betacoccus cremoris* from the pyruvic acid present. α-Acetyllactic acid is first produced, and on heating is decarboxylated and oxidised by atmospheric oxygen to biacetyl[87,90–92]:





The content of biacetyl in butter varies from 0.56 to 1.0 mg kg^{-1}.[93,95] It is often used for flavouring butter substitutes. Because of the experimental data on the mechanism of formation of biacetyl in butter, it has been proposed to add α-acetyllactic acid during the production of margarine[96]. A Japanese patent[107] for imparting an aroma to butter and margarine recommends the use of the mixture indicated in Table 7.

Until recently it was thought that, in addition to biacetyl, acetoin also plays an important part in the odour of butter and cream; in fact, acetoin purified by gas chromatography has no odour[108].

The aroma and taste of milk and especially of butter depend on the season; those of summer butter, for example, differ from those of winter butter, because of the different composition of the milk fat. Study of this composition is particularly important for the determination of possible precursors of the volatile compounds responsible for the odour.

Until recently it was thought that animal fats contain triglycerides only of straight-chain acids with an even number of carbon atoms, but it has since been established[109–116] that milk fat contains the triglycerides of C_4–C_{10} straight- and branched-chain, even and odd acids, with the exception of valeric acid.

TABLE 6. Content of some carbonyl compounds in the volatile components of milk fat, milk, and cream.

Compound	Content, mg $litre^{-1}$		Compound	Content, mg $litre^{-1}$	
	milk	cream		milk	cream
Formaldehyde	0.001–0.003	0.001–0.004	Pentanone	0.026–0.007	0.025–0.045
Acetaldehyde	0.016–0.013	0.001–0.004	Hexanone	0.007–0.011	0.017–0.018
Acetone	1.152–1.847	0.354–0.508	Heptanone	0.000–0.000	0.004–0.007
Butanone	0.077–0.079	0.154–0.177			

TABLE 7. Composition for imparting aroma to butter and margarine[7].

Mixture A, ml		Mixture B, ml		Mixture C, ml		Recommended for aroma, %	
Biacetyl	7	tetradecanal	6	ethyl acetate	9	mixture A	15
Isovaleric acid	3	lauric acid	6	ethyl lactate	9	mixture B	35
Acetaldehyde	2	vanillin	6	ethyl formate	9	mixture C	15
		butyl phthalate	18	ethyl butyrate	9	α-bromobutyric acid	35

Milk fat contains both conjugated and unconjugated unsaturated acids. McDowell[117] and Stadhouders and Mulder[118] have determined the contents of conjugated and unconjugated octadecadienoic and octadecatrienoic acids in winter and summer milk fat (Table 8).

It is interesting that the C_{18} acids contain a maximum of three double bonds. The infrared spectra of the C_{20} and C_{22} acids show them to include acids with four, five, and even six double bonds[119]; milk fat also contains a small quantity of branched-chain saturated acids[120-123].

The data so far obtained are sufficient to indicate the main pathways by which the volatile compounds present in the aromatic compositions responsible for the odour of milk, cream, and butter are produced. The chief precursors of the materials responsible for the aroma are apparently the milk fat and amino-acids present in milk. Particular importance attaches to reactions involving cleavage of the milk fat (primarily autoxidation) and to enzymic cleavage of the amino-acids. Moreover, a large part in the formation of the volatile components responsible for the odour of milk and milk products is played by reaction of the amino-acids with lactose (the Maillard reaction).

2. Cheese

The aroma of cheese is considerably different in chemical composition from that of other milk products; it contains a large number of esters and alcohols, and no unsaturated aldehydes. This is due to the technology of cheese production, which includes two most important steps — inoculation of the milk with cultures of bacteria such as *Streptococcus thermophilus*, *Lactobacillus bulgaricus*, *Propionibacterium shermanii*, *Streptococcus faecalis* *Lactobacillus lactis*, etc., and addition of rennin. The aroma and the taste of cheese are considerably affected by the microbiological and chemical composition of the milk, the types and activity of the cultures used, the amount of rennin added, the temperature and duration of ripening, the enzymes present in the cheese mass, and the enzymes which develop during its ripening.

Investigation of the aroma of cheese began with a study of the composition of the fatty acids, since butyric and propionic acids are often found in the odour of cheese. The early unsuccessful attempts to correlate the odour of cheese with the aliphatic acid content[124-128] were due to the use of insufficiently sensitive methods of analysis. In 1949 Peterson *et al.*[129], using their chromatographic method for aliphatic acids[130], studied the appearance and accumulation of acids during the ripening of Cheddar cheese, and found acetic, propionic, and butyric acids to accumulate during the first 30 days, after which hexanoic, octanoic, and decanoic acids appear. The content of C_6 and higher aliphatic acids in the cheese increases continuously as it ripens and ages. These workers suggested that the acetic acid is produced microbiologically from lactose, since the latter completely disappears from the cheese mass during the first few days of maturation. Other cheeses, such as Provolone, Rumanian, Swiss, and Blue, contain the same aliphatic acids as Cheddar, but a particular acid predominates in each type of cheese — *e.g.* acetic acid in Cheddar[131], butyric acid in Provolone and Romano cheese[132-135], and propionic acid in domestic Swiss cheese[136] (Table 9).

Russian cheeses have been studied by Chebotarev[137], who found Yaroslav cheese to contain most propionic acid, and Soviet cheese butyric.

In their study of the influence of various types of lipolytic enzyme preparations on the accumulation of free aliphatic acids in Italian cheeses (Provolone, Romano), Long and Harper showed[134,138] that the rate of formation and the concentration of butyric acid depend directly on the type of enzyme preparation (rennin) used for production of the cheese.

It can now be considered as established that, as the cheese ripens, the amount of the acid characteristic of that type of cheese increases, reaches a maximum in the mature cheese, and then decreases. The content of C_6 and higher aliphatic acids increases continuously with the time of storage of the cheese, irrespective of its type. Moreover, the suggestion made by Peterson and Johnson in 1949, that the aliphatic acids are produced by enzymatic cleavage of milk fat contained in the cheese, has also been confirmed. However, the aliphatic acids found do not reproduce the aroma of cheese, and Dacre has suggested[139] that in general fatty acids play no part in its production.

No direct relationship has been found between the quality of a cheese and its amino-acid content, but the number of free amino-acids in cheeses does not correspond to the composition of hydrolysed milk casein.[131,134,136-138,140-143] The amino-acid composition of ten types of USSR cheese has been studied by Chebotarev[137], who showed that such amino-acids as arginine, serine, methionine, and in some cheeses histidine are decomposed; ornithine and α- and γ-aminobutyric acids are produced. The accumulation of amino-acids during the ripening of Emmenthal cheese has been studied by Italian workers[144,145]. In 1956 Long and Harper suggested[138] that threonine, methionine, and histidine, which are present in small amounts in cheese,

TABLE 8. Content of conjugated and unconjugated acids in milk fat.

No. of C atoms in acid / No. of double bonds	Content in milk fat, %*	
18 : 2 conjugated	0.8–1.3;	0.58–2.81
18 : 2 unconjugated	0.2–0.7;	0.73–1.90
18 : 3 conjugated	0.03–0.04;	0.015–0.026
18 : 3 unconjugated	0.5–1;	0.35–0.96

* The first column gives McDowell's results, and the second Stadhouders and Mulder's; in each column the first figure is for winter milk fat, and the second for summer.

TABLE 9. Content of aliphatic acids in various types of cheese.

Cheese	Age of cheese	Acid content of cheese, mg g^{-1}			
		acetic	propionic	butyric	C_6 and higher
Swiss	3 months	2.6	4.4	1.2	2.4
	4 months	1.8	3.1	1.6	5.0
	11 months	3.0	5.0	1.1	24.2
Provolone	1 day	0.65	0.50	2.10	
	5 months	2.37	1.78	8.90	
	9 months	0.31	0.35	1.24	
Cheddar	mature, highest quality	23.5	1.6	0.7	11.0

play an important part in the metabolism of the bacteria, and that their conversions may be important in producing the odour of cheese. They showed that the amino-acid composition varies with the bacterial starter used, *i.e.* that the microbiological flora plays the main part in the accumulation of free amino-acids. For example, if *Lactobacillus lactis* is used in the production of Provolone cheese, the free amino-acid content is considerably greater than if *Lactobacillus bulgaricus* is used.

The accumulation of aliphatic acids and amino-acids in cheese is thus an indication of the enzymatic and bacteriological processes occurring during its production. In fact, a parallel study of the accumulation of fatty acids and amino-acids in Swiss cheese has shown[136] a clear relationship between the aroma and taste of cheese and its content of propionic acid and proline. Fig. 1 shows that, as the cheese ripens, the proline content rises from 0 to 4.5 mg × × g^{-1}, and then decreases as the cheese ages.

In cheeses of good taste and organoleptic evaluation the proline content is more than 2 mg g^{-1}, and the propionic acid content is about 4.5 mg g^{-1}. With smaller concentrations but about the same relative proportions of the two compounds (1 : 2), the odour is weak; when this proportion is disturbed, defective odours occur.

n-Butyric and glutamic acids play a definite part in the odour of Romano cheese[138], their contents in good-quality cheese being 3.0–7.1 and 4.8–6.3 mg g^{-1} respectively. Samples with less than these amounts had a poor aroma. For best-quality Provolone cheese the ratio of n-butyric to glutamic acid is about 1 : 2.

In 1960 Kristoffersen and Gould investigated the aroma of Cheddar cheese in relation to the amino-acid and aliphatic acid content[131], and concluded that the characteristic odour of the cheese is due to the simultaneous action of fat-splitting and protein-splitting agents. They followed the changes in the relative proportions of fatty acids to hydrogen sulphide (the latter being used to follow the rate of microbiological cleavage of the amino-acids) during the ripening of the cheese, and also in cheeses of various taste evaluations. The data in Table 10 show that the ratio of total aliphatic acids to hydrogen sulphide is characteristic of each type of odour. In cheese of normal odour this ratio is twice that in samples with a hydrogen sulphide odour, and half that in samples with a fatty acid odour. It is of interest that samples of the cheese with a sharp hydrogen sulphide odour contained less hydrogen sulphide than samples without this defect.

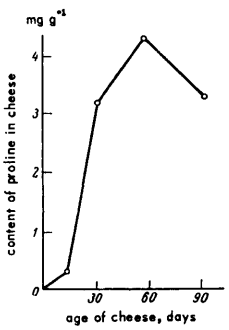


Fig.1. Variation of proline content with the time of ripening of Swiss cheese.

TABLE 10. Dependence of odour of Cheddar cheese on the relative proportions of aliphatic acids and hydrogen sulphide.

Odour	$\frac{\text{Aliphatic acids, mmoles g}^{-1}}{\text{Hydrogen sulphide, mmoles (100g)}^{-1}}$
Normal	17.6; 16.1; 13.1; 12.7; 11.7; 14.7;
Hydrogen sulphide	9.3; 8.7; 5.7; 5.1; 7.2;
Aliphatic acids	36.8; 30.0; 26.1; 22.8; 24.8; 27.8

The facts obtained in the simultaneous investigation of the rates of enzymatic splitting of fats and proteins during the making of different types of cheese thus show these rates to be an important factor in producing the odour of the cheese.

Alkyl methyl ketones, which are apparently present in all types of cheese, also play a significant role in the aroma of cheese[146-150]. In the investigation of the odour of Blue cheese in 1950, Patton isolated pentanone, heptanone, and nonanone[146]. Morgan and Anderson found the same ketones in Roquefort, Danish Blue, Gorgonzola, and Domestic Blue cheeses[147], and showed that all the samples of cheese having the typical odour contained acetone, pentan-2-one, heptan-2-one, and nonan-2-one; heptan-2--one or nonan-2-one was absent from samples having a weak aroma. Harvey and Walker[148] followed the contents of alkyl methyl ketones during the maturation of New Zealand Cheddar cheese (Fig. 2). The one-day old cheese contained acetaldehyde, acetone, butanone, and pentan-2-one. The acetone concentration fell to a minimum in two weeks, then rapidly increased to 4 mg g^{-1} in the 40-week cheese. The characteristic odour of Cheddar appeared after 8–12 weeks. The intensity of the odour increased with the content of pentan-2-one, heptan-2-one, and nonan-2-one. After 32 weeks undecanone appeared, and then rapidly increased in amount as the cheese ripened.

All the ketones, with the exception of butanone, may be produced as the result of fermentative splitting of the aliphatic acids of the milk fat, and this suggestion becomes very probable from the work of Foster[151], who showed that

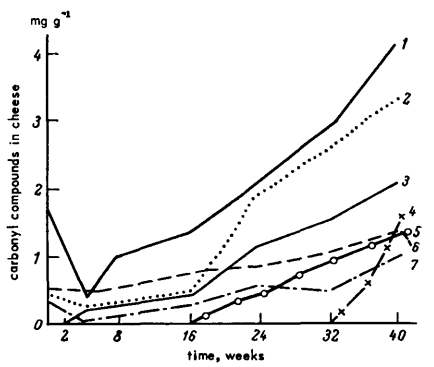


Fig.2. Change in concentration of carbonyl compounds during ripening of New Zealand Cheddar cheese:
1) acetone; 2) pentan-2-one; 3) heptan-2-one; 4) undecan-2-one; 5) nonan-2-one; 6) acetaldehyde; 7) butanone.

the enzymes produced by certain moulds, especially *Penicillium glaucum*, can convert all the individual acids from butyric to myristic into the corresponding methyl ketones:

$$R{-}CH_2{-}CH_2{-}COOH \xrightarrow{[O]} R{-}\underset{\underset{O}{\|}}{C}{-}CH_2COOH \rightarrow R{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + CO_2 .$$

The mechanism by which butanone is produced has not yet been fully elucidated; Scarpellino and Kosikowski have recently suggested[26] its formation, together with butan-2-ol, from acetoin:

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{|}{CH}{-}CH_3 \xrightarrow{2H} CH_3{-}\underset{|}{\overset{|}{CH}}{-}\underset{|}{\overset{|}{CH}}{-}CH_3 \xrightarrow{-H_2O} CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \rightarrow$$

$$\xrightarrow{H} CH_3{-}CH_2{-}\underset{|}{\overset{|}{CH}}{-}CH_3 .$$

In 1962 McGugan and Howsam[8] employed a capillary column with a flame-ionisation detector for analysis of the volatile components of cheese, and detected 42 neutral compounds in the aroma, almost twice the number that had been known previously. Unfortunately, most of these were characterised only by their retention time. Table 11 lists all the volatile compounds found in cheese by McGugan and by other workers. It is seen that 64 compounds which give cheese its odour have been detected. Unfortunately, far fewer quantitative data exist.

TABLE 11. Volatile components in the aroma of cheese.

Compound	Ref.	Compound	Ref.
Aldehydes		*Esters*	
Formaldehyde	131, 152	Ethyl formate	8
Acetaldehyde	8, 147	Butyl formate	8
Propionaldehyde	8, 152	Methyl acetate	8
n-Butyraldehyde	8, 139	Ethyl acetate	8
Isobutyraldehyde	8	Isopropyl acetate	8
n-Valeraldehyde	8	Butyl acetate	8
Isovaleraldehyde	8, 152	Pentyl acetate	8
n-Heptanal	8	Isopentyl acetate	8
		Ethyl propionate	8
Ketones		Propyl propionate	8
Acetone	8, 24, 131, 147–149, 152	Isopropyl propionate	8
		Pentyl propionate	8
Butanone	8, 24, 148, 149, 152	Methyl butyrate	8
		Ethyl butyrate	8
Pentan-2-one	8, 146–149, 152	Butyl butyrate	8
		Methyl hexanoate	8
Pentan-3-one	8		
3-Methylbutanone	8	*Sulphur compounds*	
Heptan-2-one	8, 24, 146–149, 152, 153	Hydrogen sulphide	158–160
		Methyl sulphide	24
		Methional	152
Heptan-3-one	8		
Heptan-4-one	8	*Amines*	
Octan-2-one	8		
Nonan-2-one	146–149	Putrescine	161
Undecan-2-one	148–149	Tyramine	161
Tridecan-2-one	148	Tryptamine	161
		Histamine	161
Alcohols		Cadaverine	161
		Ammonia	160, 162
Methyl	8, 153		
Ethyl	8, 24, 139		
n-Propyl	8	*Other compounds*	
Isopropyl	8		
n-Butyl	8	Diacetyl	8, 24, 152, 153
Isobutyl	8		
s-Butyl	8	Pentane-2,3-dione	8
Isopentyl	8	Acetoin	24, 152
Acids			
Formic	154		
Acetic	155, 156		
Propionic	133, 156		
n-Butyric	155, 156		
Valeric	155		
Hexanoic	155		
Decanoic	155		

Walker and Harvey[149] determined the contents of certain carbonyl compounds in Cheddar cheese. Table 12 gives their results, together with the contents of some alcohols and ketones expressed as percentages of the total volatile compounds, as found by McGugan and Howsam[8].

In addition to simple ketones and alcohols, cheese contains considerable amounts of biacetyl and acetoin, but these compounds are apparently not specific components of the aroma of cheese, since their content decreases as the cheese ripens; moreover, as already stated, pure acetoin is odourless.

The volatile components of cheese include also ammonia and various amines. Ammonia was detected in cheese in 1959 by Moller-Madsen[162]. Kristoffersen and Gould[163] followed the changes in the concentrations of ammonia and hydrogen sulphide (Table 13). They comment that considerable variation in the ammonia content has no noticeable effect on the odour of cheese.

Silverman and Kosikowski investigated 23 samples of Cheddar cheese made from untreated and pasteurised milk, and detected putrescine, tyramine, tryptamine, histamine, and, in cheeses made from untreated milk, cadaverine also[161], the concentration of the amines in such cheeses being much greater than in cheeses from pasteurised milk. These workers consider that the amines which they found are produced by degradation of amino-acids by a specific decarboxylase arising as the result of bacterial activity; they suggest the following reactions for the formation of the amines

tyrosine → tyramine + CO_2,
lysine → cadaverine + CO_2,
arginine → urea, ornithine, putrescine + CO_2,

Sulphur-containing compounds form a substantial part of the aroma of cheese (Table 11); removal of these, as with alkyl methyl ketones, leads to loss of the characteristic odour of the cheese. Sulphur compounds are apparently produced by fermentative degradation of amino-acids:

TABLE 12. Content of volatile compounds in Cheddar cheese.

Compound	Content, mg kg^{-1}	Total volatile compounds, %	Compound	Content, mg kg^{-1}	Total volatile compounds, %
Acetaldehyde	2.65		Undecan-2-one	0.83	
Acetone		2.4–5.1	Tridecan-2-one	trace	
Butanone	0.80		Methyl acetate	0.86	
Pentan-2-one	2.47	5.7	n-Propyl alcohol		7
Heptan-2-one	6.6		Isopropyl alcohol		7.6–10.4
Nonan-2-one	1.7		s-Butyl alcohol		

TABLE 13. Change in concentration of ammonia and hydrogen sulphide during ripening of Cheddar cheese.

Compound	Milk used	Time of storage of cheese, months					
		0.5	1.5	3	6	9	12
NH_3	plain	7.9*	10.9	27.0	30.3	40.6	49.0
	pasteurised	8.8	8.8	22.8	28.6	35.1	44.9
H_2S	plain	2.3	3.7	2.4	3.2	2.4	2.3
	pasteurised	1.2	2.0	1.5	1.8	1.6	1.6

* Concentrations are given in micromoles per gramme of cheese for ammonia, and micromoles per 100 g of cheese for hydrogen sulphide.

thus Kristoffersen and Nelson[158] isolated from high-quality cheese strains of *Lactobacillus casei*, which can degrade cysteine with evolution of hydrogen sulphide.

Several workers have remarked that the taste qualities of cheese are affected by hydroxy-acids and di- and tri--carboxylic keto-acids present in cheese and cheese sweat. Chebotarev detected lactic, succinic, fumaric, oxalic, and glycollic acids in Soviet cheeses, gluconic acid in Latvian and Dorogobuzh cheeses, and citric acid in grated green cheese[137].

Kristoffersen and Gould[163] found α-oxoglutaric, α-acetyllactic, oxaloacetic, glyoxylic, γ-methyl-α-oxovaleric, and citric acids in Cheddar cheese.

In 1957 the Finns Kreula and Virtanen showed[164] that lactic and propionic acid bacteria produce the same α-keto--acids as are found in Emmenthal cheese and its sweat; they isolated glyoxylic, pyruvic, hydroxypyruvic, oxaloacetic, α-oxoglutaric, β-methyl-α-oxobutyric, and γ-methyl-α-oxovaleric acids. These results suggest that keto-acids are produced in cheese by the action of lactic acid bacteria.

Many attempts have been made to formulate artificial mixtures which reproduce the odour of cheese. Thus Dacre[139] tried, in various proportions and concentrations, pure and in solution, all normal alcohols and iso-alcohols up to isopentyl inclusive, all normal aldehydes and iso--aldehydes up to isovaleraldehyde inclusive, all methyl ketones up to methyl pentyl ketone inclusive, and all symmetrical ketones up to di-n-propyl ketone; ethyl formate, acetate, propionate, butyrate, hexanoate, pyruvate, and lactate; and methylglyoxal and butane-2,3-diol. In no case did he obtain a typical cheese odour.

In 1957 Keeney and Day reported[165] the approximate reproduction of cheese aroma by carrying out the Maillard reaction with isatin and an amino-acid mixture of similar composition to casein hydrolysate.

In 1961 Walker[166] accelerated the formation of the cheese aroma in a ripening cheese mass by adding a mixture of certain alkyl methyl ketones, free aliphatic acids, and thioacetamide as a source of hydrogen sulphide; Table 14 gives his suggested mixture. This was added to 20 g of melted butter and mixed with 4 kg of the cheese curd; after 3 weeks the cheese mass had the odour of 3-month Cheddar cheese.

Much is now known about the qualitative and in part the quantitative composition of the aroma of milk, cream, butter, and cheese, but the odour of none of these has yet been created artificially, and in no case can even the qualitative picture of the aroma be considered as complete. It is possible that a more thorough investigation employing improved methods of analysis will increase the number of components known to be responsible for the aroma of milk products. It is also possible that the quantitative proportions of already known components will prove to play the basic role in the aroma of milk and milk products. At present particular attention is being paid to the quantitative determination of each component of the aroma.

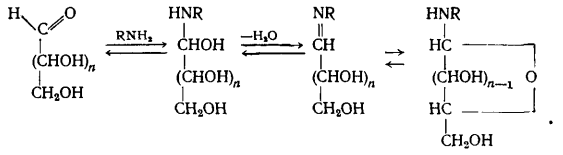
TABLE 14. Composition added to cheese curds to obtain the odour of three-month cheese in three-week-old cheese mass.

Mixture A, g		Mixture B, g		Composition recommended for 4 kg of cheese mass	
methyl ketone		acid			
Acetone	4	acetic	10	mixture A	0.3 ml
Butanone	1	n-butyric	5	mixture B	1 ml
Pentan-2-one	3	n-hexanoic	12	thioacetamide	0.1 g
Heptan-2-one	2	octanoic	14		
Nonan-2-one	1.5				
Undecan-2-one	1.5				
Tridecan-2-one	0.5				

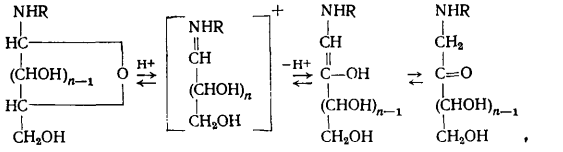
A reaction having great importance in the production of the aroma of nearly all food products is the Maillard reaction, especially where the aroma is produced by heating the foodstuff, for example in bread and meat.

The Maillard reaction. This has been the subject of several long reviews[167-169], and we shall therefore consider here only the suggested mechanism, and the attempts which have been made to obtain food odours by utilising this reaction.

The Maillard reaction is the reaction between an amino-group in an amino-acid, a peptide, or a protein and a glycosidic hydroxy-group in a sugar. The mechanism as a whole is very complex, and is not entirely clear: only the initial stages can as yet be considered proved. The first step is formation of an *N*-substituted glycosylamine



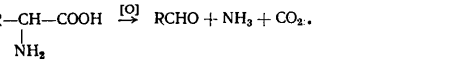
This then rearranges to produce a substituted 1-amino-1--deoxy-2-ketose (the Amadori rearrangement):



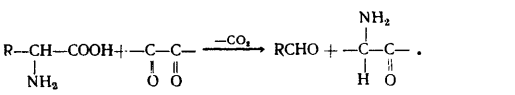
which then undergoes a series of reactions whose mechanism is not fully clear.

Products of the Maillard reaction include aliphatic aldehydes, furfural and certain furfural derivatives, formaldehyde, biacetyl, methylglyoxal, acetoin, and acetone.

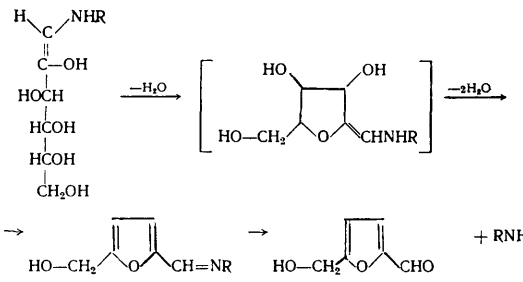
The aliphatic aldehydes are produced in the Maillard reaction by oxidative degradation of amino-acids, known as the Strecker reaction, which can be represented



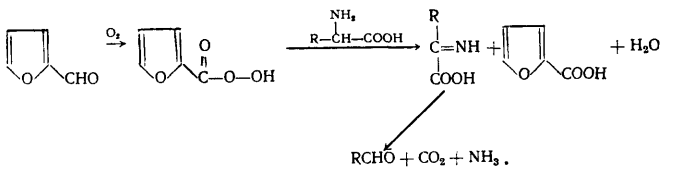
The resulting aldehyde contains one carbon atom less than the initial amino-acid. The Strecker degradation can occur by reaction of amino-acids either with the Amadori rearrangement product or with dicarbonyl compounds present in the reaction mixture



Furfural and its derivatives are produced by dehydration of the Amadori rearrangement product



According to this mechanism, furfural is produced from pentoses, hydroxymethylfurfural from hexoses, and methylfurfural from methylpentoses. Rothe and Thomas consider [170] that furfural and its derivatives can also participate in the Strecker degradation:



Other reactions of the Amadori rearrangement product have not yet been fully investigated.

The end-products of the Maillard reaction are the dark nitrogen-containing polymerisation and polycondensation products known as melanoidines; these play an important part in the darkening of food products, particularly when they are heated.

The Maillard reaction is catalysed by traces of moisture, is unaffected by atmospheric oxygen, and proceeds over a wide pH range, with an optimum in neutral or weakly alkaline media (pH 7–9). The rate of the reaction at 60° is 20 times that at 37°, but even at 37°, it is important to note, the reaction goes at an appreciable rate [167,171]. This suggests that the Maillard reaction may be involved, even at room temperature, in the formation of the substances responsible for the odour of food products.

There have been several hundred papers on the Maillard reaction, but information on the odour produced by the reaction in each particular case is very scanty.

In 1960 Herz and Shallenberger [172] investigated the aroma produced when various amino-acids are heated with glucose at 100° and 180° for 1 h; their results are given in columns 2 and 3 of Table 15. There is no definite relationship between the odour and the reaction temperature; for instance, with leucine and threonine the odour is pleasant at 100° but unpleasant at 180°, while the reverse is true with proline. With histidine an odour appears only at 180°. These workers showed that, irrespective of the temperature, glycine, α- and β-alanine, and glutamic acid produce only the odour of burnt sugar on reaction with glucose; tryptophan, tyrosine, arginine, and α-aminobutyric acid produce the burnt sugar odour only at 180°.

Keeney and Day [165] obtained various odours by heating a number of amino-acids with isatin at 100° in dilute hydrochloric acid for 15 min. No odours were produced by glycine, tryptophan, arginine, histidine, lysine, or aspartic acid (Table 15, column 1).

TABLE 15. Odours produced from amino-acids by the Maillard reaction.

Amino-acid	Odour, under the reaction conditions				
	100°, 15 min	100°, 1 h	180°, 1 h	95°, 1 h	
Glycine	none	burnt sugar	burnt sugar		
Alanine	malty	burnt sugar	burnt sugar		
Valine	apple	rye bread	penetrating, chocolate		
Leucine	malty	sweet, chocolate	burnt cheese*	rye bread	
Isoleucine	malty, apple	musty	burnt cheese*		
Proline	mushroom	burnt protein	pleasant, bakery		
Hydroxy-proline	none	none	none		
Phenylalanine	violets	violets	violets, lilac		
Tyrosine	none	none	burnt sugar		
Tryptophan	none	none	burnt sugar		
Cystine	hydrogen sulphide				
Methionine	cheesy–brothy	potato	potato		
Serine	none	none	none		maple syrup
Threonine	none	chocolate	burnt		maple syrup
Aspartic acid	none	rock candy	burnt sugar		almond
Glutamic acid		burnt sugar	burnt sugar		almond
Arginine	none	popcorn	burnt sugar		
Lysine hydro-chloride	none	none	breadlike		
Histidine	none	none	corn-bread		
α-Aminobutyric acid		none	burnt sugar		maple syrup
α-Amino-α-methyl-propionic acid					maple syrup
Asparagine		none	none		
Glutamine		chocolate	butterscotch		
Ref.	165	172	172	173	171

* Taken from Ref.172, Russian text has "burnt sugar" (Ed. of Translation).

Comparison of the results given in Table 15 shows that the same amino-acid can produce different odours in the Maillard reaction, probably because of the different reaction conditions. The considerable subjectivity in the assessment of odour must also be taken into account.

Unfortunately, there are no data on the Maillard reaction with different amino-acids under comparable conditions. The effect of the sugar on the specificity of the resulting odour has been much investigated. On the basis of their results, Kretovich and Tokareva concluded that the nature of the sugar does not affect the type of odour [173]; thus leucine reacts with xylose, glucose, and fructose to give the same odour of rye bread. However, the sugar does influence the rate of the Maillard reaction. Pentoses, especially xylose, react the most readily; with hexoses the rate is somewhat lower. The specificity of the odour is determined by the amino-acid used.

There is no doubt that the Maillard reaction requires more detailed investigation from the point of view of the "synthesis" of food odours. Such investigation might in many cases explain the occurrence of odour in food products.

IV. THE ODOUR OF BREAD

About 75 volatile compounds have been found in the aroma of bread, of which more than 60 have been identified; these are mainly carbonyl compounds, lower aliphatic acids, alcohols, esters, and some sulphur compounds. The components of the odour are produced during the making of the bread, which comprises three stages — (1) fermentation in the leaven, (2) biochemical processes

in the dough, and (3) the baking of the bread. These processes make different contributions to the final aroma of the bread. Table 16 shows the qualitative composition of the odoriferous components of the leaven, the dough, and the bread. Ketones, certain esters and alcohols are produced during the fermentation in bread ferments obtained from bread yeasts and sugar with addition of some mineral salts; however, the quantity of aliphatic aldehydes, except for acetaldehyde, is considerably smaller in the ferments than in the baked bread. At this stage of bread production lactic, succinic, malic, tartaric, and citric acids are also formed, and these play a much more important part in producing the flavour; however, their esters contribute to the aroma of bread[174].

Biochemical processes in the dough lead to the formation of the aliphatic acids from propionic to decanoic. Bacterial action in the dough also produces certain aldehydes, and the content of keto- and hydroxy-acids increases.

Kohn *et al.* [195] have studied the content of carbonyl compounds in normal and low-bacteria dough, and have established that the normal microflora of dough has no marked influence on the bread aroma. However, it has been reported that the aroma of bread is considerably improved when cultures of certain bacteria are added to the leaven or the dough[188,195,199-201]. Thus Tokareva and Kretovich have shown that enzyme preparations from the moulds *Aspergillus oryzae* and *Aspergillus awamori* reduce the fermentation time in the leaven by 39–43%, increase the content of hexoses and pentoses in the bread, and improve its taste and aroma[199].

The ferments and dough contain substances which are not produced by the Maillard reaction, mainly acids, alcohols, and esters; the content of these decreases on baking. Wiseblatt[193] studied the concentration of volatile organic acids in the dough, the bread, and the oven gases (Table 17).

Baking is the most important stage in formation of aroma, since it is here that the characteristic odour of bread is produced. The main reaction in the formation of odoriferous substances during baking is that between amino-acids and sugars (the Maillard reaction), which leads to the production of a large quantity of these substances, including furfural, hydroxymethylfurfural, and aliphatic aldehydes[170,181,182]; they are mainly formed in the crust (the hottest region), and penetrate into the soft inner part by diffusion. It is the final reaction products, the melanoidines, which give bread-crust its dark colour[174,202]. The importance of the Maillard reaction in forming the aroma of bread is shown by a number of phenomena. Thus, bread baked from overfermented dough, in which all the sugar has been used up in the fermentation, has no aroma and a pale crust. If some sugar is added to such dough before baking, the resulting bread has the normal aroma and a crust of good colour. Comparative analysis of the oven gases from the baking of overfermented and normal dough shows that in the former case almost no furfural or methylglyoxal and very little aliphatic aldehydes are produced[174,181].

Rothe and Thomas[170] studied the variation of the content of furfural and other aldehydes with duration of the period of baking of normal bread (Table 18).

TABLE 16. Compounds involved in producing the aroma of bread.

Compound	Source*	Ref.	Compound	Source*	Ref.
Aldehydes			*Acids*		
Formaldehyde	F, B	17, 175, 176	Formic	F, B	190
Acetaldehyde	F, D, B, G	17, 174–180	Acetic	F, B, G	174, 175, 178, 190–191
Propionaldehyde	F, B	176	Propionic	F, B	190–192
n-Butyraldehyde	F, D, B	176, 177	n-Butyric	F, D, B	190–193
Isobutyraldehyde	F, B	17, 181, 176	Isobutyric	F, D, B	190, 192
n-Valeraldehyde	F, B, G	17, 176	n-Valeric	F, D, B	190–192
Isovaleraldehyde	F, D, B, G	17, 176, 177	Isovaleric	F, D, B	190, 192, 193
α-Methylbutyraldehyde	F, B	17, 176, 181	Hexanoic	F, D	190, 192, 193
n-Hexanal	F, D, B	17, 176, 177	γ-Methylvaleric	F	190, 192
2-Ethylhexanal	B	180	Crotonic	F	190
Crotonaldehyde	B	180	Heptanoic	F	190
Furfural	B, G	17, 170, 174, 175, 180–185	Octanoic	F	190
Hydroxymethylfurfural	B	186, 187	Nonanoic	F	190
Benzaldehyde	D	177	Decanoic	F	190
p-Hydroxybenzaldehyde	B	188	Lauric	F	190
Phenylacetaldehyde	B	181	Myristic	F	190
Cinnamaldehyde	B	188	Palmitic	F	190
Vanillin	B	188	Lactic	F, D, B	189, 194
Syringaldehyde	B	188	Succinic	F, D, B	194
Alcohols			Malic	F, D, B	194
Ethyl	F, D, B, G	176, 179, 180, 182	Tartaric	F, D, B	194
n-Propyl	F	175, 177, 181	Citric	F, D, B	194
2-Methylbutyl	B	17	Pyruvic	F, B	185, 195
n-Hexyl	B	17	γ-Oxovaleric	B	185
Phenethyl	F	179	*Sulphur compounds*		
Ketones			Hydrogen sulphide	B	175
Acetone	F, D, B	17, 176, 177, 179, 180	Methanethiol	B	175, 196, 197
Butanone	F, B	17, 176	Methional	B	181
Hexan-2-one	D, B	177, 180	*Other compounds*		
Heptan-3-one	B	180	Ammonia	B	192
Esters			Biacetyl	F, B	179, 180, 185
Ethyl acetate	F	189	Acetoin	F, B	179, 198
Ethyl lactate	F	179, 189	Butane-2,3-diol	F	179, 197
Ethyl γ-oxovalerate	B	180, 185	Methylglyoxal	D, B, G	174, 177, 180, 181
Ethyl pyruvate	B	17, 180, 185	γ-Butyrolactone	F	179
			3-Hydroxypropyl acetate	F	179

* F = ferment (leaven); D = dough; B = bread; G = oven gases.

TABLE 17. Volatile organic acids (mg kg^{-1} of flour) in bread, dough, and oven gases.

Acid	Dough	Bread	Oven gases
Acetic	198	150	15
n-Butyric	23.1	10.6	0
Isovaleric	13.1	6.1	0
Hexanoic	6.2	0	0

TABLE 18. Variation of content of furfural and other aldehydes in bread with time of baking.

Bread	Time of baking, min	Furfurol, mg %	Other aldehydes, mg %
White	40	0.25	0.15
White	90	0.3	0.3
Black	50	0.9	0.3
Black	90	1.05	0.7
Pumpernickel	1000	2.2	4.9

Confirmation of the decisive role of the Maillard reaction in the formation of the aroma of bread is the appearance of this aroma in model experiments conducted with valine, leucine, proline, and lysine (Table 15).

Rothe and Thomas consider[170] that six amino-acids of the grain — leucine, alanine, valine, isoleucine, phenylalanine, and methionine — are of particular importance in producing the aroma of bread at the baking stage, these being precursors of the aldehydes isovaleraldehyde, acetaldehyde, isobutyraldehyde, phenylacetaldehyde, and methional. Together with furfural and hydroxymethylfurfural, these aldehydes are the main components of the aroma of bread. Reaction of the carbonyl group of the aldehydes with dimedone greatly reduces the aroma of the bread[181,182].

Kretovich and Tokareva[187] have shown the aroma of bread to depend on the hydroxymethylfurfural content. Some part in producing the aroma of bread may be played by such aromatic aldehydes as vanillin, cinnamaldehyde, and syringaldehyde, found by Tokareva by paper chromatography[188]. The presence of these aldehydes requires confirmation by other methods of analysis, since they are not found in the odours of other food products.

Sulphur compounds are assumed to be important in producing the aroma of bread. Rothe ascribes particular importance to methional[181], and Rotsch and Dörner to methanethiol and hydrogen sulphide[175,196], all of which have been found among the volatile compounds responsible for the odour of bread.

Volatile acids do not apparently play a large part, since neutralising them has no marked effect on the aroma of bread[182]. Apparently biacetyl and acetoin, which had previously been regarded as the main ingredients of the aroma of bread[198], also play no important part, since no definite relationship has been found between their concentration and the aroma of bread[181,182,203]. Similarly no correlation has been established between the concentration of esters and the aroma of bread[181].

It is important to note that the odoriferous volatile components of bread readily undergo chemical changes, which on the one hand hinder study of the actual initial aroma, and on the other lead to a worsening of the aroma of bread on storage. Apparently the change in the odour of bread as it stales is not due to drying out or to a change in the structure of the bread, but to atmospheric oxidation of the volatile aldehydes[174]. When moist air is blown over bread crumb for 4 h, the bread remains soft but takes on the odour of stale bread. On standing, the condensate from the oven gases, initially containing the volatile components of fresh bread, also develops the odour of stale bread.

Various additives have been suggested for improving the aroma of bread. The national Russian odour-improver for bread is red rye malt obtained from germinated rye seed. The chemical composition of the aromatic substances of malt has been investigated by Kretovich *et al.*[204], who suggested that the furfural, hydroxymethylfurfural, and aliphatic aldehydes found in malt are products of the Maillard reaction taking place in the germinating rye seeds during production of the malt.

Hodge and his coworkers[205,206] proposed to improve the aroma of bread by adding to the dough maltol (3-hydroxy-2-methylpyran-4-one), isomaltol (structure unknown), and galactosylisomaltol, which have been isolated from bread and are intermediates in the Maillard reaction. These decompose during baking to produce substances which improve the aroma of the bread.

The formation of odoriferous compounds when sugar and milk are fermented with yeast has been utilised to prepare the dry odour-improving additive Vico-400, which is widely recommended for the production of aromatic bread[207].

In an attempt to reproduce artificially the aroma of bread, Wiseblatt[178] found the best aroma to be given by a mixture of the composition

Ethanol	4 g
Acetaldehyde	10 mg
Acetic acid	40 mg
Furfural	20 mg
Acetoin	6 mg.

Addition of this mixture to 180 ml of water gave an odour which was pleasant, but not quite like the aroma of bread.

It is thus seen that it has not yet proved possible to reproduce the aroma of bread chemically.

V. THE ODOUR OF COCOA AND COFFEE

The aroma of coffee and cocoa is formed in the fermentation and roasting of the coffee and cocoa beans; both these processes are extremely important for the production of coffee and cocoa of good taste properties. The significance of the fermentation in cocoa production has been much studied[208-211], the microorganisms involved including moulds (*Aspergillus*, *Mucor*, *Penicillium*, *Rhizopus*, etc.), yeasts (*Saccharomyces cerevisiae*, *Candida krusei*, *Kloeckera apiculata*, *Hansenula anomala*, etc.) and lactic acid and acetic acid bacteria[208]. The enzymes produced by the microorganisms decompose the polyphenols and proteins[212] contained in the cocoa beans. Unfermented cocoa beans do not give a chocolate aroma when roasted, but a strong aroma of ordinary roasted beans; they do not have a chocolate colour. The chemical reactions of the polyphenols during the fermentation were investigated by Forsyth[211,213-216], who isolated nine polyphenols from fermented cocoa beans. The polyphenol content was 7.8%, the main one being (-)-epicatechin[214]. Decomposition of the polyphenols when the cocoa beans are roasted evidently plays an important part in formation of the aroma of cocoa, since, when the polyphenols and organic acids are precipitated from alcohol extracts of the cocoa with lead acetate, no chocolate odour is produced on roasting. Amino-acids are also apparently important precursors of the cocoa aroma. Aspartic and glutamic acids, alanine, cysteine, leucine, serine, threonine, methionine, and arginine have been found in cocoa beans[217], and during roasting these are oxidised, deaminated, and decarboxylated: *i.e.* they undergo the Strecker degradation to form aldehydes[218].

The volatile substances in the aroma of cocoa were first investigated in 1912 by Bainbridge and Davies[219]; from 2000 kg of roasted cocoa beans they separated 24 ml of an aromatic oil, 50% of which was α-linalool; 10% of the mixture comprised esters of lower aliphatic acids.

Schmalfuss and coworkers[220,221] were the first to isolate from roast cocoa biacetyl and acetoin, which they considered to be important in the formation of the chocolate aroma, but in 1936 Fincke showed[222] that addition of biacetyl to cocoa powder does not improve its aroma.

Mohr in 1958 [223] was the first to investigate the chocolate aroma by gas chromatography, and found 23 compounds.

In 1961 Dutch workers identified alcohols, aldehydes, and esters in the aroma of cocoa[224]; their findings are shown in Table 19, which also gives the amines found by Weurman and de Rooij in cocoa powder[85].

In 1962 Bailey *et al.*[218] used a high sensitivity chromatograph with a β-ionisation detector to study the aroma of six types of roasted cocoa beans — Accra, Arriba, Bahia, Trinidad, Winey, and Sanchez. The substances isolated were additionally investigated with a mass spectrometer.

The aroma compositions of the different types of roasted and raw cocoa beans were very similar, and apparently differed only in the content of certain of the components, mainly aldehydes. Thus the n-butyraldehyde content was greatest in the Bahia and Arriba types. Isovaleraldehyde, isobutyraldehyde, propionaldehyde, and acetaldehyde were present in greatest amount in all the types of cocoa bean. The accumulation of these aldehydes during the roasting of the cocoa was also studied by Bailey *et al.* (Fig. 3); the contents of all four aldehydes increase, especially that of isovaleraldehyde and isobutyraldehyde. These aldehydes are present to a negligible extent in the raw beans. The isovaleraldehyde is thought to be formed by decomposition of leucine. Sixteen compounds were found in the volatile fraction of roasted Bahia beans by the chromatographic and mass-spectrometric analysis (Table 20).

TABLE 19. Volatile compounds in the aroma of cocoa.

Class	Compound	
Alcohols	methyl ethyl propyl isopropyl isobutyl	isopentyl furfuryl linalool geraniol
Esters	ethyl acetate isopropyl acetate n-propyl acetate isobutyl acetate n-pentyl acetate	ethyl propionate pentyl propionate pentyl butyrate linalyl acetate
Carbonyl compounds	acetaldehyde α-citronellal	biacetyl 6-methylhept-5-en-2-one
Amines	methylamine isobutylamine dimethylamine	ethylamine isopentylamine

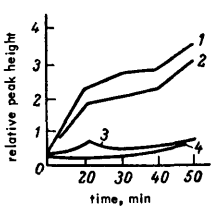


Fig.3. Accumulation of aldehydes during the roasting of cocoa beans at 148.8°:
1) isovaleraldehyde;
2) isobutyraldehyde;
3) propionaldehyde;
4) acetaldehyde.

TABLE 20. Mass-spectrometric analysis of the aroma of roasted Bahia cocoa beans.

Compound	Content, mole %	Compound	Content, mole %
Isovaleraldehyde	42.0	Methyl sulphide	0.3
Isobutyraldehyde	15.4	Methyl disulphide	0.2
Propionaldehyde	13.0	Ethanol	0.2
Methanol	9.1	Furan	0.2
Acetaldehyde	7.0	Toluene	0.1
Methyl acetate	6.3	Benzene	0.1
n-Butyraldehyde	3.0	Methylfuran	trace
Biacetyl	2.8	Acetone	trace

The number of volatile components in the aroma of liquid cocoa is much less than in the powder; Bailey and his coworkers obtained only 8 peaks in the chromatogram of the aroma of liquid cocoa, of which only 5 were identified — acetaldehyde, methyl acetate, propionaldehyde, isobutyraldehyde, and isovaleraldehyde. These compounds cannot be wholly responsible for the aroma of cocoa.

As with cocoa, the aroma of coffee is formed during the fermentation and, especially, during the roasting. Again as with cocoa, the precursors of the aroma of coffee are apparently polyphenols and amino-acids. The first gas-chromatographic investigation of the aroma of coffee was made by Rhoades in 1958.[225] The volatile components were steam-distilled from roast coffee in a current of helium and analysed on a Perkin–Elmer chromatograph. The chromatogram showed 16 peaks, of which 7 were identified. These results, together with data on the qualitative composition of the aroma of coffee obtained by other workers, are given in Table 21.

In 1960 Zlatkis and Sivetz[226] investigated quantitatively coffee aroma essence, obtained from the condensed volatiles during roasting of the coffee, and the distillate obtained by vacuum distillation of roast coffee with steam.

TABLE 21. Volatile compounds found in coffee aroma.

Compound	Ref.	Compound	Ref.	Compound	Ref.
Aldehydes		*Esters*		*Nitrogen compounds*	
Acetaldehyde	56, 225	Ethyl formate	226	Ammonia	56
Propionaldehyde	225	Methyl formate	226, 227	Methylamine	56
Butyraldehyde	226, 227	Methyl acetate	226	Trimethylamine	56
Isobutyraldehyde	226, 227	Furfuryl formate	56	Pyridine	56, 228
Valeraldehyde	227	Furfuryl acetate	56	Pyrrole	56
α-Methylbutyraldehyde	56	*Acids*		*N*-Methylpyrrole	56
Furfural	56, 226, 228	Formic	56, 226	Pyrazine	56
Ketones		Acetic	56, 226	*Other compounds*	
Acetone	56, 225, 226, 227	Propionic	56, 226	Acetoin	56, 228
Butanone	225, 227	n-Butyric	56	3-Hydroxypentane-2,4-dione	228
Pentan-3-one	56	n-Valeric	56	2,3-Dihydroxyacetophenone	56
Biacetyl	225, 227	Isovaleric	56	Isoprene	227
Pentane-2,3-dione	56, 227	α-Methylbutyric	56	n-Heptacosane	56
Alcohols		Hexanoic	56	Sylvestrene	56
Methyl	56, 225	Octanoic	56	Vanillin	56
Ethyl	56, 226	*Sulphur compounds*		Furan	56, 227
Furfuryl	56	Hydrogen sulphide	56, 227	Methylfuran	227
Phenols		Methanethiol	56, 227		
Phenol	56	Methyl sulphide	56, 227		
Cresols	56	2-Furylmethanethiol	56		
Quinol	56				
Resorcinol	56				
Eugenol	56				
Guaiacol	56				
2-Methoxy-4-vinylphenol	56				

Roast coffee contains 2×10^{-6} part of the aroma essence. The aqueous distillate of odoriferous compounds from coffee, after extraction of esters and drying, makes up 0.1% of the initial roast coffee. The coffee aroma essence contained mainly aldehydes and sulphur compounds, had a comparatively low solubility in water, and was readily oxidised in the air. It had a strong odour and gave clear yellow-green solutions in water. When sufficiently diluted with air it reproduced the aroma of coffee. The aroma of the coffee essence depended greatly on the type of coffee. The results of Zlatkis and Sivetz' chromatographic analysis of the coffee essence aroma [226] are given in Table 22.

Acetic acid (30%) and propionic acid (5%) were isolated from the distillate; the residue boiled at 90° (1 mm), and the compounds indicated in Table 21 were identified in it by gas chromatography [226]. Ketones and aldehydes containing six carbon atoms were also observed, as well as unidentified furfural derivatives. Zlatkis and Sivetz also indicate that the number of compounds present is probably far greater, since the odour of the compounds issuing from the chromatograph varied widely; for example, a pyridine-like odour was recorded, and also the sharp odour of organic acids.

The composition of the organic acids in coffee and its substitutes (barley, rye, and chicory) was studied by Schormüller *et al.* [229]; Table 23 gives their results for roast coffee. The volatile acids indicated in Table 23 undoubtedly play a part in the aroma of coffee, while the non-volatile acids affect its taste.

Several workers have attempted to reproduce the aromas of coffee and cocoa; thus in 1958 Rusoff patented the "synthesis" of the aroma of cocoa by the Maillard reaction, by heating plant and animal protein hydrolysates with sugars [230].

Meyer has reported [56] imitation of the aroma of coffee in the American food industry by using an artificial mixture comprising 10% of 2-furylmethanethiol, 3% of ethylvanillin, and 87% of an unspecified solvent. An artificial mixture reproducing the aroma of coffee has recently been developed at the Ukrainian Scientific Research Institute of the Food Industry [231]; this mixture contains furfural, methanethiol, valeraldehyde, isovaleric acid, 2-furylmethanethiol, guaiacol, quinol, and soyabean oil. Addition of 1 part of this mixture to 10 000 parts of chicory and barley malt extract gives the aroms of natural coffee.

TABLE 22. Analysis of aromatic coffee essence.

Compound	Content, wt. %	Compound	Content, wt. %
Acetaldehyde	19.9	Pentadiene	3.0
Acetone	18.7	Butanone	2.3
Biacetyl	7.5	C_4–C_7 alkanes and alkenes	2.0
n-Valeraldehyde	7.3	Methyl acetate	1.7
α-Methylbutyraldehyde	6.8	Methyl sulphide	1.0
Isovaleraldehyde	5.0	n-Butyraldehyde	0.7
Methylfuran	4.7	Ethyl formate	0.3
Propionaldehyde	4.5	Carbon disulphide	0.2
Methyl formate	4.0	Methanol	0.2
Carbon dioxide	3.8	Methanethiol	0.1
Furan	3.2	Thiophen	0.1
Isobutyraldehyde	3.0		

TABLE 23. Content of organic acids in roast coffee.

Acid	Content, mg (100 g)$^{-1}$	Percentage of total acidity	Acid	Content, mg (100 g)$^{-1}$	Percentage of total acidity
Formic	46.0	1.0	Lactic	437.5	9.3
Acetic	936.0	20.0	Succinic	283.0	6.0
Propionic	22.0	0.5	Malic	495.8	10.6
n-Butyric	35.0	0.7	Tartaric	9.0	0.2
n-Valeric	40.8	0.9	Citric	2200.0	47.0
Hexanoic	46.4	1.0	Fumaric	4.3	0.1
Octanoic	28.8	0.6	α-Oxoglutaric	20.0	0.4
			Pyruvic	77.5	1.7

VI. THE ODOUR OF MEAT AND FISH PRODUCTS

The chemical investigation of the aromas of meat and fish is far from complete, and there are very few published data.

The Aroma of Meat

The substances found in the odour of cooked meat are listed in Table 24.

Unfortunately, there are practically no data on the quantitative contents of these compounds. It is known only that, after beef has been cooked for 3 h, the broth contains 6–8 mg of hydrogen sulphide per kilogramme of meat [233], and that 79% of this hydrogen sulphide is oxidised on storage for 48 h. [232]

All workers agree that sulphur compounds and carbonyl compounds are important constituents of "meaty" odours. This cannot be said of fatty acids nor, apparently, of ammonia, since removal of the latter strengthens the odour of chicken broth [232].

During 1960–1962 it was shown by Hornstein [237,238] and by Batzer [239–241] that the phosphorus-containing glycoprotein fraction isolated from the dialysate of the aqueous extract of raw meat is a precursor of the odour of heated defatted meat. This fraction is very unstable on storage, even in a vacuum. Inosinic acid, hypoxanthine, inosine, glucose, and the amino-acids proline, isoleucine, leucine, valine, serine, and α- and β-alanine have been found as constituents of the glycoproteins. [240] Appropriate heating of the isolated fraction or a mixture of the above compounds gives the aroma of boiled or broiled meat, practically identical for beef, pork, and chicken meat. It is thought that the odour arises because of reaction between the amino-acids and the carbohydrates, for instance by a Maillard-type reaction. The absence from the glycoprotein hydrolysate of sulphur-containing amino-acids, which are precursors of the important sulphur-containing ingredients of meaty aromas, is surprising; possibly they have simply not been isolated.

TABLE 24. Compounds found in the odour of cooked meat.

Class	Compounds	Ref.
	ammonia	232, 233
Aldehydes	acetaldehydes, propionaldehyde, isobutyraldehyde, isovaleraldehyde	233–235
Ketones	acetone, butanone, acetoin, biacetyl	233–236, 236a
Sulphur compounds	hydrogen sulphide, methanethiol, ethanethiol, methyl sulphide	233–235
Fatty acids	formic, acetic, propionic, butyric, isobutyric	233

It is thus seen that fat-free meat has the same aroma irrespective of its type. The specific odours which distinguish different types of meat are thought by many to be related to the composition of the fats and their oxidation on heating[242]. Thus Hornstein and Crawe have found[238] that, when heated in a vacuum at 100°, beef fat acquires a sweet apple-like odour, and pork fat a pungent cheese-like odour[238]. These workers also investigated the composition of the carbonyl compounds isolated from fats heated in air at 100° (Table 25).

The volatile compounds of pork fat contain several times the quantity of carbonyl compounds, particularly hexanal, found with beef fat. These quantitative differences undoubtedly depend on the unsaturated acid content of the fats, and must play a part in the specificity of odour of different types of meat.

Apparently the full meaty odour and taste require the presence, in addition to the substances involved in producing the odour, of sodium *L*-monoglutamate[243], the effect of which is greatest in the pH range 5–6.5, where it exists as the glutamate ion $^{-}OCOCH(NH_3^+)CH_2CH_2COO^-$, responsible for the taste[244]. Sodium glutamate is widely used in a concentration of 0.1–0.5% to improve the taste of meat and vegetable dishes[245-248].

Unlike the meaty aroma, the odour of meat hydrolysates is due to amino-acid hydrolysis products, primarily α-oxobutyric acid produced from threonine[249-251].

Many studies have been made of the undesirable flavours and odours in fresh and prepared meat. Several unpleasant odours of fresh meat have been found to be associated with the animal feed[252,253].

γ-Irradiation is widely used for the sterilisation of meat products, and hence the nature and source of the unpleasant odours thereby produced have also been investigated. Among constituents of these odours have been identified amines, including methylamine and ethylamine[254], carbonyl compounds (n-alkanals, alk-2-enals, and ketones)[255-257], peroxides[257], and sulphur compounds (hydrogen sulphide, methanethiol, and methional)[257-259]. It should be noted that the carbonyl compounds produced when muscle tissue and fat are irradiated are greatly different[255,256]. Methional is not produced directly from methionine in γ-irradiated raw meat, but as the result of peroxide-initiated radical addition of methanethiol to acrylaldehyde[257,259]. By adding DL-methionine and glutathione labelled with ^{35}S to the meat before irradiation, Batzer and his coworkers established that most of the methanethiol is formed directly from methionine, and hydrogen sulphide from both compounds, though in small amounts[260].

TABLE 25. Carbonyl compounds isolated from fats heated in air at 100°.

Fraction	Beef fat		Pork fat	
	compounds	concn., mmole × ×(10g)$^{-1}$	compounds	concn., mmole × ×(10g)$^{-1}$
Volatile fraction	acetone, propanal	0.039	acetone, propanal, hexanal, octanal, nonanal	0.27
	acetaldehyde and 2-enals	0.072	acetaldehyde and C_7–C_{11} 2-enals deca-2,4-dienal	0.06
Fraction obtained by steam distillation	hexanal, nonanal	0.070	hexanal, octanal, nonanal, undecanal	0.24
	C_7–C_{11} 2-enals	0.028	C_7–C_{11} 2-enals	0.12
	deca-2,4-dienal	0.021	C_7, C_9, and C_{10} 2,4-dienals	0.083

The deterioration of raw and cooked meat on storage has several causes and is accompanied by the production of various odours. Decomposition of proteins and fats in raw meat is mainly due to the action of microorganisms. The main participants in the formation of the odour of bad raw meat are amines (predominantly trimethylamine) and aliphatic acids from acetic to octanoic (mainly hexanoic acid)[261]. Determination of ammonia in the meat is recognised as the best method for detecting the initial stages in decay[262,263]. Biacetyl and acetoin have also been detected in the odour of putrefying meat[264]. The microbiological decomposition of amino-acids in dehydrated conserved pork at elevated temperature produces also acetaldehyde and ammonia[265]. Other processes underlie the deterioration of cooked meat. Here the thiobarbituric method has shown that tissue lipids are rapidly oxidised, with the formation of unpleasant odours and tastes[266]. Malonaldehyde has been identified as a component of the rancid odour of cooked meat[267].

Because of the absence of data on the quantitative proportions of the ingredients of meaty odours, it is difficult to expect production of the aromas on mixing the constituents. The only attempt produced an odour only faintly resembling a meaty odour[236]. A more logical and promising method for creating this odour is to use appropriate precursors; thus May and his coworkers carried out a model Maillard reaction by heating an aqueous solution of cysteine and one or more other amino-acids with carbonyl compounds or compounds producing them[268-270]. Racemic amino-acids can be used instead of the L-isomers, or else derivatives (salts, esters, or oligopeptides) which yield the amino-acids under the experimental conditions. Carbohydrates were initially employed as carbonyl compounds[268], and it was then found possible to replace these by simpler aldehydes (propionaldehyde or glyceraldehyde)[269] or even furan derivatives[270].

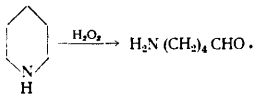
Imitation of the meaty odour by a single chemical compound is a very alluring prospect. It was long thought that methional could produce a brothlike odour[271], although all attempts to achieve this were unsuccessful. It was shown in 1959 that methional purified by gas chromatography apparently does not have this odour[272]. Serious attention is merited by a patent[273] for the production of a meaty aroma in edible compositions by the addition of 0.005–0.06 wt. % of a derivative of mercaptoacetaldehyde, which is a decomposition product of cysteine, a constituent of all suggested precursors. These compounds can also be used in admixture with sodium glutamate or other odoriferous or taste-producing compounds.

The Aroma of Fish

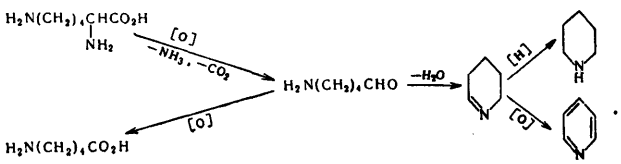
The aroma of fish products differs considerably from meaty odours. Studies of fish odours were mainly carried out on fresh and stored fish, and only since 1959 have investigations appeared on the odour of heated fish.

Obata and his coworkers showed that piperidine, pyridine, and their oxidation products δ-aminovaleraldehyde and δ-aminovaleric acid, which are found in the epidermal slime of fish, cause the odour of fresh fish[274]. They were

able to imitate the odour of fresh freshwater fish by oxidising piperidine to δ-aminovaleraldehyde with 10% hydrogen peroxide:



Addition of trimethylamine to the mixture gives the odour of fresh sea fish, which accords well with the high content of trimethylamine in sea fish [275]. The source of the compounds found by the Japanese chemists is apparently lysine, which undergoes chemical or microbiological decomposition [276]. The following mechanism could be suggested for their formation



Analogous processes occur to an even greater extent when fish is stored; thus the Japanese workers established the presence of δ-aminovaleric acid in slightly stale fish, and were able to confirm experimentally its importance in formation of the corresponding odour [274]. Methanethiol and indole were identified in fish which had deteriorated further. Amano has shown that green meat in frozen swordfish has a high concentration (12 mg per 100 mg of fish) of isovaleric acid, which is the cause of the unpleasant odour of such fish [277]. Piperidine and pyrrolidine have also been found in stale fish [278]. Hughes has shown that in stored herring trimethylamine *N*-oxide decomposes, producing mainly ammonia and trimethylamine [279]. Many carbonyl compounds have been identified in the autoxidation of the fat of salmon, which are also obtained in the oxidation of other fats [280].

Quantitative determination of the substances formed provides an objective evaluation of the freshness of fish [281-283]. The concentration of lower carbonyl compounds in fish increases linearly with its storage time. The content of higher carbonyl compounds is a maximum after 8–11 days, [284] which accords well with organoleptic analysis of the freshness of fish [285]. The content of volatile acids (formic, acetic) can also be used as a criterion of the quality of fish [286].

The odour of dried fish contains the same constituents as that of fresh and bad fish, but apparently in different proportions. Thus ammonia, trimethylamine, pyridine, piperidine, and the five fatty acids formic, acetic, propionic, butyric, and lauric have been found in a methanolic extract of katsuobushi (fish dried in pieces) [287].

There is least published information of all on the chemical composition of the odours of prepared fish — only Hughes' studies on cooked herring, which showed its odour to contain ammonia, dimethylamine, trimethylamine, methylamine, acetaldehyde, propionaldehyde, isobutyraldehyde, α-methylbutyraldehyde, and acetone [279,288]. Steam distillation from fillet of haddock has also given α-hydroxycarbonyl and dicarbonyl compounds having 2–4 carbon atoms [289], possibly acetoin and biacetyl.

When fish meat is treated with steam under pressure, the trimethylamine *N*-oxide decomposes:

$$(CH_3)_3NO \rightarrow CH_2O + (CH_3)_2NH.$$

Both these products have been detected in tinned fish, the concentration of dimethylamine being fairly high and proportional to the concentration of trimethylamine *N*-oxide in the fresh fish meat [290].

There are also very few data on the sources and precursors of the odour of prepared fish. It is thought that reactions of carbohydrates with amines and amino-acids play an important part in the formation of the aroma of fish in this case [291].

The flavour of fish products can be improved by adding sodium glutamate in a concentration of 0.15–1%, depending on the type of product [292,293]. Thus unlike the meaty odour, where sulphur compounds are the most important, the odour of prepared fish is due mainly to the presence of nitrogen compounds, particularly methylamines. Carbonyl compounds are important constituents of both types of odour.

The Odour of Smoked Products

Smoked meat and fish products have special odours of their own, produced with the participation of the curing-house smoke, which contains organic acids, phenols, and mono- and poly-carbonyl compounds [294,295]; these are absorbed by the product, where they may also undergo various reactions. Hardly any work has been done on the compounds causing the odour of smoked products. Only in 1960 did Yuditskaya and Lebedeva show that phenol, guaiacol, and *m*- and *o*-cresols are always present in fish smoked by any method [296]; depending on the method of smoking, *p*-cresol, pyrogallol methyl ethers, and two unidentified phenols may also be present. The composition of the phenols changes on storage. In meat products a higher content of phenols corresponds with a better organoleptic evaluation of the product [297]. Despite the poor knowledge of the composition of the odours of smoked products, they have been successfully imitated. It has been proposed to use a fraction of the dry distillation products of wood to imitate the odour of smoked products generally [298], and a mixture obtained by heating this fraction with cysteine and other amino-acids (or protein hydrolysates) to imitate the odour of ham [299].

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The aromas of milk, cream, butter, cheese, bread, meat, coffee, and cocoa are found to be very similar in composition, containing the same classes of chemical compounds — aldehydes, ketones, alcohols, esters, aliphatic acids, amines, heterocyclic compounds (furan and its derivatives), and sulphur compounds. Certain aldehydes and ketones are present in all the food products. However, apparently far from all the substances found in the aroma of a food product are necessary for its reproduction. For example, methanol and ethanol, which are present in the aroma of all food products, and carbon dioxide, which is found in the volatile constituents of coffee, can hardly play any substantial part. From the substances responsible for flavours in milk (Table 2) it is readily seen that the specific aroma of each food product is probably determined on the one hand by the different proportions of the components, and on the other by the presence of certain

compounds which, on the general background of the other volatile substances, produce definite and characteristic shades of flavour.

The great similarity in the various odoriferous compositions suggests the existence of general routes by which the volatile components are produced. Some of these can even be named — enzymic splitting of fats and proteins, autoxidation of fats, and the Maillard reaction. Study of these reactions is extremely important for investigating the processes by which the odoriferous compounds are produced, so that they may be utilised practically. Very important also is knowledge of the actual precursors of the aroma of a given product. The reproduction of an odour by using such precursors is beginning to be used outside the U. S. S. R.; for instance, the aroma of fresh bananas is given to preserved bananas by utilising the decomposition of three precursors by means of an enzyme obtained from fresh bananas.

Claims have recently been made in the U. S. A. to the imitation of the odours of cheese, butter, and milk with the use of lipolytic enzymes.

From the data presented in this review, it may be affirmed that knowledge of the chemistry of the odour of food products can not only considerably improve the aroma of commercial food products, but can also, in the not too distant future, provide from non-food starting materials synthetic food which is as good as, or in some cases even better than, natural food products, in respect of flavour and nutritional qualities.

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THE THERMODYNAMICS OF PROCESSES OF NEW-PHASE FORMATION

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