

Flavour formation in meat and meat products: a review

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The characteristic flavour of cooked meat derives from thermally induced reactions occurring during heating, principally the Maillard reaction and the degradation of lipid. Both types of reaction involve complex reaction pathways leading to a wide range of products, which account for the large number of volatile compounds found in cooked meat. Heterocyclic compounds, especially those containing sulfur, are important flavour compounds produced in the Maillard reaction providing savoury, meaty, roast and boiled flavours. Lipid degradation provides compounds which give fatty aromas to cooked meat and compounds which determine some of the aroma differences between meats from different species. Compounds formed during the Maillard reaction may also react with other components of meat, adding to the complexity of the profile of aroma compounds. For example, aldehydes and other carbonyls formed during lipid oxidation have been shown to react readily with Maillard intermediates. Such interactions give rise to additional aroma compounds, but they also modify the overall profile of compounds contributing to meat flavour. In particular, such interactions may control the formation of sulfur compounds, and other Maillard-derived volatiles, at levels which give the optimum cooked meat flavour characteristics. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Flavour is a very important component of the eating quality of meat and there has been much research aimed at understanding the chemistry of meat flavour, and at determining those factors during the production and processing of meat which influence flavour quality. The desirable characteristics of meat flavour have also been sought in the production of simulated meat flavourings which are of considerable importance in convenience and processed savoury foods.

Meat flavour is thermally derived, since uncooked meat has little or no aroma and only a blood-like taste. During cooking, a complex series of thermally induced reactions occur between non-volatile components of lean and fatty tissues resulting in a large number of reaction products. Although the flavour of cooked meat is influenced by compounds contributing to the sense of taste, it is the volatile compounds, formed during cooking, that determine the aroma attributes and contribute most to the characteristic flavours of meat. An examination of the literature relating to the volatile compounds found in meat, shows that over 1000 volatile compounds have been identified. A much larger number has been identified in beef than the other meats, but this

is reflected in the much larger number of publications for beef compared with pork, sheep meat or poultry (Maarse and Visscher, 1996; Mottram, 1991).

MEAT FLAVOUR PRECURSORS

The major precursors of meat flavour can be divided into two categories: water-soluble components and lipids. The main reactions during cooking, which result in aroma volatiles, are the Maillard reaction between amino acids and reducing sugars, and the thermal degradation of lipid. Early work on meat flavour, during the 1950s and 1960s, attempted to evaluate the relative contributions of fat and lean tissues to meat flavour (Hornstein and Crowe, 1960; Kramlich and Pearson, 1960; Macy *et al.*, 1964; Wasserman and Gray, 1965). That work suggested that, on heating, the fatty tissues provided species characteristics, while the lean tissues contained the precursors for the meaty flavour that are characteristic of all cooked meats. Although this view may be regarded as an over-simplification, there is no doubt that the species differences in flavour are largely explained by differences in lipid-derived volatile components.

The main water-soluble flavour precursors were suggested to be free sugars, sugar phosphates, nucleotide-bound sugars, free amino acids, peptides, nucleotides, and other nitrogenous components, such as thiamine. Reductions in the quantities of carbohydrates and amino acids were observed during heating, the most significant losses occurring for cysteine and ribose. In muscle, ribose is one of the main sugars where it is associated with the ribonucleotides, in particular, adenosine triphosphate. This nucleotide is essential for muscle function and, post-slaughter, it is converted to inosine monophosphate. Studies of the aromas produced on heating mixtures of amino acids and sugars, confirmed the important role played by cysteine and ribose in meat flavour formation and led to the classic patent of Morton *et al.* (1960) which involved the formation of a meat-like flavour by heating a mixture of these compounds. Most subsequent patent proposals for 'reaction product' meat flavourings have involved sulfur, usually as cysteine or other sulfur-containing amino acids or hydrogen sulfide (MacLeod and Seyyedain-Ardebili, 1981; MacLeod, 1986).

LIPID-DERIVED VOLATILES

Several hundred volatile compounds derived from lipid degradation have been found in cooked meat, including aliphatic hydrocarbons, aldehydes, ketones, alcohols, carboxylic acids and esters (Fig. 1). Some aromatic compounds, especially hydrocarbons, have also been reported, as well as oxygenated heterocyclic compounds such as lactones and alkylfurans. In general these compounds result from the oxidation of the fatty acid components of lipids. During long-term storage,

such reactions may lead to rancid off-flavours but, in cooked meat, the reactions occur quickly and provide a different profile of volatiles which contribute to desirable flavours. Unsaturated fatty acids undergo autoxidation much more readily than those which are saturated. The mechanism of autoxidation is free radical in nature and the reaction has been extensively reviewed (Frankel, 1980; Grosch, 1982). The phospholipids contain a much higher proportion of unsaturated fatty acids than the triglycerides and, therefore, during cooking, are an important source of volatiles.

The lean tissue of meat contains intramuscular triglycerides as well as structural phospholipids. It is not surprising, therefore, that the volatiles of all meat, whether or not it is cooked in the presence of subcutaneous fat, contain lipid-derived volatiles. Such volatiles are quantitatively dominant and it is only in meat grilled under severe conditions where the Maillard-derived volatiles are the major components (Mottram, 1985). The odour threshold values for these lipid-derived compounds are, in general, much higher than those for the sulfur- and nitrogen-containing heterocyclic compounds in meat volatiles which are derived from the water-soluble precursors. Therefore, the aroma significance of many of these lipid-derived volatiles is not as great as that for relatively low concentrations of the heterocyclic compounds. However, saturated and unsaturated aldehydes, with 6–10 carbons, are major volatile components of all cooked meats and, therefore, they probably play an important part in meat aroma. The aromas of these aldehydes are described as green, fatty, tallowy and 2,4-decadienal is reported to have an aroma of fat-fried food. It seems likely, therefore, that aliphatic aldehydes contribute to the fatty flavours of cooked meat.

The characteristic flavour of the different meat species is generally believed to be derived from lipid sources. Aldehydes, as major lipid degradation products, are probably involved in certain species characteristics. The higher proportion of unsaturated fatty acids in the triglycerides of pork and chicken, compared with beef or lamb, gives more unsaturated volatile aldehydes in these meats and such compounds may be important in determining the specific aromas of these species (Noleau and Toulemonde, 1987; Mottram, 1991). Sheep meat has been found to contain a number of methyl-branched saturated fatty acids (e.g. 4-methyloctanoic and 4-methylnonanoic acids), which have not been reported in other meats, and these acids have been associated with the characteristic flavour of mutton which results in low consumer acceptance of sheep meat in many countries (Wong *et al.*, 1975). They arise from the lipids which, in sheep unlike other species, contain significant quantities of methyl-branched fatty acids resulting from specific metabolic processes occurring in the rumen.

Recently, Guth and Grosch reported 12-methyltridecanal in the volatiles of stewed beef at a concentration of 430 $\mu\text{g}/\text{kg}$, but much lower levels in veal,

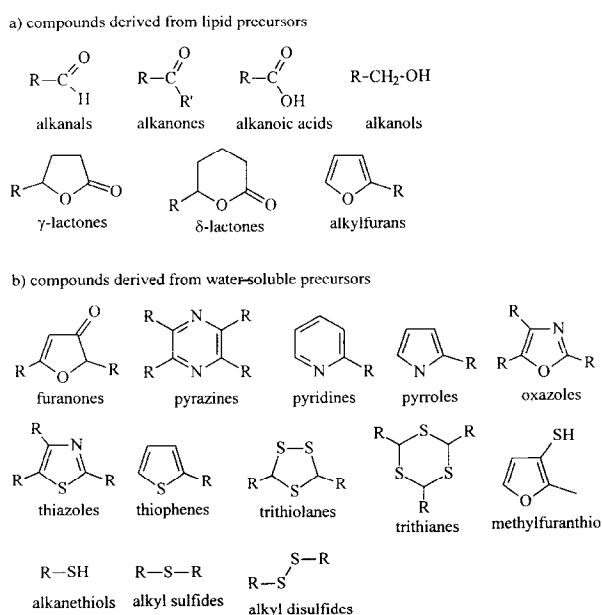


Fig. 1. Some classes of volatile compounds produced during the cooking of meat.

lamb and deer and only trace amounts in pork, chicken and turkey (Grosch *et al.*, 1993; Guth and Grosch, 1993, 1995). They reported that the compound had a tallowy, beef-like aroma and suggested that it played an important role in determining the characteristic aroma of beef. A number of other iso- and anteiso-methyl-branched aldehydes with between 11 and 17 carbon atoms have been reported in cooked beef and some have also been found in pork and chicken (Werkhoff *et al.*, 1993). It was concluded that these methyl-branched aldehydes arose from the hydrolysis of plasmalogens, which are phosphoglycerides in which one position on the glycerol moiety is linked to an aldehyde through an enol-ether link.

VOLATILES FROM THE MAILLARD REACTION

The Maillard reaction, which occurs between amino compounds and reducing sugars, is one of the most important routes to flavour compounds in cooked foods, including meat. This reaction is complex and provides a large number of compounds which contribute to flavour (Hurrell, 1982; Nursten, 1986; Tressl *et al.*, 1993; Mottram, 1994a). The initial stages of the reaction have been studied in some detail and involve the condensation of the carbonyl group of the reducing sugar with the amino compound, to give a glycosylamine. Subsequently, this rearranges and dehydrates, via deoxyosones, to various sugar dehydration and degradation products such as furfural and furanone derivatives, hydroxyketones and dicarbonyl compounds. Although the reaction has been discussed in many research papers, it is interesting to note that the mechanism proposed by Hodge in 1953 still provides the basis for our understanding of the early stages of this reaction (Hodge, 1953; Ledl and Schleicher, 1990).

The subsequent stages of the Maillard reaction involve the interaction of these compounds with other reactive components such as amines, amino acids, aldehydes, hydrogen sulfide and ammonia. It is these steps which provide the aroma compounds which characterise cooked foods and, therefore, are of particular interest to the flavour chemist. An important associated reaction is the Strecker degradation of amino acids by dicarbonyl compounds formed in the Maillard reaction. The amino acid is decarboxylated and deaminated forming an aldehyde, while the dicarbonyl is converted to an α -aminoketone or aminoalcohol. If the amino acid is cysteine, Strecker degradation can also lead to the production of hydrogen sulfide, ammonia and acetaldehyde. These compounds, together with carbonyl compounds produced in the Maillard reaction, provide a rich source of intermediates for further flavour-forming reactions (Fig. 2). These lead to many important classes of flavour compounds including furans, pyrazines, pyrroles, oxazoles, thiophenes, thiazoles and other heterocyclic compounds (Fig. 1). Sulfur-compounds,

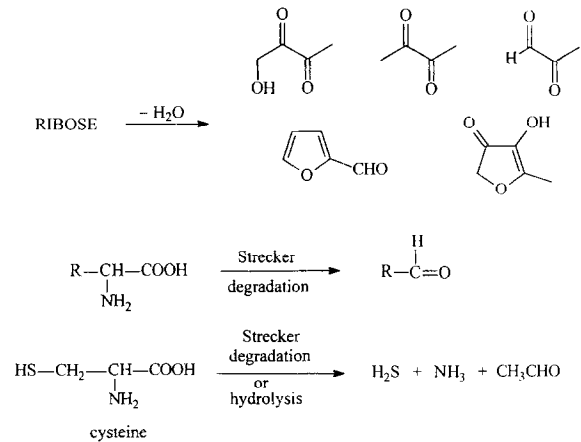


Fig. 2. Some important flavour intermediates in the Maillard reaction in meat.

derived from ribose and cysteine, seem to be particularly important for the characteristic aroma of meat. In meat, the main sources of ribose are inosine monophosphate and other ribonucleotides.

Compounds contributing to roast and boiled aromas

Roast flavours in foods are usually associated with the presence of heterocyclic compounds such as pyrazines, thiazoles and oxazoles. Many different alkyl pyrazines have been found in meat volatiles as well as two classes of interesting bicyclic compounds, 6,7-dihydro-5(H)-cyclopentapyrazines and pyrrolopyrazines (Flament *et al.*, 1976, 1977). This latter class of compounds has not been reported in any other food. Alkyl-substituted thiazoles, in general, have lower odour thresholds than pyrazines (Petit and Hruza, 1974), although they are found at lower concentrations in meat. Both classes of compound increase markedly with the increasing severity of the heat treatment and, in well-done grilled meat, pyrazines were reported to be the major class of volatiles (Mottram, 1985).

A probable route to the formation of alkylpyrazines is from the condensation of two α -aminoketone molecules produced in the Strecker degradation of amino acids by dicarbonyl compounds (Fig. 3). A mechanism for the formation of thiazoles, based on that proposed by Vernin, is shown in Fig. 4 (Vernin and Parkanyi, 1982). This also involves α -dicarbonyls, or hydroxyketones, and their reaction with hydrogen sulfide and ammonia, formed via the hydrolysis or Strecker degradation of cysteine, and an aldehyde.

One notable feature of the volatiles from cooked meat is the preponderance of sulfur-containing compounds. The majority occur at low concentrations, but their very low odour thresholds make them potent aroma compounds and important contributors to the aromas of cooked meat. A comparison of boiled and roast beef shows that many more aliphatic thiols, sulfides and disulfides have been reported in boiled meat. Heterocyclic compounds with 1, 2 or 3 sulfur atoms in 5 and 6

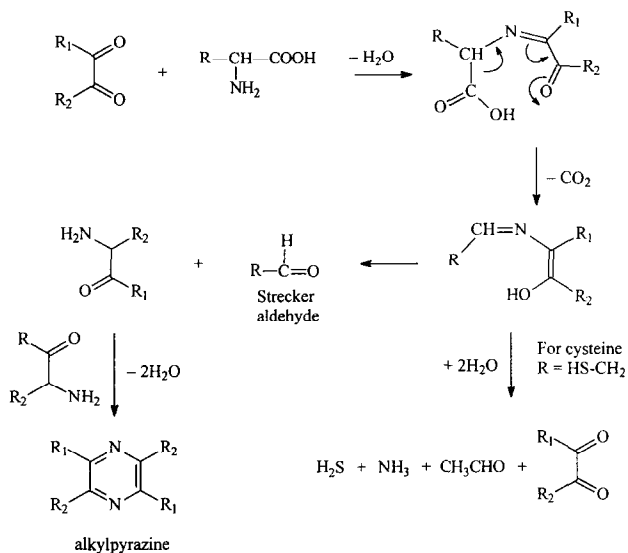


Fig. 3. Strecker degradation of amino acids, showing a route for the formation of alkympyrazines, and the formation of ammonia, hydrogen sulfide and acetaldehyde from cysteine.

membered rings (e.g. thiophenes, trithiolanes, tri-thianes) are much more prevalent in boiled than in roast meat (Mottram, 1991). Many of these sulfur compounds have low odour thresholds with sulfurous, onion-like and, sometimes, meaty aromas (Fors, 1983), and they probably contribute to the overall flavour by providing sulfurous notes which form part of the aroma of boiled meat.

'Meaty' flavours of cooked meat

All cooked meats possess a desirable 'meaty' aroma and the identification of compounds with such characteristics has been the subject of a large amount of research, much of which has been driven by the requirement for simulated meat flavourings for use in processed savoury food products. It has been known for some time that furans and thiophenes with a thiol group in the 3-position, and related disulfides, possess strong meat-like aromas and exceptionally low odour threshold values

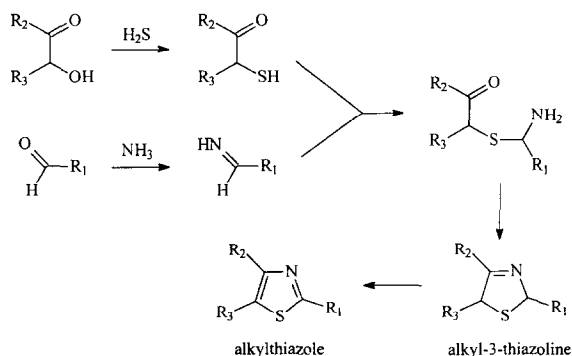


Fig. 4. Route for the formation of thiazolines and thiazoles in the Maillard reaction from the reaction of hydroxyketones, aldehydes with ammonia and hydrogen sulfide.

(Evers, 1970; van den Ouweland and Peer, 1972; Evers *et al.*, 1976). However, it was not until relatively recently that such compounds were first reported in meat itself. MacLeod and Ames (1986) identified 2-methyl-3-(methylthio)furan in cooked beef. It has been reported to have a low odour threshold value ($0.05 \mu\text{g}/\text{kg}$) and a meaty aroma at levels below $1 \mu\text{g}/\text{kg}$. Gasser and Grosch (1988) identified 2-methyl-3-furanthiol and the corresponding disulfide, bis-(2-methyl-3-furanyl) disulfide, as major contributors to the meaty aroma of cooked beef. The odour threshold value of this disulfide has been reported as $0.02 \text{ ng}/\text{kg}$, one of the lowest known threshold values (Buttery *et al.*, 1984). Other thiols and disulfides, containing, 2-furanylmethyl moieties (Fig. 5) have also been found in the volatiles of heated meat systems (Farmer and Patterson, 1991; Madruga and Mottram, 1995). Evaluation of the aromas of these compounds, by odour-port sniffing as they eluted from the gas chromatography column, indicated meaty characteristics for compounds containing 2-methyl-3-furanyl groups, while those with 2-methylfuran-yl groups had roast, nutty, burnt characteristics (Table 1). This is in agreement with earlier observations that furans with a thiol or sulfide group in the 3-position, possessed meaty odours (Evers *et al.*, 1976). These meaty and nutty aromas are detected at low concentrations ($< 1 \mu\text{g}/\text{kg}$), but at higher concentrations, the aromas are perceived as sulfurous and objectionable.

The routes involved in the formation of the various furan sulfides and disulfides are likely to be the interaction of hydrogen sulfide with dicarbonyls, furanones and furfurals to give thiols and mercaptoketones. Oxidation of these thiols then results in mixtures of symmetrical and unsymmetrical disulfides. A number of

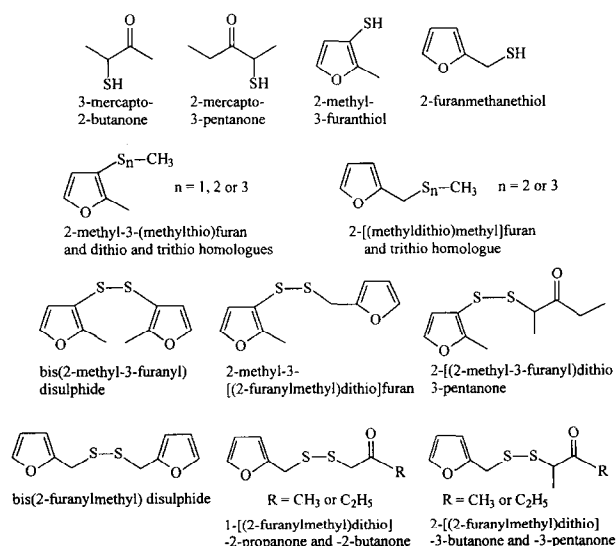


Fig. 5. Some thiols, sulfides and disulfides found in the volatiles of cooked meat (MacLeod and Ames, 1986; Gasser and Grosch, 1988; Farmer and Patterson, 1991; Madruga, 1994; Madruga and Mottram, 1995).

Table 1. Odours of some thiols and disulfides found in cooked meat volatiles; evaluated by GC odour-port assessment (Madruga, 1994)

Compound	Odour description
3-mercapto-2-butanone	fried onion, sulfury, cooked meat
2-mercapto-3-pentanone	brothy, mashed potatoes
2-methyl-3-furanthiol	meaty, roast meat, boiled meat
bis(2-methyl-3-furanyl) disulfide	meaty, boiled meat
2-methyl-3-(methylthio)furan	meaty, sulfury, fatty
2-[(2-methyl-3-furanyl)dithio]-3-pentanone	meaty
bis(2-furanylmethyl) disulfide	roast, brazil nuts, baked mushroom
2-[(methylthio)methyl]furan	brothy, spices, roast, fatty
3-[(2-furanylmethyl)dithio]-2-butanone	onion, burnt rubber, burnt wood
3-[(2-furanylmethyl)dithio]-2-pentanone	sweet, onion, roast nuts

such compounds are formed in heated model systems containing hydrogen sulfide or cysteine and pentoses or other sources of carbonyl compounds (Farmer and Mottram, 1990; Farmer *et al.*, 1989; Mottram and Whitfield, 1994), and in the thermal degradation of thiamine (van der Linde *et al.*, 1979; Werkhoff *et al.*, 1990; Güntert *et al.*, 1993). In meat, it has been proposed that ribose phosphate, from the ribonucleotides, is the principal precursor of furan and thiophenethiols. Dephosphorylation and dehydration of ribose phosphate form the important intermediate 4-hydroxy-5-methyl-3(2H)-furanone, which readily reacts with hydrogen sulfide (Fig. 6) (van den Ouweland and Peer, 1975).

INTERACTIONS BETWEEN LIPIDS AND THE MAILLARD REACTION

Saturated and unsaturated aldehydes, from lipid auto-oxidation, are major contributors to the volatile profile of cooked meats. Reactions between carbonyl compounds and amino and thiol groups are important steps in the Maillard reaction, both in the initial reactions and in the formation of aroma compounds in the later stages. It

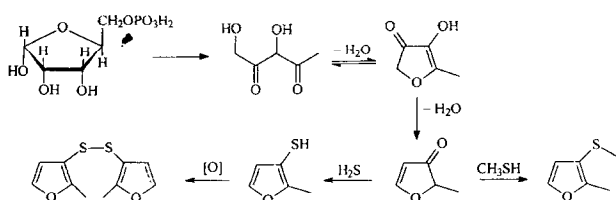


Fig. 6. Route for the formation of 2-methyl-3-furanthiol, bis(2-methyl-3-furanyl) disulfide and 2-methyl-3-(methylthio)furan from ribose phosphate (based on van den Ouweland and Peer, 1975).

could be anticipated, therefore, that lipid-derived aldehydes may participate in the Maillard reaction during the cooking of meat.

Volatiles in meat from lipid-Maillard interactions

Among the volatiles which have been identified in meat, there are a number of compounds which could be formed from the interaction of lipid with the Maillard reaction (Whitfield, 1992; Mottram, 1994b). Several thiazoles with C₄-C₈ n-alkyl substituents in the 2-position have been reported in roast beef (Hartman *et al.*, 1983) and fried chicken (Tang *et al.*, 1983). Other alkylthiazoles with much longer 2-alkyl substituents (C₁₃-C₁₅) have been reported in the volatiles of heated beef and chicken (Farmer and Mottram, 1994) with the highest concentrations in beef heart muscle. Recently, over 50 alkyl-3-thiazolines and alkylthiazoles have been isolated from cooked beef obtained from cattle which had been fed diets containing fish oil supplements (Fig. 7) (Elmore *et al.*, 1997). These appeared to be formed more readily in pressure-cooked meat than in grilled meat. Although many of the thiazoles and 3-thiazolines were also present in meat from cattle fed on normal diets, the concentrations of 3-thiazolines were much higher in meat from the cattle fed with fish oil supplements than in control samples. The cooked meat from the animals which had been fed fish oil also had considerably higher concentrations of saturated and unsaturated aldehydes than meat from the controls.

It appears that aliphatic aldehydes provide the long n-alkyl groups for these compounds. Routes to thiazole formation in heated foods involving aldehydes, hydroxyketones, ammonia and hydrogen sulfide have already been discussed and it is reasonable to assume that aldehydes, from lipid oxidation, can participate in these reactions to yield the long chain 2-alkyl thiazoles (Fig. 4). Alkylthiazoles containing C₁₃-C₁₅ alkyl groups require C₁₄-C₁₆ aldehydes, and the most likely source of these is the plasmalogens which contain long-chain alkenyl ether substituents which hydrolyse to give fatty aldehydes (Fogerty *et al.*, 1991). Heart muscle contains higher concentrations of plasmalogens which explains the higher levels of these alkylthiazoles found in heated beef heart.

Alkylpyridines have been reported in roast lamb fat (Buttery *et al.*, 1977), including 2-pentylpyridine which has also been found in all the other main species of meat (Watanabe and Sato, 1971; Tang *et al.*, 1983; Mottram,

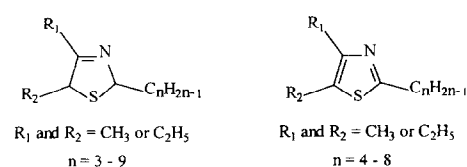


Fig. 7. Alkyl 3-thiazolines and thiazoles isolated from cooked beef (Elmore *et al.*, 1997).

1985). The reaction of 2,4-decadienal with ammonia is a likely route to 2-pentylpyridine (Fig. 8). Related reactions between dienals and hydrogen sulfide may be responsible for the formation of 2-alkylthiophenes with C₄–C₈ alkyl substituents which have been reported in pressure-cooked beef (Wilson *et al.*, 1973; Min *et al.*, 1979). Other heterocyclic compounds with long *n*-alkyl substituents found in meat include butyl and pentyl pyrazines (Tang *et al.*, 1983; Mottram, 1985), and it has been suggested that these could result from the reaction of pentanal or hexanal with a dihydropyrazine, formed by the condensation of two aminoketone molecules (Fig. 9). Pentanal and hexanal also appear to be involved in the formation of 5-butyl-3-methyl-1,2,4-trithiolane and its 5-pentyl homologue, which have both been reported in fried chicken (Hwang *et al.*, 1986) and pork (Werkhoff *et al.*, 1993). Trithiolanes can be formed from aldehydes and hydrogen sulfide and the reaction of hydrogen sulfide, acetaldehyde and pentanal or hexanal (Fig. 10) has been suggested as the route to these butyl and pentyl trithiolanes (Boelens *et al.*, 1974; Ho *et al.*, 1987).

The aroma characteristics have only been reported for a few of these alkyl-substituted heterocyclic compounds, but those which have been examined suggest that they may contribute to the fatty, fried aromas of meat (Buttery *et al.*, 1977; Ho *et al.*, 1987). Odour-port GC assessment of the alkyl-3-thiazolines and alkylthiazoles, recently found in beef, indicates that they do not possess low odour thresholds and, therefore, may not be very important odour impact compounds (Elmore *et al.*, 1997). However, the formation of these compounds provides competing reactions for the intermediates of the flavour forming reactions associated with the Maillard reaction and thereby may modify and control the generation of desirable aroma compounds.

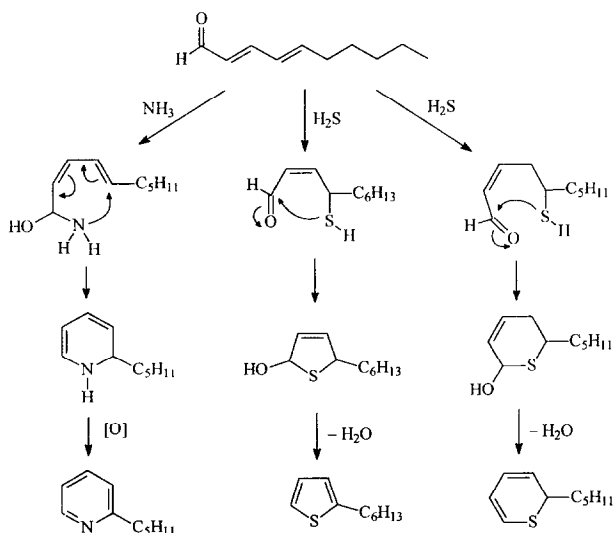


Fig. 8. Formation of 2-pentylpyridine, 2-hexylthiophene and 2-pentyl-2H-thiopyran from 2,4-decadienal, ammonia and hydrogen sulfide (adapted from Farmer and Mottram, 1990).

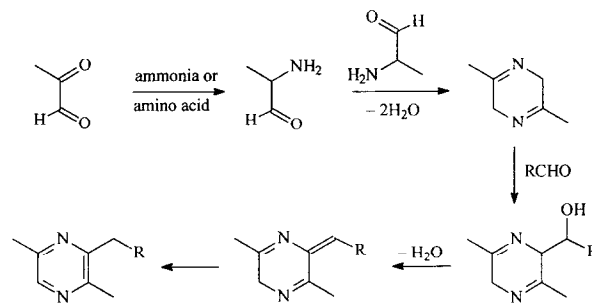


Fig. 9. Route to alkyl dimethylpyrazines from the interaction of lipid-derived aldehydes with the Maillard reaction (adapted from Ho *et al.*, 1987).

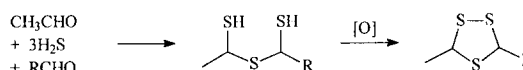


Fig. 10. Formation of alkyltrithiolanes from reaction of aldehydes and hydrogen sulfide (adapted from Boelens *et al.*, 1974).

Phospholipids and meat flavour

Phospholipids are essential structural components of all cells and contain a much higher proportion of unsaturated fatty acids than the triglycerides, including significant amounts of polyunsaturated fatty acids such as arachidonic acid (20:4). This makes them more susceptible to oxidation during heating and they have been associated with the off-flavour, known as 'warmed-over flavour', which develops in re-heated cooked meats (Pearson *et al.*, 1977). However, they may also provide lipid oxidation products during the initial cooking of meat which contribute to desirable aromas.

In an examination of the contribution which lipids make to the development of aroma during the heating of meat, the phospholipids were shown to be particularly important (Mottram and Edwards, 1983). When inter- and intramuscular triglycerides were removed from lean muscle prior to cooking using hexane, the aroma after cooking could not be differentiated from the untreated material in sensory triangle tests; both preparations being judged to be meaty. However, when a more polar solvent (chloroform-methanol) was used to extract all the lipids, phospholipids as well as triglycerides, a very marked difference in aroma resulted; the meaty aroma was replaced by a roast, biscuit-like aroma. Examination of the aroma volatiles from these meat preparations showed that the control and the material extracted with hexane had similar profiles, dominated by aliphatic aldehydes and alcohols. However, removal of phospholipids as well as triglycerides gave a very different profile; the lipid oxidation products were lost, but there was a large increase in the amounts of alkyl pyrazines. This implied that in normal meat, phospholipids or their degradation products inhibit reactions involved in the formation of heterocyclic aroma compounds from the Maillard reaction.

Effect of phospholipids on volatiles from model Maillard reaction systems

A number of studies of the effect of phospholipids on the volatile products of heated aqueous solutions of amino acids and sugars have shown that Maillard reaction products are influenced by the presence of phospholipids, confirming the earlier observations with defatted meat (Salter *et al.*, 1988; Whitfield *et al.*, 1988; Farmer *et al.*, 1989; Farmer and Mottram, 1990). The most interesting results were obtained with systems containing cysteine and ribose, which were reacted in the presence of several different phospholipid preparations, including egg-yolk phosphatidylcholine, egg-yolk phosphatidylethanolamine and phospholipids and triglycerides extracted from beef. The reaction systems gave complex mixtures of volatiles which were dominated by sulfur-containing heterocyclics, particularly thiophenes, thienothiophenes, dithiolanones, dithianones, trithiolanes and trithianes, together with 2-methyl-3-furanthiol, 2-furanmethanethiol and 2-methyl-3-thiophenethiol.

In the presence of lipids, a reduction in the amounts of many of these volatiles was observed (Table 2), compared with the system without lipid. This confirmed the observations in meat that phospholipids exert a quenching effect on the quantities of heterocyclic compounds formed in the Maillard reaction. In general, beef triglyceride showed much less effect on the levels of Maillard volatiles than the phospholipid preparations (Farmer and Mottram, 1990).

The aroma of the reaction mixture without any lipid was described as sulfurous and rubbery but with a distinct underlying meaty aroma. Addition of the beef triglyceride did not affect the aroma; however, when beef phospholipids were used the meaty aroma was more intense and the sulfurous notes less pronounced. Similarly, the addition of phosphatidylcholine or phosphatidylethanolamine gave mixtures with increased

meatiness. However, the phospholipid-containing reaction systems had lower concentrations of the meaty aroma compounds, such as 2-methyl-3-furanthiol. This anomaly may be explained in terms of a flavour-moderating role of the lipid. At high concentrations the furanthiol derivatives have strong, sulfurous odours, and it is only at low concentrations that meaty aromas become apparent. It is postulated that the lipid limits the production of these sulfur compounds and maintains their concentration at an optimum level in the reaction mixture. This hypothesis of flavour moderation and control may explain the particular role of phospholipids in the aroma of cooked meat.

The Maillard reaction mixtures containing phospholipids produced many lipid-derived volatiles, such as hydrocarbons, alkylfurans, saturated and unsaturated alcohols, aldehydes and ketones. The reaction mixtures also contained compounds derived from the interaction of lipid-derived aldehydes with Maillard reaction intermediates, the most abundant of which were 2-pentylpyridine, 2-pentylthiophene, 2-hexylthiophene and 2-pentyl-2*H*-thiapyran (Table 2). Smaller amounts of other 2-alkylthiophenes with *n*-alkyl substituents between C₄ and C₈ were found, together with 2-(1-hexenyl)thiophene. All of these heterocyclic compounds appeared to be formed by the reaction of unsaturated aldehydes with hydrogen sulfide or ammonia derived from cysteine (Fig. 8). Only trace amounts of these compounds were found in triglyceride-containing Maillard systems (Table 2). This may be explained by the much higher proportion of polyunsaturated fatty acids in the structural phospholipids than occur in the triglyceride used in the model systems. These undergo thermal oxidation much more readily than unsaturated fatty acids.

Compounds which appear to be derived from the choline moiety of phosphatidylcholine have been reported recently in the volatiles from the reaction of cysteine and ribose in the presence of phosphatidylcholine (Mottram and Whitfield, 1995). Three sulfides, 2-methyl-3-(methylthio)furan, 2(or 3)-(methylthio)thiophene and 2-methyl-3-(methylthio)thiophene, were identified in systems containing cysteine, ribose and phospholipid but could not be detected in systems without phospholipid. 2-Methyl-3-(methylthio)furan is an important aroma character-impact compound in meat and it has a very low odour threshold value (MacLeod and Ames, 1986; Werkhoff *et al.*, 1993). The corresponding thiophene was recently reported in the volatiles from the reaction of thiamin with methionine (Güntert *et al.*, 1993). It also has a meaty aroma and a low threshold value. Both 2- and 3-(methylthio)thiophenes have been tentatively identified in cooked meat and simulated meat flavours, although their odour properties have not been recorded (Golovnya *et al.*, 1983). The routes to these sulfides have been suggested to follow the same initial steps as the formation of the corresponding thiols (Whitfield and Mottram, 1996).

Table 2. Relative concentration of some selected heterocyclic compounds formed from the reaction between cysteine and ribose in the presence of different lipids (Farmer *et al.*, 1989; Farmer and Mottram, 1990)

Compound	No Lipid	BTG	BPL	PE	PC
2-mercapto-3-pentanone	1	0.72	0.49	0.53	0.53
3-mercapto-2-pentanone	1	0.77	0.47	0.49	0.50
2-methyl-3-furanthiol	1	0.40	0.15	0.24	0.27
2-methyl-3-thiophenethiol	1	0.08	0.01	0.10	0.20
2-furylmethanethiol	1	0.67	0.63	0.72	0.62
2-thiophenethiol	1	0.32	0.03	0.14	0.46
2-pentylpyridine	0	0.09	1	1.5	18.6
2-pentylthiophene	0	0	1	10.9	23.9
2-hexylthiophene	0	0.15	1	2.4	6.6
2-pentyl-2 <i>H</i> -thiapyran	0	0.01	1	4.0	11.0

BTG, beef triglyceride; BPL, beef phospholipid; PE, phosphatidylethanolamine (from egg yolk); PC, phosphatidylcholine (from egg yolk).

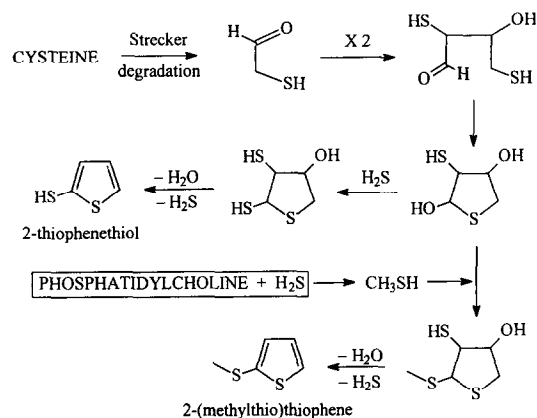


Fig. 11. Formation of 2-(methylthio)thiophene from the interaction of phosphatidylcholine in Maillard reactions involving cysteine (adapted from Mottram and Whitfield, 1995).

The formation of 2-methyl-3-furanthiol in Maillard reactions from the reaction of dehydration products of ribose with hydrogen sulfide, has been discussed above and is shown in Fig. 6. Similar mechanisms, involving replacement of oxygen in the heterocyclic ring with sulfur, explain the formation of the 2-methyl-3-thiophenethiol. Shu *et al.* (1985) suggested that 2- and 3-thiophenethiols can be formed during cysteine degradation by the condensation of two molecules of mercaptoacetaldehyde, followed by reaction with hydrogen sulfide and subsequent dehydration and loss of hydrogen sulfide (Fig. 11). The formation of the methyl sulfides requires the presence of a reactive methylthio group (e.g. methanethiol) which could participate in the later stages of these reaction pathways instead of hydrogen sulfide. It was suggested that, in the reaction systems containing cysteine, ribose and phosphatidylcholine, methanethiol was formed from the reaction of the choline moiety with hydrogen sulfide.

CONCLUSIONS

Cooked meat contains a complex mixture of volatile compounds, derived from both lipid- and water-soluble precursors. These provide roast, boiled, fatty and species-related flavours, as well as the characteristic meaty aromas associated with all cooked meats. Thermal degradation of lipid provides compounds which give fatty aromas to cooked meat and compounds which determine the flavours of the different species. The Maillard reaction is mainly responsible for the large number of heterocyclic compounds which have been found in the volatiles of cooked meat and are responsible for savoury, roast and boiled flavours. Pentoses, in particular ribose from meat ribonucleotides, and the sulfur-containing amino acid, cysteine, are important precursors for these reactions in meat. Furanthiols and furan sulfides and disulfides are very important flavour

compounds, with exceptionally low odour threshold values, which are responsible for characteristic meaty aromas.

In attempting to understand the role of the Maillard reaction in meat flavour (and other heated food flavours), the initial reaction of the sugar and the amino acid can be considered as a source of dehydration sugar products, principally furfurals, furanones and dicarbonyl compounds. Related reactions (e.g. Strecker degradation) yield other simple compounds such as aldehydes, ammonia and hydrogen sulfide. Flavour then results from many different interactions of these intermediates. Other meat components may also react with products of the Maillard reaction. Aldehydes formed during lipid oxidation have been shown to participate in the reactions of these Maillard intermediates (especially hydrogen sulfide and ammonia) to give other volatile compounds. Phospholipids are important sources of these lipid oxidation products. By participating in such interactions, the lipids appear to control the production of sulfur compounds during the cooking of meat and this is suggested to provide a mechanism by which the concentration of important sulfur compounds is maintained at optimum levels in the cooked product.

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