Maillard–Lipid Interactions in Nonaqueous Systems: Volatiles from the Reaction of Cysteine and Ribose with Phosphatidylcholine

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Equimolar mixtures of cysteine and ribose mixed with an excess of microcrystalline cellulose powder were heated at 185 °C with or without the addition of phosphatidylcholine. Volatile products were analyzed by headspace concentration and GC-MS. Sulfur-containing heterocyclic compounds dominated the volatiles, with trithiolanes, trithianes, and thiazoles among the most abundant components. Some qualitative and quantitative differences were found between the volatiles from the reactions performed with and without cellulose. The cellulose was not totally inert; volatiles were formed from its thermal degradation and its reaction with cysteine. In general, the addition of phospholipid had only a small effect on the volatile profile, with small amounts of lipid degradation products and lipid–Maillard interaction products formed. However, three methylthio-substituted furans and thiophenes were found in the phospholipid-containing systems which were not detected in the lipid-free reaction mixtures.

Keywords: *Maillard reaction; aroma; volatiles; cysteine; ribose; phospholipid*

INTRODUCTION

The Maillard reaction between amino acids and reducing sugars is a major route to flavor in cooked foods. The reaction is complex, involving many different pathways leading to a wide range of products (Vernin and Parkanyi, 1982), which helps to account for the large number of volatile compounds found in cooked foods. The reaction has been studied widely in recent years, mainly through the examination of the products of reactions between individual amino acids and sugars. It has been shown that the rate of reaction and the nature of the volatile products are affected by a number of factors, such as pH, water content, and temperature (Hurrell, 1982; Leahy and Reineccius, 1989; Ledl, 1990; Mottram, 1994). The other major source of volatile compounds in heated foods is the thermal degradation of lipids. Recent work using model systems has shown that when Maillard reactions are carried out in the presence of lipids, especially phospholipid, the quantities of Maillard reaction products are changed and a number of compounds are produced that arise from the interaction of lipid degradation products with the Maillard reaction (Whitfield et al., 1988; Farmer et al., 1989; Whitfield, 1992; Farmer and Mottram, 1994).

The Maillard reaction between cysteine and ribose has been of particular interest because of its importance in the formation of meat-like aromas. Over 180 compounds have been identified from such reaction systems (Mulders, 1973; Farmer et al., 1989; Farmer and Mottram, 1990a; Farmer and Whitfield, 1993; Mottram and Whitfield, 1995), including a number of furanthiols and disulfides which have strong meat-like aromas. In the presence of lipids or fatty acids, a number of thiophenes and formylthiophenes with long-chain alkyl substituents, pentylpyridine and pentylthiapyran, were found from the interaction of fatty acid degradation products with the Maillard reaction. A number of compounds arising from such interactions have also been found in foods (Whitfield, 1992).

Recently, we reported that the products of the Maillard reaction between cysteine, ribose, and phospholipid carried out under low moisture conditions differed greatly from those produced in aqueous solution (Mottram and Whitfield, 1995). These findings clearly demonstrated the importance of reaction conditions in determining the volatile profile produced by Maillard reactions. In food systems, the presence of structural food components such as protein, lipid, and carbohydrate also could be expected to modify the nature and concentration of volatile compounds derived from the Maillard reaction. Interactions of lipids with the Maillard reaction have already been studied in aqueous and low moisture systems. The current study was undertaken to observe how the volatile products formed in Maillard–lipid interactions could be influenced by using a microcrystalline cellulose reaction medium in the absence of water. To simulate roasting, the reaction mixtures were heated at 185 °C for up to 20 min. These conditions were chosen as they were similar to those used for the roasting of coffee beans or during the final stages for the preparation of roast meat.

EXPERIMENTAL PROCEDURES

Materials. L-Cysteine, D-(−)-ribose, and lecithin (L-α-phosphatidylcholine, type X-E from dried egg yolk) were purchased from Sigma Chemical Co. Microcrystalline cellulose powder (chromatography grade) and *n*-hexane were obtained from BDH Chemicals Ltd. Phosphate buffer (0.5 M, pH 5.6) was prepared from disodium hydrogen phosphate and sodium dihydrogen phosphate (BDH Chemicals Ltd.) in glass-distilled water. Authentic samples of volatile compounds were purchased from a range of laboratory chemical suppliers or were obtained as gifts from flavor laboratories.

Preparation of Reaction Mixtures. Cysteine (40 mg) and ribose (36 mg) were dissolved in 0.5 M phosphate buffer

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(2 mL), and the solution was added to water (8 mL) in a 50-mL round-bottom flask. Measurement of the pH at this stage gave a value of 5.8. Dry (heated at 108 °C for 5 days) cellulose powder (2 g) was added to this solution with stirring, and the mixture was allowed to stand at 20 °C for 10 min. At the end of this time, water was removed under vacuum at 60 °C with a Buchi evaporator. After removal of visible water, heat and vacuum continued to be applied for 1 h. The dry solid was removed from the flask and was ground to a fine powder in a mortar and pestle. A powder containing cysteine but not ribose was prepared similarly. Portions (500 mg) of these reaction mixtures were transferred to glass reaction tubes.

Another portion of the unheated dry reaction mixture (500 mg) was placed in a 50-mL round-bottom flask, and lecithin (38 mg) dissolved in *n*-hexane (5 mL) was added. The resultant mixture was stirred for 10 min, and the flask and contents were transferred to a Buchi evaporator. The solvent was removed under vacuum at 60 °C. The dry solid was removed from the flask, ground to a fine powder, and transferred to a glass reaction tube. Another reaction mixture was prepared using 10 times the quantity of lecithin (380 mg). Mixtures of cysteine, ribose, and lecithin in the above combinations and quantities were also prepared without the addition of cellulose or phosphate salts and transferred to reaction tubes.

After flame sealing, each tube and contents were heated in an aluminium block at 185 °C for 20 min. Samples of cellulose alone, cellulose with cysteine, and lecithin without ribose were also heated under these conditions.

Isolation of Volatile Maillard Reaction Products. After cooling, each reaction mixture was transferred to a 250-mL conical flask containing 20 mL of 0.5 M phosphate buffer (pH 5.6) and a magnetic stirrer bar. The reaction tube was rinsed twice with buffer solution (2 mL), and these washings were added to the conical flask. The volatiles were swept from the flask, maintained at 60 °C in a water bath, onto a trap containing Tenax GC using a flow of oxygen-free nitrogen (60 mL/min), as described previously (Mottram and Whitfield, 1995). The collection was continued for 1 h. At the end of this time, the flask was removed, and the trap was connected directly to the nitrogen supply for 5 min to remove moisture. An internal standard, 1,2-dichlorobenzene (65 ng, in 1 μL of diethyl ether) was added to the front end of the trap just before GC-MS analysis.

Gas Chromatography-Mass Spectrometry. The gas chromatograph was a Hewlett-Packard HP5890 gas chromatograph, equipped with a "Unijector" (Scientific Glass Engineering Pty Ltd, Australia) set in the concentrator headspace mode and fitted with a fused silica capillary column (50 m long × 0.32 mm i.d.) coated with BPX5 (Scientific Glass Engineering Pty Ltd, Australia). The gas chromatograph was directly coupled to a Hewlett-Packard HP5988A mass spectrometer controlled by a HP 59970C GC-MS Workstation. The trapped volatile components were thermally desorbed on to the GC column by heating the trap at 250 °C for 5 min while the oven was cooled at 0 °C. The column temperature was increased to 60 °C at a rate of 60 °C/min, held at that temperature for 5 min, and then increased to 250 °C at a rate of 4 °C/min. The mass spectrometer was operated in the electron impact mode with an electron energy of 70 eV and an ion source temperature of 250 °C. A continuous scan mode was employed with a scan time of 1 s over a mass range of 20–400 amu. Other conditions were similar to those published previously (Mottram and Whitfield, 1995).

Compounds were tentatively identified by comparing their mass spectra with those contained in the NIST/EPA/MSDC and Wiley mass spectral databases, in collections of mass spectra of flavor compounds (ten Noever de Brauw et al., 1980) or in previously published literature. Where possible, identifications were confirmed by comparing both mass spectra and linear retention indices (LRI) with those of authentic compounds.

The relative concentrations of the major components in the different reaction mixtures were estimated by comparing the peak areas in each total ion chromatogram with that of the dichlorobenzene internal standard (65 ng). Peaks which were >150% of the internal standard were defined as present in extra large quantities (++++), those between 50 and 150% were present in large quantities (+++), those between 10 and 50% were present in medium quantities (++), those between 1 and 10% were present in small quantities (+), and those <1% were present in trace quantities.

RESULTS AND DISCUSSION

Over 80 volatile compounds were identified in the concentrated headspace samples of the reaction mixtures. Sulfur-containing heterocyclic compounds dominated the volatiles, with trithiolanes, trithianes, and thiazoles among the most abundant components. The major components in the reaction mixtures are listed in Table 1. Most of these compounds were reported in a previous paper which examined the effect of water on the products of the Maillard reaction between cysteine and ribose (Mottram and Whitfield, 1995). As noted previously, the products of the reaction carried out in the absence of water differ markedly from those carried out in dilute aqueous solution at 140 °C (Whitfield et al., 1988; Farmer et al., 1989; Farmer and Mottram, 1990b). In the latter systems, the volatiles were dominated by thiols and thiophenones, which were absent from the dry systems reported in this present work or were only found in trace quantities.

Some qualitative and quantitative differences were found between the volatiles from the reaction between cysteine and ribose with and without cellulose (Table 1), although these were small compared with the effect of water discussed above. More thiazoles were found in the system without cellulose, and in general they were present at higher concentrations. However, in the presence of cellulose, larger quantities of pyrazines were found. The other significant difference in nitrogen-containing heterocyclics between the two systems was in the quantities of 1-(2-furanylmethyl)-1*H*-pyrrole, which occurred in much larger quantities in the system without cellulose. Most of the other sulfur-containing compounds were present at similar concentrations in the two systems, with the notable exception of dihydro-2-methyl-3(2*H*)-thiophenone, which was a major component of the cellulose containing systems but was not detected in the system without cellulose. This compound was one of the main components found when cysteine and ribose were heated at 140 °C in dilute aqueous solution (Farmer and Mottram, 1990b). It was also produced when the mixture was heated at 180 °C in the presence of a small amount of water (Mottram and Whitfield, 1995). The cellulose system may have contained a small amount of bound water that was not removed during drying following addition of the cysteine/ribose solution, and this could explain the formation of dihydro-2-methyl-3(2*H*)-thiophenone. Water inhibits the formation of 1-(2-furanylmethyl)-1*H*-pyrrole (Mottram and Whitfield, 1995), and the presence of traces of water may explain the low quantities of this compound found in the cellulose systems compared with the mixtures heated without cellulose.

A number of furan derivatives were found in the cellulose-containing system that were not detected in any of the other cysteine/ribose mixtures heated at 185 °C, or were only found in trace quantities. These included 2-acetylfuran, 5-methyl-2-furfural, 1-(2-furanyl)butan-2-one, and 2,2′-methylenebisfuran. All these compounds were also found when the cellulose was heated alone. The only other significant volatile obtained from cellulose alone was 2-furfural. There was no evidence of volatile impurities in the cellulose, and

Table 1. Volatile Compounds Obtained from Reactions between Cysteine and Ribose in the Presence and Absence of Phospholipid and Cellulose[a]

compound	LRI[b]	relative concentration[c]							method of identification[d]
		cellulose present				cellulose absent			
		C alone	C + R	C + R + L	C + R + XL	C + R	C + R + L	C + R + XL	
4,5-dimethylthiazole	933	tr	tr	tr	tr	tr	−	−	MS + LRI
5-ethylthiazole	940	tr	tr	tr	−	+	tr	−	MS[1]
trimethylthiazole	1000	++	++	+	+	+	+	+	MS + LRI
5-ethyl-2-methylthiazole	1015	++	++	+	+	+++	++	+	MS[2]
2,5-dimethyl-4-ethylthiazole	1066	tr	tr	tr	+	+	tr	+	MS + LRI
2,4-dimethyl-5-ethylthiazole	1078	+	+	+	−	+	+	−	MS + LRI
4,5-dimethyl-2-ethylthiazole	1105	−	−	−	−	tr	tr	−	MS + LRI
4,5-dimethyl-2-propylthiazole	1180	tr	−	tr	−	tr	+	−	MS + LRI
4(or 5)-ethyl-2-propylthiazole	1190	+	+	+	−	+	+	−	MS[3]
2-ethyl-5(or 6)-methylpyrazine	1005	tr	+	tr	+	−	−	tr	MS + LRI
2-ethyl-3-methylpyrazine	1010	−	+	tr	+	−	−	tr	MS + LRI
2-ethyl-3,6-dimethylpyrazine	1080	+	+	tr	tr	tr	−	tr	MS + LRI
2-ethyl-3,5-dimethylpyrazine	1088	+	+	+	+	tr	−	+	MS + LRI
1-(2-furanylmethyl)-1*H*-pyrrole	1192	−	+	+	+	++	+++	−	MS + LRI
1-(2-furanylmethyl)methyl-1*H*-pyrrole	1276	tr	tr	−	−	tr	+	−	MS[3]
1-(2-furanylmethyl)dimethyl-1*H*-pyrrole	1361	−	−	−	−	−	tr	−	MS[3]
2-acetylfuran	915	+	++	++	+	−	−	−	MS + LRI
5-methyl-2-furfural	970	+	++	+	+	−	−	−	MS + LRI
1-(2-furanyl)butan-2-one	1058	tr	+	+	−	−	−	−	MS + LRI
2,2′-methylenebisfuran	1086	+	++	+	−	tr	+	−	MS
2,2′-(1,2-ethylenediyl)bisfuran	1336	tr	tr	tr	−	++	++	+	MS
dihydro-2-methyl-3(2*H*)-thiophenone	989	tr	++	++	+	−	−	−	MS + LRI
2-acetylthiophene	1086	tr	+	+	+	tr	−	−	MS + LRI
1-(2-thienyl)-1-propanone	1188	tr	tr	tr	−	tr	−	−	MS + LRI
thieno[2,3[b]]thiophene	1212	+++	++	++	−	−++	−+	+	MS[2]
thieno[3,2[b]]thiophene	1214	+	+	+	+	+	tr	tr	MS[1]
3,5-dimethyl-1,2,4-trithiolane (*E* or *Z*)	1136	++++	++	++	+	++	++	+	MS + LRI
3,5-dimethyl-1,2,4-trithiolane (*E* or *Z*)	1148	++++	++	++	+	++	++	+	MS + LRI
3-methyl-1,2,4-trithiane	1243	++	++	++	+	++	++	+	MS + LRI
3,6-dimethyl-1,2,4,5-tetrathiane (*E* or *Z*)	1388	++	++	+	−	++	++	−	MS[4]
3,6-dimethyl-1,2,4,5-tetrathiane (*E* or *Z*)	1406	+	+	+	−	+	+	−	MS[4]
4,6-dimethyl-1,2,3,5-tetrathiane	1442	tr	tr	tr	−	+	−	−	MS[4]
2-methyl-3-(methylthio)furan	947	−	−	−	+	−	+	+	MS[5]
2(or 3)-(methylthio)thiophene	1082	−	−	tr	+	−	++	+	MS[1]
2-methyl-3-(methylthio)thiophene	1144	−	−	−	tr	−	−	+	MS[6]
bis(2-methyl-3-furanyl) disulfide	1547	−	tr	tr	−	+	−	−	MS[7] + LRI
bis(2-furanylmethyl) disulfide	1701	+	+	+	−	+	tr	−	MS[7] + LRI
1-octen-3-ol	982	−	−	++	+	−	++	+	MS + LRI
nonanal	1109	−	−	+	−	−	+	+	MS + LRI
2-heptanone	890	−	−	−	tr	−	+	+	MS + LRI
2-octanone	993	−	−	−	tr	−	+	+	MS + LRI
2-nonanone	1095	−	−	−	+	−	++	+	MS + LRI
2-decanone	1198	−	−	+	+	−	++	+	MS + LRI
2-pentylfuran	991	−	−	+	+	−	+	+	MS + LRI
2-pentylthiophene	1164	−	−	+	+	−	+	+	MS + LRI
2-hexylthiophene	1270	−	−	+	−	−	+	+	MS + LRI
2-pentylthiapyran	1317	−	−	++	++	−	+++	++	MS[3]
2-pentylpyridine	1202	−	−	+	+	−	++	+	MS + LRI

[a] C, cysteine; R, ribose; L, phospholipid (lecithin); XL, excess lecithin (10 times the amount in C + R + L). [b] Linear retention index. [c] Relative size of peaks in GC-MS chromatogram: (++++) very large; (+++) large; (++) medium; (+) small; (tr) trace; (−) not detected. [d] MS + LRI, mass spectrum and LRI agree with those of authentic compound; MS, mass spectrum agrees with literature spectrum; References of mass spectra not contained in NIST/EPA/MSDC or Wiley Mass Spectral Databases are indicated by superscript numbers: (1) ten Noever de Brauw et al., 1980; (2) Farmer et al., 1989; (3) Mottram and Whitfield, 1995; (4) Zhang et al., 1988; (5) MacLeod and Ames, 1986; (6) Güntert et al., 1993a; (7) Mottram et al., 1995.

clearly some breakdown of the cellulose occurred under these heating conditions.

The volatiles obtained when cysteine was heated in the absence of ribose are particularly interesting. Dry cysteine was thermally stable when heated alone at 185 °C, and no significant volatile compounds were found. Previous work had shown some degradation of cysteine when heated under these conditions in the presence of a small amount of water (Mottram and Whitfield, 1995). In the presence of cellulose, considerable cysteine degradation occurred with the production of large quantities of volatiles, especially 3,5-dimethyl-1,2,4-trithiolane, thieno[2,3-*b*]thiophene, and some other sulfur-containing heterocyclic compounds. Most of the volatiles found in the cysteine/cellulose system were also found in the corresponding system containing ribose. It is clear that under these heating conditions, the cellulose was not inert and underwent Maillard type reactions with cysteine.

An important part of this study was to examine the interaction of the lipid with the Maillard reaction under conditions approximating high temperature roasting. Under aqueous conditions, quantities of lipid/Maillard interaction products had been found, including alkylthiophenes, pentylpyridine, and pentylthiapyran, and other Maillard reaction products were reduced significantly (Whitfield et al., 1988; Farmer et al., 1989). In deep-fat fried foods, a number of different pyridines, thiophenes, thiazoles, and oxazoles have been identified, probably arising from reactions between the frying fat and Maillard reaction intermediates (Tang et al., 1983; Ho et al., 1987; Whitfield, 1992). Lipid degradation products were not found in very large quantities in any of the present reaction systems, which contrasts with

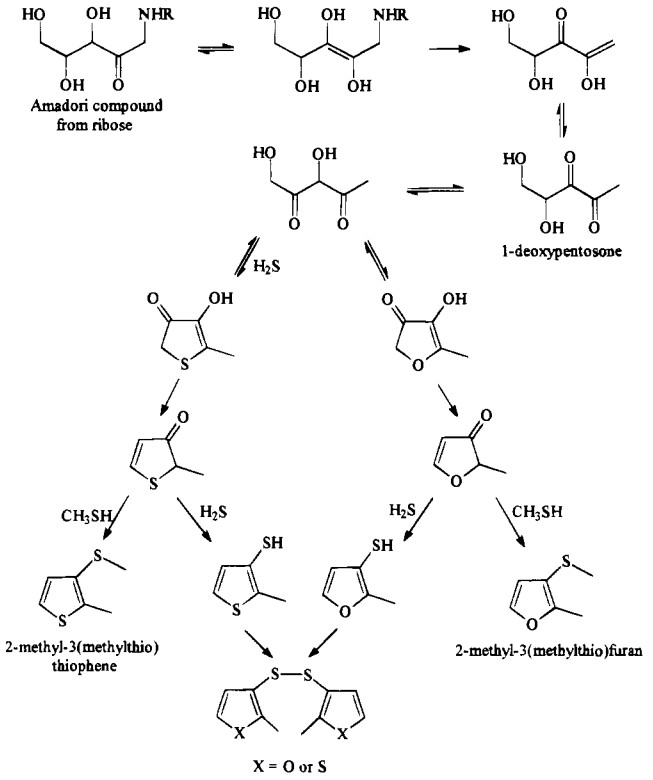

Figure 1. Possible pathways to the formation of furan and thiophene thiols, sulfides, and disulfides in Maillard reactions containing cysteine, ribose, and phosphatidylcholine.

results obtained in Maillard–phospholipid reactions carried out under aqueous conditions, where lipid degradation products dominated. In the dry systems, relatively few aldehydes and alcohols were found, the main class of lipid-derived volatiles was 2-alkanones. The addition of cellulose appeared to inhibit the production of lipid-derived volatiles. A number of Maillard–lipid interaction products were found, all of which had been previously found in cysteine–ribose–phospholipid reaction systems. However, the relative concentrations of these compounds were much lower than those obtained under aqueous conditions. No long-chain alkyl thiazoles, pyrazines, or oxazoles were found in the dry reaction systems. Such compounds are known to be formed during deep-fat frying. The failure to obtain such compounds in the model systems could be associated with the absence of water or the presence of a strongly reducing atmosphere due to cysteine degradation. Alternatively, the release of free fatty acids from the phospholipid will be inhibited in the absence of water, resulting in less oxidation products. The stability of the phospholipid under these heating conditions was further demonstrated by the systems containing a 10-fold increase in phospholipids. These systems did not exhibit an increase in lipid degradation products or lipid–Maillard interaction compounds. In fact, the excess lipid had an overall quenching effect on volatile formation.

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. Moderate concentrations were found in the absence of cellulose, but a quenching effect of cellulose was observed. These were the only compounds where the presence of excess phospholipid caused an increase in concentration. 2-Methyl-3-(methylthio)furan is an important aroma

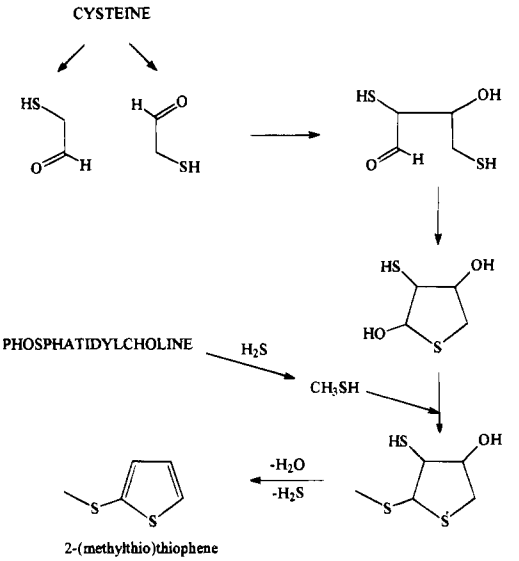

Figure 2. Proposed route to the formation of 2-(methylthio)-thiophene in reaction systems containing cysteine and phosphatidylcholine (adapted from Shu et al., 1985).

compound in meat and coffee, and it has a very low odor 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., 1993a). It also has a meaty aroma and a low threshold value. The route to 2-methyl-3-furanthiol in Maillard reactions has been suggested to be via the 2,3-enolization and dehydration of ribose Amadori products to form 1-deoxypentosone, which further dehydrates to give methylhydroxyfuranone; subsequent reaction with hydrogen sulfide produces the furanthiol (Güntert et al., 1993b; Tressl et al., 1989). Similar mechanisms involving the replacement of oxygen in the heterocyclic ring with sulfur would explain the formation of the 2-methyl-3-thiophenethiol. In Maillard systems containing cysteine, hydrogen sulfide is readily produced from the hydrolysis or Strecker degradation of cysteine. The formation of the methyl sulfides requires the presence of a reactive methylthio group (e.g., methanethiol) that could participate in these reaction pathways as shown in Figure 1. Although small amounts of methanethiol have been found among the thermal degradation products of cysteine (Mulders, 1973), such a source of methanethiol would not explain the relatively large concentrations of these sulfides nor why they were only formed in the presence of phospholipids. It is necessary to look for a source of methanethiol peculiar to the phospholipid system, and this could be provided by the action of hydrogen sulfide on the choline moiety of phosphatidylcholine (lecithin). Preliminary experiments in our laboratories have shown that methanethiol and dimethyl disulfide were formed when phosphatidylcholine, or choline itself, was heated with hydrogen sulfide (unpublished data).

The 2- and 3-(methylthio)thiophenes have been identified tentatively by Golovnya et al. (1983) in cooked meat and simulated meat flavors, although their odor properties have not been recorded. 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. The participation of methanethiol in this reaction could provide the (methylthio)-thiophene found in the present work (Figure 2). When

cysteine and lecithin were heated in the absence of ribose, the (methylthio)thiophene was among the volatile products, further substantiating the proposed pathway. Authentic samples of 2- and 3-(methylthio)-thiophene were not available; however, the pathway outlined above indicates the 2-isomer was involved, and Shu et al. (1985) report 2-thiophenethiol (not the 3-isomer) as a major product in the degradation of cysteine.

As thio-substituted furans and thiophenes are known to be important in the aroma of meat and other thermally processed foods, further investigations should be undertaken to examine the novel role of phospholipids in the formation of such compounds in food systems.

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LITERATURE CITED

Farmer, L. J.; Mottram, D. S. Recent studies on the formation of meat-like aroma compounds. In *Flavour Science and Technology*; Bessiere, Y., Thomas, A. F., Eds.; Wiley: Chichester, U.K., 1990a; pp 113–116.

Farmer, L. J.; Mottram, D. S. Interaction of lipid in the Maillard reaction between cysteine and ribose: effect of a triglyceride and three phospholipids on the volatile products. *J. Sci. Food Agric.* **1990b**, *53*, 505–525.

Farmer, L. J.; Whitfield, F. B. Some aroma compounds formed from the interaction of lipid in the Maillard reaction. In *Progress in Flavour Precursor Studies*; Schreier, P., Winterhalter, P., Eds.; Allured: Carol Stream, IL, 1993; pp 387–390.

Farmer, L. J.; Mottram, D. S. Lipid-Maillard interactions in the formation of volatile aroma compounds. In *Trends in Flavour Research*; Maarse, H., van der Heij, D. G., Eds.; Elsevier: Amsterdam, 1994; pp 313–326.

Farmer, L. J.; Mottram, D. S.; Whitfield, F. B. Volatile compounds produced in Maillard reactions involving cysteine, ribose and phospholipid. *J. Sci. Food Agric.* **1989**, *49*, 347–368.

Golovnya, R. V.; Misharina, T. A.; Garbuzov, V. G.; Medvedyev, F. A. Volatile sulfur containing compounds in simulated meat flavour and their comparison with the constituents of natural aroma. *Nahrung* **1983**, *27*, 237–249.

Güntert, M.; Bertram, H. J.; Hopp, R.; Silberzahn, W.; Sommer, H.; Werhoff, P. Thermal generation of flavor compounds from thiamin and various amino acids. In *Recent developments in flavor and fragrance chemistry*; Hopp, R., Mori, K., Eds.; VCH: Weinheim, 1993a; pp 215–240.

Güntert, M.; Bertram, H. J.; Emberger, R.; Hopp, R.; Sommer, H.; Werkoff, P. Some new aspects of the thermal generation of flavour compounds from thiamin. In *Progress in Flavour Precursor Studies*; Schreier, P., Winterhalter, P., Eds.; Allured: Carol Stream, IL, 1993b; pp 361–378.

Ho, C. T.; Carlin, J. T.; Huang, T. C. Flavour development in deep-fat fried foods. In *Flavour Science and Technology*; Martens, M., Dalen, G. A., Russwurm, H., Eds.; Wiley: Chichester, U.K., 1987; pp 35–42.

Hurrell, R. F. Maillard reaction in flavor. In *Food Flavors*; Morton, I. D., MacLeod, A. J., Eds.; Elsevier: Amsterdam, 1982; pp 399–437.

Leahy, M. M.; Reineccius, G. A. Kinetics of alkyl pyrazine formation. Effect of pH and water activity. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C. T., Eds.; American Chemical Society: Washington, DC, 1989; pp 196–208.

Ledl, F. Chemical pathways of the Maillard reaction. In *The Maillard Reaction in Food Processing, Human Nutrition and Physiology*; Finot, P. A., Aeschbacher, H. U., Hurrell, R. F., Liardon, R., Eds.; Birkhauser Verlag: Basel, 1990; pp 19–42.

MacLeod, G.; Ames, J. M. 2-Methyl-3-(methylthio)furan: a meaty character impact aroma compound identified from cooked beef. *Chem. Ind. (London)* **1986**, 175–176.

Mottram, D. S. Flavor compounds formed during the Maillard reaction. In *Microwave, Extruded and Maillard Generated Aromas*; McGorrin, R. J., Parliment, T. H., Morello, M. J., Eds.; American Chemical Society: Washington, DC, 1994; pp 104–126.

Mottram, D. S.; Whitfield, F. B. Volatile compounds from the reaction of cysteine, ribose, and phospholipid in low moisture systems. *J. Agric. Food Chem.* **1995**, *43*, 984–988.

Mottram, D. S.; Madruga, M. S.; Whitfield, F. B. Some novel meat-like aroma compounds from the reactions of alkanediones with hydrogen sulfide and furanthiols. *J. Agric. Food Chem.* **1995**, *43*, 189–194.

Mulders, E. J. Volatile components from the non-enzymatic browning reaction of cysteine/cystine-ribose system. *Z. Lebensm. Unters. Forsch.* **1973**, *152*, 193–201.

Shu, C. K.; Hagedorn, M. L.; Mookherjee, B. D.; Ho, C. T. pH effect on the volatile components in the thermal degradation of cysteine. *J. Agric. Food Chem.* **1985**, *33*, 442–446.

Tang, J.; Jin, Q. Z.; Shen, G. H.; Ho, C. T.; Chang, S. S. Isolation and identification of volatile compounds from fried chicken. *J. Agric. Food Chem.* **1983**, *31*, 1287–1292.

ten Noever de Brauw, M. C.; Bouwman, J.; Tas, A. C.; La Vas, G. F. *Compilation of Mass Spectra of Volatile Compounds in Food*; Institute for Nutrition and Food Research TNO: Zeist, The Netherlands, 1980.

Tressl, R.; Helak, B.; Martin, N.; Kersten, E. Formation of amino acid specific Maillard products and their contribution to thermally generated aromas. In *Thermal Generation of Aromas*; Parliment, T. H., McGorrin, R. J., Ho, C. T., Eds.; American Chemical Society: Washington, DC, 1989; pp 156–171.

Vernin, G.; Parkanyi, C. Mechanisms of formation of heterocyclic compounds in Maillard and pyrolysis reactions. In *Chemistry of Heterocyclic Compounds in Flavors and Aromas*; Vernin, G., Ed.; Ellis Horwood: Chichester, U.K., 1982; pp 151–207.

Werkhoff, P.; Brüning, J.; Emberger, R.; Güntert, M.; Hopp, R. Flavor chemistry of meat volatiles: New results on flavor components from beef, pork and chicken. In *Recent developments in flavor and fragrance chemistry*; Hopp, R., Mori, K., Eds.; VCH: Weinheim, 1993; pp 183–213.

Whitfield, F. B. Volatiles from interactions of Maillard reactions and lipids. *Crit. Rev. Food Sci. Nutr.* **1992**, *31*, 1–58.

Whitfield, F. B.; Mottram, D. S.; Brock, S.; Puckey, D. J.; Salter, L. J. The effect of phospholipid on the formation of volatile heterocyclic compounds in heated aqueous solutions of amino acids and ribose. *J. Sci. Food Agric.* **1988**, *42*, 261–272.

Zhang, Y.; Chien, M.; Ho, C. T. Comparison of the volatile compounds obtained from the thermal reaction of cysteine and glutathione. *J. Agric. Food Chem.* **1988**, *36*, 992–996.

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