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Analytical Methods Section

The effect of xylose on the generation of volatiles from heated thiamine

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Isolates of volatile thermal degradation products of xylose, thiamine and xylose–thiamine mixtures were prepared by continuous steam distillation-solvent extraction, and 11, 40 and 57 components were identified, respectively, from each isolate. Pentane-2,3-dione was the most abundant component of the xylose isolate at 34% of the total volatiles. Sulphur compounds predominated in both the thiamine and xylose–thiamine isolates, with 34 and 43 representatives, respectively, being identified in each sample. Thirteen compounds are reported for the first time as thiamine thermal degradation products, and include 2-methylthiophen-3-thiol, 2-methylthiophen-4-thiol, and their 2,3-dihydro and 4,5-dihydro derivatives, three other thiophen derivatives, two alicyclic sulphur compounds and two aliphatic hydroxyketones. The addition of xylose to the model system resulted in the identification of 27 components which could not be detected from xylose or thiamine alone, and 16 (15 of which are sulphur-containing) may form as a result of xylose–thiamine interactions. They include four bicyclic structures and four alicyclic sulphur components. The presence of xylose also resulted in a 4–5-fold increase in formation of the potent meaty odour compound, 2-methylfuran-3-thiol.

INTRODUCTION

Meat flavour is extremely complex and has been thoroughly reviewed by many authors (e.g. MacLeod & Seyyedain-Ardebili, 1981; Mottram, 1991). The main routes leading to the formation of meat flavour are the Maillard reaction, the thermal degradation of lipids, the Strecker degradation of amino acids and the thermal degradation of thiamine (MacLeod, 1986). In addition, these individual routes are able to interconnect, leading to a network of reactions. For example, the importance of lipid to the types of compounds formed during the Maillard reaction between ribose and cysteine has been extensively studied, and the consequent effect on the aroma formed has been established (Farmer *et al.*, 1989).

The thermal degradation of thiamine is dependent on the temperature and time of heating and on the pH of the medium (Dwivedi & Arnold, 1973), with the mechanism of degradation being greatly influenced by pH. Sixty-nine compounds have been identified among the thermal degradation products of thiamine (Arnold *et al.*, 1969; Dwivedi & Arnold, 1972; Dwivedi *et al.*, 1972, 1973; Hartman *et al.*, 1984*a*; Reineccius & Liardon, 1985; van der Linde *et al.*, 1979; Güntert *et al.*, 1990), and include aliphatic carbonyl compounds, aliphatic sulphides and thiols, furans,

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thiophens, thiazoles and alicyclic sulphur compounds. More than half the degradation products identified contain sulphur, and many possess low odour threshold values and contribute to the aroma of a number of cooked foods, particularly meat (MacLeod, 1986).

Xylose is a reducing sugar which reacts with amino compounds, e.g. lysine, to give a range of volatile compounds including aliphatic and alicyclic compounds, furans, pyrroles, pyridines and pyrazines (Apriyantono & Ames, 1990).

Thiamine possesses a free amino group, and is known to take part in Maillard-type reactions in the presence of reducing sugars (Doyon & Smyrl, 1983). de Lange and Mijll Dekker (1954) were the first to report that, when thiamine and glucose are heated at 85°C for up to 10 days, the mixture gradually darkens and the pH drops. Decreases in the concentrations of glucose and thiamine were also observed and there was an increase in fluorescence intensity. Similarities between these results and those obtained for the Maillard reaction between reducing sugars and amino acids were noted (de Lange & Mijll Dekker, 1954). The rate of reaction between thiamine and glucose is strongly influenced by pH, and, over the pH range 2·20–8·31, is greatest at values close to 7 (Lhoest *et al.*, 1958). The nature of the reducing sugar is also important and Doyon and Smyrl (1983) have shown that xylose causes a greater rate of thiamine destruction that either glucose or maltose on heating at 95°C and pH 6·75.

Seventy-eight compounds have been identified from heated model systems containing thiamine, cystine, ascorbic acid and monosodium glutamate, and sometimes xylose and lactose (Hartman *et al.*, 1984*b*,*c*; Werkhoff *et al.*, 1989*a*, 1990; Güntert *et al.*, 1990), and one additional compound has been identified in a thiamine/cysteine/hydrolysed vegetable protein mixture (Evers *et al.*, 1976). Still further reaction products were identified in a heated thiamine/cystine/ascorbic acid/monosodium glutamate mixture, but were not reported in detail (Werkhoff *et al.*, 1989*a*). Fifty-two of the components, reported have not been identified from thiamine alone. All the reactants mentioned find uses in reaction product meat flavours (MacLeod & Seyyedain-Ardebili, 1981). Compounds reported, which were not identified in model systems containing thiamine as the sole precursor, included some sulphur-substituted furans and thiophens and several furyl and thienyl sulphides. The kinetic behaviour of thiamine degradation in aqueous solution both with and without other components has recently been reported (Ramaswamy *et al.*, 1990).

Surprisingly, no reports have been published giving the identities of volatile compounds formed in binary model systems comprising thiamine and a reducing sugar. The current paper reports the nature of the volatile components formed in thiamine–xylose model systems heated at pH 7.

MATERIALS AND METHODS

Materials

D-(+)-Xylose (99+%, gold label) and thiamine hydrochloride (90–95%) were obtained from Aldrich Chemical Co. Ltd, Gillingham, UK, and diethyl ether (AnalaR grade) was obtained from BDH Chemicals Ltd, Poole, UK.

Methods

Preparation of volatile isolates

A solution of thiamine hydrochloride (0·05 mol) and xylose (1 mol) in 250 ml freshly distilled water was heated in a modified Likens and Nickerson apparatus (Maarse & Kepner, 1970) for 1h with diethyl ether (15 ml) as the extraction solvent. The pH was adjusted to and maintained at pH 7 by the addition of a total of approximately 71 ml 3 M sodium hydroxide solution before and during heating. Solvent extracts were concentrated using a Vigreux column under a reduced pressure of $8{\cdot}0 \times 10^3$ N m^{-2} (60 mm Hg), to 0·5 ml, followed by final concentration to 0·1 ml using a gentle stream of nitrogen.

Volatile isolates were also prepared using only thiamine hydrochloride and only xylose solutions in the sample flask. Blank isolates were prepared using only distilled water in the sample flask. All sample and blank isolates were prepared in triplicate and stored at −15°C prior to analyses, which were performed within one day of preparation.

Gas chromatography (GC)

Analyses were carried out using a fused silica capillary column (25 m × 0·32 mm i.d.), coated with SE52/54 (1 μm film thickness). The conditions of analysis were: helium, 1·5 ml/min; temperature programme, 40°C for 5 min followed by a ramp rate of 2°C/min to a final temperature of 200°C, held for 20 min; injector temperature, 225°C, detector temperature, 250°C, injection volume, 1μl; injection technique, Grob splitless. Retention times and quantitative data were obtained from a Hewlett Packard 3390A integrator, linked to the GC. All isolates were also analysed using a polar column (50 m × 0·32 mm i.d.) coated with CPWAX 52CB (0·2 μm film thickness) with a helium flow rate of 1 ml/min and an initial column temperature of 60°C. All other conditions of analysis were as for the SE52/54 column.

GC–mass spectrometry (GC–MS)

A Kratos MS80 mass spectrometer was used, linked to a Kratos DS90 data system and a Carlo Erba GC. The columns and relevant conditions for the GC were the same as those described above. The MS conditions of analysis were: ionisation mode, electron impact;

electron energy, 70 eV; ion source temperature, 200°C; ionisation current, 100μA; accelerating voltage, 4 kV; scan speed, 1 s/decade; mass range, 29–500; interscan time, 0·2 s.

GC–odour port assessment (GC–OPA)
The odours of the separated components were assessed as they eluted from the SE52/54 column, by two experienced assessors, using a column effluent splitter (split ratio 1 : 1). The splitter comprised two equal lengths of deactivated fused silica tubing each connected, via a two-hole ferrule, to the detector end of the GC column. One length of fused silica was connected to the FID while the second length led, via a heated (250°C) line, to an odour port.

RESULTS AND DISCUSSION

The odours of the isolates prepared from xylose alone were caramel, toffee-like and slightly buttery, and from thiamine alone, highly sulphurous, onion-like and meaty. The odour of the xylose/thiamine isolate was very similar to that of the isolate prepared from thiamine alone, but buttery notes were also present which gave the sample a more meaty character overall.

Identities of the separated components for all the isolates obtained using the SE52/54 column are given in Table 1, together with literature Kováts indices (where available) and odour descriptions (obtained by GC–OPA). Components identified using only the CPWAX 52CB column are listed in Table 2. Compounds which have previously been identified in thiamine-containing model systems, heated with or without additional components, or in heated meat, are indicated in the tables. The isolate prepared from xylose alone was the weakest, and was about 0·25 of the strength of that prepared using both xylose and thiamine. The isolate prepared from thiamine alone was the strongest, and was about 1·5 times the strength of that prepared from xylose and thiamine. It was somewhat surprising that the isolate prepared from both xylose and thiamine was weaker than that prepared from thiamine alone, especially since Doyon and Smyrl (1983) showed that the presence of xylose increased that rate of thiamine destruction, but this could be due to reactions between xylose and thiamine resulting in greater amounts of non-volatile products, which were not investigated in this study.

Volatiles from xylose

The classes of compounds represented in the isolates prepared from xylose alone were aliphatic alcohols, aliphatic aldehydes, aliphatic ketones, aliphatic acids and furan derivatives. A total of 11 compounds are reported, accounting for over 90% of the total isolate. Pentane-2,3-dione (Compound 7) was the most abundant at a level of 34%. Butanedione (Compound 2), at 13%, undoubtedly contributes to the buttery notes of this sample, while pentane-2,3-dione, along with certain of the furan derivatives, contributes to the caramel aroma.

Volatiles from thiamine

The thiamine isolate was much more complex than that prepared from xylose, and 40 compounds, representing over 87% of the total isolate, were identified. Of these, 21 have previously been identified as thermal degradation products of thiamine, as shown in Tables 1 and 2, and six components could be only partially characterised. Therefore, 13 compounds are reported here for the first time as thermal degradation products of thiamine and, of these, 12 are positive identifications and one is a tentative characterisation. They are listed in Table 3 and have been discussed in an earlier paper (Ames *et al.*, in press). In addition to the compounds listed in Table 3, three sulphur-substituted derivatives of 2-methylenetetrahydrothiophen (Compounds 54, 56 and 61) were detected at a combined level of 5%. Compound 54 was also detected as a thermal degradation product of thiamine by Reineccius and Liardon (1985). It was not fully characterised by those authors or in the current study, but it possesses a relative molecular mass of 178, a base peak of 100 and two sulphur atoms. The intensities of the eight most intense mass spectral peaks were as follows: 100(100), 85(43), *178*(38), 99(35), 117(20), 59(20), 45(12), 101(11). Compound 56 possessed an almost identical mass spectrum. The mass spectrum of the third derivative was 100(100), 85(64), 99(60), 59(36), 97(35), *210*(33), 71(31), 130(27), and it possesses three sulphur atoms. Compounds 54 and 56 were each described as 'meaty' by GC–OPA and are therefore worthy of further study.

Volatiles from the xylose/thiamine mixture

A total of 57 compounds, representing over 83% of the total volatiles, were identified from the xylose/thiamine isolate. Twenty-seven of the components reported could not be identified from either xylose or thiamine heated alone, but seven have previously been identified in heated thiamine systems and several others, e.g. Compounds 9, 11, 25 and 27, are likely thermal degradation products of xylose. Sixteen components are reported here as likely xylose–thiamine reaction products and are listed in Table 4.

2-Methylfuroate (Compound 31) was identified at a high level of 19%. It is likely to form from 2-furoic acid and methanol, both of which are sugar thermal degradation products (Sugisawa, 1966), although 2-methylfuroate was not detected in the xylose isolate. All the other components considered to be formed as a result

Table 1. Volatile components from heated xylose, thiamine and xylose/thiamine model systems (SE52/54 column)

No.	Component and Reference[a]	Previous identification[b]	R_t (min)	Kováts index (lit.)[c]	Xylose RA[d]	Thiamine RA[d]	Xylose/ thiamine RA[d]	Odour description[e]
1	Hydrogen sulphide	AC	2·64		—	1	3	Rotten eggs (T,M)
2	Butanedione	BC	6·77	575	13	—	2	Buttery (X,M)
3	Hydroxypropanone	C	9·54		—	tr	1	
4	2-Methyl-4,5-dihydrofuran	A	10·69		—	tr	tr	
5	Pentan-2-one	ABC	10·73	672	—	tr	—	Cooked cereal
6	Pentan-3-one	AC	11·00	681	—	tr	—	Caramel
7	Pentane-2,3-dione	ABC	11·00	681	34	—	1	Caramel, toffee (X), sl. buttery (M)
8	?Methanedithiol		11·93		—	—	tr	Sulphurous, cabbage
9	2,5-Dimethylfuran	C	12·45	697	—	—	tr	
10	1,1-Ethanedithiol[f]	C	13·99	792[t]	—	—	2	Raw onions
11	2-Methylbut-2-en-l-al	C	14·60		—	—	tr	
12	2(and/or 3)-Methyl-thiophen	ABC	16·76	775 (2-me)	—	2	tr	
13	Methylthiol acetate	AC	18·08		—	—	tr	
14	Hexane-3,4-dione[g]		19·01	777	3	—	—	
15	2-Methyltetrahydro-furan-3-one	ABC	19·70		—	tr	1	
16	3-Mercaptobutanone[f]	AB	20·36	787[t]	—	tr	tr	Sl. meaty (T), raw onions (M)
17	4-Methylthiazole[h]	ABC	21·14	800	—	tr	—	
18	2-Furaldehyde i.e. furfural[h]	C	22·08	815	26	—	1	
19	2-Methyl-4,5-dihydrothiophen[i]	A	23·10		—	57	27	Sulphurous, thiophen-like, raw onions, petrol (T,M)
20	2-Furanmethanol	C	23·92		11	—	—	
21	2-Methylfuran-3-thiol[j]	ABC	25·28	868[t]	—	2	14	Boiled beef (T), meaty, sl. onions (M)
22	2-Methylenetetrahydro-thiophen	B	26·16		—	1	tr	Sulphurous, sl. onions (T), meat + onions (M)
23	3-Mercaptopentanone[k]	AB	26·19	898[t]	—	tr	—	Roast beef
24	2-Methyl-4,5-dihydro-furan-3-thiol[l]	A	28·86	927[u]	—	tr	—	Beef, sweet, sulphurous
25	3-Methylcyclopent-2-enone	C	28·93		—	—	tr	Beef
26	4,5-Dimethylthiazole[h]	ABC	31·20	917	—	tr	1	Sulphurous, meaty (T), sl. roast beef, dry (M)
27	2-Propanoylfuran[m]	C	34·40	988	—	—	tr	
28	2-Methyltetrahydro-thiophen-3-one[l]	ABC	36·30	947[u]	—	12	2	
29	A C_3-substituted thiazole	C	39·90		—	tr	Offal	
30	4-Methyl-5-vinyl thiazole	AC	39·92	1011	—	—	tr	Meat pie
31	2-Methylfuroate		41·12	956	—	—	19	Sl. onions, very weak
32	2-Methylthiophen-3-thiol[l]	B	42·67	1028[v]	—	tr	tr	Roast beef, sulphurous (T), cooked onions (M)
33	2-Methyl-2,3-dihydrothiophen-4-thiol[l]		45·58		—	1	2	Roast beef, sl. onions (T), beef + onions (M)
34	1,2,4-Trithiolane[n]		46·04		—	tr	2	Onions, thiophen-like (T,M).
35	l-Methylbicyclo-[3.3.0]-2,8-dioxaoctane[o]	AB	46·92	1075[u]	—	—	tr	Sulphurous
36	1,3,5-Trithiane	C	48·10		—	—	tr	Raw onions
37	2-Methylthiophen-4-thiol[l]		48·61		—	tr	—	Onions, cooked beef

Table 1–*contd.*

No.	Component and Reference[a]	Previous identification[b]	R_t (min)	Kováts index (lit.)[c]	Xylose RA[d]	Thiamine RA[d]	Xylose/ thiamine RA[d]	Odour description[e]
38	2-Methyl-2,3-dihydro-thiophen-3-thiol[l]		48·90		—	3	2	Boiled beef sl. onions (T), sulphurous (M)
39	3,5-Dimethyl-1,2,4-trithiolane[f]	C	49·36	1099[v]	—	—	1	Boiled onions, petrol, thiophen-like
40	?1-(3-Thienyl)propan-2-one[p]		50·26		—	—	tr	
41	2-Methyl-4,5-dihydro-thiophen-4-thiol[l]		51·30		—	tr	tr	Roast beef (T), sulphurous (M)
42	2-Methyl-4,5-dihydro-thiophen-3-thiol[l]		52·57		—	1	tr	Boiled beef (T), boiled onions (M)
43	?A C_2-substituted-3-furanthiol	A	53·09		—	tr	—	
44	2-Methyl-3-oxa-8-thia bicyclo[3.3.0]octa-1,4-diene, i.e. kahweofuran[p]		53·10	1156[v]	—	—	tr	Onions
45	2-Propanoylthiophen[m]	C	53·86	1164	—	—	tr	
46	3-Methyl-1,2-dithian-4-one[k]	AB	55·99	1168[v]	—	tr	tr	Sl. meaty (T,M)
47	2-Methyl-3-(methyl-dithio)furan[q]		55·99		—	—	tr	
48	1-Methyl-bicyclo-[3.3.0]-2,4-dithia-8-oxaoctane or an isomer[r]	AB	61·69		—	tr	—	Sulphurous, sl. meaty (T) roast beef (M)
49	5–(2-Hydroxyethyl)-4-methylthiazole[s]	ABC	62·00	1241[u]	—	—	tr	
50	?4-Hydroxy-5-methyl-3(2*H*)thiophenone		63·22		—	tr	—	Dry roast beef
51	A thiazole	C	64·93		—	tr	tr	Sulphurous
52	1,2,4,5-Tetrathiane[n]		69·83		—	tr	tr	
53	?2-*n*(or *iso*)- Butyl-5-ethylthiophen		71·00		—	—	tr	
54	A derivative of 2-methylenetetrahydrothiophen	A	75·57		—	3	1	Meaty, dry roast beef (T,M)
55	*bis*-(2-Methyl-3-furyl) disulphide[t]	ABC	79·72	1494[t]	—	—	tr	Dry roast beef
56	A derivative of 2-methylenetetrahydrothiophen	A	81·00		—	1	tr	Meaty (T,M)
57	?*bis*-(5-Methyl-2-furyl) disulphide[j]		86·59		—	—	tr	
58	?2-Methyl-3-furyl-(2-methyl-4,5-dihydro-3-furyl) disulphide[s]	A	86·59		—	—	tr	
59	1,2,3,5,6-Pentathiepane[n] i.e. lenthionine	C	88·83	1590	—	—	tr	
60	1,2,3,4,5,6-Hexathiepane		92·01		—	—	tr	
61	A derivative of 2-methylenetetrahydrothiophen		95·49		—	1	tr	
62	2-Methyl-3[(2-methyl-3-thienyl)dithio]furan[t]	B	96·50	1681[t]	—	—	tr	
63	*bis*-(2-Methyl-3-furyl) trisulphide[j]		101·35		—	—	tr	

[a] Reference = *Eight Peak Index of Mass Spectra* (1983) when not cited.

[b] Compounds which have previously been identified as thermal degradation products from thiamine are indicated by A (Arnold *et al.*, 1969; Dwivedi & Arnold, 1972; Dwivedi *et al.*, 1972, 1973; van der Linde *et al.*, 1979; Hartman *et al.*, 1984*a*; Reineccius & Liardon, 1985; Güntert *et al.*, 1990). Compounds previously identified as thermal degradation products from model systems containing thiamine and other precursors are preceded by B (Evers *et al.*, 1976; Hartman *et al.*, 1984*b*,*c*; Werkhoff *et al.*, 1989*a*; 1990; Güntert *et al.*, 1990). Compounds identified in heated meat are preceded by C (Maarse *et al.*, 1989).

[c] Kováts index reference for nearest stationary phase, OV101 = Jennings & Shibamoto (1980) when not cited.

[d] Relative abundance (RA) values were calculated after exclusion of data obtained for components identified in blank isolates, 'tr', Component was identified in trace amounts but could not be accurately quantified. '—', Components could not be identified in this isolate.

[e] Odour qualities were obtained by GC–OPA. X, T, M, Odour quality was obtained from the isolate prepared from xylose, thiamine, or the mixture of xylose and thiamine, respectively. sl., Slightly.

[f] Vernin & Petitjean (1982); [g] Stoll *et al.* (1967); [h] Vitzthum & Werkhoff (1974); [i] Arnold *et al.* (1969); [j] Evers *et al.* (1976); [k] Hartman *et al.* (1984*a*); [l] van den Ouweland & Peer (1975); [m] Jennings & Shibamoto (1980); [n] Chen & Ho (1986); [o] van Dort *et al.* (1984); [p] Farmer *et al.* (1989); [q] Tressl & Silwar (1981); [r] Seifert *et al.* (1978); [s] Dwivedi & Arnold (1973); [t] Werkhoff *et al.* (1990); [u] Güntert *et al.* (1990); [v] Werkhoff *et al.* (1989*b*).

Table 2. Volatile components from heated xylose, thiamine and xylose/thiamine model systems (CPWAX 52CB column)

No.	Component and Reference[a]	Previous identification[b]	Rt (min)	Kováts index (lit.)[c]	Xylose RA[d]	Thiamine RA[d]	Xylose/ thiamine RA[d]
64	Butan-2-ol	C	[e]	1000	[e]	—	—
65	Acetic acid	ABC	7·92		2	—	tr
66	2-Acetylfuran	BC	16·74	1491	tr	—	—
67	2-Methyl-5-acetylfuran	C	20·09		tr	—	—
68	?A thiazole		22·97		—	2	—
69	1-(2-Furyl)propan-2-one	C	23·82	1502	1	—	—
70	4-Hydroxybutanoic acid lactone	C	24·11		tr	—	—
71	?3-Methylenetetrahydro-thiophen		25·23		—	—	tr
72	A thiazole	C	27·78		—	—	1
73	A C_2 substituted tetra-hydrothiophen	C	28·25		—	tr	—
74	?A dimethylthiophen	C	28·25		—	tr	—
75	5-Hydroxypentan-2-one	C	29·43		—	tr	tr
76	2-Methyl-2,3-dihydro-3-furaldehyde[f]	AC	32·00		—	—	tr
77	2-Acetylthiophen[g]	AC	32·21	1760	—	tr	tr
78	5-Methylthiophen-2-carboxaldehyde	BC	42·62	1759	—	tr	—
79	A methyl methylthio furan[h]	ABC	42·62		—	tr	—

[a,b] See Table 1.
[c] Kováts index reference Jennings & Shibamoto (1980), for PEG 20 M when not cited.
[d] See Table 1.
[e] This compound eluted under the solvent peak, and therefore R_t and RPA measurements could not be accurately determined.
[f] Vitzthum & Werkhoff (1974);
[g] ten Nover de Brauw *et al.* (1987);
[h] van der Linde *et al.* (1979).

of xylose/thiamine interactions are sulphur-containing and were identified at trace levels. Many of the thiophens and sulphur-substituted furans are likely to form as a result of interactions between furans and sulphur compounds, especially hydrogen sulphide.

Of the thiophens, 2-propanoylthiophen (Compound 45) is likely to arise from interactions between hydrogen sulphide (Compound 1) and 2-propanoylfuran (Compound 27), also present in this isolate. 1-(3-Thienyl)propan-2-one (Compound 40) has not previously been identified in thiamine model systems, but was identified in heated ribose/cysteine mixtures by Farmer and Mottram (1990). It is surprising that thiophen-2-carboxaldehyde was not identified in the xylose/thiamine isolate, since it is known to be formed from 2-furaldehyde and hydrogen sulphide (Shibamoto, 1977). The 2-methyl-3-(methyldithio)furan (Compound 47) identified has previously been found in a YEC (Ames & MacLeod, 1985), and possesses a low odour threshold value of 0·01 parts per 10^9 (Tressl & Silwar, 1981).

A total of six bicyclic sulphur-containing furan derivatives were identified in the xylose/thiamine isolate and four, i.e. Compounds 44, 57, 62 and 63, are listed in Table 4. *bis*-(2-methyl-3-furyl) trisulphide (Compound 63) is probably formed from the reaction between 2-methylfuran-3-thiol (Compound 21) and 2-methyl-3-(methyldithio)furan (Compound 47), both of which were also identified in this isolate. It possesses a brothy flavour at a level of one part per 10^6 parts of water (Evers, *et al.*, 1976). 2-Methyl-3-[(2-methyl-3-thienyl)dithio]furan (Compound 62) has previously been identified in a model system containing thiamine among the reactants (Werkhoff *et al.*, 1990), and has been prepared by oxidising a mixture of 2-methylfuran-3-thiol (Compound 21) and 2-methylthiophen-3-thiol (Compound 32) (Werkhoff *et al.*, 1989*b*). It possesses a meaty, onion, garlic aroma with fatty and metallic notes (Werkhoff *et al.*, 1989*b*). 2-Methyl-3-oxa-8-bicyclo[3.3.0]octa-1,4-diene, kahweofuran (Compound 44), is reported here for the first time as a volatile component from thiamine-containing model systems. It has previously been identified among the volatiles of a yeast extract and it is an important aroma component of coffee (Werkhoff *et al.*, 1989*b*). Its aroma has been described as cooked meat with a slight coffee character and a pleasant grilled and smoky note at concentrations of 10–100 parts per 10^9 (Werkhoff *et al.*, 1989*b*).

Interactions between xylose and thiamine are likely to be responsible for the formation of four alicyclic sulphur compounds, i.e. Compounds 36, 39, 59 and 60. 3,5-Dimethyl-1,2,4-trithiolane (Compound 39) was pre-

Table 3. Novel thermal degradation products of thiamine

No.	Identity
3	Hydroxypropanone
75	5-Hydroxypentan-2-one
78	5-Methylthiophen-2-carboxaldehyde
32	2-Methylthiophen-3-thiol
37	2-Methylthiophen-4-thiol
38	2-Methyl-2,3-dihydrothiophen-3-thiol
33	2-Methyl-2,3-dihydrothiophen-4-thiol
42	2-Methyl-4,5-dihydrothiophen-3-thiol
41	2-Methyl-4-5-dihydrothiophen-4-thiol
22	2-Methylenetetrahydrothiophen
50	?4-Hydroxyl-5-methyl-3(2*H*)thiophenone
34	1,2,3-Trithiolane
52	1,2,4,5-Tetrathiane

Table 4. Compounds likely to be formed as a result of xylose—thiamine interactons

No.	Identity
8	?Methanedithiol
10	1,1-Ethanedithiol
31	2-Methylfuroate
47	2-Methyl-(3-methyldithio)furan
57	?*bis*-(Methyl-2-furyl) disulphide
63	*bis*-(2-methyl-3-furyl) trisulphide
53	?*n*(or *iso*)-Butyl-5-ethylthiophen
45	2-Propanoylthiophen
40	?1-(3-Thienyl)propan-2-one
71	?3-Methylenetetrahydrothiophen
62	2-Methyl-32-methyl-3-thienyl)dithio]furan
44	2-Methyl-3-oxa-8-thiabicyclo[3.3.0]octa-1,4-diene, i.e. kahweofuran
39	3,5-Dimethyl-1,2,4-trithiolane
36	1,3,5-Trithiane
59	1,2,3,5,6-Pentathiepane, i.e. lenthionine
60	1,2,3,4,5,6-Hexathiepane

sent at 1% and may form from hydrogen sulphide (Compound 1) and acetaldehyde (Schutte, 1974; Shu *et al.*, 1985), which may itself derive from 2-furaldehyde (Compound 18) (Petitjean *et al.*, 1981). 1,2,3,5,6-Pentathiepane, i.e. lenthionine (Compound 59), has previously been identified among the volatiles of sheep meat (Nixon *et al.*, 1979) and the *Shiitake* mushroom (Morita & Kobayashi, 1966; Chen & Ho, 1986).

1,1-Ethanedithiol and the tentatively identified methanedithiol are listed in Table 4. The former compound has been synthesized by reacting hydrogen sulphide (Compound 1) with acetaldehyde (Werkhoff *et al.*, 1989*b*). 1,1-Ethanedithiol may react with and without hydrogen sulphide to give 1,2,3,5,6-pentathiepane (Compound 59) and 3,5-dimethyl-1,2,4-trithiolane (Compound 39), respectively (Shu *et al.*, 1985; Zhang *et al.*, 1988). Methanedithiol (Compound 8) could oxidise to give 1,2,4,5-tetrathiane (Compound 52), identified in both the thiamine and xylose/thiamine isolates.

In addition to compounds identified only in the xylose/thiamine isolate, two compounds were identified at very different levels in the xylose/thiamine isolate compared to the that prepared from thiamine alone. The yield of 2-methyltetrahydrothiophen-3-one (Compound 28) in the mixture was only 0·25 of that in the thiamine isolate. In contrast, 2-methylfuran-3-thiol (Compound 21) accounted for 14% of the total xylose/thiamine isolate, but only 2% of that prepared from thiamine alone. This represents a 4–5-fold increase in absolute yield in the mixture. The compound has been reported to possess and aroma described as 'beef broth, roast beef' (MacLeod, 1986), and, together with the corresponding disulphide, has been shown to possess the highest aroma value in cooked beef (Gasser & Grosch, 1988). Its formation in much greater amounts in the presence of xylose suggests that, as well as deriving from thiamine alone, it could conceivably be formed from 4-hydroxy-5-methyl-3(2*H*)-furanone (HMFone) and hydrogen sulphide as immediate precursors, these two compounds being formed from xylose and thiamine, respectively. The formation of higher levels of 2-methylfuran-3-thiol in the xylose/thiamine isolate is no doubt partly responsible for the identification of certain bicyclic sulphur-containing furan derivatives, i.e. Compounds 62 and 63, in this system, as discussed above.

CONCLUSION

This study has resulted in the identification of 13 components as novel thermal degradation products of thiamine. They comprise two aliphatic hydroxyketones, nine thiophens and two alicyclic sulphur compounds. Several have been described in the literature as possessing meaty aromas, and they were frequently assigned meaty odour descriptions by GC–OPA. The incorporation of xylose in the model system resulted in the identification of 27 components which could not be detected in the isolates prepared from either xylose or thiamine. Sixteen are likely to be formed as a result of xylose—thiamine interactions and 15 of them contain sulphur. They comprise two alkanedithiols, two furans (one sulphur-substituted), four sulphur-containing bicyclic furan derivatives, four thiophens and four alicyclic sulphur compounds. The other main impact of incorporating xylose in the model system was a 4–5-fold increase in the quantity of the potent meaty odour compound, 2-methylfuran-3-thiol.

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