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Volatile reaction products from a heated xylose–lysine model system

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Aqueous solutions of xylose (1 molal) and lysine monohydrochloride (1 molal) were refluxed without pH control (initial pH 4·9) for 240 min by simultaneous steam distillation–solvent extraction using a modified Likens and Nickerson apparatus. The solvent extract was replaced by fresh solvent after 15, 30, 45, 60, 120 and 180 min refluxing and subsequently concentrated to give a series of volatile isolates. Isolates were analysed by gas chromatography (GC) and GC–mass spectrometry, and a total of 44 reaction products could be identified. 2-Furfural constituted over 99% (w/w) of the volatiles in each isolate. The most numerous reaction products were monocyclic furans (20 being identified), whereas only eight nitrogen-containing compounds were noted. Yields of total reaction products increased up to 120 min refluxing, and then decreased, but if 2-furfural is excluded from the calculations, yields of the remaining reaction products increased up to 180 min before decreasing. Individual classes of compounds also tended to follow this general rule, notable exceptions being the nitrogen-containing components. Monocyclic pyrroles, 2,3-dihydro-1*H*-pyrrolizines and pyridines were identified only after 45, 45 and 60 min refluxing, respectively, whereas yields of 1-(2-furfuryl)pyrroles increased throughout the heating period.

INTRODUCTION

The aroma of heat-processed foods, such as bread, other cereal products and roasted coffee, is largely due to the Maillard reaction. Various factors, notably the temperature and time of heating and the pH and moisture content of the system, affect the reaction. Some control over the final aroma of the system can thus be exerted by careful manipulation of these factors (Shu & Ho, 1989; Ames, 1990).

Total amounts of volatiles formed in Maillard model systems generally increase with time of heating, up to a certain value, usually about 4 h (Hayase & Kato, 1985; Hayase *et al.*, 1985; Kim *et al.*, 1988). This general rule also applies to certain other classes of compound, and Huang *et al.* (1989) established that levels of total pyrazines produced in a glucose–arginine system increased up to 1 h heating. When the time of heating is extended, yields of classes or of individual components exhibit maxima at specific times of heating, and then decrease. For example, yields of pyrazines from a glucose–ammonia system reached a maximum after 4 h, followed by a rapid decrease between 4 and 6 h and a further slight decrease between 6 and 48 h (Shibamoto & Bernhard, 1976). As far as individual reaction products are concerned, Tressl *et al.* (1986) showed that, on heating an arabinose–hydroxyproline model system, 4-hydroxy-5-methyl-3(2*H*)-furanone, 1-acetonylpyrrole and 2-(1-pyrrolyl)-2-cyclopenten-1-one all exhibited maximum yields between 2 and 4 h heating.

In contrast, other reaction products may be formed in increasing amounts over several days heating. 2-Furfural and 1-(2-furfuryl)pyrrole were formed in increasing amounts up to 48 h on heating an arabinose–hydroxyproline system at 100°C (Tressl *et al.*, 1986).

The purpose of this study was to continue and extend our previous work on the low molecular weight compounds (both volatile and non-volatile) formed in a xylose–lysine model system (Banks *et al.*, 1988; Apriyantono & Ames, 1990) and of relevance to a wide range of foods. The effect of pH on the volatile compounds formed and some data on the coloured components have already been reported (Ames *et al.*, 1993; Ames & Apriyantono, in press; Apriyantono & Ames, 1993).

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MATERIALS AND METHODS

Materials

D-(+)-Xylose (99+%, Gold Label) was obtained from Aldrich Chemical Company, Gillingham, UK, and L-lysine monohydrochloride (chromatographically homogenous), diethyl ether (AnalaR) and *n*-tetradecane were obtained from BDH Chemicals, Poole, UK.

Preparation of volatile isolates

Volatile extracts were prepared by refluxing solutions of xylose (0·5 mol) and lysine monohydrochloride (0·5 mol) in degassed distilled water (500 ml) which were refluxed for 240 min in a modified Likens and Nickerson apparatus (Maarse & Kepner, 1970), using diethyl ether (15 ml) as the extraction solvent. A series of volatile extracts was prepared by replacing the solvent extract with fresh solvent after 15, 30, 45, 60, 120 and 180 min refluxing.

Each solvent extract was concentrated to a volume of 0·5–1·0 ml using a Vigreux column under a reduced pressure of $8{\cdot}0 \times 10^3$ Nm^{-2} (60 mmHg). Concentration, to a final volume of 0·05 ml, was achieved using a gentle stream of nitrogen.

Blank isolates were prepared using only distilled water in the sample flask. All isolates were prepared in at least triplicate and were stored at −20°C before analysis.

Analysis of volatile isolates

Gas chromatography (GC)

Volatile isolates were analysed using a fused silica capillary column (25 m × 0·32 mm i.d.) coated with SE 52/54 (1 μm film thickness) (Thames Chromatography, Maidenhead, UK) installed in a Perkin Elmer Sigma 3B instrument (Perkin Elmer, Beaconsfield, UK). The conditions of analysis were: helium, 1·5 ml min^{-1}; temperature programme, 60°C for 5 min followed by a ramp rate of 3°C min^{-1} to a final temperature of 200°C, held for 20 min; injector temperature, 225°C; detector temperature, 250°C; injection volume, 1 μl; injection technique, Grob splitless.

Retention times and quantitative data were obtained from a Hewlett Packard 3390A integrator (Hewlett Packard, Wokingham, UK). Linear retention index (LRI) values for individual compounds were calculated based on data obtained for a series of standard alkanes. Individual components were quantified by the use of an internal standard (tetradecane). Quantitative data were obtained for all compounds using the concentrated isolates, apart from 2-furfural, for which data were obtained before concentration.

GC–mass spectrometry (GC–MS)

Components were identified using a Kratos MS 80 RFA mass spectrometer (Kratos Analytical, Manchester, UK) equipped with a Carlo Erba MFC 500 GC and a Kratos DS 90 data system. The MS conditions of analysis were: ionisation mode, electron impact; electron energy, 70 eV; ion source temperature, 200°C; separator temperature, 250°C; ionisation current, 100 μA; accelerating voltage, 4 kV; scan speed, 1 s per decade; mass range, 30–500; interscan time, 0·2 s; resolution, 1000. Components were identified by matching the mass spectra obtained with those available in the libraries of the MS data systems and by manual comparison with published spectra.

RESULTS AND DISCUSSION

The pH of the model system dropped from 4·9 (before heating) to 2·6 after heating for 240 min, followed by cooling. The drop in pH was greatest at the start of the experiment and a drop of about 0·6 of a unit occurred while the model system was heated to boiling point. This was followed by a further drop of about 0·6 of a unit during the first 15 min of refluxing. Drops in pH of about 0·3, 0·1 and 0·1 of a unit occurred over the time intervals 15–30, 30–45 and 45–60 min refluxing, respectively. From 60 to 240 min, the total drop in pH was only 0·1 of a unit; however, a pH drop from 3·1 to 2·6 was observed on cooling to room temperature. The model system changed colour from very pale yellow (before heating) through yellow and orange to brown (after the start of heating, but before refluxing began). A series of seven volatile isolates was prepared covering the refluxing periods 0–15, 15–30, 30–45, 45–60, 60–120, 120–180 and 180–240 min. The model system and all the volatile isolates prepared from it possessed aromas described as caramel, toffee and slightly buttery.

The experimental LRI values confirmed the general elution sequence, but were higher than those published in the literature for similar stationary phases, as a result of the effect of the immense 2-furfural peak. A total of 44 volatile compounds were identified in the solvent isolates, and are listed in Table 1, together with the yield at each time interval. The cumulative yields of classes of compounds are given in Table 2. Mass spectra were also obtained for 18 unidentified compounds, but only one was present in more than trace amounts.

The main difference between the isolates prepared over successive time intervals was in the total yield of volatiles produced, i.e. in the rate of total volatiles formation. The rate of total volatiles production increased with time up to 120 min, and then decreased between 120 and 240 min refluxing. However, if 2-furfural is disregarded, total yields of the remaining volatiles increased up to 180 min, and then decreased slightly between 180 and 240 min.

The lower rate of total volatiles formation after 120 min refluxing suggests that some of the volatile reaction products may have acted as precursors in further reactions, involving the formation of non-volatile reaction products.

The volatile components were dominated by 2-furfural,

Table 1. Volatile compounds identified from a xylose–lysine model system over successive time intervals

No.	Identity and MS reference[a,b]	Yield (nmol mol^{-1} xylose)[c] Time interval (min)						
		0–15	15–30	30–45	45–60	60–120	120–180	180–240
Aliphatic compounds								
1	Butanedione (1)	tr	tr	tr	tr	tr	tr	tr
2	Acetic acid (2)	—	tr	tr	tr	—	tr	tr
Total aliphatic compounds		tr	tr	tr	tr	tr	tr	tr
Alicyclic compounds								
3	2-Cyclohexen-1-ol* (2)	tr	6·2	14·2	14·2	11·2 × 10	23·9 × 10	18·6 × 10
4	Cyclopropylethyl ketone* (2)	tr	tr	tr	tr	tr	tr	tr
5	A methylcyclohexenone* (2)	—	—	—	—	tr	tr	tr
6	A methyl-1,2-cyclopentanedione* (2,3)	—	—	3·6	5·4	—	25·0	—
Total alicyclic compounds		tr	6·2	17·8	19·6	11·2 × 10	26·4 × 10	18·6 × 10
Benzene derivatives								
7	1,2,3-Trihydroxybenzene* (2)	21·4	—	—	—	—	—	—
8	2,5-Dihydroxyacetophenone* (2,3)	—	tr	tr	tr	32·8	36·8	40·8
9	2,5-Dimethoxyacetophenone* (2)	tr	—	—	—	—	—	—
Total benzene derivatives		21·4	tr	tr	tr	32·8	36·8	40·8
Monocyclic furans								
Type I furans								
10	2(5*H*)-Furanone (4)	tr	—	7·2	7·2	64·2	86·0 × 10	10·3 × 10^2
Type II furans								
11	2-Methylfuran (2)	tr	tr	tr	tr	tr	tr	tr
12	2-Furanmethanol (2)	—	—	—	—	—	tr	tr
13	2-Furfural (2)	98·0 × 10^3	74·2 × 10^4	14·1 × 10^5	21·6 × 10^5	96·8 × 10^5	79·6 × 10^5	72·6 × 10^5
14	2-Furoic acid (2,3)	—	tr	tr	tr	tr	tr	tr
Total Type II furans		98·0 × 10^3	74·2 × 10^4	14·1 × 10^5	21·6 × 10^5	96·8 × 10^5	79·6 × 10^5	72·6 × 10^5
Type III furans								
15	5-Methyl-2-furanmethanol (2)	—	—	—	—	tr	—	tr
16	5-Methyl-2-furfural (2)	—	12·2 × 10	38·0 × 10	68·4 × 10	37·8 × 10^2	52·4 × 10^2	56·6 × 10^2
17	A dimethyl-2-furfural (4)	tr	3·2	4·8	11·2	40·4	—	—
18	2-Acetylfuran (2)	tr	10·2 × 10	35·2 × 10	81·0 × 10	50·6 × 10^2	58·2 × 10^2	48·1 × 10^2
19	2-Propionylfuran (2)	—	3·2	13·0	17·8	54·8	59·6	95·2
20	1-(2-Furyl)-2-propanone (4)	—	6·4	32·2	22·6	47·2 × 10	72·2 × 10	10·3 × 10^2
21	1-(2-Furyl)-3-butanone (3,5)	—	53·6	92·8	29·2 × 10	96·6 × 10	97·2 × 10	76·8 × 10
22	*cis*-4-(2-Furyl)-3-buten-2-one* (4)	—	17·6	15·3 × 10	29·8 × 10	69·8 × 10	45·6 × 10	34·2 × 10
23	*trans*-4-(2-Furyl)-3-buten-2-one (2,4)	88·2	23·6	88·2	19·0 × 10	81·4 × 10	93·2 × 10	75·6 × 10
24	1-(2-Furyl)-1,2-propanedione (4,6)	—	20·2	20·2	71·0	21·6 × 10	27·6 × 10	18·0 × 10
25	1-(2-Furyl)-1,2-butanedione* (6)	—	tr	—	10·6	15·7 × 10	89·4	55·2
26	A furan (2,3) 123(100), *124*(93), 43(49), 69(40), 95(32), 39(16), 96(12)	—	—	tr	tr	tr	tr	tr
27	A furan (2,3) 109(100), 110(15), *152*(13)	tr	tr	—	—	—	—	—
28	A furan (2,3) 81(100), 43(79), *152*(66), 82(37), 53(30), 95(12)	—	3·9	—	6·6	—	26·4	—
29	A furan (2,3) 81(100), 43(34), 39(18), 53(15), 123(15), *166*(14)	tr	—	—	tr	—	tr	tr
Total Type III furans		88·1	35·6 × 10	11·4 × 10^2	24·2 × 10^2	12·3 × 10^3	14·6 × 10^3	13·8 × 10^3
Total monocyclic furans		98·0 × 10^3	74·2 × 10^4	14·1 × 10^5	21·6 × 10^5	96·9 × 10^5	79·7 × 10^5	72·7 × 10^5
Dimeric furans								
30	2,2'-Bifuran (2)	—	18·0	44·8	88·0	36·9 × 10	39·3 × 10	33·7 × 10
31	2,2'-Difurylmethane (2,3,6)	—	—	—	10·8	40·6	47·2	69·0
32	2,2'-Difurylethane (2,3)	—	—	—	tr	tr	15·1 × 10	11·5 × 10
33	*cis*-2,2'-Difurylethylene (2,3)	tr	35·0	72·6	98·8	34·6 × 10	32·4 × 10	23·6 × 10
34	5-(2-Furfuryl)-2-furfural* (2,3,5)	—	—	—	8·0	tr	—	tr
35	2-Furfurylidene-4-hydroxy-5-methyl-3(2*H*)-furanone (7, 8)	—	—	—	—	tr	tr	tr
Total dimeric furans		tr	53·0	11·7 × 10	20·6 × 10	75·6 × 10	91·5 × 10	75·7 × 10

(Continued)

Table 1—*Contd.*

No.	Identity and MS reference[a,b]	Yield (nmol mol^{-1} xylose)[c] Time interval (min)						
		0–15	15–30	30–45	45–60	60–120	120–180	180–240
	Benzofurans							
36	5-Methoxy-6,7-dimethylbenzofuran* (2)	—	—	—	13·6	—	70·4	10·5 × 10
	Monocyclic pyrroles							
37	2-Pyrrolaldehyde (2)	—	—	—	tr	tr	tr	tr
	1-(2-Furfuryl)pyrroles							
38	1-(2-Furfuryl)pyrrole* (2,6)	—	—	—	—	94·0	55·8	80·2
39	1-(2-Furfuryl)-2-pyrrolaldehyde (4,6)	—	9·2	30·8	88·0	65·9 × 10	14·4 × 10^2	17·5 × 10^2
	Total 1-(2-furfuryl)pyrroles	—	9·2	30·8	88·0	75·3 × 10	15·0 × 10^2	18·3 × 10^2
	Pyridines							
40	1-Acetyl-1,2,3,4-tetrahydropyridine (2)	—	—	—	—	tr	tr	tr
	Pyrazines							
41	A propenylpyrazine (9)	tr	8·4	—	—	—	—	—
	*2,3-Dihydro-1*H*-pyrrolizines*							
42	5-Formyl-6-methyl-2,3-dihydro-1*H*-pyrrolizine* (10)	—	—	—	—	tr	—	tr
43	5-Acetyl-7-methyl-2,3-dihydro-1*H*-pyrrolizine* (10)	—	—	—	8·6	tr	43·0	tr
44	5-Propionyl-7-methyl-2,3-dihydro-1*H*-pyrrolizine* (10)	—	—	—	—	—	tr	tr
	Total pyrrolizines	—	—	—	8·6	tr	43·0	tr
	Unknowns	23·6	19·8	29·8	31·0	32·9 × 10	51·4 × 10	48·6 × 10
	Grand total	98·1 × 10^3	74·2 × 10^4	14·1 × 10^5	21·6 × 10^5	96·9 × 10^5	79·7 × 10^5	72·7 × 10^5

[a] Identifications were based on the mass spectral data.

* Tentatively identified components.

Sources of literature MS data were as follows: (1) Bondarovich *et al.* (1967); (2) Heller & Milne (1978); (3) Anon. (1983); (4) Baltes & Bochmann (1987*a*); (5) Ferretti & Flanagan (1971); (6) Stoll *et al.* (1967); (7) Ledl & Severin (1978); (8) O'Reilly (1982); (9) Baltes & Bochmann (1987*b*); (10) Tressl *et al.* (1985),

[b] The mass spectral data of the partially identified furans are given in order of decreasing intensity of peaks as m/z (relative intensity).

[c] The yields quoted are the means obtained from two runs. The precision was ±16% and was obtained from the means of the standard deviations of the values obtained from each run. Yields of less than 2 nmol mol^{-1} xylose are quoted as tr (trace). —, Compound not detected in this isolate.

which accounted for more than 99% of the total volatiles of each isolate. In terms of numbers, monocyclic furans were the most important, and only eight nitrogen-containing compounds were identified in this study.

The total yield of monocyclic furans increased over successive time intervals up to 120 min, and then decreased, but if 2-furfural is excluded from the calculations, the yield increased up to 180 min refluxing. The amounts of 2-furfural formed increased up to 120 min and then decreased, paralleling the formation of total volatiles. 2-Furfural may act as a precursor in subsequent reactions by condensing with, e.g. propanone (Baltes & Mevissen, 1988) to give *cis*- and *trans*-4-(2-furyl)-3-buten-2-one (Compounds **22** and **23**), or with 4-hydroxy-5-methyl-3(2*H*)-furanone (Severin & Krönig, 1972) to give 2-furfurylidene-4-hydroxy-5-methyl-3(2*H*)-furanone (Compound **35**). It may also act as a precursor of other volatile compounds (Shibamoto, 1977; Silwar & Tressl, 1989), including 5-methyl-2-furfural (Compound **16**) and 2-acetylfuran (Compound **18**). In addition, 2-furfural is a precursor of certain non-volatile Maillard reaction products (Ames, 1992; Ames *et al.*, 1993).

The monocyclic furans may be classified according to the number of carbon atoms they possess, relative to the sugar. Type I, Type II and Type III furans contain fewer, the same number as, and more carbon atoms than the initial sugar, respectively (Apriyantono, 1992; Ames & Apriyantono, in press; Apriyantono & Ames, 1993). Based on this classification, only one Type I furan, i.e. 2(5*H*)-furanone, was identified, and its yield increased with time over the entire experiment. Four Type II furans were formed, i.e. 2-methylfuran, 2-furfural, 2-furanmethanol and 2-furoic acid. Apart from 2-furfural, they were present in only trace amounts.

In general, yields of Type III furans increased in successive isolates up to 180 min refluxing, and then

Table 2. Cumulative yields of classes of compounds identified from a xylose–lysine model system

Class of compound	Yield (nmol mol^{-1} xylose)[a] Time interval (min)						
	0–15	15–30	30–45	45–60	60–120	120–180	180–240
Aliphatic compounds	tr	tr	tr	tr	tr	tr	tr
Alicyclic compounds	tr	6·2	24·0	43·6	15·6 × 10	42·0 × 10	60·6 × 10
Benzene derivatives	42·8	42·8	42·8	42·8	75·6	11·2 × 10	15·3 × 10
Monocyclic furans	$98{\cdot}0 \times 10^3$	$84{\cdot}0 \times 10^4$	$22{\cdot}6 \times 10^5$	$44{\cdot}2 \times 10^5$	$14{\cdot}1 \times 10^6$	$22{\cdot}1 \times 10^6$	$29{\cdot}4 \times 10^6$
Monocyclic furans, excluding 2-furfural	88·2	44·4 × 10	$15{\cdot}8 \times 10^2$	$40{\cdot}0 \times 10^2$	$16{\cdot}3 \times 10^3$	$31{\cdot}8 \times 10^3$	$46{\cdot}5 \times 10^3$
Dimeric furans	tr	53·0	17·0 × 10	37·6 × 10	$11{\cdot}3 \times 10^2$	$20{\cdot}4 \times 10^2$	$28{\cdot}0 \times 10^2$
Benzofurans	—	—	—	13·6	—	70·4	10·5 × 10
Monocyclic pyrroles	23·6	43·4	73·2	10·4 × 10	43·4 × 10	94·8 × 10	$14{\cdot}3 \times 10^2$
1-(2-Furfuryl)pyrroles	—	9·2	30·8	88·0	75·4 × 10	$15{\cdot}0 \times 10^2$	$18{\cdot}3 \times 10^3$
Pyridines	—	—	—	—	tr	tr	tr
Pyrazines	tr	8·4	8·4	8·4	8·4	8·4	8·4
2,3-Dihydro-1*H*-pyrrolizines	—	—	—	8·6	8·6	51·6	51·6
Unknowns	23·6	43·4	73·2	10·4 × 10	43·4 × 10	94·8 × 10	$14{\cdot}3 \times 10^2$
Total volatiles	$98{\cdot}1 \times 10^3$	$84{\cdot}0 \times 10^4$	$22{\cdot}6 \times 10^5$	$44{\cdot}2 \times 10^5$	$14{\cdot}1 \times 10^6$	$22{\cdot}1 \times 10^6$	$29{\cdot}4 \times 10^6$
Total volatiles, excluding 2-furfural	15·5 × 10	60·8 × 10	$19{\cdot}5 \times 10^2$	$47{\cdot}4 \times 10^2$	$19{\cdot}0 \times 10^3$	$37{\cdot}8 \times 10^3$	$56{\cdot}0 \times 10^3$

[a] See Table 1, footnote c.

decreased (see Table 1). There were, however, some exceptions to this rule: e.g. 5-methyl-2-furfural, 1-(2-furyl)-2-propanone and 2-propionylfuran were formed in increasing amounts throughout the experiment, and a dimethyl-2-furfural, *cis*-4-(2-furyl)-3-buten-2-one and 1-(2-furyl)-1,2-butanedione were formed in increasing amounts up to 120 min, and then in decreasing amounts between 120 and 240 min. The formation of Type III furans has been discussed previously (Ames & Apriyantono, in press; Apriyantono & Ames, 1993), and may involve the reaction of sugar fragmentation products, or the reaction of furans formed directly from the sugar with sugar fragmentation products, or fragmentation of melanoidins.

Total yields of dimeric furans increased up to 180 min refluxing, and then decreased. Several of these compounds were only identified in the isolates produced on refluxing for more than 45 min. It appears that the formation of dimeric furans depends on the presence of compounds formed at earlier stages of the reaction, such as monocyclic furans (Ferretti *et al.*, 1970). An example of this is the formation of 2-furfurylidene-4-hydroxy-5-methyl-3(2*H*)-furanone from 2-furfural and 4-hydroxy-5-methyl-3(2*H*)-furanone. Although this latter compound was not identified in this study, the (presumably) small amounts formed at the low pH of the model system are probably quickly exhausted in subsequent reactions. 2-Furfurylidene-4-hydroxy-5-methyl-3(2*H*)-furanone is of interest as it is coloured (Severin & Krönig, 1972; O'Reilly, 1982.

2,3-Dihydro-1*H*-pyrrolizines were tentatively identified after 45 min refluxing (see Table 1). This study is the first to report the identification of 2,3-dihydro-1*H*-pyrrolizines in a model system containing an amino acid other than proline, serine or threonine (Apriyantono & Ames, 1990, 1993; Ames & Apriyantono, in press). The formation of these compounds in this xylose–lysine model system has been discussed previously (Ames & Apriyantono, in press; Apriyantono & Ames, 1993).

1-(2-Furfuryl)pyrrole and 1-(2-furfuryl)-2-pyrrolaldehyde were both identified in increasing amounts in each isolate prepared over successive time intervals. A similar result was obtained by Tressl *et al.* (1986), who observed that, on heating arabinose with hydroxyproline at 100°C, 1-(2-furfuryl)pyrrole production increased with time up to 48 h. This suggests that these compounds could be end-products of the Maillard reaction.

Three benzene derivatives were tentatively identified (see Table 1). 1,2,3-Trihydroxybenzene and 2,5-dimethoxyacetophenone were identified only in the 0–15 min isolate, whereas 2,5-dihydroxyacetophenone was identified only after 15 min refluxing. Phenolic compounds, especially hydroxybenzenes and hydroxyacetophenones, have been identified on heating sugars with and without amino acids (Popoff & Theander, 1972; Forsskahl *et al.*, 1976; Olsson *et al.*, 1977, 1978). The formation of benzene derivatives increases when the pH of aqueous xylose solutions increases above 4·5 (Popoff & Theander, 1972; Forsskahl *et al.*, 1976), and so the presence of benzene derivatives in the 0–15 min isolate was expected.

The two aliphatic compounds identified, i.e. butanedione and acetic acid, are well-known sugar degradation products. Each alicyclic compound identified possesses more than five carbon atoms, and therefore they could arise from fragmentation of xylose followed by recombination of the fragmentation products. Although sugar fragmentation is favoured by increasing pH, some of these compounds were identified in each isolate, it seems that fragmentation of the xylose took place throughout the experiment. One benzofuran, one monocyclic pyrrole, one pyridine and one pyrazine were also identified in this study.

CONCLUSION

This study reveals the varying profile of volatile reaction products formed over successive time intervals in a xylose–lysine model system. Each isolate was dominated by 2-furfural, which accounted for more than 99% of the total volatiles. In terms of numbers, monocyclic furans were the most important reaction products, 20 representatives being identified. Six dimeric furans were also recognised in this study. In contrast, only eight nitrogen-containing compounds are reported. Yields of total volatiles increased up to 120 min, and then decreased, but if 2-furfural is disregarded, total yields of volatiles increased up to 180 min before decreasing. Classes of nitrogen-containing components tended not to follow this general rule. Monocyclic pyrroles and pyridines were detected only after 45 min and 60 min, respectively, whereas pyrazines were not detected after 45 min. Amounts of 1-(2-furfuryl)pyrroles increased from 0 to 240 min. This study is the first to report 2,3-dihydro-1*H*-pyrrolizines from a model system using lysine as the only amino acid, and three representatives were tentatively identified after 45 min refluxing.

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