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Kinetics and thermal degradation of the fructose–methionine Amadori intermediates. GC–MS/SPECMA data bank identification of volatile aroma compounds *

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ABSTRACT

Fructose-methionine Amadori intermediates, prepared from D-glucose and L-methionine, were purified by semi-preparative HPLC. Structural elucidation was achieved by ^{13}C-NMR and mass spectrometry in the FAB^+ and FAB^- modes. Constant rates of formation of glucosylamine and the Amadori intermediate, and their thermal degradation into reductones and methionine as well as into diglucosylamine, were observed. Thermal degradation of the Amadori intermediate gives not only the well-known degradation products of the sugar moiety and methional (from the Strecker degradation of methionine), but also several heterocyclic compounds (pyridines, pyrazines, pyrroles, and furans). Some of them contain a methylthiopropyl group in their side chain. These new compounds were identified by the fragmentation rules and the Kováts index additive properties. Out of the 80 compounds isolated, ~ 70 were identified.

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INTRODUCTION

Amadori intermediates resulting from the condensation of reducing sugars with α-amino acids[1–3] are the key compounds in the Maillard reaction[4], whose historical and various other aspects have been recently reviewed by several authors[5–7]. Thermal decomposition of Amadori intermediates produces a large number of volatile compounds responsible for the flavor of all processed foods[8]. Furthermore, polymerization reactions between aldimines, ketimines, and carbonyl compounds give rise to brown pigments (melanoidins) that are suspected carcinogens.

Although several papers have been devoted to the thermal degradation of Amadori intermediates[9–14], nothing is known about the behavior of the fructose–methionine Amadori intermediate and no kinetic data on its formation are available. Thus, an investigation of the various aspects of this reaction seems of interest.

RESULTS AND DISCUSSION

Structural elucidation of the Amadori intermediate.—The structure of the fructose–methionine amadori intermediate was confirmed by mass spectrometry using the FAB^+ and FAB^- modes (see Fig. 1). A proposed pathway for the fragmentation is given in Scheme 1.

The ^{13}C-NMR spectrum of the fructose–methionine intermediate is presented in Fig. 2, with the chemical shifts given in Table I. As previously reported by Moll et al.[19], these intermediates exist mainly in the β-pyranose form ($\sim 70\%$) but the α- and β-furanose forms are present as well. Also, our SPECMA data bank of mass spectra was used for positive identification (see below)[14].

Kinetics.—The use of a general-purpose, nonlinear regression program, adapted by one of us (J.L.L.) for the simulation of macroscopic kinetics, allows us to consider different experimental data. In the first step, on the basis of the data input (time and concentration), using the Runge–Kutta method, the program determines the calculated concentrations. The second step involves computation of the rate constants corresponding to each step of the suggested reaction scheme. Using these data, the program simulates the reaction and determines the residues by comparing calculated concentrations with those obtained experimentally. To minimize these residues, a subprogram optimizes the rate-constant values.

We have studied the concentration changes of glucose, methionine, and the Amadori intermediate for four glucose:methionine ratios (4:1, 2:1, 1:1, and 1:2). For each ratio, the statistical confidence range of the concentration for each compound at the point corresponding to the average value has been determined. For glucose, it varies from ± 3.38 to $\pm 4.07\%$, for methionine from ± 2.11 to 3.20%, and for the Amadori intermediate from ± 2.26 to $\pm 4.48\%$.

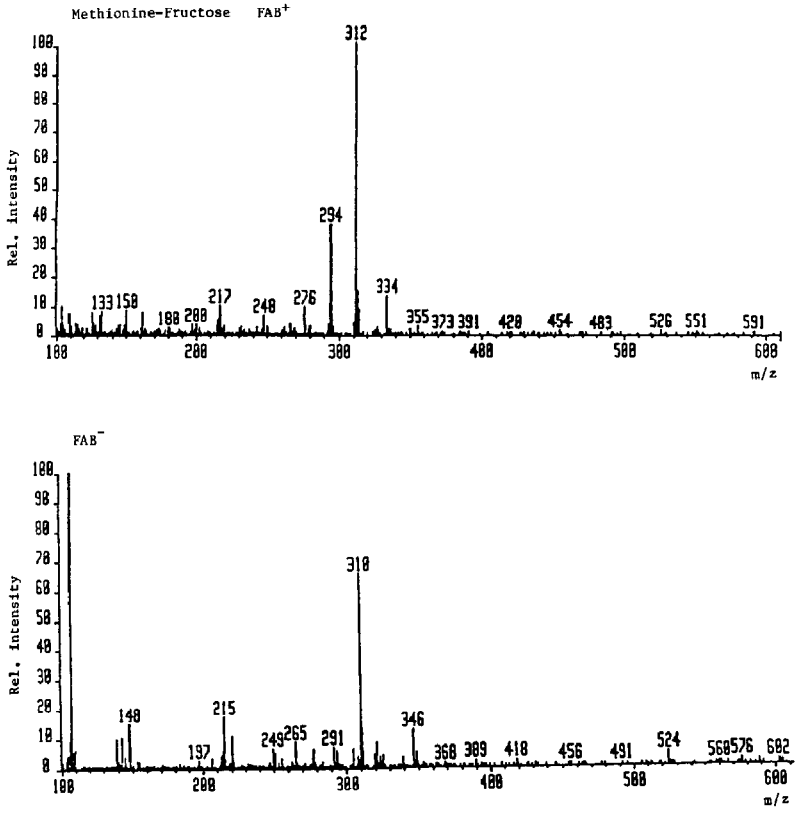


Fig. 1. Mass spectra of the fructose–methionine Amadori intermediate using the FAB^+ and FAB^- modes.

Several reaction schemes have been suggested[20]. Some of them call for a Schiff-base intermediate in the formation of the Amadori compound from the glucosylamine. However, this step is so rapid that the corresponding product has never been isolated. Because of this, the foregoing step has not been taken into account in the determination of the rate constants (see Scheme 2).

These results may be compared with those obtained elsewhere for the condensation of glucose with valine[21,22]. As with valine, glucose disappears faster than methionine. The rate constant for the first step leading to the formation of the glucosylamine is lower than the rate found for valine ($k_1 = 0.084\ mol^{-1} \cdot L \cdot min^{-1}$), implying a slower reaction. On the other hand, transformation of the glucosylamine into the Amadori intermediate is higher than in the case of valine ($k_2 = 2.1\ min^{-1}$). The thermal degradation of the Amadori intermediate into methionine and reductones is slower than with valine ($k_4 = 1.5\ min^{-1}$) and the rate constant corresponding to the formation of diglucosylamine is higher than for valine ($k_3 = 0.07\ mol^{-1} \cdot L \cdot min^{-1}$).

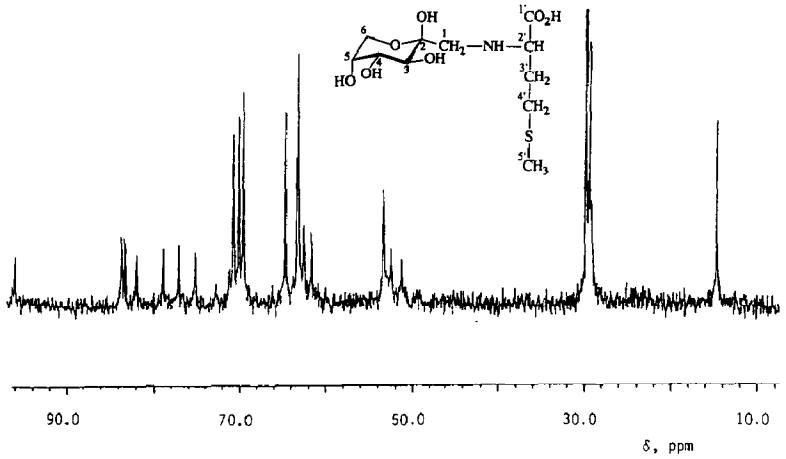
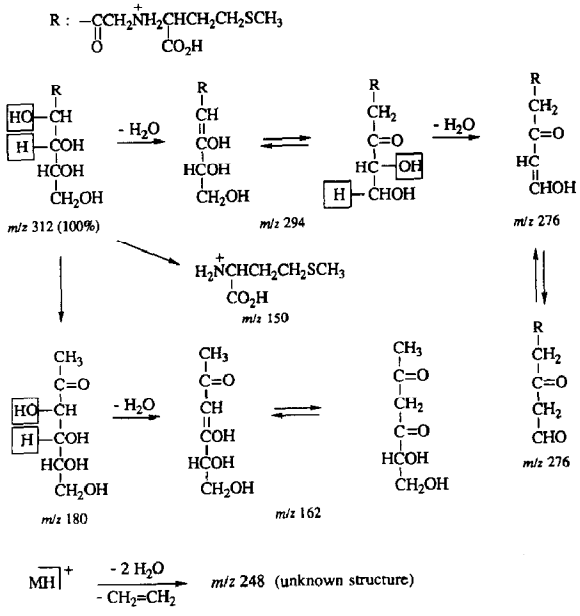


Fig. 2. ^{13}C-NMR spectrum (D_2O) at 220 MHz (Varian FT 80A) of the fructose–methionine intermediate. Chemical shifts for the various forms are given in Table I.

For each glucose:methionine ratio, the disappearance graphs for the starting materials and the appearance graph for the Amadori intermediate have been plotted. In Scheme 3, the curves for the 2:1 ratio are shown as an example. For two ratios (1:1 and 2:1) the variations are well distributed between glucose and methionine. However, for the 1:2 and 4:1 ratios, while the variations are well



Scheme 1. A hypothetical pathway for the formation of the main fragments arising from the mass-spectrometric fragmentation (FAB^+) of the fructose–methionine intermediate.

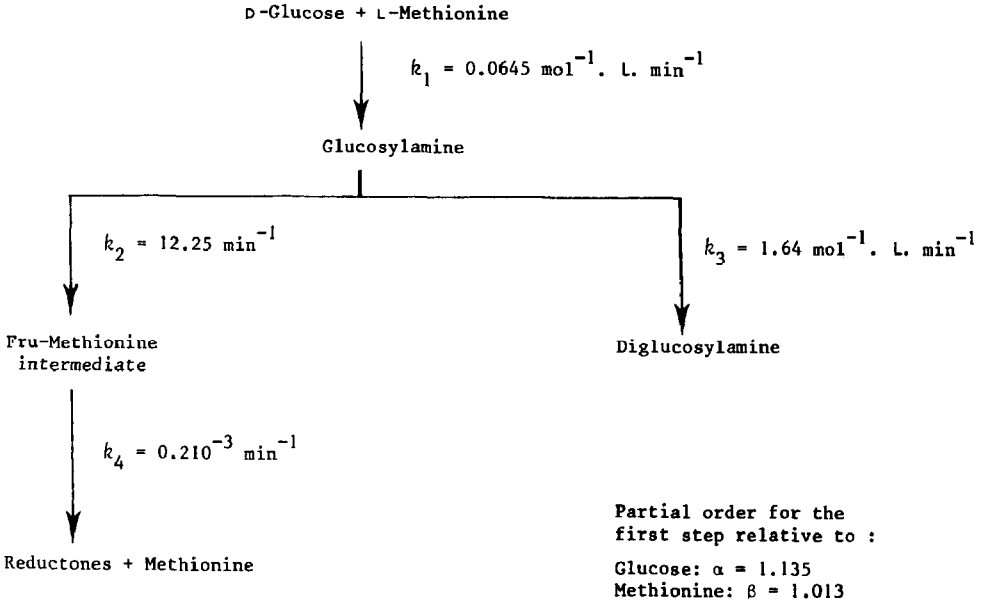
TABLE I

Chemical shifts for the various forms of the fructose–methionine intermediate

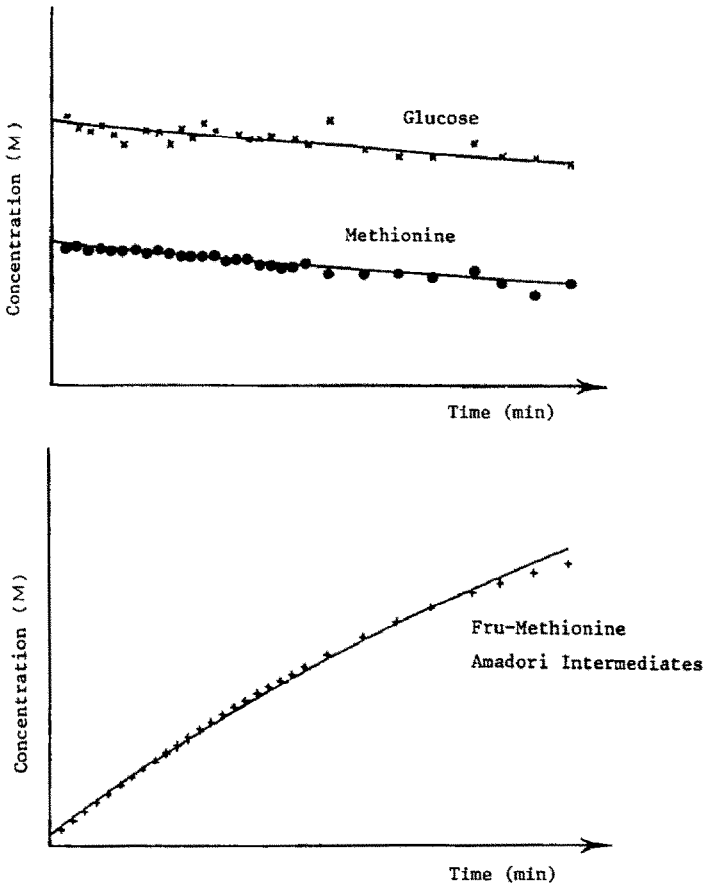
Fructose		Configuration	Methionine	
δ (ppm/Me_4Si)	Atom		δ (ppm/Me_4Si)	Atom
53.13	C-1	$\beta p, \alpha f, \beta f$	172.83	C-1′
52.32				
51.06				
95.71	C-2	βp	62.76	C-2′
			62.24	
70.46	C-3	$\beta p, \beta f, \alpha f$	29.67	C-3′
78.54				
82.99				
69.84	C-4	$\beta p, \beta f, \alpha f$	29.24	C-4′
74.87			14.57	C-5′
76.81				
69.32	C-5	$\beta p, \beta f$		
81.36				
64.31	C-6	βp		

distributed for methionine, in the case of glucose they range from 1.86% for the 4:1 ratio up to 3.14% for the 1:2 ratio.

Thermal degradation of the fructose-methionine intermediate.—The reconstructed total-ion chromatogram of the products resulting from the thermal degra-



Scheme 2. Rate constants for the reaction of D-glucose with L-methionine.



Scheme 3. Disappearance graphs for glucose and methionine and the appearance graph for the fructose–methionine Amadori intermediate.

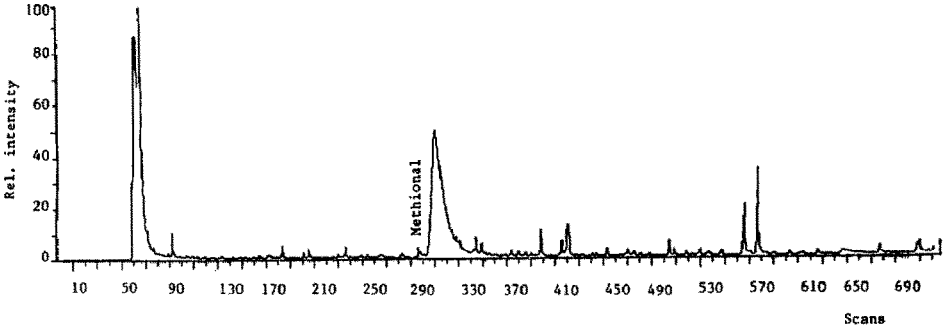


Fig. 3. Reconstructed total-ion chromatogram of the products resulting from the thermal degradation of the fructose–methionine Amadori intermediate at 260 ±5° (Ribermag R10-10, Carbowax 20M column).

dation of the Amadori intermediate at 260° is shown in Fig. 3. The major compound formed in this reaction, accounting for 70% of the reaction mixture, is methional. However, mass spectra of 82 minor compounds have also been recorded and almost 70 of them have been identified.

Identification of the compounds was accomplished by library searches using the NERMAG data bank and our own SPECMA data bank of mass spectra[15–17]. The Kováts indices were computed from the mass spectra scans using a laboratory program written in BASIC[18]. For the unknown compounds, the identification was based upon fragmentation rules and a comparison of the experimental Kováts indices with those calculated using the additivity increments. A detailed description of the use of the computer data bank for identification of flavor heterocycles can be found in our previous papers[14].

These minor products are formed mainly from three sources. The majority of heterocyclic compounds (pyridines, pyrazines, pyrroles, and furans) arise from the degradation of the sugar moiety in the presence or in the absence of ammonia. The second source includes compounds from the amino acid moiety and leads to sulfur-containing aliphatic, alicyclic, and heterocyclic compounds. Finally, the third source are the compounds obtained by recombination of the reactive products generated in the foregoing two cases.

The majority of the aliphatic compounds (compare Table II) contains the (methylthio)methyl group arising from methional. 1-Hydroxy-2-propanone, a well-known product of the retroaldolization of rearranged sugars (as well as acetoin), has also been identified. Acetic acid and propanoic acid are produced either from the hydrolytic cleavage of rearranged sugars, or by oxidation of the corresponding aldehydes. Four alicyclic compounds (see Table II) were also found, with their structures tentatively identified as methylcyclopentenes (mol wt 114 and 128). Cyclotene (2-hydroxy-3-methyl-2-cyclopenten-1-one) is a well-known dimerization product of 1-hydroxy-2-propanone ("hydroxyacetone").

Among the pyran derivatives (see Table III), an α,β-unsaturated 1,5-lactone (mol wt 112) characterized by a base peak at m/z 97 has been found. Maltol and hydroxymaltol derivatives arise from the thermal degradation of rearranged sugars and are always found among products of this kind of reaction.

The furan derivatives, along with pyrazines, constitute the two main categories of products. Most of the furans reported in Table III are well known. Among them, 2-acetylfuran, 5-methylfurfural, furfuryl alcohol, β-angelica lactone, furoic acid, and furaneol (2,5-dimethyl-3-hydroxy-2,3-dihydro-3-furanone) were easily identified. Four new derivatives containing the (methylthio)methyl group result from the condensation of methional with carbonyl compounds followed by nucleophilic heterocyclization.

The first nine pyrazines reported in Table IV are formed from α-aminoketones resulting from the Strecker degradation of α-amino acids in the presence of α-diketones. The mechanism of formation of the newly identified pyrazines is discussed later in this paper.

TABLE II

Aliphatic and alicyclic compounds identified in the thermal degradation of the fructose–methionine intermediate

Scan	Compound	Formula (mol wt)	KIP [a]	Base peak; main fragments
	Aliphatic compounds			
92	Dimethyl disulfide	$C_2H_6S_2$ (94)	1160	94;79,45,46
104	A pentanethiol (?)	$C_5H_{12}S$ (104)	1180	29;57,104
109	3,4-Hexanedione	$C_6H_{10}O_2$ (114)	1183	29;57
183	1-Hydroxy-2-propanone	$C_3H_6O_2$ (74)	1272	43;31,74
226	Vinyl butanoate	$C_6H_{10}O_2$ (114)	1323	43;71,27,86
230	3-Hydroxy-2-pentanone	$C_5H_{10}O_2$ (102)	1330	43;59,31,101
297	Acetic acid	$C_2H_4O_2$ (60)	1410	43;45,60
313	Methional [b]	C_4H_8OS (104)	1425	48;104,47,76
374	4-(Methylthio)-2-butanone [b]	$C_5H_{10}OS$ (118)	1500	43;71,118,75,61
381	Propanoic acid	$C_3H_6O_2$ (74)	1510	29;27,74,73
386	A sulfur-containing compd. [b]	$C_6H_{10}OS$ (130)	1513	57;43,29
390	Two isomers (?)	$C_6H_{10}O_3$ (130)	1518	43;57,29
420	1,3-Bis(methylthio)propane [b]	$C_5H_{12}S_2$ (136)	1554	73;61,96,136
428	A mixture	$C_6H_{12}OS$ (132)	1563	43;95,131,132
453	(*Z*)-1,3-Bis(methylthio)propene [b]	$C_5H_{10}S_2$ (134)	1593	87;45,134
471	A methyl ester (?)	$C_4H_8O_2S$ (132)	1615	74;43,132,61
481	3-(Methylthio)propyl acetate [b]	$C_6H_{12}O_2S$ (148)	1625	43;73,88,61
488	Methyl 4-(methylthio)butanoate [b]	$C_6H_{12}O_2S$ (148)	1636	74;75,148
504	(*E*)-1,3-Bis-(methylthio)propene [b]	$C_5H_{10}S_2$ (134)	1654	87;45,134
566	3-(Methylthio)-1-propanol [b]	$C_4H_{10}OS$ (106)	1725	61;106,31
1066	3-(Methylthio)propanoic acid [b]	$C_4H_8O_2S$ (120)	2320	61;120,45
	Alicyclic compounds			
172	x-(Methylthio)cyclopentene [b](?)	$C_6H_{10}S$ (114)	1260	67;41,39
			1267	67;41,39
241	x,y-Bis-(methylthio)cyclopentenes [b] (2 isomers)	$C_7H_{12}S$ (128)	1340	128;113,85
677	2-Hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene)	$C_6H_8O_2$ (112)	1830	112;55,69,41,27

[a] Kováts index (polar column). [b]Contains a (methylthio)methyl group.

Some pyridine and pyrrole derivatives (Table V) were also identified and, unless stated differently, they are the common thermal degradation products of the Amadori intermediate.

We stress here that, although the results obtained using our thermal degradation set-up are not very quantitative, their qualitative importance is undisputable and the products identified in the work are definitely formed in the indicated temperature-range.

Mechanisms.—The Strecker degradation of methionine consists of several different steps. The first step involves the decarboxylation of methionine leading to the corresponding (methylthio)propylamine. Although this compound was not found in the reaction mixture, its formation is highly probable because it constitutes the major product of the thermal degradation of methionine, carried out

TABLE III

Pyran and furan derivatives identified in the thermal degradation of the fructose–methionine intermediate

Scan	Compound	Formula (mol wt)	KIP [a]	Base peak; main fragments
	Pyran derivatives			
445	6-Methyl-3,4-dihydropyran-2-one	$C_6H_8O_2$ (112)	1585	97;41,43,39,112
874	5-Hydroxy-6-methyl-2,3-dihydropyran-4-one (2,3-dihydromaltol)	$C_6H_8O_3$ (128)	2090	43;128,57,29,85
1048	3-Hydroxy-2,3-dihydromaltol	$C_6H_{10}O_4$ (144)	2300	43;44,144,101
	Furan derivatives			
133	2,4-Dimethyltetrahydrofuran	$C_6H_{12}O$ (100)	1210	85;43,68,55
283	5-Methyl-2(3*H*)-furanone	$C_5H_6O_2$ (98)	1390	55;98,43
331	2-(Methylthio)methylfuran [b]	C_6H_8OS (128)	1450	81;53,128
344	3-(Methylthio)methylfuran [b]	C_6H_8OS (128)	1463	81;53,128
350	2-Acetylfuran	$C_6H_6O_2$ (110)	1470	95;110,53
400	2-(Methylthio)methyl-4-methylfuran [b]	$C_7H_{10}OS$ (142)	1530	95;142,43
415	5-Methylfurfural	$C_6H_6O_2$ (110)	1550	110;109,53,81
510	Furfuryl alcohol	$C_5H_6O_2$ (98)	1660	39;41,98,97,81
518	5-Methyl-2(5*H*)-furanone (β-angelica lactone)	$C_5H_6O_2$ (98)	1673	55;43,83,98
577	Furoic acid	$C_5H_4O_3$ (112)	1740	95;112,43
707	Furaneol	$C_6H_8O_3$ (128)	1895	43;128,44
1002	2,x-Bis(methylthio)methylfuran [b]	$C_7H_{12}O_2S$ (188)	2246	141;94,188

[a] Kováts index (polar column). [b] Contains a (methylthio)methyl group.

under the same conditions as for the Amadori intermediate. Condensation of this amine with an α-diketone gives rise to a ketimine which, upon rearrangement, affords an imine and an enediol in equilibrium with an acyloin. The imine is hydrolyzed into methional which is then thermally decomposed into methanethiol and acrolein. While methanethiol is oxidized to dimethyl disulfide, the reaction of

TABLE IV

Pyrazine derivatives identified in the thermal degradation of the fructose–methionine intermediate

Scan	Compound	Formula (mol wt)	KIP [a]	Base peak; main fragments
164	2-Methylpyrazine	$C_5H_6N_2$ (94)	1250	94;67,39,26
201	2,5-Dimethylpyrazine	$C_6H_8N_2$ (108)	1293	42;39,108
205	2,6-Dimethylpyrazine	$C_6H_8N_2$ (108)	1300	42;108,39
217	2,3-Dimethylpyrazine	$C_6H_8N_2$ (108)	1312	67;108
249	2-Ethyl-6-methylpyrazine	$C_7H_{10}N_2$ (122)	1350	121;122
254	2-Ethyl-5-methylpyrazine	$C_7H_{10}N_2$ (122)	1356	121;122
266	2,3,6-Trimethylpyrazine	$C_8H_{12}N_2$ (136)	1370	42;122
523	5-Methyl-2,3-(α-methyltrimethylene)pyrazine	$C_9H_{12}N_2$ (148)	1676	133;148,147
536	3-Acetyl-2-methylpyrazine	$C_7H_8N_2O$ (136)	1692	43;136,94,93
845	2-(Methylthio)methyl-3,5,6-trimethylpyrazine [b]	$C_8H_{14}N_2S$ (182)	2060	61;135,182
922	2-(Methylthio)ethyl-3,x-dimethylpyrazine	$C_8H_{14}N_2S$ (182)	2150	61;135,82
1013	2,3-Dimethyl-6-(3-methylthio)propylpyrazine [b]	$C_9H_{16}N_2S$ (196)	2260	122;135,196

[a] Kováts index (polar column). [b] Contains a (methylthio)methyl group.

TABLE V

Pyridine and pyrrole derivatives identified in the thermal degradation of the fructose–methionine intermediate

Scan	Compound	Formula (mol wt)	KIP [a]	Base peak; main fragments
	Pyridine derivatives			
179	2-Ethylpyridine (?)	C_7H_9N (107)	1267	A mixture
441	2-Acetylpyridine	C_7H_7NO (121)	1580	79;78,121,43
475	x-Acetoxypyridine	$C_7H_7NO_2$ (137)	1620	43;137
786	2-(Methylthio)methylpyridine [b]	C_7H_9NS (139)	1990	92;139
889	x-Methyl-2-(methylthio)methylpyridine [b]	$C_8H_{11}NS$ (153)	2110	106;153,77,79
	Pyrrole derivatives			
109	1-Methylpyrrole	C_5H_7N (81)	1180	81;80,39,42
571	1-Methyl-2-acetylpyrrole	C_7H_9NO (123)	1735	80;27,123
752	1-(Methylthio)propylpyrrole [b]	$C_8H_{13}NS$ (155)	1950	80;81,155
810	2-Acetylpyrrole	C_6H_7NO (109)	2020	94;109,66
922	5-Methylpyrrole-1-carboxaldehyde	C_6H_7NO (109)	2100	109;108,80,53

[a] Kováts index (polar column). [b] Contains a (methylthio)methyl group — uncommon during thermal degradation.

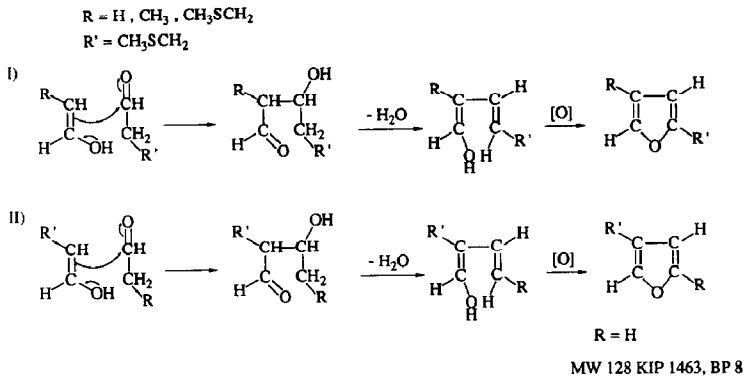
ammonia with acyloin gives an aminediol whose dehydration leads to α-aminoketones. These ketones are subsequently dimerized into the various substituted pyrazines. The role of acrolein in the next steps of the reaction is not clear.

The formation of 1,3-bis(methylthio)propene isomers (mol wt 134) may be attributed to the condensation of methanethiol with methional. The dehydration of the adduct gives the corresponding *cis*- and *trans*-isomers. The experimental and calculated Kováts indices, KIP, are in approximate agreement (*cis*-isomer: KIP_{exp} 1595, KIP_{calc} 1550; *trans*-isomer: KIP_{exp} 1655, KIP_{calc} 1580). Furthermore, the fragmentation is in good agreement with the proposed structures. The reduced compound, 1,3-bis(methylthio)propane (mol wt 136, KIP 1554) gives the characteristic fragments (electron impact, EI) at *m/z* 121,75, 73 (base peak), 61, and 45.

The 2-formyl-5-methyl- and 2-acetylfurans and -pyrroles may be formed from 1-hydroxy-2-propanone and pyruvaldehyde in the presence or in the absence of ammonia, and the 2-acetyl derivatives from glycolaldehyde and biacetyl. Another interesting possibility is the formation of 2-acylpyrroles by reaction of ammonia with the corresponding furan.

The formation of 2-(methylthio)methylfuran derivatives substituted in position 4 ($R = H$, CH_3, CH_2SCH_3) may be explained as due to aldolization reactions between aldehydes (RCH_2CHO) and methional (Scheme 4). The compounds obtained after dehydration, heterocyclization, and subsequent oxidation give base peaks (EI) corresponding to the loss of a methylthio radical. The isomeric 3-(methylthio)methylfuran can be obtained by a mechanism including nucleophilic attack of the activated group of methional upon the enol form of the aldehyde.

The formation of two amino intermediates, **A** and **B**, in the synthesis of 2,3-dimethyl-6-(3-methylthio)propylpyrazine is shown in Scheme 5. Starting from



Scheme 4. Formation of 2- and 3-(methylthio)methylfurans.

methional and glycolaldehyde, the intermediate **A** is formed after the reaction of ammonia with the enol form of 5-methylthio-2-oxopentanal. The intermediate **B** is readily formed from ammonia and acetoin. Nucleophilic attack of the amino groups on the carbonyl groups leads to the dihydropyrazine ring after dehydration and, subsequently, gives the expected product via proton transfer. This compound (mol wt 196, KIP 2260) gives a base peak (EI) at m/z 122, characteristic of 2,3-dimethyl-5(or 6)-alkylpyrazines and corresponding to the well-known McLafferty rearrangement.

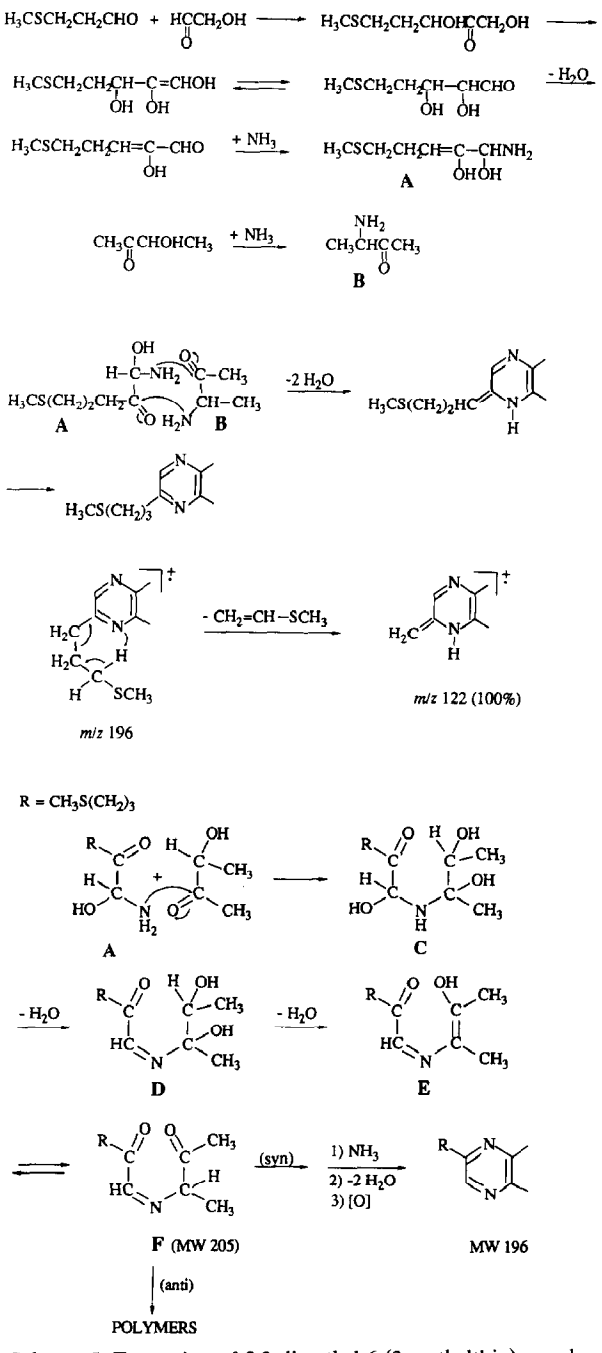
Instead of the formation of a heterocycle by reaction with an α-aminoketone, **A** can also react with acetoin to give the imino compound **D** (after dehydration of the intermediate **C**). Subsequent dehydration gives the intermediate **E** in equilibrium with the keto form **F** (both in *syn*- and *anti*-conformations). While the *syn*-form leads to the corresponding pyrazine by reaction with ammonia, the *anti*-form leads to polymers. Intermediates similar to **F** have been previously isolated and characterized in the case of acetoin and ammonia and also with the acetoin–2-methylpropanal–ammonia model-system[23].

Although the last two mechanistic schemes (Schemes 4 and 5) are at least somewhat speculative, similar schemes are generally accepted in the literature.

EXPERIMENTAL

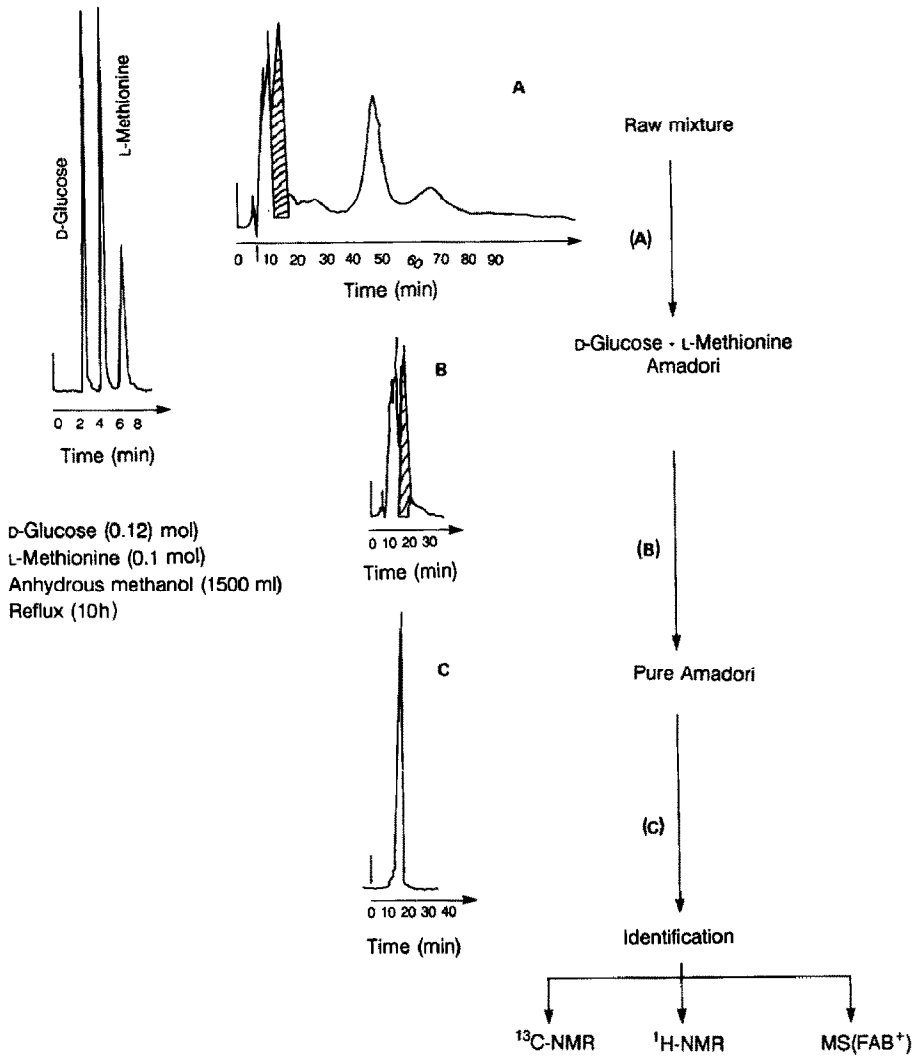
Synthesis of the fructose–methionine Amadori intermediate (new intermediate).— The synthesis was performed by a modification of a previous method[19,24]. There are other similar procedures in the literature referring to the synthesis of the various Amadori intermediates[21,22,25–35].

A mixture of D-glucose (21.6 g, 0.12 mol) and L-methionine (14.9 g, 0.1 mol) was refluxed in abs MeOH (1500 mL) for 10 h with stirring. After reaction, the solvent was evaporated to dryness, the residue was dissolved in purified water, and 1 mL was taken for HPLC analysis on an RP-18, 5-μm reverse-phase column (250 × 4 mm i.d.). The column was eluted with water. The products were detected with UV



Scheme 5. Formation of 2,3-dimethyl-6-(3-methylthio)propylpyrazine and its identification.

light at 254 nm, revealing some by-products which had to be eliminated. A summary of the operations involved in the purification procedure is presented in Scheme 6.



Scheme 6. Various steps in the HPLC purification of the fructose–methionine Amadori intermediate. (A) Semi-preparative HPLC: column RP-18 40–63 μm (310 × 25 mm i.d.); eluent, water; detection, UV 254 nm. (B) Semi-preparative HPLC: column μBondapack RP-18 (610 × 7.8 mm i.d.); eluent, water; detection, UV 254 nm. (C) Analytical HPLC: column RP-18 5 μm (254 × 4 mm i.d.); eluent, water; detection, refractometry.

The first step was a repeated separation of the heavy products from 5 mL of the aqueous solution by semi-preparative HPLC (PR-18, 40–63-μm column, 310 × 25 mm i.d.). This was followed by a repeated separation of the Amadori intermediate from D-glucose and L-methionine using semi-preparative HPLC (RP-18, 37–50-μm column, 610 × 7.8 mm i.d.). The final step of the purification procedure was accomplished on an analytical RP-18, 5-μm column (250 × 4 mm i.d.). The yield of the product was between 15 and 20%.

The chromatographic system used included a water pump (M-45 G), a Rheodyne injection device (750 μL), and a detector, either connected to a Delsi integrator or to a servotrace recording giving both the peak areas and the retention times. The calibration curves were established for the three compounds — glucose, methionine, and the Amadori intermediate. The correlation coefficient for the relationship between the injected amount and the detector response was equal to 0.995. The reproducibility of the injections has been verified by injecting each sample six times, for the three compounds under study.

Identification: mass spectrum, FAB^+ mode (Fig. 1): m/z, 312 $[(MH)^+$, base peak, quasimolecular ion], 294 $[(MH - H_2O)^+]$, 276 $[(MH - 2\ H_2O)^+]$, 248 $[(MH - 2\ H_2O - C_2H_4)^+]$. FAB^- (Fig. 1): m/z, 310 (base peak, molecular ion). ^{13}C-NMR spectrum (Fig. 2): the individual chemical shifts for the fructose and methionine components are given in Table I.

Thermal degradation of the fructose–methionine intermediate.—The Amadori intermediate (1.0 g) was placed in an Erlenmeyer flask (25 mL) specifically designed for introduction of N_2 gas on one side and connected to a flask filled with Freon 11 ($CFCl_3$) (20 mL) cooled with dry ice. While a stream of N_2 was being passed through the flask, it was quickly heated to 260 $\pm 5°$ with a Bunsen burner (in a silicone oil bath). Nitrogen carried out the volatile compounds which were trapped in Freon 11. The reaction time was 3–5 min. After evaporation of the solvent, the residue [possessing the characteristic flavor of boiled potatoes (methional)] was analyzed by gas chromatography and GLC–MS.

Analytical methods.—The gas chromatograms were recorded on an Intersmat IGC 120 FL instrument connected to an Intersmat integrator, model ICR 1B (using a WCOT fused silica capillary column, 50 m × 0.22 mm i.d., stationary phase Carbowax 20M). The oven temperature ranged from 70 to 210° with a linearly programmed rate of 2°/min. The injector-block temperature was 260° with an injection volume of 0.1 μL and a split of 1 : 20. The carrier gas flow rate (He) was 1 mL/min. The air and H_2 flow rates were 25 mL/min at 1 bar.

In the GLC–MS studies, gas chromatograms were recorded on a Girdel instrument with a Carbowax 20M column (50 m × 0.33 mm i.d.). The oven temperature ranged from 60 to 200° with a linearly programmed rate of 3°/min and an injector-block temperature of 250°. The mass spectra were recorded on a Ribermag R10-10 spectrometer at low resolution. The ionization current was 100 μA and the ionizing voltage 70 eV. The source temperature was 200°.

CONCLUSIONS

Our data bank of mass spectra, SPECMA, makes it possible to identify a substantially higher number of compounds than the commercially available data banks. This is especially true in the case of heterocyclic compounds. Because of the very large number of compounds formed in the Maillard reaction, including the

products of thermal degradation of the Amadori intermediate and the Strecker degradation of α-amino acids, not all of them could be identified.

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