

Volatile Compounds Generated from Thermal Reaction of Methionine and Methionine Sulfoxide with or without Glucose

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Methionine and methionine sulfoxide were mixed with or without glucose in distilled water, individually. These solutions were heated in closed sample cylinders at 180 °C for 1 h. The volatile compounds generated were extracted using methylene chloride and analyzed by GC and GC-MS. Pyrazine compounds, especially 2,5-dimethyl-, 2-ethyl-5-methyl-, trimethyl-, and methylpyrazines were the predominant compounds among those generated from thermal interactions of glucose and methionine or methionine sulfoxide. The formation of methional or those compounds derived from methional was found to be more favorable from the thermal degradation of methionine, whereas the formation of dimethyl polysulfides, especially dimethyl disulfide and dimethyl trisulfide, was found to be more favorable from the thermal degradation of methionine sulfoxide. Glucose was found to have a catalytic effect on the formation of volatile compounds from the thermal degradation of methionine or methionine sulfoxide.

Keywords: *Methionine; methionine sulfoxide; methional; methyl sulfides; volatiles*

INTRODUCTION

L-Methionine is one of the essential amino acids for man (Rose et al., 1955; Meister, 1965; Irwin and Hegsted, 1971). Methionine also has been widely used in the flavor and food industries to produce reaction flavors such as baked potato, fried potato, coffee, and meat flavors (Herz and Shallenberger, 1960; Ballance, 1961; Hodge, 1967; Chen, 1968; Lee et al., 1973; Mielniczuk et al., 1977; Fan and Yueh, 1980; Silwar and Tressl, 1989). The contribution of methionine to flavor formation was found mainly through thermal degradation itself or through thermal interactions with other food ingredients, especially reducing sugars. Herz and Shallenberger (1960) reported that heating methionine and glucose in an aqueous solution at 100 °C or in mineral oil at 180 °C would generate a potato aroma. Contrarily, El-Ode et al. (1966) indicated that heating methionine and sugars in water at 100 °C yielded a cabbage-like aroma. Casey et al. (1965) reported that methionine was degraded by compounds such as glucose to produce methional, dimethyl sulfide, and dimethyl disulfide. Shigematsu et al. (1977) reacted six sugars with methionine and cysteine. A mixture of equimolar amounts of sugar and amino acids was heated at 190 °C for 15 min under reduced pressure. They reported that in most cases the main product was the Strecker aldehyde methional or products derived from this aldehyde, such as the corresponding alcohol. Besides dimethyl sulfides and methional, several volatile compounds were identified from the thermal degradation of methionine with or without glucose or dicarbonyl compounds (Fujimaki et al., 1969; Rijike et al., 1981; Ho et al., 1982; Hartman and Ho, 1984; Tressl et al., 1989). However, no quantitative results for the formation of these compounds were presented.

Methionine has been found to be oxidized to methionine sulfoxide easily, especially when oxidized lipid or other oxidizing agents, such as hydrogen peroxide, are present. Heat treatment and/or alkali treatment can sometimes lead to this kind of chemical change. In a few cases methionine can even be oxidized into methionine sulfone (Slump and Schreuder, 1973; Walker et al., 1975; Cheftel, 1977; Cuq et al., 1973, 1978). Methionine sulfone has been found to be biologically nonavailable, and the availability of methionine sulfoxide is generally expected to be less than that of methionine (Cuq et al., 1978). Methionine sulfoxide has been detected in meat (Happich, 1975), soy concentrate (Happich et al., 1975), untreated fish protein (Sjoberg and Bostrom, 1977), untreated fish protein and casein (Slump and Schreuder, 1973), native porcine pepsin (Kido and Kassel, 1975), and casein, egg, gelatin, fish, milk, beans, gluten, soy, and rapeseed meals (Njaa, 1980). Besides the nutritional availability, flavor or aroma is also considered to be one of the important attributes for the overall food qualities. It is, therefore, interesting to study the changes of flavor or aroma after methionine oxidation. Flavor generations from methionine and methionine sulfoxide with or without glucose, therefore, were compared in this study.

EXPERIMENTAL PROCEDURES

Thermal Reaction of Methionine or Methionine Sulfoxide with or without Glucose in Water. DL-Methionine (0.01 mol) (Sigma, grade 1, purity >99%) or DL-methionine sulfoxide (0.01 mol) (Aldrich, 98% purity) was mixed with or without 0.01 mol of α -D-glucose (Aldrich, 96% purity) in 200 mL of distilled water. The solutions were added to 0.3 L Hoke SS-DOT sample cylinders (Hoke Inc., Clifton, NJ) and sealed, individually. These cylinders were then heated at 180 °C in a GC oven for 1 h. After being cooled to room temperature, the reaction solutions of methionine or methionine sulfoxide with or without glucose were obtained.

Isolation of the Volatile Compounds. The total reaction mass prepared was mixed with 10 mL of internal standard stock solution (0.077 g of hexadecane in 200 mL of methylene chloride) and then extracted by 200 mL of redistilled methyl-

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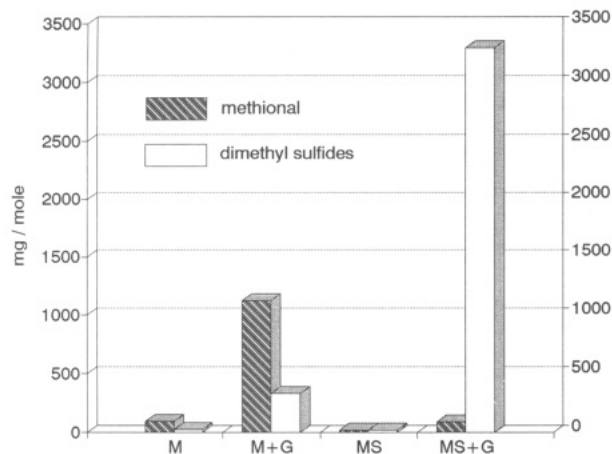


Figure 1. Comparisons of the yields of methional and dimethyl sulfides generated in methionine alone (M), methionine + glucose (M+G), methionine sulfoxide alone (MS), and methionine sulfoxide + glucose (MS+G) model systems.

ene chloride for 3 h. After being separated, the methylene chloride layer was dried over anhydrous sodium sulfate and filtered. The filtrate was then concentrated to minimum volume using a Kuderna-Danish apparatus fitted with a Vigreux distillation column. The flavor isolate was then slowly concentrated further under a stream of nitrogen in a small sample vial to a final volume of 0.2 mL.

Gas Chromatographic Analysis. A Varian 3400 gas chromatograph equipped with a fused silica capillary column (60 m \times 0.25 mm i.d.; 1 μ m thickness, DB-1, J&W Scientific Inc.) and a flame ionization detector was used to analyze the volatile compounds. The operating conditions were as follows: injector temperature, 270 $^{\circ}$ C; detector temperature, 300 $^{\circ}$ C; helium carrier flow rate, 1 mL/min; temperature program, 40 $^{\circ}$ C (5 min), 2 $^{\circ}$ C/min, 260 $^{\circ}$ C (60 min). A split ratio of 50:1 was used. The quantities of volatile compounds were expressed as milligrams per mole of methionine or methionine sulfoxide by comparing their GC peak areas with that of the internal standard.

Gas Chromatography–Mass Spectrometry (GC–MS) Analysis. The concentrated isolate was analyzed by GC–MS using a Varian 3400 gas chromatograph coupled to a Finnigan MAT 8230 high-resolution, double-focusing magnetic sector mass spectrometer equipped with a direct split interface and the same column as used for the gas chromatography. The operating conditions in the GC part were the same as described above. Mass spectra were obtained by electron ionization at 70 eV and an ion source temperature of 250 $^{\circ}$ C.

Identification of the Volatile Compounds. Identification of the volatile compounds in the isolate was based mostly on gas chromatography–mass spectrometry (GC–MS), and information from the GC retention index (I_k) used a C₅–C₂₅ mixture as the reference standard. The structural assignment of volatile compounds was accomplished by comparing the mass spectral data with those of authentic compounds available from the Browser–Wiley computer library, the NBS computer library, or previously published literature (Guntert et al., 1993; Hartman and Ho, 1984). The retention indices were used for the confirmation of structural assignments. Due to the lack of standard mass spectra, some compounds (as shown in Table 3) were identified only by mass fragment interpretation. Therefore, the identification of these compounds can only be considered tentative.

RESULTS AND DISCUSSION

Odor Descriptions. The odor descriptions of the model reaction systems are shown in Table 1, and the odor of each sample was slightly different. More baked potato odor was detected in the methionine system with or without glucose. More sulfuryl and black mushroom odor was detected from the methionine sulfoxide system

Table 1. Odor Descriptions of the Thermal Reaction Aqueous Solution of Methionine or Methionine Sulfoxide with or without Glucose

sample	odor description
methionine	fermented radish or cabbage note with baked potato undertone
methionine + glucose	fermented radish or cabbage note with burned, caramellic, and baked potato undertone
methionine sulfoxide	sulfuryl, fermented radish-like, with black mushroom undertone
methionine sulfoxide + glucose	sulfuryl, fermented radish-like, burned, caramellic with black mushroom and baked potato undertone

with or without glucose. More burned, caramellic odor was detected in those samples containing glucose.

The volatile compositions of the model reaction samples prepared in this study are shown in Table 2. A comparison of the yields of methional and dimethyl sulfides of the model reaction samples is shown in Figure 1. As shown in Table 2 and Figure 1, more methional was found to be generated in methionine systems than in methionine sulfoxide systems. More dimethyl sulfides were found to be generated in methionine sulfoxide systems than in methionine systems. Since methional has a baked or boiled potato flavor and dimethyl sulfides, especially dimethyl disulfide and dimethyl trisulfide, have cabbage, fermented radish, black mushroom-like flavor, the difference in the odor sensations between the methionine and methionine sulfoxide systems, therefore, is believed to result from the difference in the different yields of methional and dimethyl sulfides in these systems. The results shown in Table 1, therefore, are worthy to be used to predict the flavor changes of food systems after methionine is changed into methionine sulfoxide.

Comparison of Volatile Compounds Generated.

The identification and quantification of the volatile compounds generated from the thermal reaction of methionine and methionine sulfoxide with or without glucose are shown in Table 2. Due to the lack of standard mass spectra, the identification of some of the compounds is considered to be only tentative. Table 3 shows the mass spectra of these tentatively identified volatile compounds.

As shown in Table 2, the volatile compounds generated from the model systems can be grouped into those generated from the thermal degradation of methionine or methionine sulfoxide, those generated from the thermal degradation of glucose, and those generated from the thermal interactions of glucose and methionine or methionine sulfoxide.

1. Volatile Compounds Generated from the Thermal Degradation of Methionine or Methionine Sulfoxide. As shown in Table 2, methional was found to be the predominant volatile compound generated from the thermal degradation of methionine with or without glucose, whereas dimethyl disulfide and dimethyl trisulfide were found to be the predominant volatile compounds generated from the thermal degradation of methionine sulfoxide with or without glucose. A comparison of the yields of methional and dimethyl sulfides generated in the model systems is shown in Figure 1. The formation of methional was found to be more favorable in methionine systems, whereas the formation of dimethyl sulfides was found to be more favorable in methionine sulfoxide systems. The addition of glucose to methionine significantly increased the yield of me-

Table 2. Volatile Compounds Identified from the Thermal Reaction of Methionine or Methionine Sulfoxide with or without Glucose

compound	MW ^a	RI ^b	mg/mol of methionine or methionine sulfoxide			
			M ^c	M+G ^c	MS ^c	MS+G ^c
Compounds Generated from the Thermal Degradation of Methionine or Methionine Sulfoxide						
dimethyl disulfide	94	731	19.1	332.2	96.1	2528.7
methional	104	875	90.5	1126.9	14.8	87.6
(methylthio)cyclopentane	116	943	17.1	nd ^d	23.9	nd
dimethyl trisulfide	126	957	2.5	nd	39.1	748.4
S-methyl methylthiosulfonate	126	1092	nd	nd	3.1	15.6
2-methyl-5-(methylthio)furan	128	1196	1.5	nd	3.4	15.8
dimethyl tetrasulfide	158	1206	nd	nd	4.5	24.8
2,6-dithianone	164	1316	2.2	nd	0.9	nd
1,1,3-tris(methylthio)propane	182	1510	nd	44.1	nd	nd
2-[(methylthio)methyl]-5-(methylthio)-2-pentenal	190	1567	nd	72.5	nd	nd
Compounds Generated from the Thermal Degradation of Glucose						
2-butanone	72	564	nd	18.6	nd	8.9
1-hydroxy-2-propanone	74	625	nd	76.8	nd	61.6
acetoin	88	690	nd	2.8	nd	27.7
3-hydroxy-2-pentanone	102	783	nd	13.7	nd	14.1
2,3-pentanedione	100	790	nd	8.1	nd	5.8
furfural	96	829	nd	14.5	nd	17.6
furfuryl alcohol	98	849	nd	9.1	nd	41.9
5-methyl-2-furfural	110	950	nd	3.6	nd	21.7
2-hydroxycyclohexanone	114	971	nd	13.3	nd	16.7
phenol	94	981	nd	15.2	nd	24.1
cyclotene	112	1005	nd	56.6	nd	117.1
2-hydroxy-3-methylbenzaldehyde	136	1125	nd	9.9	nd	7.6
2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	144	1144	nd	nd	nd	9.1
5-(hydroxymethyl)furfural	126	1228	nd	nd	nd	13.3
Compounds Generated from the Thermal Interactions of Glucose and Methionine or Methionine Sulfoxide						
ethanethioic acid S-methyl ester	90	671	nd	3.4	nd	1.5
pyrazine	80	716	nd	97.7	nd	80.4
pyridine	79	753	nd	nd	nd	13.7
methylpyrazine	94	802	nd	94.1	nd	170.7
3-methylpyridine	93	845	nd	23.9	6.5	86.3
2,5-dimethylpyrazine	108	891	nd	165.1	nd	192.5
ethylpyrazine	108	895	nd	1.38	nd	55.6
2,3-dimethylpyrazine	108	899	nd	66.2	nd	63.2
vinylpyrazine	106	922	nd	0.3	nd	18.1
1,1-bis(methylthio)ethane	122	935	nd	2.4	nd	nd
3-hydroxy-2-thiabutane	92	941	nd	1.3	nd	nd
4-(methylthio)-2-butanone	118	962	nd	64.5	nd	nd
2-ethyl-5-methylpyrazine	122	985	nd	75.7	nd	160.8
2-formylthiophene	112	987	nd	nd	1.3	nd
trimethylpyrazine	122	992	nd	128.9	nd	91.7
2-vinyl-5-methylpyrazine	120	999	nd	0.6	nd	13.2
2-acetylpyrrole	109	1051	nd	20.1	nd	12.3
2-ethyl-3,5-dimethylpyrazine	126	1065	nd	17.8	nd	6.6
3-ethyl-2,5-dimethylpyrazine	126	1071	nd	12.3	nd	35.1
2-methyl-5-[(methylthio)methyl]furan	142	1080	nd	32.5	nd	nd
2-methyl-5-(1-propenyl)pyrazine	134	1110	nd	7.2	nd	6.8
2-formyl-5-methylthiophene	126	1129	nd	nd	0.8	2.3
3-(methylthio)propanoic acid methyl ester	134	1142	nd	119.6	nd	nd
3,5-diethyl-2-methylpyrazine	150	1152	nd	nd	nd	4.4
3,4-dihydro-2H-thiopyran-3-one	114	1155	nd	nd	0.7	nd
3-(methylthio)propanoic acid ethyl ester	148	1167	nd	23.1	nd	nd
2-formylpyrrole	95	1234	nd	nd	nd	20.3
3-[(methylthio)methyl]pyridine	139	1243	nd	37.3	nd	nd
5,6,7,8-tetrahydroquinoline	133	1257	nd	nd	nd	31.5
2-pyridinemethanol	109	1305	nd	nd	nd	24.4
5-[(methylthio)methyl]furfuryl alcohol	158	1335	nd	nd	nd	6.5
2-[(methylthio)methyl]-3-(2-furyl)acrolein	182	1456	nd	25.1	nd	nd
2-[(methylthio)methyl]-3-(2-furyl)acrolein	182	1468	nd	17.1	nd	nd
2-[(methylthio)methyl]-3-(3-furyl)acrolein	182	1480	nd	44.1	nd	nd
2-[(methylthio)methyl]-3-(3-furyl)acrolein	182	1488	nd	11.3	nd	nd
1-[3-(methylthio)propyl]-2-formylpyrrole	183	1504	nd	103.5	nd	nd
2,3-dimethyl-5-[(methylthio)propyl]pyrazine	196	1556	nd	10.3	nd	nd
2,5-dimethyl-3-[(methylthio)propyl]pyrazine	196	1601	nd	31.3	nd	nd



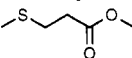
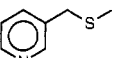
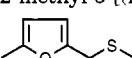
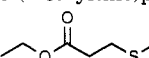
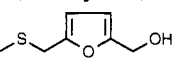

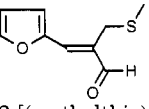
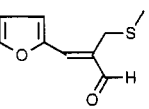
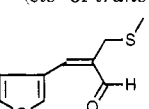
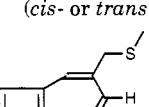
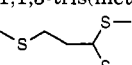
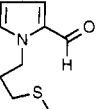
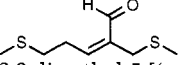
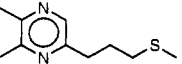
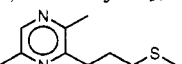
^a MW, molecular weight. ^b RI, Kovat's retention index. ^c M, methionine; M+G, methionine + glucose; MS, methionine sulfoxide; MS+G, methionine sulfoxide + glucose. ^d nd, not detected.

thional; the addition of glucose to methionine sulfoxide significantly increased the yield of dimethyl sulfides.

Methional has been reported to be generated from methionine through the Shigematsu reaction (Shigematsu et al., 1971, 1972, 1977; Rijke et al., 1981). The

methional detected in the methionine system without glucose is therefore proposed to be generated from methionine through the same reaction, i.e., through the decarboxylation and deamination of this amino acid. Some of the methional could then break down further

Table 3. Mass Spectra of Some Tentatively Identified Volatile Compounds from the Thermal Interactions of Methionine or Methionine Sulfoxide with Glucose

compound	MW	MS, <i>m/e</i> (relative intensity)
3-hydroxy-2-thiabutane 	92	45 (100), 92 (40), 48 (36), 47 (21), 49 (18), 43 (16), 75 (6), 71 (5), 94 (4)
1,1-bis(methylthio)ethane 	122	47 (100), 75 (96), 45 (58), 122 (58), 48 (50), 59 (37), 76 (16)
3-(methylthio)propanoic acid methyl ester 	134	61 (100), 75 (50), 47 (30), 134 (22), 41 (20), 45 (20), 103 (16), 59 (12), 49 (10)
3-[(methylthio)methyl]pyridine 	139	92 (100), 139 (50), 65 (26), 41 (16), 69 (12), 93 (11), 39 (10), 43 (10), 63 (10), 121 (7), 140 (6)
2-methyl-5-[(methylthio)methyl]furan 	142	95 (100), 43 (26), 142 (23), 40 (10), 41 (10), 51 (8), 53 (8), 67 (8), 39 (7), 65 (7), 96 (6)
3-(methylthio)propanoic acid ethyl ester 	148	61 (100), 43 (58), 57 (16), 105 (16), 148 (15), 45 (14), 74 (12), 62 (10), 87 (10), 40 (9), 47 (6)
5-[(methylthio)methyl]furfuryl alcohol 	158	110 (100), 55 (64), 83 (41), 158 (40), 45 (30), 65 (29), 39 (25), 51 (24), 94 (18)
2,6-dithianonane 	164	88 (100), 61 (86), 73 (58), 45 (56), 41 (54), 164 (54), 40 (38), 47 (36), 39 (29), 69 (28), 68 (26), 87 (18), 149 (14), 103 (12), 89 (10), 136 (10), 116 (6), 117 (5)
2-[(methylthio)methyl]-3-(2-furyl)acrolein (<i>cis</i> - or <i>trans</i> -) 	182	135 (100), 61 (50), 167 (48), 39 (41), 42 (38), 53 (21), 136 (21), 154 (21), 107 (16), 41 (14), 40 (12), 133 (12), 54 (11), 45 (10), 80 (9), 66 (8), 81 (8), 182 (7)
2-[(methylthio)methyl]-3-(2-furyl)acrolein (<i>cis</i> - or <i>trans</i> -) 	182	135 (100), 39 (44), 167 (42), 61 (39), 154 (38), 40 (28), 42 (22), 66 (22), 136 (20), 53 (18), 54 (17), 123 (14), 80 (10), 107 (10), 121 (10), 168 (6)
2-[(methylthio)methyl]-3-(3-furyl)acrolein (<i>cis</i> - or <i>trans</i> -) 	182	135 (100), 61 (55), 39 (37), 167 (37), 53 (28), 42 (22), 52 (22), 154 (22), 136 (18), 45 (12), 51 (12), 80 (11), 107 (9), 150 (7), 134 (6), 182 (6)
2-[(methylthio)methyl]-3-(3-furyl)acrolein (<i>cis</i> - or <i>trans</i> -) 	182	135 (100), 61 (90), 167 (78), 39 (50), 136 (50), 154 (38), 53 (32), 121 (30), 133 (28), 165 (16), 182 (14), 120 (12), 183 (5)
1,1,3-tris(methylthio)propane 	182	108 (100), 39 (26), 121 (12), 107 (11), 41 (10), 53 (10), 55 (10), 109 (10), 80 (8), 182 (6)
1-[3-(methylthio)propyl]-2-formylpyrrole 	183	136 (100), 93 (50), 108 (46), 39 (18), 94 (18), 183 (16), 43 (12), 66 (11), 41 (10), 65 (10), 92 (10), 137 (10), 80 (8), 67 (9)
2-[(methylthio)methyl]-5-(methylthio)-2-pentenal 	190	61 (100), 143 (40), 67 (38), 39 (26), 41 (25), 45 (24), 95 (20), 142 (18), 65 (16), 66 (15), 115 (11), 127 (8), 129 (6), 190 (2)
2,3-dimethyl-5-[(methylthio)propyl]pyrazine 	196	122 (100), 42 (15), 39 (14), 149 (14), 53 (10), 135 (10), 123 (9), 61 (8), 196 (3)
2,5-dimethyl-3-[(methylthio)propyl]pyrazine 	196	122 (100), 61 (60), 67 (26), 39 (25), 41 (23), 95 (20), 142 (18), 47 (16), 80 (16), 135 (16), 45 (12), 196 (3)

and generate methanethiol. The oxidation of the methanethiol then resulted in the formation of dimethyl sulfides (Schonberg and Moubacher, 1952; Casey et al., 1965; Rijke et al., 1981; Tressl et al., 1989; Guntert et al., 1993). The decarboxylation and the deamination of methionine sulfoxide were proposed to generate methional sulfoxide first. A small portion of methional sulfoxide was further proposed to transform to methional, whereas most of the methional sulfoxide generated was proposed to break down easily into methanethiol, thus favoring the formation of dimethyl sulfides.

Besides the Shigematsu reaction, Strecker degradation was proposed to be involved in the formation of methional and methional sulfoxide, the Strecker aldehydes of methionine and methionine sulfoxide, respectively, when glucose was added (Schonberg and Moubacher, 1952; Ballance, 1961; Pokorny, 1980; Tressl, 1989). A very high amount of the Strecker aldehyde, i.e. methional or methional sulfoxide, was proposed to be generated from methionine or methionine sulfoxide with glucose. Only a small portion of methional was transformed into dimethyl sulfides, whereas most of the methional sulfoxide was transformed into these dimethyl sulfides. Methionine sulfoxide was also proposed to break down to acrolein plus methanesulfenic acid, and the latter compound may then undergo disproportionation to form methyl sulfides and methanesulfonic acid.

Besides methional and dimethyl sulfides, some sulfur-containing compounds were also considered to be generated from the thermal degradation of methionine or methionine sulfoxide. Among these compounds, 1,1,3-tris(methylthio)propane probably was generated from the interactions of one molecule of methional and two molecules of methanethiol. 2-[(Methylthio)methyl]-5-(methylthio)-2-pentenal probably was generated from the interactions of two molecules of methional through the dehydration process.

2. Volatile Compounds Generated from the Thermal Degradation of Glucose. As shown in Table 2, 1-hydroxy-2-propanone and cyclotene were found to be the predominant volatile compounds generated from the thermal degradation of glucose. Some furan-type compounds, such as furfural, furfuryl alcohol, 5-methyl-2-furfural, and 5-(hydroxymethyl)furfural, were also detected. Most of the formation mechanisms of these compounds have been well studied (Vernin and Vernin, 1982; Vernin and Parkanyi, 1982).

3. Volatile Compounds Generated from the Thermal Interactions of Glucose and Methionine or Methionine Sulfoxide. *a. Pyrazines.* Several pyrazines were detected from the thermal reaction systems of glucose and methionine or methionine sulfoxides. The occurrence and the formation mechanisms of these pyrazines have been reviewed (Maga, 1982). Among these pyrazines, 2,5-dimethyl-, trimethyl-, methyl-, 2-ethyl-5-methyl-, 2,3-dimethylpyrazine, and pyrazine were found to be the predominant compounds. Most of these pyrazines have also been identified in baked potato, potato chips, and related model systems (Buttery et al., 1971; Deck et al., 1973; Pareles and Chang, 1974; Coleman and Ho, 1980). Therefore, we feel confident in saying that these pyrazines contribute some of the baked or fried potato notes detected in the thermal reaction systems of glucose with methionine or methionine sulfoxide. Two pyrazines, i.e. 2,3-dimethyl-5-[(methylthio)propyl]pyrazine and 2,5-dimethyl-3-[(methylthio)propyl]pyrazine, were considered to be two of the methionine specific volatile com-

pounds. 2,3-Dimethyl-5-[(methylthio)propyl]pyrazine probably was generated from the interactions of 2,3-dimethylpyrazine or its precursor, 2,3-dimethyl-dihydropyrazine, and methional; 2,5-dimethyl-3-[(methylthio)propyl]pyrazine was probably generated from the interactions of 2,5-dimethylpyrazine or its precursor, 2,5-dimethyldihydropyrazine, and methional. The occurrence of 2,5-dimethyl-3-[(methylthio)propyl]pyrazine also has been reported by Rijke et al. (1981).

b. Miscellaneous Other Products. The formation pathways of some of the non-pyrazine compounds which were generated from the thermal interactions of glucose and methionine or methionine sulfoxide were proposed as follows: (1) Ethanethioic acid, *S*-methyl ester, was generated from the interactions of one molecule of acetic acid, one of the thermal degradation products of glucose, and one molecule of methanethiol. (2) 1,1-Bis(methylthio)ethane comes from the interactions of one molecule of acetaldehyde, one of the thermal degradation products of glucose, and two molecules of methanethiol. (3) 3-Hydroxy-2-thiabutane occurs from the interactions of one molecule of acetaldehyde and one molecule of methanethiol. (4) 3-(Methylthio)propanoic acid methyl ester comes from the esterification of 3-(methylthio)propanoic acid, one of the oxidation products of methional, and methanol, one of the thermal degradation products of glucose. (5) 3-(Methylthio)propanoic acid, ethyl ester, comes from the esterification of 3-(methylthio)propanoic acid and ethanol, one of the thermal degradation products of glucose. (6) 3-[(Methylthio)methyl]pyridine comes from the interactions of methanethiol, methional, ammonia, and 2-propenal, which can be generated from both the thermal degradation of glucose and methional. (7) 2-[(Methylthio)methyl]-3-(2-furyl)acrolein and 2-[(methylthio)methyl]-3-(3-furyl)acrolein were generated from the aldol condensation/dehydration of 2-furfurylaldehyde and 3-furfurylaldehyde with methional, respectively. The occurrence and the formation pathways of some of the thermal interaction volatile compounds of glucose and methionine have also been reported by Rijke et al. (1981) and Tressl et al. (1989).

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LITERATURE CITED

- Ballance, P. E. Production of volatile compounds related to the flavor of foods from the Strecker degradation of DL-methionine. *J. Sci. Food Agric.* **1961**, *12*, 532-536.
- Buttery, R. G.; Ling, L. C. Characterization of nonbasic steam volatile components of potato chips. *J. Agric. Food Chem.* **1972**, *20*, 698-700.
- Buttery, R. G.; Seifert, R. M.; Guadagni, D. G.; Ling, L. C. Characterization of volatile pyrazine and pyridine components of potato chips. *J. Agric. Food Chem.* **1971**, *19*, 969-971.
- Casey, J. C.; Self, R.; Swain, T. Factors influencing the producing of low boiling volatiles from foods. *J. Food Sci.* **1965**, *30*, 33-34.
- Cheftel, J. C. Chemical and nutritional modifications of food proteins due to processing and storage. In *Food Proteins*; Whitaker, J. R., Tannenbaum, S. R., Eds.; AVI Publishing: Westport, CT, 1977.
- Chen, S. S. The generation of volatile flavor compounds by amino acids under the conditions of deep fat frying. *Proc. Potato Chip Inst.* **1968**, 9-20.

- Coleman, E. C.; Ho, C.-T. Chemistry of baked potato flavor. 1. Pyrazines and thiazoles identified in the volatile flavor of baked potato. *J. Agric. Food Chem.* **1980**, *28*, 66–68.
- Cuq, J. L.; Provansal, M.; Gulleaux, F.; Cheftel, J. C. Oxidation of methionine residues of casein by hydrogen peroxide. Effects on *in vitro* digestibility. *J. Food Sci.* **1973**, *38*, 11–15.
- Cuq, J. L.; Bresancon, P.; Chartier, L.; Cheftel, J. C. Oxidation of methionine residues of food protein and nutritional availability of protein bond methionine sulphoxide. *Food Chem.* **1978**, *3*, 85–90.
- Deck, R. E.; Pokorny, J.; Chang, S. S. Isolation and identification of volatile compounds from potato chips. *J. Food Sci.* **1973**, *38*, 345–349.
- El-Ode, K. E.; Dornseifer, T. P.; Keith, S.; Powers, J. J. Effects of pH and temperature on the carbonyls and aromas produced in heated amino acid-sugar mixtures. *J. Food Sci.* **1966**, *31*, 351–354.
- Fan, T. Y.; Yueh, M. H. Potato flavor generation—an approach to the flavor improvement of dehydrated potato products. *J. Food Sci.* **1980**, *45*, 748–749.
- Fujimaki, M.; Kato, S.; Kurata, T. Pyrolysis of sulfur-containing amino acids. *Agric. Biol. Chem.* **1969**, *33* (8), 1144–1151.
- Guntert, M.; Bertram, H.-J.; Hopp, R.; Silberzahn; Sommer, H.; Werkhoff, P. Thermal generation of flavor compounds from thiamine and various amino acids. In *Recent Development in Flavor and Fragrance Chemistry—Proceedings of the 3rd International Haarmann & Reimer Symposium*; Hopp, R., Mori, K., Eds.; 1993, VCH: New York, 1993; pp 215–240.
- Happich, M. L. Protein nutritive value of selected present and potential meat extenders. In *Protein Nutritional Quality of Foods and Feeds*; Friedman, M., Ed.; Dekker: New York, 1975; Vol. 1, part 2.
- Happich, M. L.; Swift, C. E.; Nagaski, J. Equations for predicting PER from amino acid analysis—a review and current scope of application. In *Protein Nutritional Quality of Foods and Feeds*; Friedman, M., Ed.; Dekker: New York, 1975; Vol. 1, part 2.
- Hartman, G. J.; Ho, C.-T. Volatile products of the reaction of sulfur-containing amino acids with 2,3-butanedione. *Lebensm. Wiss. Technol.* **1982**, *15*, 368–371.
- Herz, W. J.; Shallenberger, R. S. Some aromas produced by simple amino acid, sugar reactions. *Food Res.* **1960**, *25*, 632–635.
- Ho, C.-T.; Hartman, G. J.; Jin, Q. Z. The formation of oxazoles and oxazolines in the Strecker degradation of DL-methionine and L-cystine with 2,3-butanedione. *Lebensm. Wiss. Technol.* **1982**, *15*, 368–371.
- Hodge, J. E. Origin of flavor in food. Nonenzymic browning reactions. In *Chemistry and Physiology of Flavor*; Schulz, H. W., Day, E. A., Libbey, L. M., Eds.; AVI Publishing: Westport, CT, 1967.
- Irwin, M. I.; Hegsted, D. M. A conspectus of research on amino acid requirements of man. *J. Nutr.* **1971**, *101*, 539–566.
- Kido, K.; Kassell, B. Oxidation of methionine residues of porcine and bovine pepsins. *Biochemistry* **1975**, *14*, 631–635.
- Lee, S. C.; Reddy, B. R.; Chang, S. S. Formation of a potato chip-like flavor from methionine under deep-fat frying conditions. *J. Food Sci.* **1973**, *38*, 788–790.
- Maga, J. A. Pyrazines in Flavour. In *Food Flavours—Part A. Introduction*; Morton, I. D., Macleod, A. J., Eds.; Elsevier Scientific Publishing: New York, 1982; pp 283–318.
- Meister, A. The role of amino acids in nutrition. In *Biochemistry of the Amino Acids*; Academic Press: New York, 1965; Vol. 1, p 201–230.
- Mielniczuk, Z.; Barylko, P. N.; Daniewski, M. Main group components of aroma in amino acid-sugar model systems. *Acta Aliment. Pol.* **1977**, *2* (3), 213–221.
- Njaa, I. R. A method for determination of unoxidized and total methionine in protein concentrates, with special reference to fish meals. *Br. J. Nutr.* **1980**, *43*, 339–345.
- Pareles, S. R.; Chang, S. S. Identification of compounds responsible for baked potato flavor. *J. Agric. Food Chem.* **1974**, *22*, 339–340.
- Pokorny, J. Effect of browning reactions on the formation of flavour substances. *Nahrung* **1980**, *24*, 115–120.
- Rijke, D.; Dort, J. M. V.; Boelens, H. Shigematsu variation of the maillard reaction. In *Flavour '81*; de Gruyter: Berlin, 1981; pp 417–431.
- Rose, W. C.; Coon, M. J.; Lockhart, H. B.; Lambert, G. F. The amino acid requirements of man. XI. The threonine and methionine requirements. *J. Biol. Chem.* **1955**, *215*, 101–110.
- Schonberg, A.; Moubacher, R. The Strecker degradation of α -amino acids. *Chem. Rev.* **1952**, *50*, 261–270.
- Shigematsu, H.; Kurata, T.; Kato, H.; Fujimaki, M. Formation of 2-(5-hydroxymethyl-2-formylpyrrole-1-yl)alkyl acid lactones on roasting alkyl- α -amino acid with D-glucose. *Agric. Biol. Chem.* **1971**, *35*, 2097–2105.
- Shigematsu, H.; Kurata, T.; Kato, H.; Fujimaki, M. Volatile compounds formed on roasting DL-alanine and D-glucose. *Agric. Biol. Chem.* **1972**, *36*, 1631–1637.
- Shigematsu, H.; Shibata, S.; Kurata, T.; Kato, H.; Fujimaki, M. Thermal degradation products of several amadori compounds. *Agric. Biol. Chem.* **1977**, *41*, 2377–2380.
- Silwar, R.; Tressl, R. Gas chromatographic-mass spectrometric investigation of aroma compounds from the reaction of cysteine and methionine with furfural under roasting condition. *Z. Lebensm. Unters. Forsch.* **1989**, *189*, 205–211.
- Sjoberg, L. B.; Bostrom, S. L. Studies in rats on the nutritional values of hydrogen peroxide treated fish protein and the utilization of oxidized sulphur amino acids. *Br. J. Nutr.* **1977**, *38*, 189–195.
- Slump, P.; Schreuder, H. A. W. Oxidation of methionine and cystine in foods treated with hydrogen peroxide. *J. Sci. Food Agric.* **1973**, *24*, 657–660.
- 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., McGorin, R. J., Ho, C.-T., Eds.; ACS Symposium Series 409; ACS: Washington, DC, 1989; pp 156–169.
- Vernin, G.; Parkanyi, C. Mechanisms of formation of heterocyclic compounds in Maillard and pyrolysis reactions. In *Chemistry of Heterocyclic Compounds in Flavour and Aromas*; Vernin, G., Ed.; Ellis Horwood: West Sussex, England, 1982; pp 151–201.
- Vernin, G.; Vernin, G. Heterocyclic aroma compounds in foods: occurrence and organoleptic properties. In *Chemistry of Heterocyclic Compounds in Flavour and Aromas*; Vernin, G., Ed.; Ellis Horwood: West Sussex, England, 1982; pp 72–140.
- Walker, H. G., Jr.; Kohler, G. O.; Kuzmicky, D. D.; Witt, S. C. Problems in analysis for sulfur amino acids. In *Protein Nutritional Quality of Foods and Feeds*; Friedman, M., Ed.; Dekker: New York, 1975; part 1.

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