Volatile Chemicals Formed in the Headspace of a Heated D-Glucose/L-Cysteine Maillard Model System

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Volatile chemicals formed from heated D-glucose, L-cysteine, or D-glucose/L-cysteine were collected in three traps (20, 0, and −78 °C) connected in series, recovered, and analyzed. A total of 130 chemicals was positively identified: 41 identified in the samples from D-glucose heated alone, 52 in the samples from L-cysteine heated alone, and 93 in the samples from L-cysteine/D-glucose heated together. The heterocyclic compounds identified were 16 thiophenes, 16 furans, 11 pyridines, 10 pyrazines, 9 thiazoles, 8 thiazolidines, 7 pyrroles, 2 thiazolidines, and 1 oxazole. Thialdine and 3,5-dimethyl-1,2,4-trithiolane were also identified. Carbonyl compounds (14 ketones and 3 aldehydes) were produced from D-glucose alone. The L-cysteine/D-glucose system produced 2-methylthiazolidine and thialdine as major volatile components; L-cysteine alone produced 2-methylthiazolidine as a major component. Pyridines and pyrroles were found both in the L-cysteine/D-glucose system and in L-cysteine alone, whereas pyrazines and thiazoles were found mainly in the L-cysteine/D-glucose system.

Keywords: *D-Glucose/cysteine; Maillard reaction; volatile compounds*

INTRODUCTION

Since Maillard first proposed the theory of nonenzymatic browning reactions in 1912, studies based upon the Maillard reaction have been actively performed in many different fields including flavor chemistry, food engineering, analytical chemistry, and toxicology. Generally, the Maillard reaction is a result of the chemical reaction between amino acids and reducing sugars in foods. Among various studies associated with the Maillard reaction, the isolation and identification of volatile flavor chemicals have been conducted most frequently (Hodge, 1967; Hurrell, 1982; Shibamoto, 1989) because the Maillard reaction is known to produce desirable flavor in cooked food. Even though real food systems consist of many chemical components besides amino acids and sugars, the Maillard system serves as a simple model to study the chemistry of flavor compounds under various simulated cooking conditions. Consequently, there have been numerous investigations into cooked food flavors using amino acid/sugar Maillard model systems (Scanlan et al., 1973; Shibamoto, 1983; Yeo and Shibamoto, 1991a).

For flavor studies, D-glucose and L-cysteine have been most commonly used as reactants in Maillard model systems mainly because D-glucose is one of the most abundant reducing sugars found in food materials and L-cysteine contains a nitrogen and a sulfur, necessary atoms in heterocyclic flavor chemicals (Scanlan et al., 1973; Mulders, 1973; Yeo and Shibamoto, 1991a). Some heterocyclic compounds have specific cooked food flavors; for example, furans give a caramel-like flavor, thiazoles have a cooked beef flavor, and pyrazines possess a roasted or toasted flavor.

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In the late 1970s, improvement of gas chromatography/mass spectrometry technology allowed the identification of large numbers of so-called Maillard browning reaction products. Most of these flavor chemicals were recovered by an organic solvent extraction from the reaction mixture; this method generally yields a gas chromatogram that contains over 1000 peaks. While most of the major peaks have now been identified, there are still many unknown compounds present in samples obtained from sugar/amino acid browning model systems. In the present study, volatile chemicals formed from D-glucose, L-cysteine, and a D-glucose/L-cysteine model system were heated by a newly developed method and then identified by gas chromatography/mass spectrometry.

EXPERIMENTAL PROCEDURES

Materials. L-Cysteine and D-glucose were bought from Sigma Chemical Co. (St. Louis, MO). Authentic chemicals were obtained from Tokyo Chemicals Co., Ltd. (Tokyo, Japan), Wako Fine Chemicals Co., Ltd. (Osaka, Japan), Aldrich Chemical Co. (Milwaukee, WI), and Fluka Chemical Co. (Ronkonkoma, NY) or synthesized according to reliable methods. Glass beads (0.177−0.25 mm diameter) were washed with distilled water and dried at 160 °C for 5 h before use. Glass beads were used to transfer the heat uniformly to sample powders. Also, the glass tubing would become plugged by the polymers produced without glass beads and then purging would be impossible.

Authentic thiazolidine derivatives were synthesized according to the method reported previously (Sakaguchi and Shibamoto, 1978). A dichloromethane solution (30 mL) containing 1.29 g (15 mmol) of butane-2,3-dione and 1.15 g (15 mmol) of cysteamine was refluxed for 4 h. After the reaction solution was washed with 20 mL of saturated sodium chloride solution, it was dried over anhydrous sodium sulfate for 12 h. The solvent was removed under reduced pressure. Approximately 2 g of 2-acethyl-2-methylthiazolidine was obtained (yield percentage = 93). Using cysteamine, 2-(2-furyl)thiazolidine, 2-(5-methyl-2-furyl)thiazolidine, 2-methyltetrahydrofuran-3-spiro-2′-thiazolidine, and 2-methyl-4,5-dihydrofuran-5-spiro-

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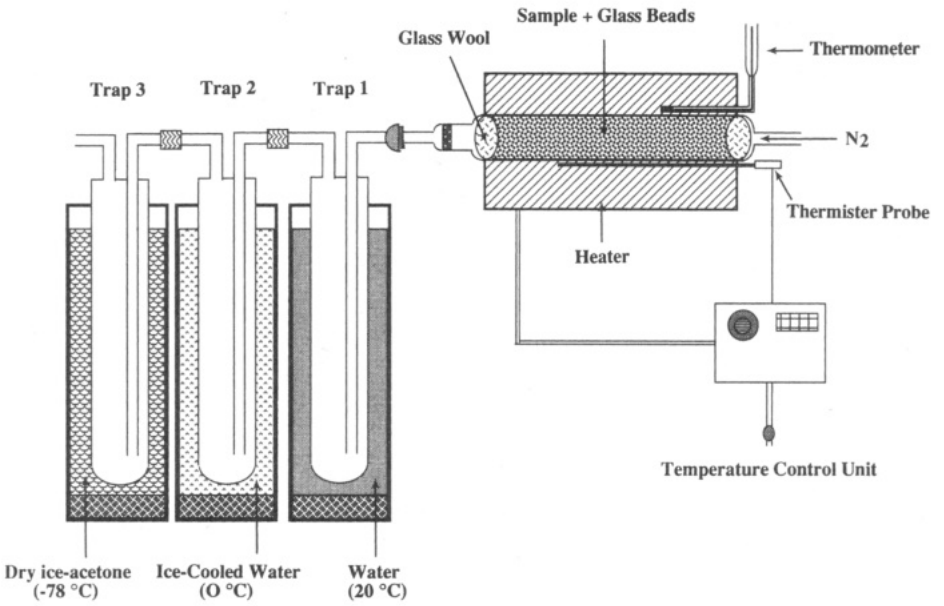

Figure 1. Apparatus used to produce and trap Maillard reaction products.

Table 1. Mass Spectral Data of Newly Identified Thiazolidines

compound	MW	I[a]	MS data, *m/z* (rel intensity)
2-acetyl-2-methylthiazolidine	145	1789	102 (100), 42 (55), 43 (26), 61 (23), 59 (20), 44 (18), 56 (9), 45 (9), 41 (7), 58 (5)
2-methyltetrahydrofuran-3-spiro-2′-thiazolidine	159	2024	114 (100), 115 (86), 60 (64), 59 (38), 61 (36), 43 (35), 159 (32), 45 (31), 54 (30), 116 (20)
2-methyl-4,5-dihydrofuran-5-spiro-2′-thiazolidine	157	2152	98 (100), 55 (56), 42 (33), 157 (30), 82 (19), 45 (18), 59 (16), 39 (14), 56 (14), 142 (12)
2-(2-furyl)thiazolidine	155	2192	165 (100), 81 (56), 96 (47), 39 (41), 109 (35), 80 (35), 156 (30), 45 (27), 94 (25), 108 (24)
2-(5-methyl-2-furyl)thiazolidine	169	2251	169 (100), 95 (58), 43 (37), 109 (37), 123 (36), 108 (28), 51 (27), 53 (25), 81 (23), 94 (23)
2,4,6-trimethyl-1,3,5-dithiazine (thialdine)	163	1747	44 (100), 59 (69), 60 (53), 42 (39), 70 (27), 58 (25), 56 (23), 71 (18), 163 (17), 43 (15)

[a] Kovats retention index on DB-Wax.

2′-thiazolidine were synthesized from furfural, 5-methylfurfural, 2-methyltetrahydrofuran-3-one, and α-angelicalactone (5-methyl-2,3*H*-furanone), respectively, with the same method used for 2-acetyl-2-methylthiazolidine. However, the reflux time for 2-methyl-4,5-dihydrofuran-5-spiro-2′-thiazolidine synthesis was extended to 24 h. The MS data of those thiazolidines are shown in Table 1.

Sample Preparation. D-Glucose (7 g), L-cysteine (7 g), or a mixture of L-cysteine (7 g) and D-glucose (7 g) was mixed with 150 g of glass beads and then placed in a 275 mm × 30 mm (o.d.) glass tube connected to three in-line traps. The glass tube was maintained at 180 °C by an electric heater. Volatile compounds formed from the sample were purged into the three traps with purified nitrogen gas for 2 h at 1 mL/s. A schematic diagram of the apparatus is shown in Figure 1. The temperatures of traps 1, 2, and 3 were 20 °C (water cooled), 0 °C (ice cooled), and −78 °C (dry ice/acetone cooled), respectively. Volatile chemicals collected in each trap were recovered with 12 mL of diethyl ether. The diethyl ether solutions were dried over anhydrous sodium sulfate for 12 h. After removal of sodium sulfate, the solvent was removed by distillation using a Vigreux column. The solvent was removed further with a purified nitrogen stream. Final weight of the each sample was adjusted to 100 mg.

Analysis of Volatiles. Identification of volatile chemicals collected in each trap was made by comparison of their Kovats gas chromatographic retention indices and mass spectra to those of authentic compounds. For some compounds, authentic samples were not available to confirm positive identification. If the mass spectrum matched precisely that of published data and the retention could be estimated from the published data, the compound was listed as tentatively identified.

Instruments. A Hewlett-Packard (HP) Model 5890 gas chromatograph (GC) equipped with a 60 m × 0.25 mm i.d. DB-Wax fused silica capillary column (J&W Scientific, Folsom, CA) and a flame ionization detector (FID) were used for routine analysis. The oven temperature was held at 40 °C for 2 min and then programmed to 200 °C at 2 °C/min. The detector and injector temperatures were 250 °C. The linear velocity of the helium carrier gas was 30 cm/s, with a split ratio of 1:30.

A Varian 3500 gas chromatograph interfaced to a Finnigan MAT Model 800 ion trap detector was used for mass spectral (MS) identification of the GC components. Column and oven conditions were as stated above.

RESULTS AND DISCUSSION

The yields (w/w) of total volatile compounds collected in traps 1, 2, and 3 from heated cysteine were 1.55%, 0.379%, and 0.508%, respectively. The yields (w/w) of total volatile compounds collected in traps 1, 2, and 3 from heated D-glucose were 0.547%, 0.315%, and 0.439%, respectively. The yields (w/w) of total volatile compounds collected in traps 1, 2, and 3 from a heated L-cysteine/D-glucose were 0.964%, 0.266%, and 0.368%, respectively. Generally, volatiles formed in the Maillard reaction systems are recovered with an organic solvent extraction (Shibamoto, 1983; Zhang and Ho, 1991). Headspace collection is also widely used because the composition of samples obtained should be close to that responsible for the typical smell of the reacted models. However, a major disadvantage of the headspace collection is that the sample obtained is very small. The newly developed method used in the present study could recover volatile chemicals in large amounts. Table 2 shows volatile compounds identified in traps 1−3 from heated D-glucose, L-cysteine, and D-glucose/L-cysteine model systems. A total of 130 chemicals was positively

Table 2. Volatile Compounds Identified in Traps 1 (T-1), 2 (T-2), and 3 (T-3) from Heated D-Glucose, L-Cysteine, and D-Glucose/L-Cysteine Model Systems

		GC peak area %								
		D-glucose			L-cysteine			D-glucose/L-cysteine		
compound	I[a]	T-1	T-2	T-3	T-1	T-2	T-3	T-1	T-2	T-3
acid										
acetic acid	1448	48.10	10.79	1.06						
formic acid	1499	1.12								
propionic acid	1541	2.44	0.53	9.17						
butyric acid	1642	1.24	0.22							
alcohols										
ethanol	932	0.98	1.45	5.94	0.06	0.27	8.98			0.06
allyl alcohol	1111									0.05
aldehydes										
acetaldehyde	714	0.07	0.12	0.82						
crotonaldehyde	1038			0.03						
2-ethyl-2-butenal	1145									*c*
esters										
ethyl formate	825	0.32	0.20	0.83						
ethyl acetate	912	0.26	0.28	0.76						
ethyl propionate	967			0.09						
ethyl pyruvate	1268			0.03						
furfuryl formate	1497	0.14	0.54	1.26						
ethyl (*E*,*Z*)-2,6-nonadienoate	1704			0.04						
furans										
2-methylfuran	863								0.02	0.73
2,5-dimethylfuran	949							0.03	0.07	3.20
2-methyltetrahydrofuran-3-one	1263	0.46	1.54	1.48						0.25
2-methyl-3(2*H*)-furanone[b]	1407	0.83	3.77	1.43						
5-methyl-2(3*H*)-furanone	1429	0.69	1.10	0.98						
furfural	1461	13.36	54.09	55.08						
2-acetylfuran	1499	0.35	5.37	2.04				1.02	1.29	1.10
furfuryl acetate	1538		1.14	0.44						
5-methylfurfural	1570	1.86	4.66	0.61						
methyl 2-furoate	1578			0.70						
5-methyl-2-acetylfuran	1608							0.12	0.06	
ethyl 2-furoate	1622			0.03						
furfuryl alcohol	1663	10.77	3.14	0.09				0.12	0.37	
5-methylfurfuryl alcohol	1722							0.65	0.06	
2-furyl-4-methyl-1,3-dioxolane	1676			0.07						
2(5*H*)-furanone	1746	0.36	0.09							
3-(2-furyl)-2-propenal	1851	0.08	0.09							
2-oxoprop-2-yltetrahydrofuran[b]	1857	0.13								
methylfuranone derivative[b]	2079	0.24								
hydrocarbons										
benzene	938								0.16	0.26
toluene	1038			0.04	0.01	0.03	0.06		0.11	0.11
ethylbenzene	1126						0.10			
1,4-dimethylbenzene	1133						0.06			0.04
d-limonene	1199						0.04			
hydroxyl ketones										
3-hydroxybutan-2-one	1277	0.32	0.75	4.48						
hydroxyacetone	1298	8.28	0.98	0.20						
3-hydroxypentan-2-one	1340	0.06	0.05							
ketones										
2-butanone	912			0.12					0.01	0.86
1-buten-3-one	945			0.10						
butane-2,3-dione	967	0.03	0.14	2.25						
2-pentanone	975						0.09		0.02	0.52
1-penten-3-one	1020			0.03						
3-hexanone	1050						0.17			0.16
pentane-2,3-dione	1055	0.03	0.15	3.26						
2-hexanone	1078									*c*
2-methylcyclopentanone	1192						0.04		0.03	0.27
2-methyl-2-cyclopenten-1-one	1366			0.03						
acetoxy-2-propanone	1465	0.23								
cyclopentene-3,4-dione[b]	1580	1.00	3.62	0.43						
mercaptans										
methyl mercaptan	699									*c*
ethyl mercaptan	731								0.04	0.03
1,2-ethynedithiol	1318							1.49	0.64	0.71
5-methylfurfuryl mercaptan	1497							0.35	*c*	
nitriles										
acetonitrile	1003						0.01			0.02
propionitrile	1023						0.04			0.09
butyronitrile	1100						0.53		0.01	0.50
oxazole										
2,4,5-trimethyloxazole	1197									*c*

Table 2 (Continued)

compound	I[a]	GC peak area %: D-glucose T-1	D-glucose T-2	D-glucose T-3	L-cysteine T-1	L-cysteine T-2	L-cysteine T-3	D-glucose/L-cysteine T-1	D-glucose/L-cysteine T-2	D-glucose/L-cysteine T-3
pyrazines										
2-methylpyrazine	1262							0.31	0.17	4.13
2,5-dimethylpyrazine	1320							0.23	0.23	0.49
2,6-dimethylpyrazine	1326							0.25	0.48	0.42
2-ethylpyrazine	1333						0.01	0.08	0.07	0.15
2,3-dimethylpyrazine	1343							0.07	0.14	
2-ethyl-6-methylpyrazine	1382							*c*	0.12	0.04
2-ethyl-5-methylpyrazine	1390							*c*	*c*	
2-ethyl-3-methylpyrazine	1403							0.16	0.26	*c*
2-ethyl-3,6-dimethylpyrazine	1449							0.23	0.65	0.79
2-ethyl-3,5-dimethylpyrazine	1460							0.22	0.60	0.83
pyridines										
pyridine	1183						0.18	0.15	0.24	2.16
2-methylpyridine	1216				0.52	1.39	7.37	0.64	0.66	5.32
2-ethylpyridine	1284				*c*	*c*	0.02			*c*
3-methylpyridine	1291							0.06	0.07	*c*
4-methylpyridine	1298				0.15	0.36	0.59	0.81	0.98	1.64
2,5-dimethylpyridine	1326				0.07	0.11		0.09		
2,4-dimethylpyridine	1338				*c*			0.03	0.06	0.05
2,3-dimethylpyridine	1358							*c*	*c*	0.07
3-ethylpyridine	1380				0.04	*c*	*c*	6.97	6.81	1.52
5-ethyl-2-methylpyridine	1413				6.89	2.96	0.83	0.35	0.47	
2-methyl-5-vinylpyridine[b]	1509				0.12	0.06				
3-ethyl-4-methylpyridine	1545				0.10			0.53	0.44	
pyrroles										
1-ethylpyrrole	1181						0.32		0.08	1.81
1*H*-pyrrole	1513				0.24	0.32	0.79	0.83	1.84	2.94
2,5-dimethypyrrole	1601				0.05			0.31	0.44	
2-ethylpyrrole	1619							0.22	0.05	
2-acetyl-1-ethylpyrrole	1635							*c*	0.03	
1-(2-furyl)pyrrole	1823							0.24		
2-acetylpyrrole	1967							0.14		
thiazoles, thiazolines, thiazolidines										
2-methylthiazole	1239				*c*	0.02	0.16	0.09	0.13	1.08
thiazole	1248						0.37	0.13	0.16	2.52
4-methylthiazole	1278							0.05	0.05	0.27
2,4-dimethylthiazole	1283							0.07	0.10	0.21
2-methyl-2-thiazoline	1299				0.56	0.18	0.26	0.45	0.59	1.06
2-ethylthiazole	1304				*c*	*c*	0.01	*c*	*c*	0.30
5-ethylthiazole[b]	1315							0.18		
2-ethyl-2-thiazoline	1368				0.02	0.03	0.04	0.31	0.37	0.18
4,5-dimethylthiazole	1371							0.03	0.06	0.05
2,4,5-trimethylthiazole	1377							0.56	1.29	0.76
2-propylthiazole	1381				0.12	0.19	0.20	0.05	0.07	0.03
2-methylthiazolidine	1422				78.98	86.37	48.85	33.93	51.18	5.79
alkylthiazole[b]	1470				1.24	1.27	1.18	3.33	4.42	1.91
2-ethylthiazolidine	1514				0.14	*c*		0.30	*c*	
2-propylthiazolidine	1615				0.73	0.14	0.01	0.82	1.42	
2-acetylthiazole	1641							0.00	0.15	0.02
2-acetyl-2-methylthiazolidine	1789							*c*		
2-methyltetrahydrofuran-3-spiro-2′-thiazolidine	2024							*c*		
2-methyl-4,5-dihydrofuran-5-spiro-2′-thiazolidine	2152							*c*		
2-(2-furyl)thiazolidine	2192							0.11		
2-(5-methyl-2-furyl)thiazolidine	2251							*c*		
thiophenes										
thiophene	1022				*c*	0.02	4.84		0.02	6.19
2-methylthiophene	1095						0.17		0.05	1.01
2,3-dihydrothiophene	1104									0.59
tetrahydrothiophene	1109						0.06			0.06
2-methyltetrahydrothiophene	1116						0.07			0.20
3-methylthiophene	1120						0.08		0.03	0.33
2-methyl-4,5-dihydrothiophene	1148						0.05			
2,5-dimethylthiophene	1157				0.01	0.02	0.63	0.03	0.04	0.86
2-ethylthiophene	1173						0.68	0.02	0.02	0.82
3-ethylthiophene	1211				0.01	0.02	0.68	0.02	0.02	0.53
2,3-dimethylthiophene	1212				*c*	0.02	0.50	0.03	0.06	0.71
2-vinylthiophene	1298						0.16	*c*	0.11	0.61
3-vinylthiophene	1343				0.03	0.06	0.45	0.10	0.11	0.88
2-pentylthiophene	1460				0.03					
2-acethylthiophene	1762							*c*		
2-thiophenemethanol	1937							0.03		
trithiolanes										
3,5-dimethyl-1,2,4-trithiolane, 1st	1597						0.05	0.10	0.05	0.15
3,5-dimethyl-1,2,4-trithiolane, 2nd	1618						0.03	*c*	0.02	0.36
3-methyl-1,2,4-trithiolane[b]	1857				0.11	0.14	0.06	1.42	0.06	0.11

Table 2 (Continued)

compound	I[a]	GC peak area %								
		D-glucose			L-cysteine			D-glucose/L-cysteine		
		T-1	T-2	T-3	T-1	T-2	T-3	T-1	T-2	T-3
miscellaneous										
acetaldehyde diethyl acetal	898			0.09						
1,4-dioxane	1015				*c*	*c*	1.52			
acetic anhydride	1236			0.34						
1,2-dithiane	1489				0.46	0.09	0.05	0.32	*c*	
γ-butyrolactone	1620	0.49								
2,4,6-trimethyldihydro-1,3,5-dithiazine (thialdine)	1747							12.39	4.36	23.24
4-methyl-6-isopropyl-α-pyrone[b]	1862	0.02	0.18							
2,6-di-*tert*-butyl-4-methylphenol	1912	0.29	1.00	0.39	0.06	0.32	0.63	0.05	0.28	0.21
dibutyl phthalate	2683	0.08	0.26	0.45	0.02	0.07	0.10			

[a] Kovats index on DB-Wax. [b] Tentatively identified. [c] GC peak area % less than 0.01.

identified in the three systems. Forty-one chemicals were identified in the samples from D-glucose heated alone, 52 chemicals were found in the samples from L-cysteine heated alone, and 93 chemicals were identified in the samples from L-cysteine/D-glucose heated together. Among the chemicals identified, 33 were unique to D-glucose, 5 were unique to L-cysteine, and 36 were unique to D-glucose/L-cysteine.

Oxygenated Compounds. In the present study, when D-glucose was heated alone, high levels of furfural and acetic acid were formed, which is consistent with previous reports (Hodge, 1967). However, furfural was not detected in the sample from the L-cysteine/D-glucose system, suggesting that furfural was consumed completely by the reaction with L-cysteine and its breakdown products. The same phenomenon was observed in the cases of aliphatic acids, aliphatic aldehydes, aliphatic esters, and hydroxy ketones. Some acetic acid formed might react with alcohols such as ethanol to form acetate esters. It is proposed that carbonyl compounds, alcohols, and esters formed from sugar degradation (Hodge, 1967) undergo secondary reactions with amines to form heterocyclic flavor compounds (Schirle-Keller and Reineccius, 1992).

Nitrogen-Containing Compounds. In the present study, pyrazines and pyridines were the most abundant compounds found in the samples from the L-cysteine/D-glucose model system. Pyrazines are one of the major volatile chemicals produced in the Maillard reaction system and possess a roasted or toasted flavor (Maga and Sizer, 1973; Shibamoto, 1983); they have been widely used in imitation flavors such as cooked meat flavor. Among 10 pyrazines identified in the L-cysteine/D-glucose model system, 2,5- and 2,6-dimethylpyrazines were recovered in relatively high levels. 2-Ethylpyrazine was the only pyrazine detected in the samples from L-cysteine heated alone.

The first pyridine derivative reported in a browning model system was unsubstituted pyridine formed in a lactose/casein model system (Ferretti and Flanagan, 1971). Generally, pyridines possess less pleasant odors than pyrazines and have not received much attention as flavor chemicals (Buttery et al., 1977). In the present study, 10 pyridines were identified in the samples from the L-cysteine/D-glucose model system. Many pyridines were also found in the samples from L-cysteine heated alone, with 3-ethylpyridine the most abundant. 5-Methyl-2-methylpyridine was the most abundant pyridine in the L-cysteine system alone. It is interesting that all pyridines except 3-methylpyridine found in the samples from L-cysteine/D-glucose model system were also found in the samples from L-cysteine heated alone. The formation mechanisms of pyridines have not yet been well investigated; however, Buttery et al. (1977), who identified 13 pyridines in the volatile components of roasted lamb fat, proposed that pyridines were formed from the reaction of fatty aldehydes and ammonia.

Pyrroles began to appear in the reports of Maillard reaction products in the late 1960s (Kato and Fujimaki, 1968; Kobayashi and Fujimaki, 1965). Pyrroles have not received much attention as flavor chemicals because most pyrroles do not possess desirable food flavors. However, pyrroles are among the most widely distributed heterocyclic compounds in heat-processed foods such as coffee (Maga, 1981). The L-cysteine/D-glucose model system produced seven pyrroles and L-cysteine gave three pyrroles upon heating. Some oxygenated pyrroles such as 2-acetylpyrrole and 1-furfurylpyrrole were formed only from the L-cysteine/D-glucose model system, suggesting that the formation of these requires D-glucose. Three nitriles were identified in the samples both from the L-cysteine/D-glucose model system and from L-cysteine alone. The kinds and relative quantities of these nitriles were consistent in the two systems, indicating that these nitriles formed from cysteine degradation rather than from a reaction between L-cysteine and D-glucose.

Sulfur-Containing Compounds. Thiophenes were also one of the major products from the L-cysteine/D-glucose system and L-cysteine alone; they yielded 14 and 13 thiophenes, respectively. All thiophenes were common to the two systems except for 2-acetylthiophene, which formed from L-cysteine/D-glucose. There have been many reports on thiophene formation from the Maillard model systems consisting of sugar and sulfur-containing amino acids (Mulders, 1973; Sakaguchi and Shibamoto, 1978); however, it has been shown that most thiophenes found in the Maillard model systems can be formed from L-cysteine alone upon oxidative degradation (Sheldon and Shibamoto, 1987), acylthiophenes cannot. Mulders (1973) found five acylthiophenes in a pentane–ether extract of a cysteine/cystine–ribose model system and proposed that acylthiophenes were formed through a Michael addition of the thiol group of cysteine to the α,β-unsaturated carbonyl compounds formed from a sugar.

Many polysulfur heterocyclic compounds, with five- or six-membered rings, have been reported in the Maillard model systems (Mottram, 1991). 3,5-Dimethyl-1,2,4-trithiolane was first isolated from boiled beef (Chang et al., 1968) and subsequently found in various other cooked foods (Mottram, 1994). It was also reported as the major product in the volatile compounds formed from the thermal reaction of glucose with cysteine (Zhang and Ho, 1991). In the present study,

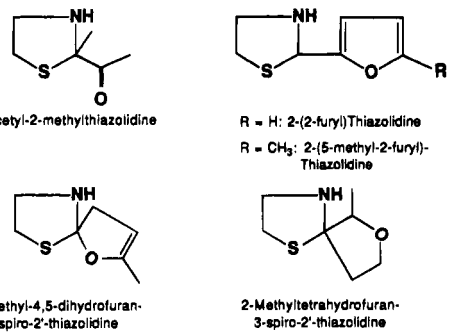

Figure 2. Chemicals formed from cysteamine and D-glucose degradation products.

three trithiolanes were identified both in L-cysteine/D-glucose and in L-cysteine alone.

Nitrogen- and Sulfur-Containing Compounds. The L-cysteine/D-glucose system produced 2-methylthiazolidine and 2,4,6-trimethyldihydro-1,3,5-dithiazine (thialdine) as major components in the present study. Thermal degradation of cysteine also produced thialdine in large amount (Zhang et al., 1988). It has been hypothesized that thiazolidines form from cysteamine, which is a decarboxylated cysteine, and carbonyl compounds such as acetaldehyde and glyoxal (Sakaguchi and Shibamoto, 1978). When cysteamine and D-glucose were heated together, thiazolidine and 2-methylthiazolidine formed as major volatile components (Sakaguchi and Shibamoto, 1978). There was no report on the formation of thiazolidines from a cysteine/glucose browning model system in the early era of the study of Maillard reaction products (Scanlan et al., 1973). Later, it was shown that the formation of thiazolidines from cysteine is pH dependent. At pH lower than 8, the amino group ($pK_a = 10.7$) of cysteine does not react with a carbonyl group due to its protonation. On the other hand, the mercapto group ($pK_a = 8.3$) on cysteine reacts with a carbonyl group to form an intermediate hemimercaptal, which forms a thiazolidine followed by decarboxylation and dehydration reactions (Yeo and Shibamoto, 1991b). This leads to the conclusion that pH 8 is optimum for thiazolidine formation. In fact, many browning systems were conducted at pH values higher than 8 to promote sugar degradation for production of carbonyl compounds (Hodge, 1967).

In the present study, L-cysteine alone also produced 2-methylthiazolidine as a major component. Oxidative degradation of L-cysteine by UV light also produced 2-methylthiazolidine (Sheldon and Shibamoto, 1987). It was proposed that L-cysteine decomposed to hydrogen sulfide, carbon dioxide, ammonia, and acetaldehyde; the latter reacts with cysteine to give 2-methylthiazolidine upon oxidation (Obata and Tanaka, 1965). Thiazolidines such as 2-acetyl-2-methylthiazolidine formed from the reaction between glucose degradation products such as butane-2,3-dione and cysteamine were found in the L-cysteine/D-glucose system in the present study. These compounds are shown in Figure 2.

Conclusion. It is generally recognized that the samples obtained directly from headspace resemble most closely the flavors which one actually smells in cooked foods. Most chemicals formed in the Maillard reaction system have been recovered by liquid–liquid extraction; there are only a few reports on analysis of headspace volatiles of the Maillard reaction systems. In the present study, volatile chemicals were satisfactorily recovered from the three traps using liquid–solid extraction. This system has an advantage over one requiring liquid–liquid extraction, where the aqueous phase may alter the structure or the recovery of certain compounds. Additionally, the advantage of this method over headspace systems is that many compounds are recovered in greater quantity and they are not in contact with appreciable amounts of water.

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