

Formation of Sulfur-Containing Compounds from the Reaction of D-Glucose and Hydrogen Sulfide

Thirty-nine compounds produced from the reaction of D-glucose with hydrogen sulfide in aqueous solution were identified by a GC-MS technique. The major volatiles obtained from this reaction system were sugar degradation products and sulfur-containing heterocyclic compounds. Most compounds identified were found in foods and some of them give characteristic odors to particular foods. The formation of flavor compounds in this system indicates that sugar and hydrogen sulfide may be precursors of cooked food flavors.

A large number of sulfur-containing compounds are found in cooked meat (Wilson and Katz, 1972; Persson and von Sydow, 1973; Mussinan and Walradt, 1974). Degradation of sugar yields carbonyl compounds which can react with hydrogen sulfide formed by decomposition of sulfur-containing amino acids. According to Shibamoto and Russell (1977) this reaction may result in the formation of sulfur-containing compounds which may contribute to the flavor of cooked meat. They found twenty-six sulfur-containing compounds in their D-glucose-hydrogen sulfide-ammonia model system; these included thiols, sulfide thiophenes, thiazoles, and thiazolines. Hydrogen sulfide seems to play an important role in the production of sulfur-containing compounds associated with cooked meat flavors. Several researchers have reported that a sugar-amino acid browning system produces hydrogen sulfide (Obata and Tanaka, 1965; Fujimaki et al., 1969). Kobayashi and Fujimaki (1965) have postulated the formation pathway of hydrogen sulfide from cysteine. van den Ouweland and Peer (1975) investigated the volatile compounds produced by the reaction of 4-hydroxy-5-methyl-3(2*H*)-furanone, which forms in the sugar decomposition reaction (Hodge, 1967), with hydrogen sulfide. They reported the formation of fifteen sulfur-containing compounds from the reaction of their model system. Shibamoto (1977) identified six sulfur-containing compounds from the reaction of furfural, which is also a sugar decomposition product, with hydrogen sulfide and ammonia. In this study, we have identified sulfur-containing compounds from the reaction of D-glucose with hydrogen sulfide in order to investigate the origin of meat flavor.

EXPERIMENTAL SECTION

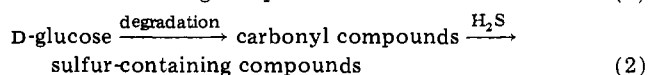
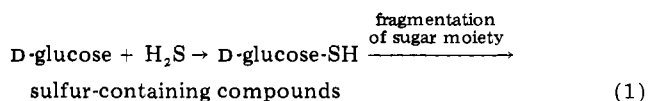
Sample Preparation. Hydrogen sulfide gas was bubbled through an aqueous solution (100 mL) containing 0.1 mol of D-glucose for 10 min at 0°C in a Kjeldahl flask. The pH 10 is not a food cooking condition. This reaction, however, produces acid (Hayami, 1961) and the pH of the final reaction mixture becomes acidic (pH 4). The pH of the solution was adjusted to 10 in order to promote sugar fragmentation. The neck of the flask was flame-sealed and the flask placed in an oven at 100 °C for 5 h. Volatiles were isolated from the reaction mixture with 200 mL of methylene chloride using a liquid-liquid continuous extractor for 6 h. Volatiles were identified by the gas chromatographic-mass spectrometric method (Shibamoto and Russell, 1976).

Gas-Liquid Chromatography-Mass Spectrometry. A Hewlett Packard Model 5710 A gas chromatograph equipped with a flame ionization detector and a 100 m × 0.25 mm i.d. glass capillary column coated with Carbowax 20M was used. The oven temperature was programmed from 70 to 170 °C at 1 °C/min. The Hitachi M-52 gas chromatograph-mass spectrometer was used for GC-MS

analysis. The gas chromatographic column and oven conditions were the same as for the Hewlett Packard instrument.

RESULTS AND DISCUSSION

The compounds identified from the reaction of D-glucose with hydrogen sulfide at pH 10 are listed in Table I, and their gas chromatogram is shown in Figure 1. The identification of volatiles was conducted by the comparison of GC retention indices and mass spectra of unknowns to those of authentic samples. The compounds analyzed by MS fragmentation alone, that is, those that were not compared with authentic samples (due to lack of authentic samples), were classified as tentatively identified. The volatiles which were found in this reaction mixture can be classified into two groups. One group comprises the sugar degradation products (e.g., 2-butanone, 2-methylfuran, acetoin, furfural, etc.). The other comprises the sulfur-containing compounds yielded from the reaction of hydrogen sulfide and the sugar degradation products (e.g., thiophene, 1,2,4-trithiolane, etc.). Two possible formation pathways can be proposed for these sulfur-containing compounds:



Shibamoto and Russell (1977) reported the formation of sulfur- and nitrogen-containing compounds from the reaction of D-glucose with hydrogen sulfide and ammonia. They found sulfides, thiophenes, furans, thiazoles, and pyrazines. The sulfides and thiophenes are apparently products of the reaction of sugar and hydrogen sulfides. In the present study, we found cyclic methylene polysulfides which were not reported in their study; *s*-trithiane has been found in chicken meat and gives a pungent sulfurous odor (Minor et al., 1965). In addition to polysulfides, this reaction system yielded many compounds which give characteristic odors to particular foods (e.g., 2,4-acetyl-3-methylthiophene: fried onion; methyl furfuryl sulfide: coffee; 2-acetyl-3-methylthiophene: nuts; etc.). The flavor compounds which were found in this reaction usually make a dominant contribution to the overall flavor impression of foods. Odor descriptions of identified compounds were made by five experienced flavorists and they are shown in Table I.

The formation pathways of these flavor compounds in cooked foods are not yet clearly understood. But one may conclude that some of these compounds come from the reaction of sugar and hydrogen sulfide which is formed

Table I. Compounds Identified from the Reaction of D-Glucose with Hydrogen Sulfide at pH 10

Peak no.	Compounds	Odor description	Occurrence in foods	MS references
1	Acetone	Ethereal	Peanuts ^a	Stenhagen et al. (1974a)
2	2-Butenal	Pungent		Stenhagen et al. (1974b)
3	2-Butanone	Ethereal, sweet	Coffee, ^b beef ^c	Stoll et al. (1967)
4	2-Methyl-4,5-dihydrofuran	Ethereal		Stenhagen et al. (1974c)
5	Solvent (methylene chloride)			Stenhagen et al. (1974d)
6	2-Pentanone	Burnt, green	Coffee, ^b beef ^c	Stoll et al. (1967)
7	2-Methylfuran	Ethereal	Coffee, ^b chicken ^d	Stoll et al. (1967)
8	2,5-Dimethylfuran	Ethereal	Beef ^c	Stenhagen et al. (1974e)
9	Solvent impurity (trichloromethane)			Stenhagen et al. (1974f)
10	Thiophene	Sickly, pungent	Coffee, ^b beef ^c	Porter and Bladas (1971)
11	2,3-Pentanedione	Sickly, buttery	Coffee, ^e	van den Ouweland and Peer (1975)
12	2-Methylthiophene	Heated onion	Chicken, ^d beef ^c	Budzikiewicz et al. (1964)
13	3-Methylthiophene	Fatty, winey	Beef ^c	Cornu and Massot (1966)
14	2,5-Dimethylthiophene	Greenish	Beef ^c	Boelens et al. (1971)
15	2-Ethylthiophene	Styrene-like	Beef ^e	Kato et al. (1973)
16	2,4-Dimethylthiophene	Fried onion	Onion ^f	Boelens et al. (1971)
17	2-Methyltetrahydrofuran-3-one	Sweet, roasted	Pork liver ^g	Ferretti and Flanagan (1971)
18	Acetoin	Creamy, fatty	Pork liver, ^g beef ^h	Ferretti and Flanagan (1971)
19	Acetol	Sweet, caramellike	Pork liver ^g	Ferretti and Flanagan (1971)
20	3-Hydroxy-2-pentanone	Sweet, fruity	Coffee, ^b pork liver ^g	Mussinan and Walradt (1974)
21	2-Hydroxy-3-pentanone	Sickly, ethereal	Coffee, ^b pork liver ^g	Mussinan and Walradt (1974)
22	Furfural	Sweet, caramellike	Coffee, ^b popcorn ⁱ	Stoll et al. (1967)
23	Methyl furfuryl sulfide	Coffee-like	Coffee ^b	Stoll et al. (1967)
24	2-Acetylfuran	Tobacco-like	Beef, ^c coffee ^b	Stoll et al. (1967)
25	Unknown			
26	Methyl furfuryl ketone	Mild sweet	Coffee, ^b beef ^j	Stoll et al. (1967)
27	Unknown			
28	Unknown			
29	2-Methyl tetrahydrothiophen-3-one	Acetylenic	Beef, ^k coffee ^b	Kato et al. (1973)
30	Tetrahydrothiophen-3-one	Acetylenic	Coffee, ^b filberts ^l	Stoll et al. (1967)
31	Methylthiofuroate	Cabbage-like	Coffee ^b	Stoll et al. (1967)
32	Ethyl 2-furyl ketone	Sweet, caramellike	Coffee ^b	Stoll et al. (1967)
33	Unknown			
34	3-Hydroxy-2-methyltetrahydrofuran	Fatty		van den Ouweland and Peer (1975)
35	2-Acetyl-5-methylfuran	Caramellike	Coffee ^b	Stoll et al. (1967)
36	Unknown			
37	Furfuryl alcohol	Mild warmy, oily	Coffee, ^b pork liver ^g	Mussinan and Walradt (1974)
38	Furfuryl methyl ether (tentative)			Stenhagen et al. (1974g)
39	Unknown			
40	Thiophene-2-carboxaldehyde	Coconut-like	Bread, ^m coffee ^b	Mussinan and Walradt (1974)
41	Tetrahydrothiophene-2,3-dione (tentative)			
42	5-Methylthiophene-2-carboxaldehyde	Cherry, almond	Peanuts ^a	Stoll et al. (1967)
43	2,5-Dimethylthiophene-3-carboxaldehyde (tentative)			Mussinan and Walradt (1974)
44	Unknown			
45	Unknown			
46	2-Acetylthiophene	Mustard-like	Coffee, ^b peanuts ^a	Mussinan and Walradt (1974)
47	1,2,4-Trithiolane	Sulfurous		Morita and Kobayashi (1967)
48	2-Acetyl-3-methylthiophene	Nutty	Coffee ^b	Stoll et al. (1967)
49	Unknown			
50	2-Acetyl-5-methylthiophene	Sweet, flowery	Coffee ^b	Stoll et al. (1967)
51	Unknown			
52	Unknown			
53	2-Hydroxy-3-methyl-2-cyclopenten-1-one (tentative)			
54	2-Thienyl methyl ketone (tentative)			
55	Unknown			
56	Unknown			
57	(2-Thienyl)-1-propane-1,2-dione	Woody	Coffee ^b	Stoll et al. (1967)
58	2-Acetyl-4-methylthiophene (tentative)			
59	Unknown			
60	Unknown			
61	Unknown			
62	2-Thienyl alcohol	Burnt	Coffee, ^b beef ^k	Stoll et al. (1967)
63	s-Trithiane	Pungent, sulfurous	Chicken ⁿ	Minor et al. (1965)
64	Methyl-2-thienylcarboxylate (tentative)		Coffee ^b	Stoll et al. (1967)

^a Walradt et al. (1971). ^b Stoll et al. (1967). ^c Persson and von Sydow (1973). ^d Boelens et al. (1971). ^e Stoffelsma et al. (1968). ^f Nonaka et al. (1967). ^g Mussinan and Walradt (1974). ^h Liebich et al. (1972). ⁱ Walradt et al. (1970). ^j Watanabe and Sato (1972). ^k Wilson et al. (1973). ^l Kinlin et al. (1972). ^m von Sydow and Anjou (1969). ⁿ Minor et al. (1965)

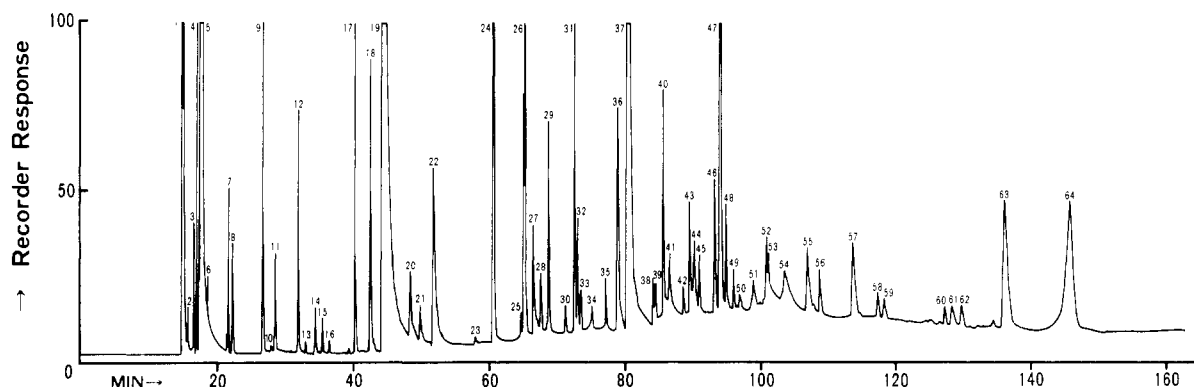


Figure 1. Gas chromatogram of compounds produced from the reaction of D-glucose and hydrogen sulfide at pH 10: column, 100 m \times 0.25 mm i.d. glass capillary coated with Carbowax 20M, programmed from 70 to 170 $^{\circ}$ C at 1 $^{\circ}$ C/min and held. Nitrogen carrier gas flow was 15 cm/s. See Table I for peak identification.

from amino acid degradation (Kato et al., 1973). Further study will be necessary to clarify the precise formation pathways of flavor compounds in cooked foods.

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