

# Some Novel Meatlike Aroma Compounds from the Reactions of Alkanediones with Hydrogen Sulfide and Furanthiols

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The products of reactions of hydrogen sulfide with 2,3-butanedione and with 2,3-pentanedione in dilute ethanolic solution were analyzed by GC-MS and GC-odor port analysis. Components were also collected from the GC column and analyzed by  $^1\text{H}$  NMR. Mercaptoketones were formed which readily oxidized to the corresponding disulfides with traces of mono- and trisulfides. When 2-methyl-3-furanthiol or 2-furylmethanethiol was added to the reaction mixtures, a series of disulfides containing alkanone, 2-methyl-3-furyl and 2-furanmethyl moieties were formed. Some of these compounds have been found recently in the volatiles of cooked meat and in meatlike model systems. GC-odor port evaluation of the components of the reaction systems showed that disulfides containing the 2-methyl-3-furyl group had meaty aromas, whereas those without this group were sulfurous or onion-like in character.

**Keywords:** *Aroma; meat; mercaptoketones; disulfides*

## INTRODUCTION

Sulfur-containing furans and thiophenes and related disulfides are known to possess strong meatlike aromas and exceptionally low odor threshold values. In 1976 it was reported that furans and thiophenes with a thiol group in the 3-position possessed meatlike aromas (Evers et al., 1976), and the corresponding disulfides formed by oxidation of furan and thiophene thiols were also found to have meatlike characteristics and exceptionally low odor threshold values (Buttery et al., 1984). A number of such compounds are formed in heated model systems containing hydrogen sulfide or cysteine and pentoses or other sources of carbonyl compounds (Farmer and Mottram, 1990; Farmer et al., 1989; Mottram and Whitfield, 1994), and in the thermal degradation of thiamin (Güntert et al., 1993a,b; van der Linde et al., 1979; Werkhoff et al., 1990). A few compounds of this type have been reported in meat itself (Farmer and Patterson, 1991; Gasser and Grosch, 1988; MacLeod and Ames, 1986).

During recent studies in our laboratories with model reaction mixtures and heated meat systems we isolated a number of sulfides and disulfides which contained alkanone, 2-methyl-3-furyl, or 2-furylmethyl moieties (Madruga, 1994). A number had meatlike odors at low concentration, and they appeared to originate from the oxidation of mercaptoketones and furanthiols. The routes involved in the formation are likely to be the interaction of hydrogen sulfide with dicarbonyls, furanones, and furfurals, all of which are important intermediate products of the Maillard reaction.

This paper reports on the disulfides and their mono- and trisulfide homologues which were formed in reactions between hydrogen sulfide with  $\alpha$ -diketones. Other

disulfides formed when the reaction was carried out in the presence of 2-methyl-3-furanthiol and 2-furylmethanethiol are also reported.

## EXPERIMENTAL PROCEDURES

**Reaction Mixtures.** Aliquots (2 mL) of a solution of 2,3-butanedione (Aldrich Chemical Co.) in ethanol (2.5% v/v) were placed in 5 mL glass ampules in an ice-salt mixture (temperature  $-15^\circ\text{C}$ ). Hydrogen sulfide from a lecture bottle was passed through the solutions for 40 min at a flow of approximately 30 mL/min. 2-Methyl-3-furanthiol (50  $\mu\text{L}$ ) (Aldrich) was then added to one reaction mixture, and a similar amount of 2-furylmethanethiol (Aldrich) was added to another. Hydrogen sulfide was passed through each solution for a further 5 min. A third reaction mixture received no further treatment. The ampules were allowed to reach room temperature, and then nitrogen was blown through each reaction mixture until excess hydrogen sulfide was removed. Finally the ampules were held at room temperature for 30 min before analysis. A similar set of reaction mixtures were prepared using 2,3-pentanedione and a 1:1 mixture of 2,3-butanedione and 2,3-pentanedione. A mixture of 2-methyl-3-furanthiol and 2-furylmethanethiol (50  $\mu\text{L}$  each) in 2 mL of ethanol was also prepared and allowed to stand at room temperature for 1 h before analysis.

**Gas Chromatography.** A split/splitless injection was used to introduce 1  $\mu\text{L}$  aliquots of each reaction mixture onto a fused silica capillary column installed in a Hewlett-Packard HP5890 gas-chromatograph. The column effluent was split equally between a flame ionization detector and an odor port, where the aromas of the eluting components could be evaluated. The column was a 30 m  $\times$  0.32 mm (i.d.) capillary column coated with DB-5 at 1  $\mu\text{m}$  film thickness (J&W Scientific Inc). Helium at 2 mL/min was used as carrier gas. The oven was held at  $60^\circ\text{C}$  for 5 min and then programmed at  $4^\circ\text{C}/\text{min}$  to  $250^\circ\text{C}$ . A solution containing  $\text{C}_6$ - $\text{C}_{20}$  *n*-alkanes was chromatographed before each new reaction mixture was analyzed to allow calculation of linear retention indices (LRI) for each sample component. Each reaction mixture was assessed by GC-odor port evaluation using four individuals, experienced in aroma evaluation, who provided descriptions for each aroma detected.

**Gas Chromatography-Mass Spectrometry (GC-MS).** The reaction mixtures were also analyzed by GC-MS using a

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Hewlett-Packard HP5988A mass spectrometer fitted with an HP 5890 GC and an HP Chemstation data system. The GC column and conditions used were the same as those described above. The following conditions were used for the mass spectrometer: source temperature, 250 °C; ionizing voltage, 70 eV; scan range,  $m/z$  29–290, with 1 scan/s.

#### Nuclear Magnetic Resonance Spectroscopy (NMR).

Prior to NMR analysis, components eluting from the gas chromatograph were collected in cooled glass capillary tubes (Microcaps). The GC effluent was split between an FID and a collection port. When a component of interest eluted from the column, a 100  $\mu$ L Microcap (1.42 mm o.d.) was pushed into a tight-fitting PTFE sleeve within the collection port to collect the sample. During collection the tube was surrounded by solid carbon dioxide. For each component of interest, three collections within one tube (between 5 and 50  $\mu$ g) were made from separate GC analyses. One end of the tube was then sealed in a microflame, and 99.96% deuteriobenzene (7  $\mu$ L, Merck Sharp and Dohme Canada Limited) was added. The contents of the tube were concentrated at the sealed end by spinning in a centrifuge, and the open end was then sealed.

The NMR spectra were recorded on a Bruker CXP 100 spectrometer fitted with a  $^1\text{H}$  microprobe head. The sealed Microcap was inserted into a PTFE sleeve fitted to an inverted NMR tube (5 mm o.d.), and the tube was positioned in the spinner so that the center of the solution corresponded to the center of the coil in the microprobe. Depending on the size of the sample, between 1000 and 12 000 scans (1–12 h) were required to obtain definitive spectra. Spectral analyses were carried out by assuming first-order principles.

## RESULTS

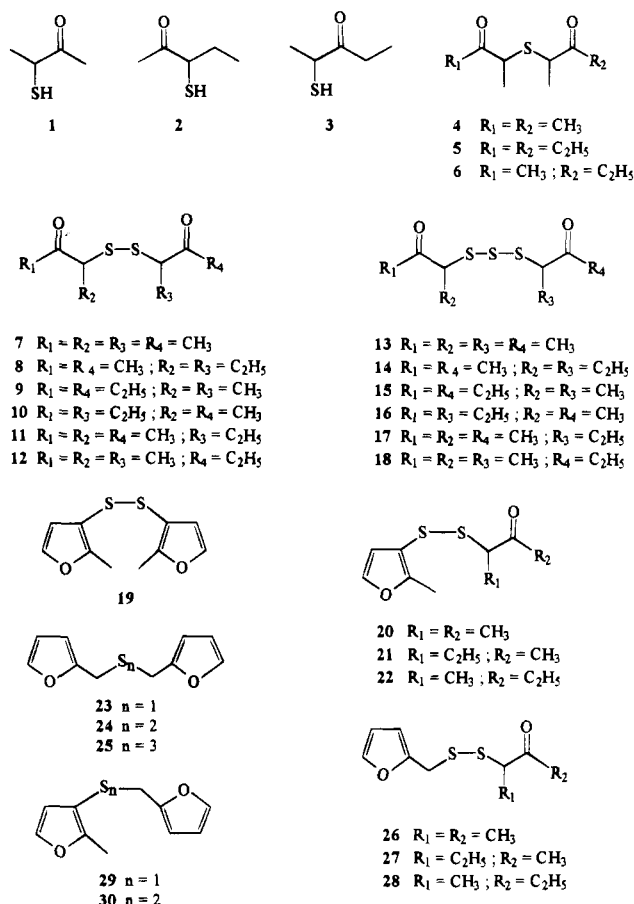
**Reaction of Alkanediones with Hydrogen Sulfide.** The major compounds from the reactions of 2,3-butanedione, 2,3-pentanedione, and a 1:1 combination of these compounds with hydrogen sulfide, in dilute ethanolic solution, are shown in Figure 1. With the butanedione there were three major GC peaks corresponding to 3-mercapto-2-butanone (1) and the corresponding disulfide, bis(1-methyl-2-oxopropyl) disulfide (7). The latter compound contains two asymmetric centers, one on each 1-methyl-2-oxopropyl moiety, and the two diastereoisomers were resolved into separate GC peaks. Small amounts of the corresponding mono-sulfide 4 and trisulfides 13 were also found, although diastereoisomers were not evident.

The mass spectra of all these sulfides showed a base peak at  $m/z$  43 ( $\text{CH}_3\text{CO}^+$ ), similar to the parent mercaptobutanone, with a small peak at  $m/z$  103 resulting from fission of the sulfide link (Table 1). They all showed molecular ions and  $M + 2$  ions arising from the  $^{34}\text{S}$  isotope.

The  $^1\text{H}$  NMR spectra of 1 and 7 are characterized by their distinctive methyl resonances (Table 1). In the spectrum of the mercaptan, the protons of the methyl  $\alpha$  to the methinethiol group resonated as a doublet at  $\delta$  1.09 and those of the acetyl methyl at  $\delta$  1.75. In the disulfide the protons of the two methyls  $\alpha$  to the methine disulfide group resonated as a doublet at  $\delta$  1.08; however, those of the two acetyl methyls resonated as two singlets at  $\delta$  1.86 and 1.90. The two diastereoisomers of 7 eluted closely on the GC column and were trapped together; thus, the noncoincidence of the latter resonances is attributed to a difference in symmetry in the two diastereoisomers.

GC-odor port analysis of the reaction mixture gave onion-like descriptions for bis(1-methyl-2-oxopropyl) disulfide and its mono- and trisulfide homologues (Table 1).

The reaction of 2,3-pentanedione and hydrogen sulfide gave a mixture of 3-mercapto-2-pentanone (2) and



**Figure 1.** Sulfur compounds formed from the reaction of alkanediones, hydrogen sulfide, 2-methyl-3-furanthiol, and 2-furylmethanethiol.

2-mercapto-3-pentanone (3). Symmetrical disulfides 8 and 9 and the unsymmetrical disulfide 10, produced from the oxidation of these two mercaptoketones, were the major components formed in the reaction, and on the GC column they were each resolved into two diastereoisomeric pairs. The corresponding three trisulfides 14–16 were also formed, but only one related sulfide, bis(1-methyl-2-oxobutyl) sulfide (5), was produced.

The two mercaptopentanone isomers could be readily identified from their mass spectra, which agreed with published spectra (Hartman et al., 1984). Both had small molecular ions ( $m/z$  118), and 3-mercapto-2-pentanone had a base peak at  $m/z$  43 ( $\text{CH}_3\text{CO}^+$ ) and a major fragment at  $m/z$  75 ( $\text{C}_2\text{H}_5\text{CHSH}^+$ ) due to the fission of the pentanone at C2. With the 2-mercapto-3-pentanone, fission at C3 gave a base peak  $m/z$  57 ( $\text{CH}_3\text{-CH}_2\text{CO}^+$ ) and another strong ion  $m/z$  61 ( $\text{CH}_3\text{CHSH}^+$ ). Mass spectra of all the symmetrical and unsymmetrical mono-, di-, and trisulfides gave clear molecular ions and characteristic fragmentations (Table 1). The abundant ion at  $m/z$  57 was characteristic for compounds formed from the oxidation of 2-mercapto-3-pentanone, while compounds with an abundant ion at  $m/z$  43 were oxidation products of 3-mercapto-2-pentanone. Unsymmetrical compounds which were obtained from a mixture of the two mercaptoketones showed abundant ions at both  $m/z$  57 and 43.

The  $^1\text{H}$  NMR spectra of 2, 3, and 8–10 are recorded in Table 1 and, similar to the spectra of 1 and 7, they are dominated by their characteristic methyl resonances. In the spectrum of the mercaptan 2 the protons

**Table 1. Spectral Data, Linear Retention Indices (LRI), and Odor Descriptions for Sulfur Compounds Obtained from the Reaction of Alkanediones, 2-Methyl-3-furanthiol, 2-Furylmethanethiol, and Hydrogen Sulfide**

no.	compound	LRI	spectral data: MS ( <i>m/z</i> , %) and <sup>1</sup> H NMR (100 MHz, C <sub>6</sub> D <sub>6</sub> , TMS)	odor port description	reaction mixture <sup>a</sup>
1	3-mercapto-2-butanone	815	43 (100), 61 (75), <b>104</b> (47), 60 (25), 35 (9), 105 (3), 106 (2) δ 1.09 (d, <i>J</i> = 8 Hz, 3H), 1.40 (d, <i>J</i> = 10 Hz, 1H), 1.75 (s, 3H), 2.68 (m, 1H)	burnt bread, burnt cereal, burnt vegetables, sulfury, burnt hamburger	A, C, D, F
2	3-mercapto-2-pentanone	899	43 (100), 41 (53), 75 (50), 74 (38), <b>118</b> (18), 57 (16), 45 (14) δ 0.72 (t, <i>J</i> = 7 Hz, 3H), 1.40 (d, <i>J</i> = 9 Hz, 1H), 1.73 (m, 2H), 1.95 (s, 3H), 2.60 (bm, 1H)	sulfury, hydrogen sulfide	B, C, E, G
3	2-mercapto-3-pentanone	904	57 (100), 61 (59), <b>118</b> (23), 43 (16), 41 (9) δ 0.97 (t, <i>J</i> = 3 Hz, 3H), 1.17 (d, <i>J</i> = 8 Hz, 3H), 1.40 (d, <i>J</i> = 10 Hz, 1H), 2.12 (m, 2H), 2.60 (bm, 1H)	sulfury, rotten meat, hydrogen sulfide	B, C, E, G
4	bis(1-methyl-2-oxopropyl) sulfide	1359	43 (100), <b>174</b> (40), 87 (28), 59 (27), 103 (17), 115 (12), 128 (5), 71 (6), 175 (3), 176 (2)	chopped onions, sulfury, rotten egg, cooked cabbage	A, C
5	bis(1-methyl-2-oxobutyl) sulfide	1460	57 (100), 43 (33), 113 (26), 153 (18), <b>202</b> (14), 164 (13), 135 (9)	sulfury, cooked vegetables	B, C
6	2-[(1-methyl-2-oxopropyl)-thio]-3-pentanone	1498	43 (100), 57 (23), 117 (5), 71 (4), 85 (2), <b>188</b> (2), 129 (1), 142 (1), 159 (1)	sulfury, freshly cut spring onion	C
7	bis(1-methyl-2-oxopropyl) disulfide	1476/1489	43 (100), 71 (18), 72 (16), <b>206</b> (14), 103 (17), 59 (15), 93 (10), 119 (9), 163 (8), 207 (2), 208 (1) δ 1.08 (d, <i>J</i> = 8 Hz, 6H), 1.86 (s, 3H), 1.90 (s, 3H), 3.01 (m, 2H)	fried onion, chopped onion	A, C, D, F
8	bis(1-ethyl-2-oxopropyl) disulfide	1606/1615	43 (100), 85 (36), 73 (21), <b>234</b> (15), 107 (15), 117 (14), 191 (7) δ 0.70 (t, <i>J</i> = 7 Hz, 3H), 0.72 (t, <i>J</i> = 7 Hz, 3H), 1.71 (bm, 4H), 1.92 (s, 6H), 2.96 (m, 2H)	sulfury, burnt onion	B, C, E, G
9	bis(1-methyl-2-oxobutyl) disulfide	1640/1649	57 (100), 117 (27), 43 (16), 85 (15), <b>234</b> (11), 175 (6), 133 (6) δ 0.97 (t, <i>J</i> = 9 Hz, 3H), 1.00 (t, <i>J</i> = 9 Hz, 3H), 1.16 (d, <i>J</i> = 8 Hz, 3H), 1.18 (d, <i>J</i> = 7 Hz, 3H), 2.25 (bm, 4H), 3.09 (bm, 2H)	roasted, sulfury, hydrogen sulfide	B, C, E, G
10	3-[(1-methyl-2-oxobutyl)-dithio]-2-pentanone	1629/1631	57 (100), 43 (96), 85 (42), 117 (27), <b>234</b> (21), 177 (8), 191 (4), 235 (2), 236 (2) δ 0.71 (t, <i>J</i> = 7 Hz, 3H), 0.98–1.02 (t, <i>J</i> = 8 Hz, 3H), 1.18 (d, <i>J</i> = 9 Hz, 3H), 1.71 (bm, 2H), 1.92 (s, 3H), 2.25 (bm, 2H), 2.96 (bm, 1H), 3.09 (bm, 1H)	rotten egg, burnt, onion	B, C, E, G
11	3-[(1-methyl-2-oxopropyl)-dithio]-2-pentanone	1544/1550	43 (100), 71 (10), 57 (9), 85 (7), <b>220</b> (5), 101 (3), 117 (3), 129 (20), 143 (2) δ 0.70–0.72 (t, <i>J</i> = 7 Hz, 3H), 1.10 (d, <i>J</i> = 8 Hz, 3H), 1.70 (bm, 2H), 1.88 (s, 3H), 1.93 (s, 3H), 2.96 (bm, 1H), 3.10 (bm, 1H)	oniony, freshly cut spring onion, sulfury	C
12	2-[(1-methyl-2-oxopropyl)-dithio]-3-pentanone	1562/1567	57 (100), 43 (95), 59 (19), 71 (13), 103 (11), 85 (10), 117 (10), <b>220</b> (7), 163 (4), 129 (3), 145 (2), 177 (2) δ 0.96–1.00 (t, <i>J</i> = 8 Hz, 3H), 1.08–1.11 (d, <i>J</i> = 7 Hz, 3H), 1.18 (d, <i>J</i> = 8 Hz, 3H), 1.88 (s, 3H), 2.26 (bm, 2H), 2.96 (bm, 1H), 3.10 (bm, 1H)	roast, chopped onion, sulfury	C
13	bis(1-methyl-2-oxopropyl) trisulfide	1731	43 (100), 59 (18), 93 (14), <b>238</b> (10), 71 (8), 195 (4), 103 (3), 123 (2), 240 (1)	freshly cut onion	A, C,
14	bis(1-ethyl-2-oxopropyl) trisulfide	1877	43 (100), 85 (15), 105 (10), 57 (11), 73 (11), 149 (8), <b>266</b> (7), 117 (7)	sulfury, oniony, rotten egg	B, C
15	bis(1-methyl-2-oxobutyl) trisulfide	1899	57 (100), 43 (12), <b>266</b> (7), 149 (6), 117 (6), 85 (6)	sulfury, burnt, hydrogen sulfide	B, C
16	3-[(1-methyl-2-oxobutyl)-trithio]-2-pentanone	1888	57 (100), 43 (85), 149 (16), <b>266</b> (14), 117 (10), 85 (13), 73 (10), 105 (8)	sulfury, burnt, cooked cabbage	B, C
17	3-[(1-methyl-2-oxopropyl)-trithio]-2-pentanone	1805	43 (100), 59 (8), 71 (6), 85 (6), 135 (6), 105 (4), <b>252</b> (4), 117 (4), 209 (3), 149 (2), 167 (2)	sulfury, freshly cut onion, fried	C
18	2-[(1-methyl-2-oxopropyl)-trithio]-3-pentanone	1820	57 (100), 43 (67), 59 (18), 85 (7), 117 (7), 135 (6), <b>252</b> (4), 149 (3), 177 (1), 209 (1)	fried onions, sulfury, freshly cut spring onion	C
19	bis(2-methyl-3-furyl) disulfide	1547	113 (100), <b>226</b> (44), 43 (30), 114 (14), 69 (13), 85 (12), 45 (13), 115 (7), 155 (5), 227 (5), 228 (4), 183 (2)	beefy, meaty, meat soup	D, E, H
20	3-[(2-methyl-3-furyl)dithio]-2-butanone	1510	113 (100), 43 (79), <b>216</b> (36), 114 (29), 59 (18), 45 (14), 81 (13), 173 (11), 217 (6), 218 (5)	meaty, burnt meat, sulfury	D
21	3-[(2-methyl-3-furyl)dithio]-2-pentanone	1580	43 (100), 113 (92), <b>230</b> (43), 114 (34), 145 (27), 85 (15), 81 (14), 187 (13), 231 (6), 232 (5)	meaty, boiled meat, roast beef, sulfury	E
22	2-[(2-methyl-3-furyl)dithio]-3-pentanone	1593	113 (100), 57 (78), <b>230</b> (37), 114 (32), 43 (29), 173 (14), 85 (12), 145 (7), 231 (5), 232 (4)	roast meat, boiled meat	E
23	bis(2-furylmethyl) sulfide	1416	81 (100), 53 (15), <b>194</b> (12), 113 (8), 43 (7), 195 (2)	overcooked stew, burnt, sulfury	F, G, H
24	bis(2-furylmethyl) disulfide	1701	81 (100), 53 (14), <b>226</b> (7), 69 (5), 112 (4), 193 (2)	spring onion, freshly cut onion, fried onion, roasted, rubbery	F, G, H
25	bis(2-furylmethyl) trisulfide	1879	81 (100), 53 (20), 43 (10), 45 (8), 161 (6), 113 (3), <b>258</b> (1)	sulfury, hydrogen sulfide	F, G, H
26	3-[(2-furylmethyl)dithio]-2-butanone	1589	81 (100), 43 (14), 53 (13), 45 (5), <b>216</b> (2), 185 (2)	sulfury, onion	F
27	3-[(2-furylmethyl)dithio]-2-pentanone	1671	81 (100), 43 (14), 53 (11), <b>230</b> (2), 113 (1), 196 (1)	rubbery, oniony	G
28	2-[(2-furylmethyl)dithio]-3-pentanone	1686	81 (100), 53 (13), 45 (4), <b>230</b> (2), 113 (1)	roasted, oniony	G
29	2-methyl-3-[(2-furylmethyl)thio]furan	1501	81 (100), 53 (21), <b>194</b> (17), 113 (13), 45 (11), 126 (7), 195 (1)	bland meat	H
30	2-methyl-3-[(2-furylmethyl)dithio]furan	1649	81 (100), 113 (18), 53 (18), 43 (14), <b>226</b> (9), 45 (12), 85 (11), 162 (1)	meat, burnt meat, roast meat, roast coffee	H

<sup>a</sup> Reaction mixtures in which compounds were found: A, 2,3-butanedione + hydrogen sulfide; B, 2,3-pentanedione + hydrogen sulfide; C, 2,3-butanedione + 2,3-pentanedione + hydrogen sulfide; D, 2,3-butanedione + 2-methyl-3-furanthiol + hydrogen sulfide; E, 2,3-pentanedione + 2-methyl-3-furanthiol + hydrogen sulfide; F, 2,3-butanedione + 2-furylmethanethiol + hydrogen sulfide; G, 2,3-pentanedione + 2-furylmethanethiol + hydrogen sulfide; H, 2-methyl-3-furanthiol + 2-furylmethanethiol.

of the methyl  $\beta$  to the methinethiol group resonated as a triplet at  $\delta$  0.72 and those of the acetyl methyl as a singlet at  $\delta$  1.95. With the mercaptan **3** the protons of the methyl  $\alpha$  to the methinethiol group resonated as a doublet at  $\delta$  1.17 and those of the propionyl methyl as a triplet at  $\delta$  0.97. However, in the symmetrical disulfide **8** the protons of the two methyls  $\beta$  to the methine disulfide group appeared as a pair of triplets at  $\delta$  0.70 and 0.72, while in the disulfide **9** the protons of the two methyls  $\alpha$  to the methine disulfide group appeared as a pair of doublets at  $\delta$  1.16 and 1.18 and those of the two propionyl methyls as a pair of triplets at  $\delta$  0.97 and 1.00. Again in the spectrum of the unsymmetrical disulfide **10** the protons of the single propionyl methyl appeared as a pair of triplets at  $\delta$  0.98 and 1.02. As before, these multiple signals are attributed to a difference in symmetry of the diastereomeric pairs present in the samples.

The product from the system containing 2,3-pentanedione and hydrogen sulfide had a strong onion-like and sulfury odor. In the GC-odor port analysis of the reaction mixture, similar descriptions were applied to the odors of the individual disulfides.

The reaction of the 1:1 mixture of 2,3-butanedione, 2,3-pentanedione, and hydrogen sulfide gave, in addition to those compounds identified in the individual reactions, two mixed disulfides **11** and **12**, two corresponding trisulfides **17** and **18**, and one monosulfide **6**. Like the other disulfides, GC analysis of the reaction mixtures resolved these compounds into two diastereoisomeric pairs. The mass spectra of these compounds gave clear molecular ions and characteristic fragmentations (Table 1). The abundant ion  $m/z$  43 was characteristic of compounds **6**, **11**, and **17** formed from the 3-mercapto-2-alkanones **1** and **2**, whereas compounds **12** and **18** obtained from the combination of **1** and **3** showed abundant ions at  $m/z$  57 and 43.

In the  $^1\text{H}$  NMR spectrum of **11** the protons of the two acetyl methyls resonated as single signals at  $\delta$  1.88 and 1.93, those of the methyl  $\alpha$  to the methine disulfide group as a doublet at  $\delta$  1.10, and those of the methyl  $\beta$  to this group as a pair of triplets at  $\delta$  0.70 and 0.72 (Table 1). Similarly, in the spectrum of **12** the protons of one methyl  $\alpha$  to the methine disulfide group resonated as a doublet at  $\delta$  1.18, while those of the other  $\alpha$  methyl appeared as a pair of doublets at  $\delta$  1.08 and 1.11. The protons of the acetyl methyl resonated as a singlet at  $\delta$  1.88 and those of the propionyl methyl as a pair of triplets at  $\delta$  0.96 and 1.00. Again these multiple signals are attributed to a difference in symmetry of the diastereoisomers present in the samples.

**Reaction between Mercaptoketones, 2-Methyl-3-furanthiol, and 2-Furylmethanethiol.** Addition of 2-methyl-3-furanthiol to the reaction mixture containing 3-mercapto-2-butanone led to formation of 3-[(2-methyl-3-furyl)dithio]-2-butanone (**20**), together with bis(2-methyl-3-furyl) disulfide (**19**) and the disulfide **7** obtained from two molecules of the mercaptobutanone.

3-[(2-Methyl-3-furyl)dithio]-2-pentanone (**21**) and 2-[(2-methyl-3-furyl)dithio]-3-pentanone (**22**) were produced when the 2,3-pentanedione/hydrogen sulfide reaction system was mixed with 2-methyl-3-furanthiol. A large amount of compound **19** was also formed, together with the two symmetrical disulfides **8** and **9**, and the mixed disulfide **10** formed from the two mercaptopentanones. Related sulfides and trisulfides were not found. The mass spectra of these mixed disulfides were clearly identified from the fragments originating from the

fission of the disulfide link. An ion at  $m/z$  113 derived from compounds containing the 2-methyl-3-furyl group, and a strong  $m/z$  43 ion ( $\text{CH}_3\text{CO}^+$ ) was observed for the disulfides containing the 2-pentanone group, while the  $m/z$  57 ion ( $\text{CH}_3\text{CH}_2\text{CO}^+$ ) was a major fragment in the spectra of the disulfide with the 3-pentanone. The molecular ions and the associated  $M + 2$  ions were clear in all spectra.

As expected, the reaction mixture containing 3-mercapto-2-butanone and 2-furylmethanethiol resulted in generation of 3-[(2-furylmethyl)dithio]-2-butanone (**26**). The chromatogram of the reaction mixture showed other large peaks corresponding to bis(2-furylmethyl) disulfide (**24**) and compound **7**, with smaller peaks containing bis(2-furylmethyl) sulfide (**23**) and its trisulfide homologue **25**. The reaction of 2-furylmethanethiol with the mixture of mercaptopentanones generated two disulfides containing the 2-furylmethyl group and joined to either 2-pentanone or 3-pentanone by a disulfide link (**27** and **28**). Mass spectra of these sulfur compounds containing the 2-furylmethyl moieties were all similar. The main feature of their fragmentation was the cleavage of the sulfur-carbon bond, giving an intense fragment at  $m/z$  81, with very small molecular ions.

When 2-methyl-3-furanthiol and 2-furylmethanethiol were mixed in ethanol, 2-methyl-3-[(2-furylmethyl)dithio]furan (**30**) and a small amount of the corresponding monosulfide **29** were produced together with the two symmetrical disulfides **19** and **24**. The mass spectra of compounds **29** and **30** were very similar to those of the corresponding bis(2-furylmethyl) compounds, with a base peak at  $m/z$  81 and small molecular ions of  $m/z$  194 and 226, respectively. A small, but significant,  $m/z$  113 ion was observed for these compounds.

GC-odor port analysis of these reaction mixtures confirmed previous observations that furans with a thiol group in the 3-position possess meatlike aromas (Evers et al., 1976). The aromas detected for the volatiles containing the 2-methyl-3-furyl moieties were described as "meaty, beefy, boiled meat, roast meat". However, "sulfury, burnt, oniony, rubbery" notes were mainly used to describe the compounds containing the 2-furylmethyl group (Table 1).

## DISCUSSION

A number of compounds produced by the reactions described above have not been reported previously in the literature. Compounds **4-6**, **8**, **13-18**, and **26-29** are reported here for the first time. Mercaptoketones, compounds **1-3**, have been found previously as products of the reaction between  $\alpha$ -dicarbonyl compounds and hydrogen sulfide (Takken et al., 1976). Compound **19** was first reported by Evers et al. (1976), who described its aroma as meaty at low concentrations. It is now regarded as an important contributor to meat aroma. Compound **30**, which contains both 2-methyl-3-furyl and 2-furylmethyl moieties, has been reported in model systems (Farmer and Mottram, 1990), and recently, Zhang and Ho (1991) described the formation of the disulfide **24** and the trisulfide **25**, containing two 2-furylmethyl groups, from a reaction system containing 5'-inosine monophosphate and cysteine. The mixed disulfide **20** was reported as a product from a reaction mixture containing 2-methyl-3-furanthiol and 3-mercapto-2-butanone (Evers et al., 1977). We have recently found compounds **7**, **9-12**, and **20-22** in a heated model system containing 4-hydroxy-5-methyl-3(2*H*)-furanone and cysteine or hydrogen sulfide (Whitfield et al., 1993).

The thermal degradation of thiamin has been shown to give rise to many thiols, sulfides, and disulfides, including some compounds reported in this paper and other closely related compounds. An important thiamin degradation product is 5-hydroxy-3-mercapto-2-pentanone, and this very reactive compound is the intermediate for a number of thiols including 2-methyl-4,5-dihydro-3-furanthiol and 2-methyl-3-furanthiol as well as the mercaptoketones 1–3 (Güntert et al., 1993b; Hartman et al., 1984; van der Linde et al., 1979). In recent studies on flavor compounds from thiamin-containing systems, Güntert and co-workers have reported the aroma properties of a large number of sulfides and disulfides, many of which had been synthesized. These included some monosulfides similar to some of the disulfides reported in this paper, namely 3-[(2-methyl-3-furyl)thio]-2-butanone, 3-[(2-methyl-3-furyl)dithio]-2-pentanone, and 2-[(2-methyl-3-furyl)thio]-3-pentanone (Güntert et al., 1993b). The odor threshold values of such compounds were found to be in the low micrograms per kilogram range, and most of those containing the 2-methyl-3-furyl group had meaty aromas.

Only a few disulfides of this type, namely **19**, **24**, and **30**, have actually been reported in meat volatiles (Farmer and Mottram, 1990; Farmer and Patterson, 1991; Gasser and Grosch, 1988). However, all of the thiols discussed in this paper have been found among the volatiles of cooked meat. The work reported here demonstrates the ready formation of both symmetrical and unsymmetrical disulfides, and therefore, more compounds of this type are likely to be present in the volatiles of cooked meat where they may make important contributions to meat aroma.

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