

Organic Sulfur Compounds from Fatty Aldehydes, Hydrogen Sulfide, Thiols, and Ammonia as Flavor Constituents

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Fatty aldehydes, hydrogen sulfide, thiols, and ammonia are often constituents of food flavors. Therefore, we studied the reaction products of these compounds by a combination of gas chromatographic and mass spectrometric techniques. Saturated aldehydes react with gaseous hydrogen sulfide (molar ratio 5:1) with the formation of 2,4,6-trialkyl-1,3,5-dioxathianes, 2,4,6-trialkyl-1,3,5-oxadithianes, and 2,4,6-trialkyl-1,3,5-trithianes. Reaction of aldehydes with liquid hydrogen sulfide (molar ratio 2:3) yields 1,1-alkanedithiols and, not previously reported, bis(1-mercaptoalkyl) sulfides. Bis(1-mercaptoalkyl) sulfides can be converted into 3,5-dialkyl-1,2,4-trithiolanes (oxidation), 2,4,6-trialkyl-1,3,5-trithianes

(treatment with boron trifluoride), 2,4,6-trialkyl-dihydro-1,3,5-dithiazines, 2,4,6-trialkyltetrahydro-1,3,5-thiadiazines (reaction with ammonia), and di- and trisulfides (thermolysis). Saturated aldehydes, hydrogen sulfide, and thiols produced 1,1-dialkylthioalkanes and 1-alkylthio-1-alkane-thiols. The latter can be converted into disulfides and 1-alkylthioalkyl alkyl disulfides by heating. Unsaturated aldehydes react with hydrogen sulfide and thiols to give mainly addition products to the carbon-carbon double bond. The organoleptic aspects of the reaction mixtures and some of the isolated compounds have been evaluated.

Nowadays the importance of organic sulfur compounds in food flavors is generally recognized. The important role of sulfur compounds to meat flavor was first demonstrated by Minor *et al.* (1965). In 1970, after extensive studies, Herz and Chang suggested research on flavor producing reactions may need to concentrate on the chemistry of compounds like hydrogen sulfide and ammonia under the conditions of their release from proteins by heat in the presence of other compounds such as carbonyls. Gordon (1972) published a survey of recent work about meat and poultry flavor, and also mentioned the important role of hydrogen sulfide and its reaction products with carbonyl compounds in this field. A review on the genesis of volatile sulfur-containing food flavors was made by Schwimmer and Friedman (1972). Wasserman (1972) discussed the formation of sulfur-containing compounds in a study on thermally produced flavor compounds in the aroma of meat and poultry.

In 1952 Barch claimed that flavoring materials were obtained when hydrogen sulfide was bubbled through a solution of an aliphatic aldehyde or an aliphatic methyl ketone. Pippen and Mecchi (1969) suggested that hydrogen sulfide should be a direct and potentially indirect contributor to cooked chicken aroma. Kurasawa and Homma (1971) reported that water extracts of rice cake contained hydrogen sulfide, ammonia, carbon dioxide, and some carbonyl compounds. An aqueous solution of a mixture of these compounds should develop the typical flavor of rice cake. Wiener (1972) found that onion- and bacon-like flavors were produced by reaction of hydrogen sulfide or certain sulfides with aldehydes.

Brinkman *et al.* (1972) identified in beef broth 1-methylthio-1-ethanethiol, which smells like fresh onions. Schutte and Koenders (1972) proposed as natural precursors for this compound ethanal, methanethiol, and hydrogen sulfide.

Kato *et al.* (1973) studied the volatile compounds produced by the reaction of L-cysteine or L-cystine with the carbonyl compounds D-glucose or pyruvaldehyde. Ledl and Severin (1973) investigated the thermal decomposition of cysteine and xylose in tributyrin. They found 41 volatile sulfur compounds. Very recently (1974) the same

authors reported the formation of 2,4,6-trimethyldihydro-1,3,5-dithiazine (thialdine), 2,x-dimethyldihydro-1,3,5-dithiazine, x-methyldihydro-1,3,5-dithiazine, 3-methyl-1,2,4-trithiolane, and 3,5-dimethyl-1,2,4-trithiolane from the reaction of methanal and ethanal with hydrogen sulfide and ammonia.

Mulders (1973) published the formation of 45 volatile components from the nonenzymatic browning reaction of the cysteine/cystine-ribose system, comprising thiophenes, thiazoles, and a trithiane. Mussinan and Katz (1973) isolated and identified over 20 sulfur compounds present in two model systems approximating cooked meat. Scanlan *et al.* (1973) reported the identification of volatile compounds from heated L-cysteine-HCl/D-glucose, among which were 15 thiophene derivatives.

Wilson *et al.* (1973) isolated and identified 46 sulfur chemicals present in pressure cooked beef. Schutte (1974) studied the role of sulfur compounds, derived from 4-hydroxy-5-methyl-2,3-dihydro-3-furanone, in meat flavor.

Because fatty aldehydes, hydrogen sulfide, thiols, and ammonia have been found in many flavors, especially in the aromas of meat, allium species, rice, and animal fats, we studied the reactions between these compounds. The reaction products were analyzed by the combined glc-mass spectral technique. The organoleptic aspects of the reaction mixtures and some of the isolated compounds have been evaluated.

EXPERIMENTAL SECTION

Materials. 2,4,6-Trimethyl-1,3,5-dioxathiane, 2,4,6-trimethyl-1,3,5-oxadithiane, 2,4,6-trimethyl-1,3,5-trithiane, and the triethyl compounds were prepared by reacting ethanal and propanal, respectively, with hydrogen sulfide at atmospheric pressure and room temperature for 24 hr (molar ratio 5:1) (see Apparatus section). These compounds were isolated by preparative glc, and the spectral data for the new products are listed in Table I, part a.

Bis(1-mercaptoalkyl) sulfides were obtained by treating ethanal, propanal, isobutanal, and n-hexanal with liquid hydrogen sulfide in a closed glass vessel at room temperature for 48 hr (molar ratio 2:3) (see Apparatus section). These compounds were isolated from the reaction mixture *via* extraction with cold potassium hydroxide solution (10%), acidification with acetic acid, extraction with hexane, and distillation. Yields and physical and spectral data are listed in Table I, part b.

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Table I. Physical and Spectral Data



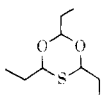
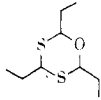
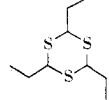
Compd. formula	Spectral data	Lit.
(a) Oxathianes and Trithianes		
2,4,6-Trimethyl-1,3,5-dioxathiane 	Mass 148 (5), 104 (2), 61 (2), 60 (100) , 59 (14), 45 (13), 43 (29); nmr δ 1.32 (3 H, d, $J = 5$ Hz), 1.47 (6 H, d, $J = 6$ Hz), 4.70 (1 H, q, $J = 5$ Hz), 4.95 (2 H, q, $J = 6$ Hz); ir ^b	Lebedew and Platonow (1926)
2,4,6-Trimethyl-1,3,5-trithiane 	Mass 180 (29), 120 (16), 115 (10), 92 (12), 88 (13), 74 (12), 61 (30), 60 (100) , 59 (82), 58 (19); nmr δ 1.56 (9 H, d, $J = 7$ Hz), 3.97 (3 H, q, $J = 7$ Hz); ir ^b	Barch (1952) Wilson <i>et al.</i> (1973)
2,4,6-Triethyl-1,3,5-dioxathiane ^a 	Mass 190 (2), 132 (7), 74 (100) , 59 (7), 58 (14), 57 (19), 47 (5), 45 (15), 41 (32); nmr δ 0.93 (3 H, t), 1.01 (6 H, t), 1.4-2.1 (6 H, m), 4.50 (1 H, t, $J = 5$ Hz), 4.82 (2 H, t, $J = 6$ Hz); ir ^b	
2,4,6-Triethyl-1,3,5-oxadithiane ^a 	Mass 206 (6), 148 (13), 115 (6), 106 (6), 74 (100) , 73 (22), 58 (9), 41 (37); nmr δ 1.05 (6 H, t), 1.10 (3 H, t), 1.5-2.1 (6 H, m), 4.22 (1 H, t, $J = 6.5$ Hz), 4.61 (2 H, t, $J = 6$ Hz); ir ^b	
2,4,6-Triethyl-1,3,5-trithiane 	Mass 222 (13), 157 (5), 148 (8), 83 (14), 74 (100) , 73 (30), 59 (12), 45 (40), 41 (65); nmr δ 1.14 (9 H, t), 1.90 (6 H, q), 3.97 (3 H, t, $J = 6.3$ Hz); ir ^b	Douglass and Martin (1950)
(b) Bis(1-mercaptoalkyl) Sulfides		
Bis(1-mercaptoethyl) sulfide ^a <chem>CH3C(SH)HSC(SH)HCH3</chem>	Mass 154 (6), 121 (13), 120 (6), 95 (15), 94 (4), 61 (100) , 60 (56), 59 (57), 58 (22), 57 (12), 45 (44), 35 (12); nmr, isomer A, δ 1.67 (6 H, d, $J = 6.8$ Hz), 1.98 (2 H, d, $J = 7.8$ Hz), 4.15 (2 H, d of q, $J = 7.8-6.8$ Hz); isomer B, δ 1.70 (6 H, d, $J = 7$ Hz), 1.90 (2 H, d, $J = 8.6$ Hz), 4.27 (2 H, d of q, $J = 8.6-7$ Hz); ir; ^b yield 50%; bp 77° (5 mm); n_D^{20} 1.5659	
Bis(1-mercaptopropyl) sulfide ^a <chem>C2H5C(SH)HSC(SH)HC2H5</chem>	Mass 182 (7), 149 (7), 148 (5), 108 (13), 75 (93), 74 (55), 73 (20), 59 (11), 58 (9), 47 (36), 46 (14), 45 (54), 41 (100) , 39 (27); nmr, isomer A, δ 1.14 (6 H, t), 1.5-2.2 (4 H, m), 1.90 (2 H, d, $J = 7.6$ Hz), 4.03 (2 H, m); isomer B, δ 1.14 (6 H, t), 1.5-2.2 (4 H, m), 1.75 (2 H, d, $J = 8.6$ Hz), 4.17 (2 H, m); ir; ^b yield 44%; bp 110° (5 mm); n_D^{20} 1.5489	
Bis(1-mercaptoisobutyl) sulfide ^a <chem>i-C3H7C(SH)HSC(SH)H-i-C3H7</chem>	Mass 210 (16), 154 (4), 145 (14), 88 (69), 73 (83), 59 (33), 57 (78), 55 (100) , 47 (19), 45 (75), 43 (47), 41 (78), 39 (50); nmr, isomer A, δ 1.1 (12 H, d), 1.75 (2 H, d, $J = 7.8$ Hz), 2.1 (2 H, m), 4.03 (2 H, d of d, $J = 4-7.8$ Hz); isomer B, δ 1.1 (12 H, d), 1.67 (2 H, d, $J = 8.5$ Hz), 2.1 (2 H, m), 4.20 (2 H, d of d, $J = 4-8.5$ Hz); ir; ^b yield 29%; bp 120° (4 mm); n_D^{20} 1.5352	

Table I (continued)

Compd. formula	Spectral data	Lit.
Bis(1-mercaptohexyl) sulfide ^a $C_5H_{11}C(SH)HSC(SH)HC_5H_{11}$	Mass 266 (5), 148 (20), 117 (16), 116 (10), 115 (8), 73 (25), 60 (23), 59 (31), 57 (30), 56 (35), 55 (44), 43 (100), 41 (78); nmr, isomer A, δ 0.93 (6 H, t), 1.1–2.1 (16 H, m), 1.92 (2 H, d, $J =$ 7.6 Hz), 4.08 (2 H, m); isomer B, δ 0.93 (6 H, t), 1.1–2.1 (16 H, m), 1.81 (2 H, d, $J = 8.6$ Hz), 4.19 (2 H, m); ir; ^b yield 26%; bp 150° (1 mm); n_D^{20} 1.5161 (c) Trithiolanes	
3,5-Dimethyl-1,2,4-trithiolane 	Mass, nmr, and ir ^b	Asinger <i>et al.</i> (1959); Asinger and Fischer (1967); Tjan <i>et al.</i> (1972); Chang <i>et al.</i> (1968)
3,5-Diethyl-1,2,4-trithiolane 	Mass, nmr, and ir ^b	Asinger <i>et al.</i> (1959); Asinger and Fischer (1967); Tjan <i>et al.</i> (1972)
2,4,6-Trimethyldihydro-1,3,5- dithiazine (thialdine) 	(d) Thiazines Mass, nmr, and ir ^b	Wöhler and von Liebig (1847); Brinkman <i>et al.</i> (1972)
2,4,6-Trimethyltetrahydro- 1,3,5-thiadiazine ^a 	Mass spectrum not available (decomposes on glc); nmr δ 0.0 (2 H, br), 1.20 (3 H, d, $J = 6$ Hz), 1.34 (6 H, d, $J =$ 6.5 Hz), 4.08 (2 H, q, $J = 6.5$ Hz); ir; ^b (e) 1-Alkylthio-1-alkanethiols	
1-Methylthio-1-ethanethiol $CH_3CH(SH)(SCH_3)$	Mass, nmr, and ir; ^b yield 38%; bp 58° (26 mm); n_D^{20} 1.5274	Schutte (1971); Peer <i>et al.</i> (1971)
1-Methylthio-1-propanethiol $C_2H_5CH(SH)(SCH_3)$	Mass, nmr, and ir; ^b yield 49%; bp 60° (21 mm); n_D^{20} 1.5193	Schutte (1971); Peer <i>et al.</i> (1971)
1-Ethylthio-1-ethanethiol $CH_3CH(SH)(SC_2H_5)$	Mass, nmr, and ir; ^b yield 29%; bp 56° (17 mm); n_D^{20} 1.5140	Schutte (1971); Peer <i>et al.</i> (1971)
1-Propylthio-1-propanethiol ^a $C_2H_5CH(SH)(SC_3H_7)$	Mass 150 (12), 117 (46), 75 (62), 74 (50), 73 (15), 47 (44), 45 (43), 43 (43), 41 (100); nmr δ 1.00 (3 H, t), 1.07 (3 H, t), 1.3–2.1 (4 H, m), 1.77 (1 H, d, $J = 7$ Hz), 2.5–2.8 (2 H, m), 3.77 (1 H, q, $J = 6.5$ –7 Hz); ir; ^b yield 30%; bp 42° (3 mm); n_D^{20} 1.5033	
1-Methylthio-1-hexanethiol ^a $C_5H_{11}CH(SH)(SCH_3)$	Mass 164 (12), 131 (44), 116 (20), 87 (24), 83 (50), 73 (50), 67 (16), 61 (67), 60 (90), 55 (100), 48 (42), 47 (8); nmr δ 0.90 (3 H, t), 1.1–2.0 (8 H, m), 1.77 (1 H, d, $J = 7$ Hz), 2.17 (3 H, s), 3.77 (1 H, q, $J = 6$ –7 Hz); ir; ^b yield 20%; bp 79° (6 mm)	
1-Methylthiopropyl methyl disulfide ^a $C_2H_5CH(SCH_3)SSCH_3$	(f) 1-Alkylthioalkyl Alkyl Disulfides Mass 168 (1), 89 (76), 79 (7), 75 (11), 74 (9), 73 (13), 64 (4), 61 (26), 59 (11), 49 (10), 47 (22), 45 (40), 41 (100); nmr δ 1.07 (3 H, t), 1.6–2.2 (2 H, m), 2.18 (3 H, s), 2.46 (3 H, s), 3.63 (1 H, m)	

Table I (continued)

Compd. formula	Spectral data	Lit.
1-Methylthiopropyl ethyl disulfide ^a $C_2H_5CH(SCH_3)SSC_2H_5$	Mass 182 (1), 89 (100), 79 (5), 73 (14), 64 (3), 61 (31), 59 (9), 49 (8), 47 (17), 45 (32), 41 (95); ir; ^b nmr δ 1.07 (3 H, t), 1.33 (3 H, t, $J = 7$ Hz), 1.6–2.2 (2 H, m), 2.20 (3 H, s), 2.75 (2 H, q, $J = 7$ Hz), 3.60 (1 H, m); ir ^b	
(g) Reaction Products of Unsaturated Aldehydes, Hydrogen Sulfide, and Thiols		
3-Methylthiohexanal $C_3H_7CH(SCH_3)CH_2CHO$	Mass, nmr, and ir ^b	Givaudan (1971)
1,3-Dimethylthiohex-1-ene ^a $C_3H_7CH(SCH_3)CH=CH(SCH_3)$	Nmr δ 0.92 (3 H, t), 1.1–1.8 (4 H, m), 1.92 (3 H, s), 2.23 (3 H, s), 3.05 (1 H, m), 5.10 (1 H, d of d, $J = 9$ and 15 Hz), 5.97 (1 H, d, $J = 15$ Hz); mass and ir ^b	
1,1-Dimethylthiohex-2-ene ^a $C_3H_7CH=CHCH(SCH_3)_2$	Nmr δ 0.92 (3 H, t), 1.1–1.8 (2 H, m), 2.0 (2 H, m), 2.03 (6 H, s), 4.08 (1 H, br d, $J = 6$ Hz), 5.5 (2 H, m); mass and ir ^b	

^a Not previously reported. ^b Available on request.

3,5-Dialkyl-1,2,4-trithiolanes were prepared in 80% yield by oxidation of bis(1-mercaptoalkyl) sulfides with iodine in ethanol and pyridine at room temperature (see Table I, part c).

2,4,6-Trialkyl-1,3,5-trithianes were obtained in quantitative yield by disproportionation of bis(1-mercaptoalkyl) sulfides with boron trifluoride-acetic acid at room temperature for 3 hr (see Table I, part a).

Bis(1-mercaptoalkyl) sulfides were isomerized in 50% yield to a mixture of alkyl di- and trisulfides by heating at 140–150° for 5 hr.

2,4,6-Trimethyldihydro-1,3,5-dithiazine and 2,4,6-trimethyltetrahydro-1,3,5-thiadiazine were obtained when bis(1-mercaptoethyl) sulfide was allowed to react with ammonia at room temperature for 24 hr (molar ratio 2:5) (see Table I, part d). The same products were detected in the reaction mixture of ethanal, hydrogen sulfide, and ammonia (molar ratio 1:1:1) in a closed glass vessel for 24 hr.

1-Alkylthio-1-alkanethiols were prepared by reaction of ethanal or propanal with hydrogen sulfide and methanethiol, ethanethiol, or propanethiol in a closed glass vessel at room temperature for 48 hr (molar ratio 1:1:1). These compounds were also isolated as described for bis(1-mercaptoalkyl) sulfides. From the nonalkaline soluble part an amount of 1,1-dialkylthioalkanes could be isolated. Yields and physical and spectral data are listed in Table I, part e.

Dialkyl disulfides were obtained in 50% yield when 1-alkylthio-1-alkanethiols were heated at 140–150° for 5 hr. The main by-products were 1-alkylthioalkyl alkyl disulfides (see Table I, part f).

Hex-2-enal and deca-2,4-dienal were allowed to react with hydrogen sulfide and methanethiol in a closed glass vessel for 40 hr at room temperature (molar ratio 1:1:1). The crude reaction mixtures were analyzed by glc-mass spectrometry (see Table I, part g).

Apparatus. Reactions of fatty aldehydes with excess liquid hydrogen sulfide, thiols, or ammonia, respectively, were carried out in a 100-ml Carius tube (pyrex glass, wall thickness 4 mm, maximum pressure 300 psi), with a Teflon-coated screw locking. During the reaction the tube is protected by a metal sleeve.

Reactions under atmospheric pressure were carried out in a 500-ml reaction flask with magnetic stirrer. The

closed flask is connected with a supplier of hydrogen sulfide.

Mass spectra were recorded on a Varian MAT/CH 5 mass spectrometer coupled with a Varian Aerograph Model 1220 gas chromatograph. The separations were performed in an all-glass system as described previously (Boelens *et al.*, 1971).

Preparative scale gas chromatographic separations were performed in a Varian Aerograph gas chromatograph Model 90-P. Purified materials were obtained by gas chromatography on a 7 ft × 0.25 in. (i.d.) glass column, packed with 60–80 mesh Embacel, coated with 10% OV-17. A hydrogen flow rate of 60 ml/min was maintained, under isothermal conditions.

Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrophotometer; the cell thickness was 0.015 mm.

Nuclear magnetic resonance (nmr) spectra were recorded on a Varian Associates A 60A instrument. Compounds were run in 10% v/v carbon tetrachloride solutions using tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

Primary and Secondary Reactions of Saturated Aldehydes with Hydrogen Sulfide. The formation of ethanal, hydrogen sulfide, and ammonia from cysteine has been studied by Obata and Tanaka (1965) and by Fujimaki *et al.* (1969).

Propanal is an important flavor component of onion (Virtanen, 1967), and other lower saturated aldehydes derived by Strecker degradation of amino acids or oxidation of fatty acids are frequently found in flavors.

When such saturated aldehydes were allowed to react with hydrogen sulfide at atmospheric pressure and room temperature, we obtained 2,4,6-trialkyl-1,3,5-dioxathianes, 2,4,6-trialkyl-1,3,5-oxadithianes, and 2,4,6-trialkyl-1,3,5-trithianes; the trimethyl derivative of the latter has been found in pressure cooked beef (Wilson *et al.*, 1973). The formation of the cyclic oxygen-containing sulfur compounds must be due to the fact that the aldehydes are in excess (molar ratio 5:1). Figure 1a shows a gas chromatogram of the reaction mixture of propanal with hydrogen sulfide at atmospheric pressure.

If the reaction of saturated aldehydes with hydrogen

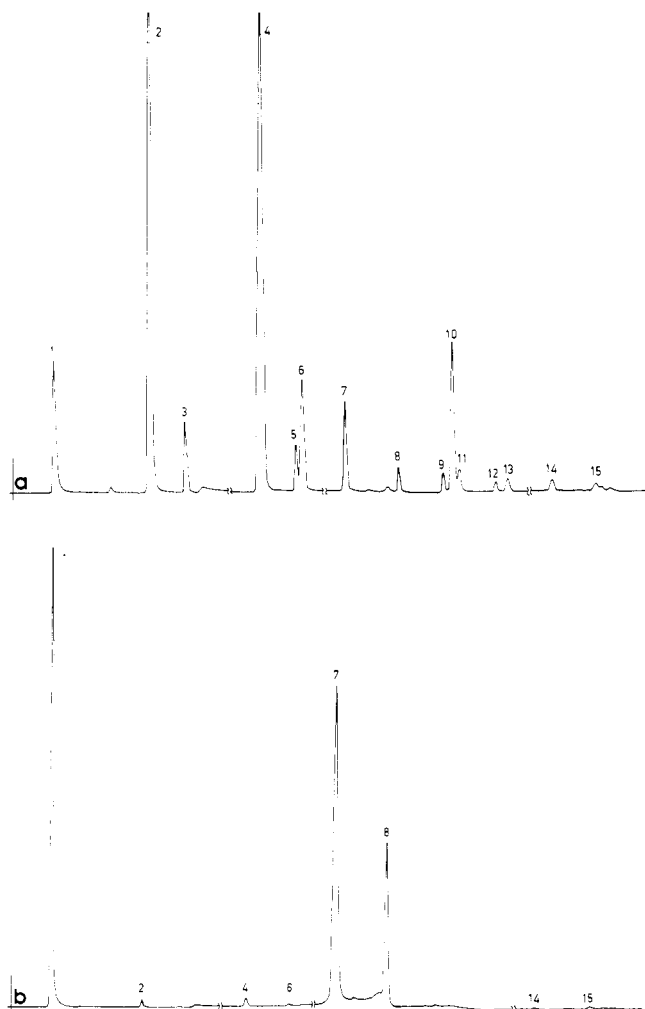


Figure 1. (a) Gas chromatogram of the reaction mixture of propanal and gaseous hydrogen sulfide (molar ratio 5:1); (b) gas chromatogram of the reaction mixture of propanal and liquid hydrogen sulfide (molar ratio 2:3): (1) 1,1-propanedithiol; (2,3) 2,4,6-triethyl-1,3,5-trioxane (two isomers); (4,5,6) 2,4,6-triethyl-1,3,5-dioxathiane (three isomers); (7,8) bis(1-mercaptopropyl) sulfide (two isomers); (9,10,11) 2,4,6-triethyl-1,3,5-oxadithiane (three isomers); (12,13) unknown; (14,15) 2,4,6-triethyl-1,3,5-trithiane (two isomers).

sulfide (molar ratio 2:3) was carried out in a closed glass vessel, the main products were 1,1-alkanedithiols and bis-(1-mercaptoalkyl) sulfides. A gas chromatogram of the reaction mixture of propanal with excess hydrogen sulfide is given in Figure 1b.

Bis(1-mercaptoalkyl) sulfides have not been reported previously, and are probably the key products for several aroma components. These compounds were easily oxidized to 3,5-dialkyl-1,2,4-trithiolanes. 3,5-Dimethyl-1,2,4-trithiolane has been found in the aroma of boiled meat (Chang *et al.*, 1968; Wilson *et al.*, 1973), in beef broth (Brinkman *et al.*, 1972), and in potatoes (Buttery *et al.*, 1970).

When bis(1-mercaptoalkyl) sulfides were treated with acids, they disproportionated to 2,4,6-trialkyl-1,3,5-trithianes; the trimethyl form of this also occurs in pressure cooked meat (Wilson *et al.*, 1973). By heating in the presence of oxygen the bis(1-mercaptoalkyl) sulfides were converted into a mixture of dialkyl di- and trisulfides, which occur in the flavor complex of onion (Boelens *et al.*, 1971) and in boiled meat (Wilson *et al.*, 1973). Bis(1-mercaptoalkyl) sulfides reacted with ammonia to give 2,4,6-trialkyl-dihydro-1,3,5-dithiazines and 2,4,6-trialkyl-tetrahydro-1,3,5-thiadiazines. 2,4,6-Trimethyldihydro-1,3,5-

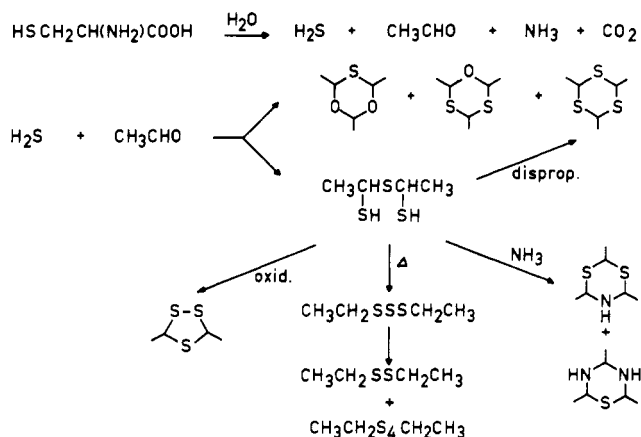


Figure 2.

dithiazine (thialdine) has been found in beef broth (Brinkman *et al.*, 1972) and in boiled meat (Wilson *et al.*, 1973).

In Figure 2 a survey is given of the organic sulfur compounds which were formed from ethanal with hydrogen sulfide and ammonia and therefore can be derived from cysteine.

Primary and Secondary Reactions of Saturated Aldehydes with Hydrogen Sulfide and Thiols. When saturated aldehydes were allowed to react with equimolar amounts of hydrogen sulfide and thiols in a closed glass vessel at room temperature the main products were 1,1-dialkylthioalkanes and 1-alkylthio-1-alkanethiols. 1-Methylthio-1-ethanethiol, formed from ethanal, hydrogen sulfide, and methanethiol, has been found in beef broth (Brinkman *et al.*, 1972).

1-Alkylthio-1-alkanethiols are converted into dialkyl disulfides and 1-alkylthioalkyl alkyl disulfides by heating. Dialkyl disulfides occur in the flavor complex of allium species and boiled meat (Wilson *et al.*, 1973). These products can be expected in each aroma that is formed by heating of a mixture in which cysteine (precursor for ethanal and hydrogen sulfide), methionine (precursor for methanethiol), and possibly other fatty aldehydes are present.

Reactions of Unsaturated Aldehydes with Hydrogen Sulfide and Methanethiol. Reaction of hex-2-enal with hydrogen sulfide and methanethiol (molar ratio 1:1:1) gave as main products: 3-methylthiohexanal, 1,1-dimethylthiohex-2-ene, and 1,3-dimethylthiohex-1-ene; a trace of 2-ethylthiophene was also found. The use of 3-methylthiohexanal has been claimed for application in flavor compositions (Givaudan, 1971).

Reaction of deca-2,4-dienal with a mixture of hydrogen sulfide and methanethiol gave as main products: 1,1-dimethylthiodeca-2,4-diene, 1,3-dimethylthiodeca-1,4-diene, and 1,5-dimethylthiodeca-1,3-diene; a little 2-hexylthiophene was also identified. Thus 2-alkylthiophenes, which occur in the flavor of boiled meat (Wilson *et al.*, 1973) and cranberries (Anjou and von Sydow, 1967), may be formed from unsaturated aldehydes and hydrogen sulfide.

Odor Evaluation. The organoleptic aspects of the reaction mixtures and some of the isolated compounds listed in Table II were evaluated by seven expert flavorists. They were asked to describe the odor and taste of the product dissolved in water.

The usefulness of some of the reaction mixtures and isolated compounds was tested (1-5% v/v) in allium (steam-distilled onion oil), meat (fried beef extract), and fruity (durian) flavors. Improvement of the organoleptic quality was obtained with: (a) a reaction mixture of propanal with excess hydrogen sulfide, bis(1-mercaptoalkyl) sul-

Table II. Organoleptic Properties

Reaction mixtures of	Organoleptic aspects
Ethanal and hydrogen sulfide	Allium (onion)
Propanal and hydrogen sulfide	Allium (strongly fresh onion), mustard
Hexanal and hydrogen sulfide	Strongly green, weak allium
Ethanal, hydrogen sulfide, and methanethiol	Allium (onion), green, earthy
Hexanal, hydrogen sulfide, and methanethiol	Allium (onion), mango
Hex-2-enal and hydrogen sulfide	Strongly green, weak allium
Hex-2-enal, hydrogen sulfide, and methanethiol	Allium (onion), green bellpepper and cauliflower
Deca-2,4-dienal, hydrogen sulfide, and methanethiol	Allium (onion, leek), meaty, tomato soup
Isolated compounds	Organoleptic aspects
Bis(1-mercaptoethyl) sulfide	Allium (onion, chives), meaty
Bis(1-mercaptopropyl) sulfide	Green fruity, allium (onion, garlic)
Bis(1-mercaptoisobutyl) sulfide	Allium (onion), mushroom and soup
Bis(1-mercaptohexyl) sulfide	Allium (onion), green fatty
1-Ethylthio-1-ethanethiol	Allium (onion, leek), blackcurrant
1-Methylthio-1-propanethiol	Allium (onion), meaty
1-Propylthio-1-propanethiol	Allium (onion), blackcurrant
1-Methylthio-1-hexanethiol	Allium (onion), blackcurrant, rhubarb, and green bellpepper
1,1-Propanedithiol	Allium (strongly fresh onion)
1,1-Dimethylthioethane	Allium (onion)
1,1-Dimethylthiohexane	Weak allium, strongly green, privet, oleander blossom
3-Methylthiohexanal	Strongly green, privet
1,3-Dimethylthio- (and 1,1-dimethylthio)hexane	Strongly green, weak allium
2,4,6-Trimethyl-1,3,5-trithiane	Dusty, earthy, nutty
2,4,6-Triethyl-1,3,5-trithiane	Green, allium (onion, garden cress)

fides, and 1-alkylthio-1-alkanethiols in onion oil; (b) 3,5-dialkyl-1,2,4-trithiolanes, 2,4,6-trialkyldihydro-1,3,5-dithiazines, and 2,4,6-trialkyltetrahydro-1,3,5-thiadiazines in meat flavor; and (c) a reaction mixture of hex-2-enal with hydrogen sulfide and methanethiol, 3,5-dialkyl-1,2,4-trithiolanes, and 1-alkylthio-1-alkanethiols in fruit flavor.

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LITERATURE CITED

- Anjou, K., von Sydow, E., *Acta Chem. Scand.* **21**, 2076 (1967).
 Asinger, F., Fischer, M., *J. Prakt. Chem.* **35**, 81 (1967).
 Asinger, F., Thiel, M., Lipfert, G., *Justus Liebigs Ann. Chem.* **627**, 195 (1959).
 Barch, W. E. (to Standard Brands), U. S. Patent 2,594,379 (1952).
 Boelens, M., de Valois, P. J., Wobben, H. J., van der Gen, A., *J. Agr. Food Chem.* **19**, 984 (1971).
 Brinkman, H. W., Copier, H., de Leuw, J. J. M., Tjan, S. B., *J. Agr. Food Chem.* **20**, 177 (1972).
 Buttery, R. G., Seifert, R. M., Ling, L. C., *J. Agr. Food Chem.* **18**, 538 (1970).
 Chang, S. S., Hirai, C., Reddy, B. R., Herz, K. O., Kato, A., Sipma, G., *Chem. Ind.*, 1639 (1968).
 Douglass, I. B., Martin, F. T., *J. Org. Chem.* **15**, 795 (1950).
 Fujimaki, M., Kato, S., Kurata, T., *Agr. Biol. Chem.* **33**, 1144 (1969).
 Givaudan, Netherlands Patent Application 71,17,965 (1971).
 Gordon, A., *The Flavour Industry*, 1972, p 445.
 Herz, K. O., Chang, S. S., *Advan. Food Res.* **18**, 68 (1970).
 Kato, S., Kurata, T., Fujimaki, M., *Agr. Biol. Chem.* **37**, 539 (1973).
 Kurasawa, F., Homma, M., *Niigata Norin Kenkyu No.* **23**, 85 (1971).
 Lebedew, S. W., Platonow, M., *Berichte* **59**, 762 (1926).
 Ledl, F., Severin, Th., *Chem. Mikrobiol. Tech. Lebensm.* **2**, 155 (1973).
 Ledl, F., Severin, Th., *Z. Lebensm. Unters. Forsch.* **154**, 29 (1974).
 Minor, L. J., Pearson, A. M., Dawson, L. E., Schweigert, B. S., *J. Food Sci.* **30**, 686 (1965).
 Mulders, E. J., *Z. Lebensm. Unters. Forsch.* **152**, 193 (1973).
 Mussinan, C. J., Katz, I., *J. Agr. Food Chem.* **21**, 43 (1973).
 Obata, Y., Tanaka, H., *Agr. Biol. Chem.* **29**, 191 (1965).
 Peer, H. G., van der Heyden, A., Tjan, S. B., van Orden, T. L., *Syn. Commun.* **1**, 277 (1971).
 Phippen, E. L., Mecchi, E. P., *J. Food Sci.* **34**, 443 (1969).
 Scanlan, R. A., Kayser, S. G., Libbey, L. M., Morgan, M. E., *J. Agr. Food Chem.* **21**, 673 (1973).
 Schutte, L., *Tetrahedron Lett.*, 2321 (1971).
 Schutte, L., *Crit. Rev. Food Technol.*, in press (1974).
 Schutte, L., Koenders, E. B., *J. Agr. Food Chem.* **20**, 181 (1972).
 Schimmer, S., Friedman, M., *The Flavour Industry*, 1972, p 137.
 Tjan, S. B., Haakman, J. C., Teunis, C. J., Peer, H. G., *Tetrahedron* **28**, 3489 (1972).
 Virtanen, A. I., *Nutr. Dieta* **9**, 1 (1967).
 Wasserman, A. E., *J. Agr. Food Chem.* **20**, 737 (1972).
 Wiener, C. (to Polak Frutal Works), U. S. Patents 3,645,754 and 3,650,771 (1972).
 Wilson, R. A., Mussinan, C. J., Katz, I., Sanderson, A., *J. Agr. Food Chem.* **21**, 873 (1973).
 Wöhler, F., von Liebig, J., *Ann. Chem. Pharm.* **61**, 1 (1847).

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