Phenolic, Sulfur, and Nitrogen Compounds in Food Flavors

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Furans Substituted at the Three Position with Sulfur

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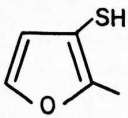
During recent years the analysis of cooked meats and of model systems has been reported by numerous investigators; leading references include Wilson et al (1), Mussinan and Katz (2), Persson and von Sydow (3), Schutte (4), and van den Ouweland and Peer (5).

We now report the isolation, identification and synthesis of two important meat flavor and aroma chemicals, 2-methyl-3-furanthiol (1) and bis (2-methyl-3-furyl) disulfide (2).



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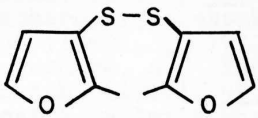

2

While preparing small batches (1000 g) of a processed meat flavor which consisted of a mixture of L-cysteine hydrochloride, thiamine chloride hydrochloride, hydrolyzed vegetable protein and water heated at reflux for four hours (6), it was noted that the condensate possessed an intense roasted aroma. The material responsible for the aroma proved to be extractable with methylene chloride but when the methylene chloride was removed, only a minute amount of material remained. In order to obtain workable quantities of aroma material for analysis a large scale preparation was undertaken. This reaction totaled 4,000 lbs. and gave 40 gallons condensate from which 16 liters of methylene chloride extract was obtained. Careful solvent removal of the extract under mild vacuum and final concentration with a stream of nitrogen gave

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50 ml of concentrate possessing a powerful roast aroma.

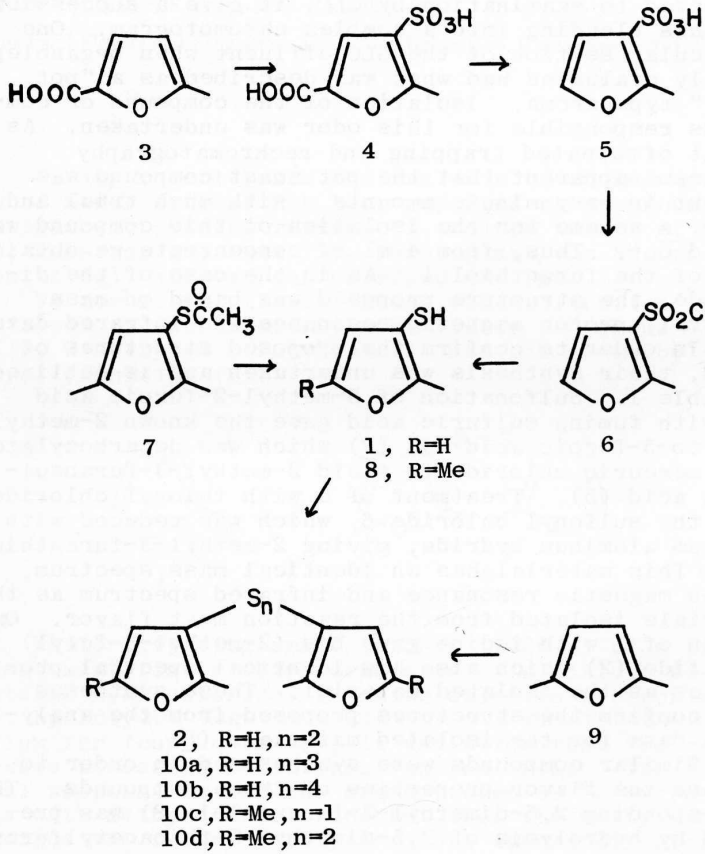
Thin-layer chromatography of the concentrate indicated the presence of a readily isolable compound near the solvent front. Repeated preparative thin-layer chromatography gave, from 2.4 g of concentrate, a 66 mg sample of the disulfide 2. The structure is assigned on the basis of mass spectral, proton magnetic resonance and infrared data. When the concentrate was subjected to examination by GLC, it gave a succession of peaks blending into a complex chromotogram. One particular section of the GLC effluent when organoleptically evaluated had what was described as a "pot roast" type aroma. Isolation of the compound or compounds responsible for this odor was undertaken. As a result of repeated trapping and rechromatography it became apparent that the pot roast compound was present in very minute amounts. With much trial and error, a scheme for the isolation of this compound was worked out. Thus, from 4 ml of concentrate we obtained 2-3 λ of the furanthiol 1. As in the case of the disulfide, the structure proposed was based on mass spectral, proton magnetic resonance and infrared data.

In order to confirm the proposed structures of 1 and 2, their synthesis was undertaken and is outlined in Table I. Sulfonation of 5-methyl-2-furoic acid (3) with fuming sulfuric acid gave the known 2-methyl-3-sulfo-5-furoic acid (4) (7) which was decarboxylated with mercuric chloride to yield 2-methyl-3-furansulfonic acid (5). Treatment of 5 with thionyl chloride gave the sulfonyl chloride 6, which was reduced with lithium aluminum hydride, giving 2-methyl-3-furanthiol (1). This material has an identical mass spectrum, proton magnetic resonance and infrared spectrum as the materials isolated from the reaction meat flavor. Oxidation of 1 with iodine gave bis (2-methyl-3-furyl) disulfide (2) which also has identical spectral properties as the isolated material. These syntheses thus confirm the structures proposed from the analytical data for the isolated materials (8).

Similar compounds were synthesized in order to compare the flavor properties of these compounds. The corresponding 2,5-dimethyl-3-furanthiol (8) was prepared by hydrolysis of 2,5-dimethyl-3-thioacetylfuran (7) (10).

Treatment of 2,5-dimethyl furan with either sulfur monochloride or sulfur dichloride gave, in low yield, a mixture containing both bis (2,5-dimethyl-3-furyl) sulfide (10c) and bis (2,5-dimethyl-3-furyl) disulfide (10d). The corresponding tri- and tetrasulfides of 2 were also prepared. Thus the reaction of 1

TABLE I


HOOC
O
3
HOOC
SO3H
O
4
SO3H
O
5
O
SCCH3
O
7
SH
R
O
1, R=H
8, R=Me
SO2Cl
O
6
Sn
R
O
O
R
2, R=H,n=2
10a,R=H,n=3
10b,R=H,n=4
10c,R=Me,n=1
10d,R=Me,n=2
O
9

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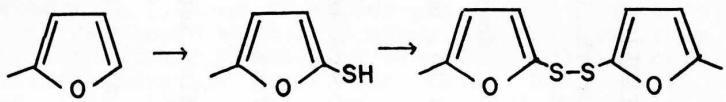
with sulfur dichloride gave bis (2-methyl-3-furyl) trisulfide (10a) and the reaction of 1 with sulfur monochloride gave bis (2-methyl-3-furyl) tetrasulfide (10b). For comparison, 5-methyl-2-furanthiol (12) and bis (5-methyl-2-furyl) disulfide (13) were prepared. Treatment of the lithio derivative of sylvan (11) with sulfur gave the thiol 12 which was oxidized with iodine to give 13.



11 12 13

A summary of the organoleptic evaluations of the various compounds is contained in Table II. It is apparent from a brief study of the table that all of the furans where the sulfur atom is bound to the β carbon have meaty aroma and taste characteristics. However, when the sulfur atom is in the α position only hydrogen sulfide like, burnt and chemical notes are observed. It is somewhat surprising that a one carbon shift in substitution would produce this substantial change in flavor character.

Experimental

Isolation of 1 and 2. In a suitable vessel a mixture of 35 lbs. of thiamine chloride hydrochloride, 35 lbs. of L-cysteine hydrochloride, 1,238 lbs. of vegetable protein hydrolysate (carbohydrate free) and 2,692 lbs. of water was heated at reflux for four hours. After 45 minutes, 40 gallons of condensate was removed during $3\frac{1}{4}$ hrs. Each gallon was extracted with 400 ml of CH_2Cl_2 and the extracts were combined and dried with sodium sulfate. Solvent removal in mild (100 mm) vacuum and final concentration with a stream of dry nitrogen gave 50 ml of concentrate.

2-Methyl-3-furanthiol (1): Preparative GLC of the concentrate (2 x 2 ml) on an 8' x 3/4", 25% SE 30 on A/W DMCS column, programmed from 70° to 225°C at 1°/min yields about 300 λ containing a strong pot roast aroma. Rechromatography of the 300 λ on a 10' x 3/8", 20% CBW 20M A/W DMCS column programmed from 80° to 225°C at 1°/min yields about 100 λ of material containing a very intense pot roast aroma. Final chromatography of this material on a 10' x 1/4" glass, 20% Apiezon L column gave 2-3 λ of 2-methyl-3-furanthiol

TABLE II

Flavor Characteristics

Compound	Medium	Description
2-Methyl-3-furanthiol (1)	Water	Sweet meat, beef broth, HVP like. Roasted meat aroma.
2,5-Dimethyl-3-furanthiol (8)	Water	Strong meaty taste. Roasted meat aroma.
5-Methyl-2-furanthiol (12)	Water	Hydrogen sulfide like, burnt, sulfury-not meaty.
Bis-(2-methyl-3-furyl) disulfide (2)	Bouillon 0.05 ppm	Meat fullness. Cooked meat aroma.
Bis-(2,5-dimethyl-3-furyl) disulfide (10d)	Bouillon 0.05 ppm	Meaty taste and aroma.
Bis-(2,5-dimethyl-3-furyl) sulfide (10c)	Bouillon 0.05 ppm	Bloody aroma. Boiled meat taste.
Bis-(5-methyl-2-furyl) disulfide (13)	Bouillon 0.05 ppm	Chemical, rubbery aroma and taste.
Bis-(2-methyl-3-furyl) trisulfide (10a)	Water 1 ppm	Brothy
Bis-(2-methyl-3-furyl) tetrasulfide (10b)	Water 10 ppb	Braised beef aroma and taste.

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having: ir (neat, KBr plates) 3120, 2960, 2925, 2540 (-SH), 1595, 1514, 1222, 1136, 1092, 938, 888 and 730 cm^{-1}; nmr (CCl_4) δ 2.32 (s,3, α ring CH_3), 2.47 (s,1 β SH), 6.19 (d,1,J=1.5Hz, β ring H), 7.15 ppm (d,1, J=1.5Hz, α ring H); mass spectrum (70 ev) m/e (rel. intensity) 116 (5), 115 (8), 114 (100), 113 (29), 86 (10), 85 (23), 71 (14).

bis (2-Methyl-3-furyl) disulfide (2): Repeated preparative thin-layer chromotography on 8"x 8" plates coated with 1.25 mm of silica-gel G (200 λ portions per plate, developed with 1:10 ether/hexane) gave from 2.4 g of concentrate 0.066 g of bis (2-methyl-3-furyl) disulfide having: ir (neat, KBr plates) 3120, 2955, 2920, 1580, 1512, 1222, 1120, 1085, 936, 885, 730 cm^{-1}; nmr (CCl_4) δ 2.08 (s,3, α ring CH_3), 6.27 (d,1,J=1.5Hz, β ring H), and 7.16 ppm (d,1,J=1.5 Hz, α ring H); mass spectrum (70 ev) m/e (rel intensity) 228 (6), 227 (9), 226 (60), 115 (5), 114 (17), 113 (100), 85 (13).

2-Methyl-3-sulfo-5-furoic acid (4): The barium salt of 4a was prepared in 93% yield from 3 according to Scully and Brown (7). The free acid was isolated for nmr by treating the barium salt with H_2SO_4 followed by filtration and evaporation under vacuum. Nmr (D_2O) δ 2.62 (s,3, α ring CH_3) and 7.47 ppm (s,1, β ring H).

2-Methyl-3-furansulfonic acid (5): A solution of 33 g of the barium salt of 4a in 450 ml of H_2O was treated with 20% H_2SO_4 until no further precipitation was observed. After filtration, the filtrate was adjusted to pH 7 with solid $NaHCO_3$. After addition of 26.3 g of mercuric chloride the resulting mixture was heated at reflux and monitored for CO_2 evolution. When CO_2 evolution had stopped, the mixture was cooled to room temperature and treated with hydrogen sulfide. After standing overnight precipitated mercuric sulfide was removed by decantation and filtration. The solution was evaporated to dryness *in vacuo* and the residue recrystallized from a minimum of boiling water to give 4.25 g of 2-methyl-3-furan sulfonic acid as the sodium salt. Ir (nujol mull) 3140, 1240, 1229, 1190, 1110, 1075, 1018, 898 cm^{-1}; nmr (D_2O) δ 2.48 (s,3, α ring CH_3), 6.62 (d,1,J=2Hz, β ring H) and 7.43 ppm (d,1,J=2Hz, α ring H).

2-Methyl-3-furansulfonyl chloride (6): A mixture of 80 g of 5 (sodium salt), 880 g thionyl chloride and 15 drops of dimethyl formamide was heated at reflux for 100 min, cooled to room temperature and filtered. After washing the filter cake with benzene (20 ml) and combining with the filtrate, concentration *in vacuo* gave 58 g of a brown oil. Distillation of the oil gave 45.4 g of 2-methyl-3-furansufonyl chloride as a light yellow liquid boiling at 55°C at 0.55

torr. and having: ir (neat, KBr plates) 3115, 1570, 1520, 1380, 1360, 1220, 1158, 1129, 1092, 1024, 948, 880, 740 cm^{-1}: nmr (CCl_4) δ 2.71 (s,3, α ring CH_3), 6.86 (d,1,J=2Hz, β ring H) and 7.52 ppm (d,1,J=2Hz, α ring H); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 145, 97, 53, 43, 180, and intensity of P+2 (182) is 43% of P.

2-Methyl-3-furanthiol (1): A solution of 45.4 g of 2-methyl-3-furansulfonyl chloride (6) in 540 ml of anhydrous ether was added dropwise to a solution of lithium aluminium hydride in 1200 ml ether. After heating at reflux one hour, excess hydride was destroyed by the addition of ethyl acetate. The resulting mixture was poured into 1,500 ml water and the ether layer separated. The aqueous phase was extracted with ether (4 x 250 ml) and the ether extracts were combined, washed with 5% $NaHCO_3$ solution (150 ml), water (2 x 200 ml) and dried over sodium sulfate. Solvent removal *in vacuo* gave 18 g crude 1. Distillation gave 11.6 g of 2-methyl-3-furanthiol boiling at 57-58.5° at 36 torr and having: ir, (neat, KBr plates) 3110, 2955, 2925, 2540 (SH), 1594, 1512, 1223, 1134, 1092, 937, 889, 732 cm^{-1}; nmr (CCl_4) δ 2.34 (s,3, α ring CH_3), 2.47 (s,1, β ring SH), 6.19 (d,1,J=1.5 Hz, β ring H) and 7.15 ppm (d,1,J=1.5 Hz, α ring H); mass spectrum (70 eu) m/e (rel. intensity) 116 (5), 115 (8), 114 (100), 113 (29), 86 (10), 85 (23), 71 (13).

bis (2-Methyl-3-furyl) disulfide (2): A solution of 7.4 g of sodium hydroxide, 10 g of sodium carbonate and 21 g of 2-methyl-3-furanthiol (1) in 344 ml of water was prepared. To this solution was added a solution of 77.3 g of potassium iodide and 23.2 g of iodine in 780 ml of water until the iodine color persisted for 1 min. After rendering the solution colorless with 0.1 sodium thiosulfate solution, the mixture was extracted with pentane (3 x 150 ml). The pentane extracts were combined, washed with water (2 x 100 ml) and dried over sodium sulfate. Solvent removal *in vacuo* gave 10 g of an amber oil. Distillation of the oil gave 15.4 g of bis (2-methyl-3-furyl) disulfide (2) boiling at 77-78° at 0.3 torr and having: ir (neat, KBr plates) 3120, 2955, 2920, 1580, 1512, 1222, 1122, 1082, 938, 885, 730 cm^{-1}; nmr (CCl_4) δ 2.07 (s,3, α ring CH_3), 6.25 (d,1,J=1.5 Hz, β ring H) and 7.14 ppm (d,1,J=1.5 Hz, α ring H); mass spectrum (70 ev) m/e (rel. intensity) 228 (6), 227 (10) 226 (61), 115 (4), 114 (16), 113 (100), 85 (13).

bis (2,5-Dimethyl-3-furyl) sulfide (10c) and bis (2,5-dimethyl-3-furyl) disulfide (10d): A mixture of 175 g of 2,5-dimethyl-furan (9) and 0.4 g of stannic chloride was cooled to -20° and 75.3 g of sulfur

dichloride was added while maintaining a temperature of -20°. After stirring at -20° for 100 mins., the reaction mixture was warmed to 34° and poured into ice water (1 liter). Extraction with hexane, and concentration in vacuo, after drying over sodium sulfate, gave 64.8 g of residue. Column chromatography of the residue on 1625 g of silicic acid with ether/hexane (1:20) gave 14.4 g of a mixture of 10c and 10d. Distillation of 11 g of the mixture gave 3.8 g of bis (2,5-dimethyl-3-furyl) sulfide, b.p. 81-85°C at 0.15 torr, and 5.1 g of bis (2,5-dimethyl-3-furyl) disulfide, b.p. 112-116°C at 0.45 torr.

10c: ir (neat, KBr plates) 3100, 2940, 2910, 1600, 1560, 1425, 1372, 1330, 1220, 1110, 1060, 979, 918, 790 cm^{-1}; nmr (CCl_4) δ 2.2 (s,3, α ring $C\underline{H}_3$), 2.3 (s,3, α ring $C\underline{H}_3$) and 5.78 ppm (s,1, β ring $\underline{H}$); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 43, 222, 126, 125, 179, 96, intensity of P+2 is 5% of P.

10d: ir (neat, KBr plates) 3100, 2942, 2910, 1598, 1560, 1423, 1372, 1330, 1218, 1110, 1060, 979, 918, 790 cm^{-1}; nmr (CCl_4) δ 2.1 (s,3, α ring $C\underline{H}_3$), 2.27 (s,3, α ring $C\underline{H}_3$) and 6.0 ppm (s,1, β ring $\underline{H}$); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 127, 43, 254, 128, 39, intensity of P+2 is 8% of P.

Repeating the above experiment but replacing the sulfur dichloride with 98.5 g of sulfur chloride gave a 54 g residue which when chromatographed gave 13.9 g of mono- and disulfide. Distillation of 11 g of the mixture gave 1.96 g of a 40/60 mixture of mono- and disulfide and 6.6 g of bis (2,5-dimethyl-3-furyl) disulfide boiling at 115° at 0.45 torr.

bis (2-Methyl-3-furyl) trisulfide (10a): To a mixture of 5 g of 2-methyl-3-furanthiol (1), 8.7 g of sodium bicarbonate and 25 ml of ether cooled to -30° was added a solution of 2.24 g of sulfur dichloride in 20 ml of ether during 24 min. After standing 5 min the mixture was allowed to warm to -5° and poured into 125 ml of ice water. Extraction with ether (2 x 25 ml), drying the ether extracts (sodium sulfate) and concentration in vacuo gave 5.1 g of crude 10a. Chromatography on 15 g of silicic acid with hexane gave 3.6 g of bis (2-methyl-3-furyl) trisulfide as a light yellow oil, homogeneous by tlc and having: ir (neat, KBr plates) 3120, 2950, 2919, 1580, 1512, 1384, 1225, 1122, 1085, 935, 885, 730 cm^{-1}; nmr ($CDCl_3$) δ 2.36 (s,3, α ring $C\underline{H}_3$), 6.35 (d,1,J=2H_2, β ring $\underline{H}$) and 7.21 ppm (d,1,J=2Hz, α ring $\underline{H}$); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 113, 43, 258, 45, 51, 145, 226, 194.

bis (2-Methyl-3-furyl) tetrasulfide (10b): To a mixture of 1.65 g 2-methyl-3-furanthiol (1), 10 ml ether and 3 g sodium bicarbonate cooled to -30°C was added dropwise a solution of 1.0 g of sulfur monochloride in 10 ml ether. After standing 45 min at -30° the reaction mixture was poured into water (75 ml), the upper layer was separated and washed with 25 ml water. After extracting the combined aqueous and wash layers with 25 ml ether, the ether layers were combined, washed with water (2 x 25 ml) and dried (sodium sulfate). Solvent removal *in vacuo* gave 1.6 g of crude 10b. Chromatography on 60 g of silicic acid with hexane gave 1.1 g of bis (2-methyl-3-furyl) tetrasulfide as a light yellow oil homogeneous by tlc and having: ir (neat, KBr plates) 3100, 2900, 1570, 1510, 1435, 1380, 1225, 1122, 1086, 938, 887, 730 cm^{-1}; nmr (CCl_4) δ 2.37 (s,3, α ring CH_3) 6.38 (d,1,J=2Hz, β ring H), 7.20 ppm (d,1,J=2Hz, α ring H); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 113, 114, 43, 45, 51, 226, 85, 69, 64, 290, 145.

5-Methyl-2-furanthiol (12): Preparation of 12 according to Goldfarb and Danyushevskii (9) gave, from 45.1 g of 2-methylfuran (11), 5.9 g of 5-methyl-2-furanthiol boiling at 56.5° at 33 torr (lit. 44-46° at 17 torr, (9)) and having: ir (neat, KBr plates) 3130, 2965, 2940, 2538, 1590, 1510, 1450, 1345, 1222, 1200, 1120, 1024, 960, 930, 790 cm^{-1}; nmr (CCl_4) δ 2.4 (s,3, α ring CH_3), 3.4 (s,broad,1, α ring SH), 6.15 (m,1, β ring H) and 6.58 (m,1, β ring H); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 114, 43, 71, 53, 85, 86, P+2 intensity 5.5% of P.

bis (5-Methyl-2-furyl) disulfide (13): A 3.0 g sample of 5-methyl-2-furanthiol (12) was oxidized with an aqueous potassium iodide/iodine solution as in the preparation of 2. A 2.6 g sample of crude 13 was obtained. Chromatography on 81 g of silicic acid with ether/hexane (1:9) as eluent gave 2.2 g of bis (5-methyl-2-furyl) disulfide (13) as a bright yellow oil having: ir (neat, KBr plates) 3135, 2965, 2938, 1590, 1485, 1450, 1224, 1198, 1118, 1022, 960, 929, 790 cm^{-1}; nmr (CCl_4) δ 2.47 (s,3, α ring CH_3), 6.22 (m,1,J=3Hz, β ring H), 6.66 (d,1,J=3Hz, β ring H); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 114, 113, 43, 71, 53, 85, 84, 226, 150, 160, 194, P+2 intensity 8.5% of P.

2,5-Dimethyl-3-furanthiol (8): A mixture of 35 g of 2,5-dimethyl-3-thioacetylfuran (10) and 350 ml of 15% aqueous sodium hydroxide solution was heated at reflux for 1 hr, cooled to room temperature, acidified to pH 1 with 20% sulfuric acid, and extracted with ether (3 x 100 ml). The combined extracts were washed

with sat. salt solution (4 x 75 ml) and dried (sodium sulfate). Solvent removal in vacuo gave 26 g of crude 8 which on distillation gave 17.3 g of 2,5-dimethyl-3-furanthiol boiling at 79° at 43 torr and having: ir (neat, KBr plates) 3110, 2980, 2950, 2920, 2530, 1610, 1572, 1445, 1430, 1378, 1222, 1063, 982, 920, 790 cm^{-1}; nmr ($CDCl_3$) δ 2.2 (s,3, α ring CH_3), 2.25 (s,3, α ring CH_3), 2.59 (s,1, β ring SH) and 5.86 ppm (s,1, β ring H); mass spectrum (70 ev) m/e (decreasing intensity, mol. ion) 43, 128, 85, 127, 95, 113 (P+2 intensity 4.5% of P).

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