The Odor and the Infrared Spectra of Furfuryl Sulfides

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By using furfuryl mercaptan as the starting material, the following sulfides have been prepared: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, isoamyl, *n*-hexyl, *n*-octyl, *n*-decyl, allyl, prenyl (3-methyl-2-butenyl), benzyl, propargyl, β -hydroxyethyl furfuryl sulfides.

Most of these compounds showed grassy or spicy odor which is distinguishable from the roasted-coffee aroma of furfuryl mercaptan. The infrared spectra of furfuryl alcohol, furfuryl mercaptan and the furfuryl sulfides in carbon tetrachloride have also been compared to find the characteristic absorptions for furfuryl sulfides and a medium band has been detected at 1130 cm^{-1} , which could be useful in identifying furfuryl sulfide group.

Furfuryl mercaptan has been characterized as an agent of roasted-coffee aroma.^{1,2)} The odor of the mercaptan in high concentration is extremely disagreeable and causes headache. However, when diluted with water or glycerol it shows a strong coffee aroma. The roasted-coffee odor is also recognized in several other vegetable products. Obata et al.³⁾ have prepared furfuryl mercaptan from furfuryl chloride and thiourea according to Kirner and Richter,⁴⁾ and suggested the usefulness of the mercaptan as a flavoring agent in tobacco processing. Chierici and Sardella⁵⁾ have reported difurfuryl mercaptols prepared by the action of gaseous hydrogen chloride on mixture of furfuryl mercaptan and the corresponding aldehydes or ketones and described that some of these compounds showed a better coffee-flavor than the mercaptan.

On the other hand, the literature contains little information about the odor and biological activities of furfuryl sulfides. Kirner and Richter⁴⁾ reported the first preparation of this series from ethyl bromide and furfuryl mercaptan and described the product, ethyl furfuryl sulfide, as a colorless liquid of pungent odor. Gilman and Hewlett⁶⁾ prepared β -chloroethyl and γ -chloropropyl furfuryl sulfides from furfuryl mercaptan obtained by the reduction of furfuryl disulfide which was prepared from furfuryl aldehyde and sodium hydrosulfide. They showed that the β -compound had a marked vesicant action which was not so great as that of mustard gas ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$), whereas the γ -chlorosulfide produced no skin irritation.

Recently, in a patent⁷⁾ which was published while this work was in progress, several furfuryl sulfides are prepared as the intermediate of furfuryl sulfoxides, useful as sedatives.

This experiment reported here was undertaken to obtain information about the odor of

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5) L. Chierici and M. Sardella, *Chimica* (Milan) **8**, 119 (1953). C.A. **48**, 4501i.

6) H. Gilman and A. P. Hewlett, *J. Am. Chem. Soc.* **52**, 2141 (1930).

7) Fujisawa Pharmaceutical Co., Ltd. (by Haruo Saikachi), Japan **16**, 267 (1962), Oct. 11, Appl. Oct. 9, 1959; C.A., **59**, 11425e.

the furfuryl sulfides and to find new flavoring agent for foodstuff. The infrared spectra of furfuryl sulfides, furfuryl mercaptan, and furfuryl alcohol were also studied to provide the basic information for diagnosis of the structure for furfuryl sulfides.

Although none of furfuryl sulfides has been isolated or detected in nature, the occurrence of several compounds containing furan nucleus suggests a possible presence or formation of furfuryl sulfides.

EXPERIMENTAL AND RESULTS

Furfuryl mercaptan (2-Furanmethanethiol)

Furfuryl mercaptan was prepared from furfuryl alcohol with thiourea and concentrated hydrochloric acid followed by the decomposition of the intermediate S-2-furfuryl isothiurea and steam distillation as described in *Organic Syntheses*.⁸⁾

In this method, the use of the very unstable and difficultly available furfuryl halides was avoided and furfuryl mercaptan was obtained in good yield (56~57%) after the distillation under nitrogen at reduced pressure, b.p. 45~47°C/12 mm.

Furfuryl sulfides

Slight variation of the procedure of Kirner and Richter⁴⁾ was adequate for the preparation of the entire series reported here. The furfuryl mercaptan (11.4 g, 0.1 mole) was converted into the sulfides by treatment of its sodium derivative with 0.1 mole of alkyl or substituted alkyl halide in methanolic solution (50 ml).

All of the alkyl or substituted alkyl halide except prenyl bromide were commercially available. Prenyl bromide (3-methyl-2-butenyl bromide) was prepared from isoprene and hydrogen bromide⁹⁾ in 70% yield, b.p. 50~51°C/40 mm.

The reaction mixture was refluxed on a water bath for one hour. On cooling the

solution was added 80 ml of ethyl ether and separated from the sodium halide by filtration. The methanol-ether solution was evaporated and the residue distilled in a nitrogen atmosphere. The products, colorless or faint yellow liquid of disagreeable odor were collected and analyzed. Yields and properties are summarized in Tables I and II.

Several products turned to brown on standing. Propargyl furfuryl sulfide was most unstable and turned to colored syrup in one week in sealed tube under nitrogen.

Infrared spectra

Infrared spectra were determined with Hitachi infrared spectrophotometer EPI-S2. Furfuryl mercaptan and furfuryl sulfides were run as 5% solutions in carbon tetrachloride using 1 mm cells.

Freshly distilled furfuryl alcohol, b.p. 70°C/11 mm, was used as 2% solution in the same solvent. Carbon tetrachloride of reagent grade, obtained from the Kanto Chemical Company, was used without further purification. Several of the curves are given in Figs. 1 and 2.

The bands found to be common to all spectra of furfuryl sulfides, furfuryl mercaptan and furfuryl alcohol are as follows: 3150 (weak),¹⁰⁾ 1720 (weak), 1665 (weak), 1595,¹¹⁾ 1505,^{10,11)} 1460, 1380,¹¹⁾ 1230~1250, 1155,¹¹⁾ 1075,¹¹⁾ 1005,¹¹⁾ 930,¹¹⁾ 885^{10,11)} cm⁻¹

Yamaguchi¹⁰⁾ pointed out several characteristic bands of furans; 3165~3115 cm⁻¹ due to C-H vibrations, 1577~1558 cm⁻¹ and 1511~1504 cm⁻¹ due to C-C vibrations, and also suggested that the characteristic absorption band at 885~873 cm⁻¹ could be most useful in identifying the furan nucleus. Katritzky and Logowski¹¹⁾ have recorded and discussed the characteristic infrared bands of 2-mono-substituted furans in chloroform solution.

Trotter and Thompson¹²⁾ have pointed out

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9) H. Staudinger et al. *Helv. Chim. Acta.*, 5, 743 (1922).

11) A. R. Katritzky and J. M. Logowski, *J. Chem. Soc.* 1959, 657.

12) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.* 1946, 481.

TABLE I. FURFURYL SULFIDES, -CH₂-S-R

R	Halide* ¹ used	B. p. °C/mm	Yield %	Formula	Analyses, % * ²			
					Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found.
Methyl	i)	61~61/12	* ³	C ₆ H ₈ OS	56.25	56.22	6.25	6.11
Ethyl* ⁴	b)	77/14	47	C ₇ H ₁₀ OS	59.15	58.94	7.04	6.81
<i>n</i> -Propyl* ⁵	b)	90~92/15	46	C ₈ H ₁₂ OS	61.54	61.36	7.69	7.54
Isopropyl* ⁵	i)	79~80/12	32	C ₈ H ₁₂ OS	61.54	61.77	7.69	7.53
<i>n</i> -Butyl* ⁵	b)	102~103/13	60	C ₉ H ₁₄ OS	63.53	63.14	8.24	8.25
Isobutyl	i)	94~96/16	39	C ₉ H ₁₄ OS	63.53	63.18	8.24	8.05
<i>n</i> -Amyl	b)	117~120/15	56	C ₁₀ H ₁₆ OS	65.22	65.12	8.70	8.52
Isoamyl* ⁵	b)	108~110/15	43	C ₁₀ H ₁₆ OS	65.22	65.31	8.70	8.61
<i>n</i> -Hexyl	b)	130~131/13	43	C ₁₁ H ₁₈ OS	66.67	66.83	9.09	9.16
<i>n</i> -Octyl	c)	160/15	24	C ₁₃ H ₂₂ OS	69.03	69.03	9.73	9.71
<i>n</i> -Decyl	b)	180~183/13	57	C ₁₅ H ₂₆ OS	70.87	70.89	10.24	10.23
Benzyl	c)	160~162/17	53	C ₁₂ H ₁₂ OS	70.59	70.75	5.88	5.87
Allyl* ⁵	b)	87~88/12	49	C ₈ H ₁₀ OS	62.34	62.35	6.49	6.20
Prenyl	b)	119~121/16	40	C ₁₀ H ₁₄ OS	65.93	66.14	7.69	7.68
Propargyl	b)	70/12	6	C ₈ H ₈ OS	63.16	63.22	5.26	5.15
β -Hydroxyethyl	c)	136~137/13	51	C ₇ H ₁₀ O ₂ S	53.16	53.07	6.32	6.66

*¹ i), Iodide; b), bromide; and c), chloride.*² The analytical data reported in this paper were determined by Mrs. Toyoko Toma in the Department of Pharmacology, Hokkaido University.*³ Furfuryl methyl sulfide was prepared by Mr. Kenichi Hashizume in his graduation thesis, Department of Agricultural Chemistry, Hokkaido University, 1963. The yield from furfuryl mercaptan and dimethyl sulfate was 58%. The sulfide was obtained in 40% yield when the reaction mixture of sodium furfuryl mercaptide and methyl iodide was processed after standing overnight at room temperature without refluxing.*⁴ Reference 4.*⁵ Reference 7.

TABLE II. ODOR OF FURFUYL SULFIDES

Furfuryl sulfide	
Methyl	Pungent, spicy, soysauce-like
Ethyl	Slightly pungent, cool, grassy
<i>n</i> -Propyl	Somewhat grassy, spicy, slightly mint-like
Isopropyl	Somewhat sharp, spicy, mint-like
<i>n</i> -Butyl	Slightly cool, grassy, somewhat fruity
Isobutyl	Somewhat cool, spicy
<i>n</i> -Amyl	Grassy
Isoamyl	Grassy, slightly cool
<i>n</i> -Hexyl	Slightly cool, fruity (grape) but unpleasant
<i>n</i> -Octyl	Something like fresh cut grass
<i>n</i> -Decyl	Fatty, mild, slightly peanut-like
Benzyl	Strong, grassy, fresh Matsutake-like
Allyl	Leek or garlic-like, mild
Prenyl	Grassy, cool, unpleasant
β -Hydroxyethyl	Cool, slightly mint-like

that the band in the region of 600~700 cm⁻¹ is characteristic of the C-SH and C-S-C bands. In this study, the frequency associated with the C-S band remains approximately constant at 700 cm⁻¹ throughout the series of furfuryl sulfides and furfuryl mercaptan. However, the intensity of this band is comparatively low and the deeply absorbing aromatic band in this area obscures the C-S band (cf. Fig. 2, Benzyl furfuryl sulfide).

On the basis of comparative spectral study it can be concluded that medium but sharp band at 1130 cm⁻¹ is associated with the furfuryl sulfide group. The 1130 cm⁻¹ band is not present in the spectrum of furfuryl alcohol nor in that of furfuryl mercaptan. No absorption at 1130 cm⁻¹ also could be detected

FIG. 1. Infrared Absorption Spectra of Furfuryl Mercaptan (I) and Furfuryl Sulfides. II; Methyl, III; *n*-propyl, IV; Isopropyl

FIG. 2. Infrared Absorption Spectra of Furfuryl Sulfides.

V; *n*-Octyl, VI; Allyl, VII; Benzyl, VIII; β-Hydroxyethyl

in the following compounds:¹³⁾ Octyl methyl sulfide, β -phenyl- β -hydroxyethyl methyl sulfide, benzyl methyl sulfide, tetrahydrofurfuryl methyl sulfide, linalyl methyl sulfide, linalyl benzyl sulfide, geranyl methyl sulfide and geranyl benzyl sulfide. The 1130 cm^{-1} band may be used as the characteristic band of furfuryl sulfide group for the identification of this structure when it is considered together with the furan bands.

The infrared absorption curves of *n*-octyl furfuryl sulfide and of *n*-decyl furfuryl sulfide were superimposable except very minor difference at 1300 cm^{-1} .

13) Unpublished data of this laboratory.