Flavor Components of Onion Oil

M. H. Brodnitz, C. L. Pollock, and P. P. Vallon

The components of onion oil were examined by combined gas-liquid chromatography–mass spectrometry. The various components of the oil were also separated by preparative-scale gas chromatography and examined individually by infrared, nuclear magnetic resonance, and mass spectral techniques. 3,4-Dimethylthiophene, methyl *cis*-propenyl disulfide, methyl *trans*-propenyl disulfide, *cis*-propenyl propyl disulfide, *trans*-propenyl propyl disulfide, two methyl propenyl trisulfides, and two propenyl propyl trisulfides not previously reported as occurring in onions were found to be important components of onion oil.

Although the volatile components of the onion have been studied for over 70 years, there is still no general agreement regarding the nature and composition of onion oil. The most important volatile flavor constituents of *Allium cepa* are reported to be sulfur-containing compounds (Bernhard, 1966; Carson, 1967; Wahlroos and Virtanen, 1965).

Semmler (1892b) obtained an oil possessing the characteristic onion odor by steam distillation of fresh bulbs of *A. cepa*. A major constituent of this oil is an organic sulfide of the same empirical formula as allyl propyl disulfide, but possessing a different boiling point. Challenger and Greenwood (1949) identified 1-propanethiol in headspace above chopped onions. The presence of propyl disulfide in a low temperature–low pressure distillate of fresh onions was demonstrated by Niegisch and Stahl (1956).

Gas chromatographic analysis by Carson and Wong (1961) led to the identification of methyl, propyl, and methyl propyl disulfides and trisulfides in onions. All six possible compounds were positively identified in the distillate. Neither allyl propyl disulfide nor any other allyl-containing sulfide was found in significant amounts in the onion distillates by Carson and Wong, in agreement with the conclusions of Niegisch and Stahl (1956). Saghir *et al.* (1964) determined by gas chromatography the composition of sulfides in the vapor above several species of freshly chopped *Alliums*. In the onion cultivars studied, allyl propyl disulfide accounted for 4 to 9% of the sulfides measured, while lower concentrations of allyl disulfide and allyl methyl disulfide were also observed.

Previously (Brodnitz and Pollock, 1968), the presence of methyl and propyl propenyl in onion oil polysulfides was reported. This paper describes the isolation and identification of the major sulfide constituents of onion oil.

EXPERIMENTAL

Materials. Onion oil distilled at a Dutch facility of International Flavors & Fragrances, Inc., during the winter of 1967 was used in this study. The oil was drawn from the bulked product obtained by the distillation of hundreds of tons of field-run onions of mixed varieties, maturities, and sizes. Authentic reference samples of methyl disulfide, methyl trisulfide, propyl disulfide, propyl trisulfide, allyl methyl disulfide, and allyl propyl disulfide were obtained commercially. Methyl propyl disulfide, methyl propyl trisulfide, allyl methyl trisulfide, and allyl propyl trisulfide were synthesized according to the methods of Carson and Wong (1959). 3,4-Dimethylthiophene was synthesized from 2,3-dimethylsuccinic acid according to the method of Linstead *et al.* (1937). The methyl propenyl and propenyl propyl disulfides were obtained from W. J. Evers, who prepared them by condensing lithium propene with an alkyl disulfur chloride (Evers, 1967).

Apparatus and Method. Preparative scale gas chromatographic separations were performed in an Aerograph 200 with a 10-to-1 effluent splitter. Purified materials were obtained by gas chromatography on 8-foot by 1/4-inch (o.d.) stainless steel columns packed with 60/80-mesh acid-washed, DMCS-treated Chromosorb W coated with 25% Carbowax 20M. A helium flow rate of 75 ml. per minute was maintained while the temperature was programmed from 70° to 180° C. at 2° C. per minute. Individual components for spectroscopic analysis were trapped in thin-walled glass capillaries (Jennings *et al.*, 1964). Only fractions which contained less than 2% impurities on rechromatography on a 50-foot by 0.02-inch support coated open tubular capillary (SCOT) column containing Apiezon-L liquid phase, were considered purified.

Mass spectral analyses of the volatile fractions of the onion oil were carried out on a Perkin-Elmer Hitachi Model RMU-6E mass spectrometer. Samples for analysis were injected into an Aerograph 1520 gas chromatograph equipped with a SCOT column coupled through a Biemann helium separator to the mass spectrometer. SCOT columns, 50-foot by 0.02-inch bore, containing Carbowax 20M or Apiezon-L liquid phases were used. The mass spectrometer source temperature and oven temperature were maintained at 200° and 180° C., respectively, and the temperature of the 5-foot coupling tube between the gas chromatograph and the mass spectrometer was maintained at 150° C. A helium flow rate of 6 ml. per minute was maintained while the column was programmed from 50° to 175° C. at 2° C. per minute. Effluent from the gas chromatographic column was split 1 to 5 between the flame ionization detector and the Biemann separator. Samples up to 0.5 μl. were injected into the glass-lined injector block of the gas chromatograph. Infrared spectra were obtained on sodium chloride microdisks employing a Beckman Model IR4 recording infrared spectrophotometer. Nuclear magnetic resonance spectra (NMR) were obtained using a Varian HR100 spectrometer. All compounds were run in dilute carbon tetrachloride solutions using tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

A typical chromatogram of the distilled onion oil obtained on a SCOT Carbowax 20M column is shown in Figure 1.

International Flavors & Fragrances, Inc., 1515 Highway 36, Union Beach, N. J. 07735

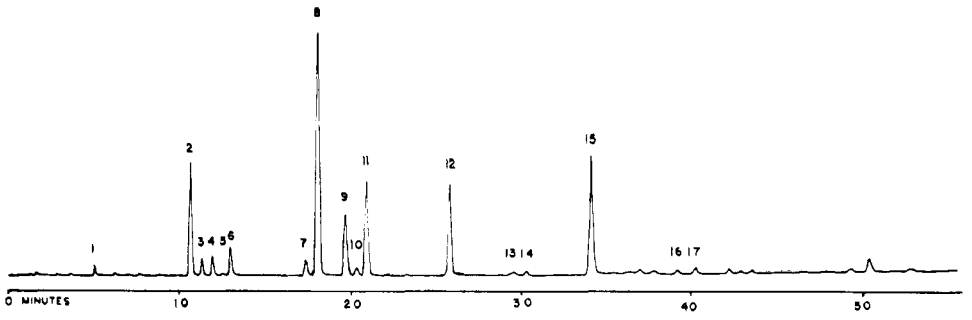

Figure 1. Capillary column gas chromatogram of onion oil

0.02-inch × 50-foot SCOT Carbowax 20M column programmed 70° to 180° C., 2° C. per minute

Table I. Identification of Compounds

Peak No.	Compound	I_E Value
1	Methyl disulfide	4.2
2	Methyl propyl disulfide	5.9
3	3,4-Dimethylthiophene	6.0
4	Methyl *cis*-propenyl disulfide	6.1–6.2
5	Allyl methyl disulfide	6.2–6.3
6	Methyl *trans*-propenyl disulfide	6.4
7	Methyl trisulfide	7.3
8	Propyl disulfide	7.4
9	*cis*-Propenyl propyl disulfide	7.6–7.7
10	Allyl propyl disulfide	7.7–7.8
11	*trans*-Propenyl propyl disulfide	7.8–7.9
12	Methyl propyl trisulfide	8.8
13	Methyl propenyl trisulfide[a]	9.1
14	Methyl propenyl trisulfide[b]	9.1–9.2
15	Propyl trisulfide	10.1
16	Propenyl propyl trisulfide[a]	10.6
17	Propenyl propyl trisulfide[b]	10.7

[a] Probably cis.
[b] Probably trans.

The order of elution on the Apiezon-L SCOT column was different, but no additional components of the oil were separated on it. Identifications of the compounds and their relative retention time indices calculated as I_E values (van den Dool and Kratz, 1963) are listed in Table I. All of the identified components of the oil contain at least one sulfur atom per molecule and, except compound 3, all are aliphatic polysulfides.

All of the possible methyl and propyl disulfide and trisulfide derivatives were identified in the oil (peaks 1, 2, 7, 8, 10, and 15) by comparing their retention times and mass spectral patterns with those of the authentic compounds.

A cyclic compound not previously reported to occur in *Alliums* was found in the oil. The mass spectrum of component 3 had abundant ions of *m/e* 112, 111, and 97, suggesting that the compound was a dimethyl-substituted thiophene. NMR analysis showed two signals, one at 2.14 and one at 6.76 p.p.m., with an integral ratio of 3 (2.14 p.p.m.) to 1. This restricted the possibilities to the symmetric thiophenes. A comparison with authentic samples of 2,5- and 3,4-dimethylthiophene confirmed that the isolate was the 3,4-dimethylthiophene.

Components of Molecular Weight 120. Components 4, 5, and 6 had molecular weights of 120 and according to MS, all

Table II. Mass Spectral Data of Natural and Synthetic Unsaturated Disulfides

(Per cent total ionization)

	Methyl *cis*-Propenyl Disulfide		Allyl Methyl Disulfide		Methyl *trans*-Propenyl Disulfide		*cis*-Propenyl Disulfide		Allyl Propyl Disulfide		*trans*-Propenyl Disulfide	
m/e	Syn.	Nat.	Syn.	Nat.	Syn.	Nat.	Syn.	Nat.	Syn.	Nat.	Syn.	Nat.
27	1.94	0.85	2.00	1.50	1.30	0.99	4.68	2.28	2.82	3.04	4.79	2.77
28	9.98	5.96	8.05	22.64	2.48	6.57	1.55	3.29	16.44	10.31	1.79	3.63
39	6.51	4.26	16.10	4.72	5.26	4.48	5.85	3.80	5.17	5.24	5.99	4.18
41	7.76	4.68	23.80	16.98	6.95	5.47	12.87	8.11	14.80	16.22	12.57	10.07
43	0.03	0.02	0.01	0.02	0.01	0.01	9.95	6.08	7.98	9.30	9.58	7.05
45	11.64	8.51	9.39	4.72	11.22	9.95	8.19	5.33	3.38	3.99	8.38	6.29
47	3.47	2.55	2.41	1.89	3.28	2.99	2.40	1.85	1.78	2.20	2.39	2.02
71	2.30	2.55	1.00	0.90	3.28	2.99	1.80	1.27	0.85	0.68	1.32	1.51
72	5.54	6.81	1.00	0.94	7.94	7.66	4.15	2.84	0.94	1.35	3.47	3.02
73	3.19	3.40	2.00	1.57	4.47	3.98	3.66	2.84	2.35	2.54	3.59	4.53
74	2.36	2.13	0.67	0.94	2.98	2.99	2.41	2.03	1.41	1.62	2.30	2.52
75	4.16	4.77	0.80	0.63	6.95	5.97	1.20	0.76	0.70	0.68	1.19	1.07
78	0.20	0.05	0.02	0.01	0.02	0.02	1.99	1.93	1.27	1.35	1.25	2.26
79	0.83	0.85	2.00	1.76	1.49	1.00						
80	2.50	3.15	1.61	2.04	4.17	3.58						
81	1.08	0.26	0.15	0.25	0.15	0.20						
82	0.28	0.43	0.15	0.38	0.30	0.50						
87	0.69	1.28	0.67	0.57	1.99	1.50						
88			0.67	0.58								
105	0.58	0.85	0.10	0.28	1.49	1.19						
106							10.5	9.13	7.80	7.44	10.77	12.08
120	9.40	14.04	9.39	11.19	17.20	18.90						
148							12.3	11.66	13.15	9.30	13.17	14.35

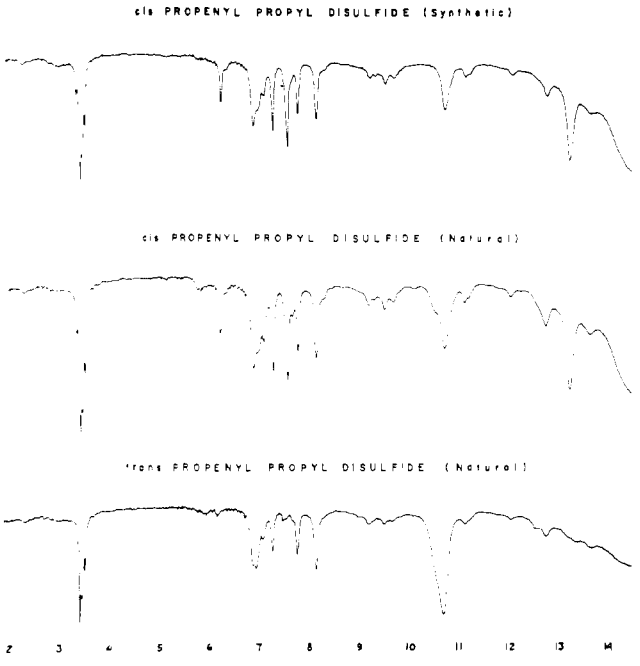

Figure 2. Infrared spectra of natural and synthetic propenyl propyl disulfides (microns)

contained a methyl group and two sulfur atoms. The mass spectra of components 4 and 6 were essentially identical, while that of 5 was slightly different (Table II). All three spectra contained characteristic ions of *m/e* 120 and 105 (M minus CH_3). Mass spectrum and retention time on both the Carbowax 20M and the Apiezon-L columns for component 5 agreed closely with those of allyl methyl disulfide. The spectral similarity of components 4 and 6 to that of allyl methyl disulfide and the presence of two isomers suggested that the two components were the methyl *cis*- and *trans*-propenyl disulfides (Table II). The infrared spectrum of compound 4 was identical with that of authentic methyl *cis*-propenyl disulfide, with absorptions (microns) at 3.35 (m) shoulder, 3.45 (s), 3.51 (w) shoulder, 6.21 (m), 6.90 (s), 7.05 (s) shoulder, 7.25 (m), 7.53 (s), 7.64 (m), 8.25 (w), 9.70 (w), 10.48 (m), 10.63 (m), 11.58 (w), 12.75 (w), 13.23 (s). The strong absorption at 13.23 microns was assigned to the cis double bond. The infrared spectrum of compound 6 was identical to that of authentic methyl *trans*-propenyl disulfide with absorptions (microns) at 3.35 (m) shoulder, 3.45 (s), 3.52 (m), 6.15 (m), 6.97 (s), 7.05 (m) shoulder, 7.25 (m), 7.64 (m), 7.73 (m), 8.11 (m), 8.83 (w), 9.03 (w), 10.50 (s) shoulder, 10.78 (s), 12.52 (w), 13.33 (w). The strong absorption at 10.78 microns was assigned to the trans double bond.

The NMR spectra of the natural components also agreed with those of the synthetic methyl *cis*- and *trans*-propenyl disulfides. That the unsaturation in the molecule was at the propenyl carbon of the C_3 chain is demonstrated by the absence of the characteristic allylic A_2B pattern at 5.1 to 6.5 p.p.m. in compounds 4 and 6.

Components of Molecular Weight 148. Components 9, 10, and 11 had molecular weights of 148 and contained a propyl radical and two sulfur atoms. Here, too, two of the mass spectra (components 9 and 11) were essentially identical, while the third component had a similar but slightly different pattern (Table II). All three spectra contained characteristic ions of *m/e* 148 and 106 (*M* minus C_3H_6). The third component was identified as allyl propyl disulfide by comparing mass spectra and retention times with an authentic sample. As indicated in Figure 2, the infrared spectrum of compound 9 was identical with that of authentic *cis*-propenyl propyl disulfide, with absorptions (microns) at 3.4 to 3.5 (s), 6.20 (m), 6.85 (m), 7.08 (m) shoulder, 7.27 (m), 7.54 (s), 7.75 (m), 8.12 (m), 9.19 (w), 9.50 (w), 9.68 (w), 10.52 (w) shoulder, 10.72 (m), 11.12 (w), 12.05 (w), 12.78 (w), 13.25 (s), 13.67 (w). The strong absorption at 13.25 microns was assigned to the cis double bond. The infrared spectrum of compound 11 was identical with that of authentic *trans*-propenyl propyl disulfide with absorptions (microns) at 3.4 to 3.5 (s), 6.15 (w), 6.92 (m), 7.08 (m) shoulder, 7.27 (m), 7.48 (w), 7.77 (m), 8.14 (m), 9.20 (w), 9.50 (w), 9.68 (w), 10.70 (s), 11.13 (w), 12.08 (w), 12.55 (vw), 12.76 (w), 13.25 (vw), 13.38 (w), 13.68 (w). The strong absorption at 10.70 microns was assigned to the trans double bond.

The NMR spectra of the natural samples also agreed with those of synthetic *cis*- and *trans*-propenyl propyl disulfide. The absence of the characteristic allylic A_2B pattern at 5.1 to 6.5 p.p.m. also shows that the unsaturation in compounds 9 and 11 occurs at the propenyl position in the C_3 chain of these molecules.

Components of Molecular Weights 152 and 180. Components 13 and 14 had identical spectra and a molecular weight of 152, which were similar to but somewhat different from those of allyl methyl trisulfide. On the basis of their mass spectra, both components contained three sulfur atoms as well as a methyl group and an alkenyl radical, and hence were the cis and trans isomers of methyl propenyl trisulfide. As can be seen in Figure 3, the two isomers of the trisulfide are difficult to separate by preparative gas chromatography, and hence, infrared and NMR confirmation of struc-

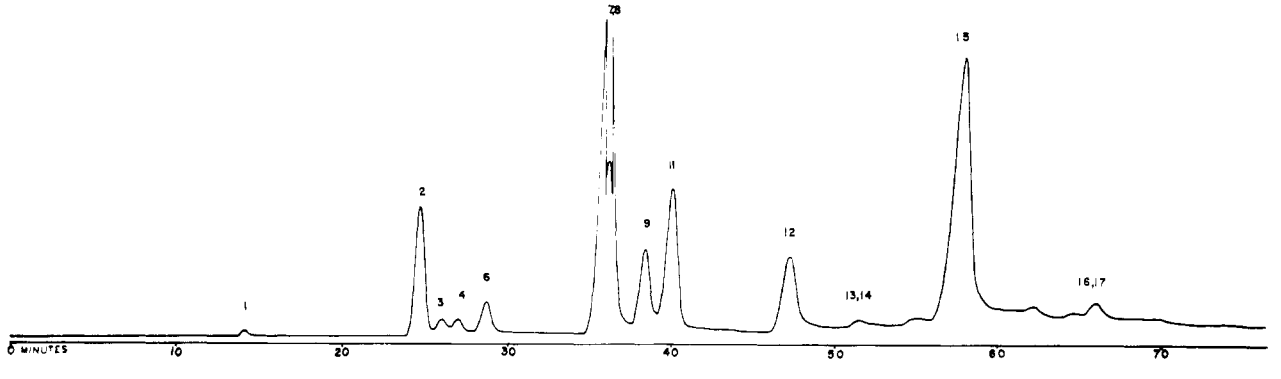

Figure 3. Preparative gas chromatogram of onion oil

1/4-inch × 8-foot Carbowax 20M column programmed 70° to 180° C., 2° C. per minute

ture was not possible. Based on the pattern observed for the propenyl disulfide, it appears reasonable that component 13 is the cis isomer, while component 14 is methyl *trans*-propenyl trisulfide.

By mass spectrometry, components 16 and 17 were found to be trisulfides with a molecular weight of 180. Their spectra were identical and bore some resemblance to that of allyl propyl trisulfide. These two components could not be separated by preparative-scale GLC. Based on analogy with the propenyl disulfides, it is reasonable to assume that component 16 is the cis isomer, while 17 is *trans*-propenyl propyl trisulfide.

Origin of Components of Onion Oil. Stoll and Seebeck (1949) demonstrated that garlic (*A. sativum*) contains an enzyme, allinase, capable of converting odorless *S*-allyl cysteine sulfoxide to diallyl thiosulfinate, pyruvic acid, and ammonia. The thiosulfinate, however, is unstable, and a thiosulfonate and a disulfide are known to be the products of its decomposition (Barnard, 1957), thereby explaining the origin of the allyl propyl disulfide and allyl propyl trisulfide first reported in garlic oil by Semmler (1892a).

Methyl disulfide, methyl trisulfide, propyl disulfide, propyl trisulfide, methyl propyl disulfide, and methyl propyl trisulfide were identified in onion distillates by Carson and Wong (1961).

Methyl disulfide, methyl propyl disulfide, and propyl disulfide were found in the volatiles of fresh onions as well as in dehydrated onion powder (Bernhard, 1968; Saghir *et al.* 1964).

Virtanen and Matikkala (1959) identified *S*-methyl cysteine sulfoxide and *S*-propyl cysteine sulfoxide in raw onions. An allinase capable of splitting these sulfoxides was also isolated from *A. cepa* (Kupiecki and Virtanen, 1960; Schwimmer *et al.*, 1960), suggesting the origin of the saturated di- and trisulfides identified in the onion.

Virtanen and Spāre (1961) isolated *S*-propenyl cysteine sulfoxide from onions. By analogy, the presence of propenyl disulfides might be expected in onions. Yet, no evidence of the presence of these unsaturated sulfides in *A. cepa*, and only incomplete identification of some of the propenyl sulfides in chives (*A. schoenoprasum*) (Wahlroos and Virtanen, 1965), have been reported until now. Schwimmer (1968) suggested recently that the flavor, odor, and lacrimation perceived upon comminution of onion tissue result from enzymatic activity on *trans* (+)-*s*-1-propenyl-L-cysteine-*S*-oxide. Our organoleptic evaluation of propenyl-containing polysulfides obtained in this study revealed that these compounds possess the flavor of cooked onions. It is clear now that the propenyl sulfides, and especially the propenyl propyl disulfides, are significant components of commercially distilled onion oil (Brodnitz and Pollock, 1968), while allyl disulfides are only minor components of that onion oil. This is in contradiction to the results Saghir *et al.* (1964) and Bernhard (1968) reported for freshly macerated onions. The origin of the allyl derivatives is not completely clear. Analysis of commercial garlic oil revealed the presence of trace concentrations of the cis and trans isomers of both methyl propenyl disulfides and propenyl propyl disulfides. Possibly, allyl and propenyl sulfides undergo reversible isomerization. More likely, however, yet unisolated trace concentrations of *S*-propenyl cysteine might occur in garlic.

The absence of mercaptans, alcohols, and carbonyls in the oil indicates that the commercial process employed in the production of onion oil selectively recovers the di- and trisulfides of the onion. This is significant because, as pointed out by Saghir *et al.* (1964), Carson (1967), and Bernhard (1968), the composition of the di- and trisulfides is undoubtedly the determining factor in the flavor of the members of the *Allium* family.

ACKNOWLEDGMENT

The authors thank W. J. Evers for supplies of methyl and propyl propenyl polysulfides and S. K. Freeman and M. Jacobs for assistance in obtaining and interpreting the infrared and NMR spectral data.

LITERATURE CITED

Barnard, D., *J. Chem. Soc.* **1957,** 4675.
Bernhard, R. A., *Advan. Chem. Ser.*, No. **56,** 131 (1966).
Bernhard, R. A., *J. Food Sci.* **33,** 298 (1968).
Brodnitz, M. H., Pollock, C. L., 28th meeting, Institute of Food Technologists, Philadelphia, Pa., May 1968.
Carson, J. F., in "Chemistry and Physiology of Flavors," p. 390. Avi, Westport, Conn., 1967.
Carson, J. F., Wong, F. F., J. AGR. FOOD CHEM. **9,** 140 (1961).
Carson, J. F., Wong, F. F., *J. Org. Chem.* **24,** 175 (1959).
Challenger, F., Greenwood, D., *Biochem. J.* **44,** 87 (1949).
Evers, W. J., International Flavors & Fragrances, Inc., Union Beach, N. J., private communication, 1967.
Jennings, W. G., Creveling, R. K., Heinz, D. E., *J. Food Sci.* **29,** 730 (1964).
Kupiecki, F. P., Virtanen, A. I., *Acta Chem. Scand.* **14,** 1913 (1960).
Linstead, R. D., Noble, E. G., Wright, J. M., *J. Chem. Soc.* **1937,** 911.
Niegisch, W. D., Stahl, W. H., *Food Res.* **21,** 657 (1956).
Saghir, A. R., Mann, L. K., Bernhard, R. A., Jacobsen, J. V., *Proc. Am. Soc. Hort. Sci.* **84,** 386 (1964).
Schwimmer, S., *Phytochemistry* **7,** 401 (1968).
Schwimmer, S., Carson, J. F., Makower, R. V., Mazelis, M., Wong, F. F., *Experientia* **16,** 449 (1960).
Semmler, F. W., *Arch. Pharmacol.* **230,** 434 (1892a).
Semmler, F. W., *Arch. Pharmacol.* **230,** 443 (1892b).
Stoll, A., Seebeck, E., *Helv. Chim. Acta* **32,** 197 (1949).
van den Dool, H., Kratz, P., *J. Chromatog.* **11,** 463 (1963).
Virtanen, A. I., Matikkala, E. J., *Acta Chem. Scand.* **13,** 1898 (1959).
Virtanen, A. I., Spāre, C. G., *Suomen Kemistitehti* **B34,** 72 (1961).
Wahlroos, O., Virtanen, A. I., *Acta Chem. Scand.* **19,** 1327 (1965).

Received for review October 9, 1968. Accepted January 15, 1969. Division of Agricultural and Food Chemistry, 156th Meeting, ACS, Atlantic City, N. J., September 1968.