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Synthesis and Flavor Evaluation of Some Alkylthiophenes. Volatile Components of Onion

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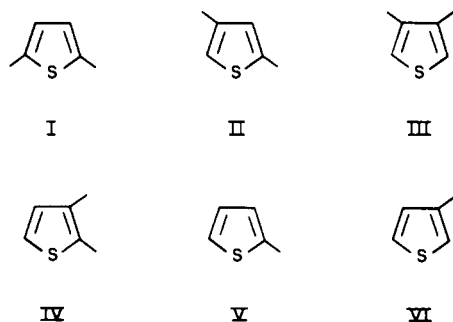
Pure samples of 2,4-, 2,5-, and 3,4-dimethylthiophene have been obtained. These compounds, upon organoleptic evaluation, have been determined not to contribute significantly to the flavor of fried onion when examined alone, in combination, or when added to artificial or natural onion oils. These findings are contrary to those previously reported in the literature. Pure samples of 2-methyl- and 3-methylthiophene, as well as 2,3-dimethylthiophene, have also been purified and evaluated organoleptically.

The complex and characteristic flavor of the onion is readily recognized and enjoyed by people in much of the world. Depending on its state and method of preparation the onion's flavor can be described as either fresh-green, cooked-boiled, or fried and at the same time distinctly that of onion.

The fresh, raw onion flavor notes are due primarily to the presence of alkyl thiosulfonates (Brodnitz and Pascale, 1973) and alkyl thiosulfonates (Brodnitz et al., 1973; Naarden International, 1974; Boelens et al., 1971). The alkyl di- and trisulfides are primarily responsible for the cooked onion flavor (Boelens et al., 1971) which is characteristic of steam-distilled onion oil. Several recent patents describe the role of these polysulfides in artificial onion oils (Brodnitz and Pascale, 1973; Galetto and Pace, 1973).

Recently, Boelens et al. (1971) in their extensive and detailed analyses of onion oil identified three thiophenes: the 2,5-dimethyl (I), the 2,4-dimethyl (II), and the 3,4-dimethyl (III) isomers. Furthermore, they described the odor of two of these compounds (II and III) as being "distinctly that of fried onion". The same three thiophenes have more recently been found in shallots by Dembele and Dubois (1973). Brodnitz et al. (1969) had previously identified 3,4-dimethylthiophene in onion oil but did not discuss its flavor characteristics.

Our interest in obtaining a better understanding of the components contributing to fried onion flavor has prompted us to purify and organoleptically evaluate all four of the possible isomers of dimethylthiophene (I-IV)



as well as the two possible methylthiophenes (V and VI).

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MATERIALS AND METHODS

Chemicals and Analytical Equipment. 2-Methylthiophene and 2,5-dimethylthiophene (Aldrich Chemical Co.) and 3-methylthiophene and 3,4-dimethylthiophene (Marstan Chemical Co.) were obtained commercially. All compounds were purified by fractional distillation at atmospheric pressure and were chromatographically and analytically (NMR, MS) pure.

Gas-liquid chromatography (GLC) analyses were performed on a Hewlett-Packard 5702A instrument equipped with a thermal conductivity detector. The column was made of glass (8 ft × 0.25 in. o.d., 0.16 in. i.d.) and packed with 5% Carbowax 20M coated on Chromosorb WAW, 80-100 mesh.

NMR data were obtained on a Varian EM-360 instrument, ir data with a Perkin-Elmer 257 grating spectrophotometer, and MS data on a Du Pont 21-490 mass spectrometer.

2,3-Dimethylthiophene (IV). Using standard procedures, 50 g of 3-methylthiophene-2-carboxaldehyde containing 20% of the 2,4-isomer via GLC was converted to 70 g of the corresponding semicarbazone. Four recrystallizations from methanol yielded white needles free of the 2,4-isomer by NMR analysis, 36 g, mp 219-221 °C.

3-Methylthiophene-2-carboxaldehyde semicarbazone (36 g) was reduced via a modified Wolff-Kishner reaction (Shepard, 1932). It was first mixed with 47.5 g of powdered KOH and then heated over an open flame. The distillate, 20 g (95%), was carefully redistilled to yield a center cut of 5.7 g of chromatographically pure 2,3-dimethylthiophene [bp 140-141 °C; n_D^{20} 1.5187; lit. bp 139.5-140.5 °C, n_D^{20} 1.5188 (King and Nord, 1949)]. The MS, NMR, and ir spectra were in complete accord with the proposed structure.

2,4-Dimethylthiophene (II). Following the general procedure of Sice (1954a) and Ramanathan and Levine (1962) with the substitution of phenyllithium for butyllithium, 49 g of 3-methylthiophene was first treated with an equivalent amount of phenyllithium in 30% ether in benzene at room temperature and then the mixture was added to a cold solution of dimethylformamide in ether. Distillation of the crude product gave 50.5 g (80%) of a product, bp 67-69 °C (2 mm) which was shown to be a 4:1 mixture of the 2,4- and 2,3-isomeric aldehydes by GLC analysis.

The methylthiophenecarboxaldehyde mixture (50 g) was converted to 66.5 g of its semicarbazone. This derivative

Table I. Threshold of Thiophene Compounds

Thiophene compd	Threshold, ppm
2-Methyl- (V)	3
3-Methyl- (VI)	5
2,3-Dimethyl- (IV)	5
2,4-Dimethyl- (II)	3
2,5-Dimethyl- (I)	3
3,4-Dimethyl- (III)	5
Mixture ^a	5

^a Compounds III, II, and I in the approximate natural ratio of 100:13.5:1.5.

was recrystallized four times from methanol yielding 35.6 g of white needles, mp 215–218 °C, which by NMR analysis were free of the 2,3-isomer.

The semicarbazone, 35.5 g, was reduced and distilled as before (16 g yield) and redistilled to give 4.3 g of a chromatographically pure center fraction of 2,4-dimethylthiophene: bp 139 °C; n_D^{20} 1.5129; lit. bp 139 °C (740 mm); n_D^{20} 1.5120 (Sice, 1954a); n_D^{20} 1.5130 (Sice, 1954b). The MS, NMR, and ir spectra were in complete agreement with the proposed structure.

Threshold Determinations. The detection thresholds of each of the thiophenes and a blend of dimethylthiophenes (see Table I) were determined by 14 or 15 panelists. A 30-ml portion of each sample was presented to the panelists in coded 2.5 oz plastic cups at 0.0, 0.001, 0.01, 0.1, 1.0, 3.0, 5.0, and 10.0 ppm levels in bottled spring water. A 30-ml portion of each sample at 50 ppm in water was also presented in a watchglass-covered 5 oz plastic cup for aroma descriptions. Panelists first tasted the blank, then progressively stronger solutions. They were asked to record the sample's code and taste description of the lowest level at which they could detect something other than water. The panelists then described the taste of the 10.0 ppm sample and the aroma of the 50.0 ppm sample. The detection threshold level reported is the level at which at least 75% of the panelists could detect something other than water.

A group of six flavorists also described the flavor characteristics of the thiophenes in aqueous solutions at the threshold and next higher concentration.

The threshold of 3,4-dimethylthiophene was also determined by a series of triangle tests conducted on separate days. A panel of 22 to 24 experienced tasters evaluated aqueous solutions of the thiophene at 0.002, 0.02, 0.2, 2.0, and 5.0 ppm. A predetermined triangle test design was used to balance the order of sample presentation. A 15 ml portion of each solution was served in coded 1 oz odor free plastic medicine cups.

The blend of dimethylthiophenes was also evaluated in natural onion oil at 0.8% and in artificial onion oil at 0.2, 1.0, and 3.0% levels. Four triangle tests were conducted, each on a different day, to compare the onion oils with added thiophenes to the controls. The oils were tasted in bottled spring water at 0.05 ppm by 20 to 24 experienced panelists. The order of sample presentation and sample codes were rotated using predetermined triangle test designs.

RESULTS AND DISCUSSION

Both 2-methyl- and 3-methylthiophene have been found in a number of products including canned beef (Perrson and Von Sydow, 1974; Wilson, 1973), heated soy and fish proteins (Qvist and Von Sydow, 1974), and in the reaction product of heated xylose–cysteine–water (Mussinan and Katz, 1973). In addition, the 2-methyl isomer has been reported in cooked pork liver (Mussinan and Waldrad, 1974), boiled chicken (Nonaka et al., 1967), heated thi-

Table II. Triangle Test Results, 3,4-Dimethylthiophene Threshold

Concn of 3,4-dimethylthiophene in water, ppm	No. of panelists	No. of correct responses	Statistically significant at 95%
0.002	22	10	No
0.02	24	6	No
0.2	23	11	No
2.0	24	11	No
5.0	24	17	Yes ^a

^a Statistically significant at the 99.9% level.

amine (Arnold et al., 1969) and pyrolyzed cysteine reaction products (Kato et al., 1973), and in coffee (Walter and Weidemann, 1969). Kato et al. (1973) found 3-methylthiophene in a cysteine–pyruvaldehyde reaction mixture.

Reported comments on the aroma of the monomethylthiophenes are typically slightly unpleasant and solvent-like. Arnold et al. (1969) described the aroma of 2-methylthiophene as heated onion or sulfury, while van den Ouweland and Peer (1975) have reported its odor at the GLC exhaust as onion-like, gasoline-like, and paraffinic. The flavorists in our laboratories described the 2-methyl isomer as having a sweet, carbon tetrachloride, onion-like aroma and a slight aromatic solvent-like taste along with waxy, fruity, and woody notes. The 3-methyl isomer has a more pronounced solvent-like taste with plastic and fruity notes and a benzene–sulfur aroma. Neither has any fried onion character, in either taste or aroma. The detection threshold of 2-methylthiophene was 3 ppm; that of 3-methylthiophene was 5 ppm.

In addition to the reported dimethylthiophenes of onion and shallots previously mentioned, Perrson and Von Sydow (1974) have tentatively found the 2,3- and 2,5-dimethyl isomers in canned beef. No odor response was mentioned.

We have found (Table I) that the detection threshold of the 2,4-dimethyl- and 2,5-dimethylthiophenes is 3 ppm and that of the 2,3-dimethyl- and 3,4-dimethylthiophenes is 5 ppm. These compounds have a distinct solvent, plastic-like flavor best described as toluene–benzene-like. They had slight, secondary flavor notes generally described as vegetative and earthy. The mixture of the three thiophenes approximating the composition in onion oil had a threshold of 5 ppm and a taste and aroma similar to the individual dimethyl compounds described above.

The onion oils with the added thiophene mixture were not significantly different from the oils without added thiophenes as evaluated by a triangle test design. None of the panelists indicated that the samples of onion oil with added thiophene were fried onion-like in flavor characteristics.

The results shown in Table I are considerably higher than those reported by Boelens et al. (1971); for example, they found a threshold of 0.0013 ppm for the 3,4-dimethyl isomer. In order to resolve the large difference between the reported threshold for this compound and our observed value, a series of triangle tests was conducted. The results (Table II) clearly show that the panelists, as a group, cannot detect 3,4-dimethylthiophene at 2.0 ppm or lower levels. None of the panelists noted a fried onion flavor at any of the five levels tasted.

The above cited authors in their evaluation of 2,4-dimethylthiophene apparently used a mixture of the 2,4- and 2,3-dimethyl isomers (4:1). To avoid any uncertainty in evaluation of the individual compound's flavor character we carefully resolved the two isomers and, in fact, re-

crystallized the key intermediates four times from methanol to make absolutely certain no impurities were being carried along in the synthetic steps.

We must conclude that methyl- and/or dimethylthiophenes are not responsible for the fried character of onion flavor.

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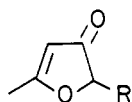
Synthesis and Flavor Evaluation of Several Alkylfuranones Found in *Allium* Species (Onions, Shallots, and Leeks)

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Recently, the identification of two alkylfuranones (I and II) in the essential oils of several *Allium* species (onions, shallots, and leeks) has been reported. Their interesting structures and presence in significant quantitative amounts have prompted us to synthesize and organoleptically evaluate these compounds. We have found their flavor characteristics to be of a fatty-waxy nature, similar to aliphatic aldehydes and alcohols. They do not make a significant contribution to the flavor of the essential oil of onion.

In their study of the volatile components of onion oil Boelens et al. (1971) isolated and identified, by spectroscopic means, the novel alkylfuranone (II). More recently Dembele and Dubois (1973) reported the same compound as well as its higher homolog (I) in the essential oil of shallots. Schreyen et al. (1976) have identified both compounds in leek oil. These latter identifications in both cases were based primarily on mass spectral analysis.

Prior to our becoming aware of the work of Dembele and Dubois we had isolated and identified furanone (I) from the oil of onion (*Allium cepa*) and had assigned to it the name Capanone. The other cyclic ketone (II) with the *n*-hexyl side chain we refer to as Norcepanone.



R = C₈H₁₇, Capanone (I)

R = C₆H₁₃, Norcepanone (II)

The synthesis and the organoleptic evaluation of these two heterocyclic compounds are the subjects of this report.

EXPERIMENTAL SECTION

Materials. Crude undecyl-1,3-diyne-5-ol and tridecyl-1,3-diyne-5-ol were custom synthesized by Farchan

Chemical Company using the general procedure of Cook et al. (1952). Their initial attempts to purify the C₁₁ alcohol by vacuum distillation resulted in detonation (Chanan, 1972). The reason is unknown; similar compounds have been routinely purified by distillation, see, e.g., Cook et al. (1952). Armitage et al. (1952), however, had a similar experience with iodocta-1,3-diyne. We utilized the crude, undistilled alcohols which contained a small amount of the starting aldehyde reactant as the only significant impurity.

Norcepanone (II). This compound was prepared using the general method reported by Nazarova et al. (1967) for the cyclization of diacetylene alcohols using mercuric salts. Approximately 40 g of crude undecyl-1,3-diyne-5-ol, 40 ml of water, 100 ml of ethanol, and 4 g of HgSO₄ were combined and stirred at room temperature for 20 h forming a heavy precipitate and a yellow supernate. The reaction mixtures from two such reactions were combined and filtered, yielding a tarry solid and a yellow filtrate. The solid was stirred with several portions of ether; the ether was combined and concentrated. The resulting oil was steam distilled to give 15.6 g of crude furanone. The original filtrate upon vacuum concentration formed two phases. The organic phase, 16 g, contained about 44% of product by GLC analysis.

An aliquot of the combined crude product was purified by distillation: bp 78 °C (0.15 mm); *n*_D²⁰ 1.4682 [lit.

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