

## Identification of a New Volatile Compound in Onion (*Allium cepa*) and Leek (*Allium porum*): 3,4-Dimethyl-2,5-dioxo-2,5-dihydrothiophene

3,4-Dimethyl-2,5-dioxo-2,5-dihydrothiophene was isolated and identified for the first time from onion and leek. An original procedure of synthesis of this compound is described and its mass, infrared, and nuclear magnetic resonance spectral data are reported; its detection threshold was measured in water.

The flavors of *Allium* species, and more particularly those of onion and leek, have been extensively studied during recent years (Galetto and Bednarczyk, 1975; Galetto and Hoffman, 1976; Herrman, 1977; Schreyen et al., 1976a,b; Van Straten et al., 1977). Volatile sulfur components appeared to be of qualitative and quantitative importance in the aroma of these vegetables. Dembele and Dubois (1973) have previously reported the identification of three dimethylthiophenes and Ledl (1975) identified a 3,4-dimethyl-2,5-dihydrothiophen-2-one. In this communication, we report the isolation and characterization of another derivative of thiophene in onion and leek.

### EXPERIMENTAL SECTION

**Aroma Recovery.** Onions were cut without any special paring and slurried with water. The slurry was extracted three times by Freon 11, and the organic phase was concentrated through a Vigreux column. Volatile components were then vacuum distilled from the residual paste on a cold finger ( $-30^{\circ}\text{C}$ ) in a little sublimator heated at  $30^{\circ}\text{C}$  and washed from the cold finger with small volumes of Freon 11.

**Gas Chromatography.** Aroma concentrates were analyzed on a Girdel 3000 chromatograph equipped with a glass capillary column (0.6 mm i.d., 40 m) coated with Carbowax 20 M and fitted with a flame ionization detector. Individual components eluted from column were sniffed using a splitter.

**Gas Chromatography-Mass Spectrometry (GC/MS).** GC/MS identifications were performed using a Varian M.A.T. Model CH5 mass spectrometer linked with the capillary column described above via a Watson-Bieman glass separator.

**NMR and IR Spectroscopy.**  $^1\text{H}$  NMR spectra were recorded with a WP 80 Bruker instrument in  $\text{CDCl}_3$  solutions with  $\text{Me}_4\text{Si}$  added and IR spectra with a Perkin-Elmer Model 457, using microcells (1-mm pathlength, NaCl, internal volume of  $20\ \mu\text{L}$ ) and a beam condenser with about  $40\ \mu\text{g}$  of compound isolated from onion or in KBr disks with 3 mg of synthetic compound.

**Synthesis.** Sodium sulfide (1 g, 0.012 M) was dissolved in 4 mL of water and the solution was added to 1 g of pyrocinchonic anhydride (PCA, 0.008 M) in 4 mL of acetone. The mixture was allowed to stand for 2 h at room temperature. The solution was extracted with 40 mL of chloroform. The extract contained about 170 mg of thiopyrocinchonic anhydride (TPCA) (yield 16%) and 70 mg of PCA. PCA (0.7 g) was obtained after acidification of the water phase. TPCA was isolated by GC on a column (6 m  $\times$  4 mm) with 20% DEGS on Chromosorb W (60-80 mesh) at  $170^{\circ}\text{C}$ .

**Odor Evaluation.** The threshold of 3,4-dimethyl-2,5-dioxo-2,5-dihydrothiophene was measured from aqueous solutions by using the procedure described by Salo (1970). The panel consisted of four experienced persons, and 40 results were computed for each dilution.

Table I. Volatile Components in Onion Identified by Mass Spectrum

methylthiomethane
2-methylbut-2-enal
2-methylpent-2-enal
1-(methylthio)propane
2,5-dimethylthiophene
2,4-dimethylthiophene
3,4-dimethylthiophene
1-(propylthio)propane
cis-1-(1-propenylthio)propane
trans-1-(1-propenylthio)propane
1-(methyltrithio)propane
1-(propyltrithio)propane

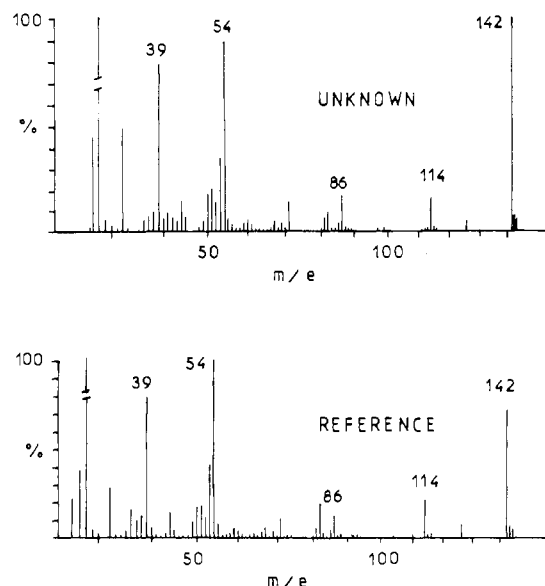
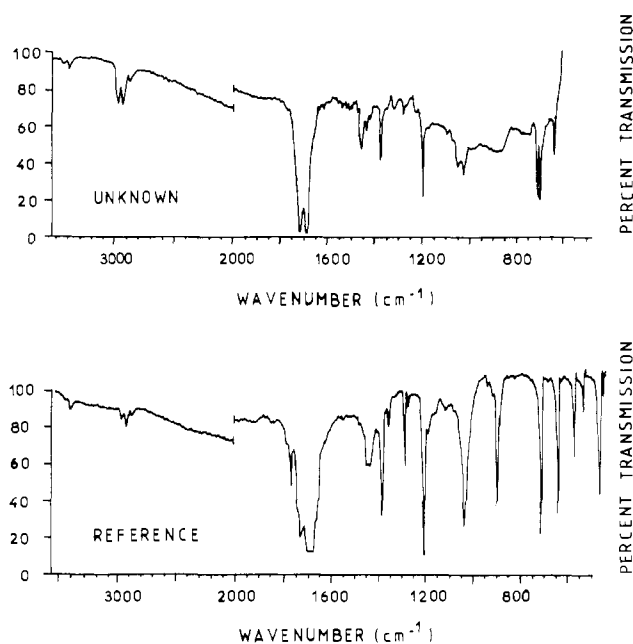
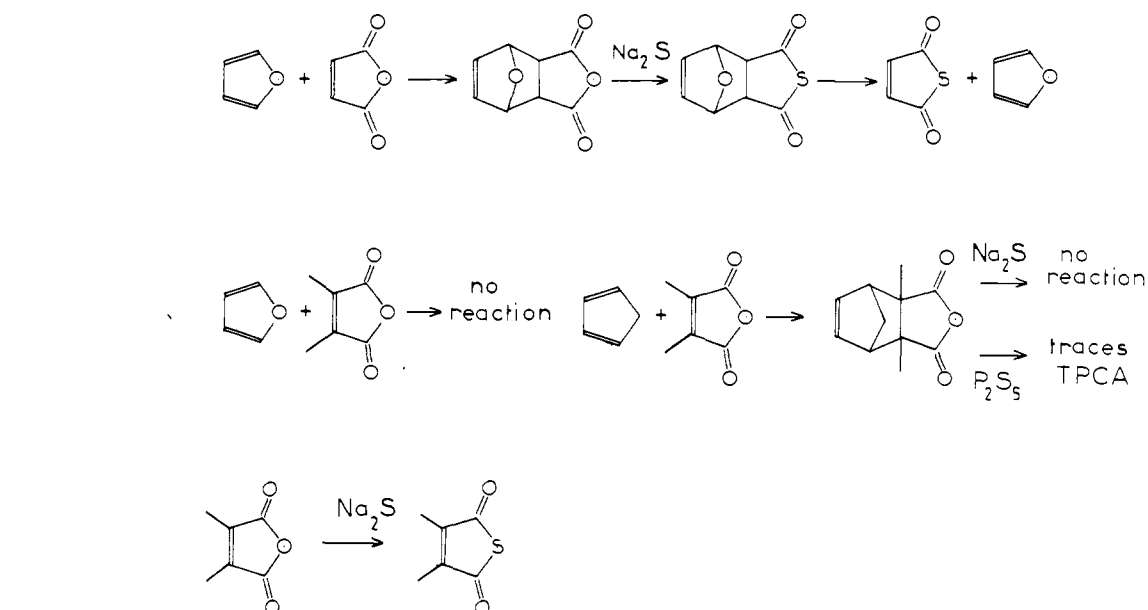


Figure 1. Mass spectra of the unknown component isolated from onion and of the synthetic TPCA.

### RESULTS AND DISCUSSION

Among the main volatiles we have identified (Table I), most of which have been previously reported in onion (Van Straten et al., 1977), we observed an unknown component which was eluted after 1-(propyltrithio)propane. The mass spectrum of the component (Figure 1) indicated two successive losses of carbonyl fragments from the molecular ion  $\text{M}^+$  142; the isotopic abundance of the  $m/e$  144 ion implied the presence of a sulfur atom in the molecule. The two fragment ions  $m/e$  39 and 54 could be assigned to a substituted 1,2-dimethylethylene group. These data indicated a 3,4-dimethyl-2,5-dihydrothiophene structure. This hypothesis was confirmed by the IR spectrum (Figure 2) and the NMR spectrum, which exhibited a singlet at 2.09 ppm. This signal is similar to the spectrum of 2,3-dimethylmaleic anhydride (singlet at 2.11 ppm). The assumed structure was confirmed by synthesis of 3,4-di-

Scheme I



**Figure 2.** Infrared spectra of the unknown compound occurring in onion (tetrachloroethylene solution) and of the synthetic TPCA (KBr disk).

methyl-2,5-dioxo-2,5-dihydrothiophene (TPCA). A patent (Jennings, 1966) describes the vapor phase oxidation of thiophene, 3-methylthiophene, and 3,4-dimethylthiophene into corresponding thioanhydrides without giving any physical properties. The well-known method for the synthesis of thiomaleic anhydride involves the action of sodium sulfide without solvent on the adduct of furan and maleic anhydride and a subsequent retro-Diels reaction (Tamura et al., 1977). The same sequence was not applicable to the synthesis of TPCA because furan does not react with 3,4-dimethylmaleic anhydride (PCA) (Diels and Olsen, 1940). Consequently furan was replaced by cyclopentadiene in the adduct, but the reaction with sodium sulfide failed. Phosphorus pentasulfide, in refluxing pyridine on the same adduct, gave only traces of TPCA which were isolated by GC (the retro-Diels probably takes place in the chromatograph). Finally, TPCA was obtained with a low yield by reacting sodium sulfide with PCA in a water-acetone solution. This low yield was due partly

to the transformation of PCA into the sodium salt of 3,4-dimethylmaleic acid and partly to the reduction of the TPCA to a volatile product (Scheme I). The spectroscopic data and retention time of this molecule are identical in all respects with those of the product isolated from onions although different sampling techniques used involve differences between IR spectra of natural and synthetic compounds.

The synthetic compound, the purity of which was checked by GC, exhibited a strong odor which could be described as H<sub>2</sub>S-like. Its threshold, measured in water, was about 7 ppb. In another investigation, the same compound was similarly identified in leek.

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Michel Albrand<sup>1</sup>  
 Pierre Dubois<sup>2</sup>  
 Patrick Etievant<sup>\*2</sup>  
 René Gelin<sup>1</sup>  
 Barbara Tokarska<sup>3</sup>

<sup>1</sup>INSA Laboratoire de Chimie Organique  
 F 69621 Villeurbanne Cedex, France

<sup>2</sup>INRA Laboratoire de Recherches sur les Arômes  
 21034 Dijon Cedex, France

<sup>3</sup>Institut de l'Industrie de la Fermentation  
 02-532 Varsovie, Poland

Received for review November 19, 1979. Accepted February 29, 1980.