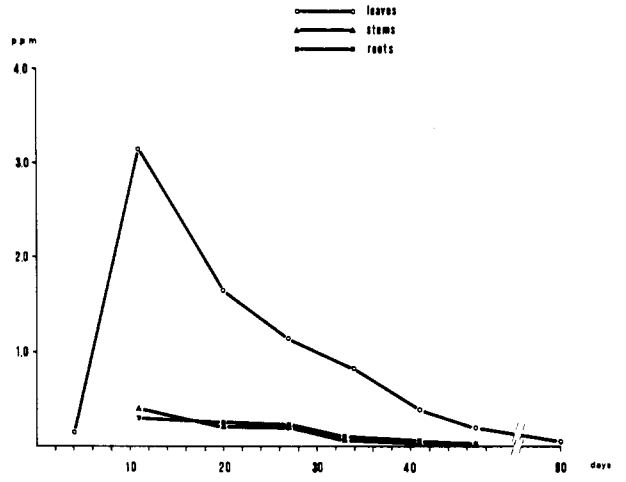

Figure 3. Uptake and persistence of Metalaxyl in sunflower when applied as a seed dressing (Ridomil: 25% Metalaxyl as a wettable powder at the rate of 600 g/100 kg of seeds).

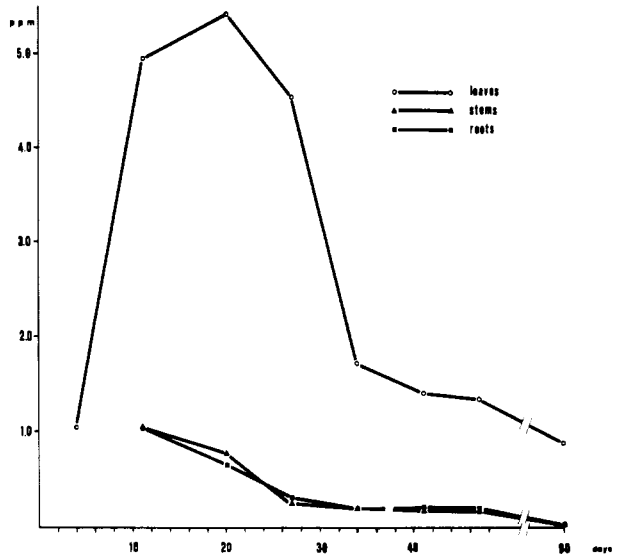

Figure 4. Uptake and persistence of Metalaxyl in sunflower when applied into the soil (granular Ridomil: 5% Metalaxyl at the rate of 2 g/m^2).

masses: 279, 248, 220, and 206 (Figure 1). The fragmentography was therefore focused on these masses to detect the presence of Metalaxyl in the plant extracts.

The mass fragmentograph was especially useful for low active principle concentrations (0.02–0.01 ppm). At these concentrations the NPD detector was not suited for a precise determination because of the interference peaks due to coextracted substances.

The results reported in Figure 2–4 show that Metalaxyl was rapidly absorbed and translocated either when applied as a seed dressing or incorporated into the soil.

The fungicide reached the maximum concentration in the leaves 11 days after planting when applied as a seed dressing (Figures 2 and 3) and 20 days after planting when applied to the soil (Figure 4).

There was then a progressive decrease, and 34 days after planting the concentration of Metalaxyl in the leaves was 70% lower than the maximum concentration, regardless of the treatments (Figures 2–4). Although the concentration of the fungicide was progressively declining, its presence in the leaves was still detected 90 days after planting. The residues detected in the roots and the stems followed a similar pattern, but the concentration was much lower than in the leaves. The presence of Metalaxyl in these organs was detectable for 47 days after planting when applied as a seed dressing and for 90 days when applied into the soil.

The concentration of Metalaxyl in the seeds was always less than the lowest limit of sensitivity of the analysis (0.01 ppm). Figures 2 and 3 show that the Metalaxyl concentration in the leaves decreased from 3–5 to 0.1–0.2 ppm in the range 11–90 days; the weight of leaves however, increased about 25-fold in the same period. For this reason we believe that the decreased concentration of the fungicide in all plant organs has to be attributed to a variation of the ratio between weight of Metalaxyl and weight of either leaves, roots, or stems rather than to a degradation of the active principle (Figures 2 and 3). By comparison of Figures 2 and 3, it can be concluded that, for equal doses of an active ingredient, a higher absorption was found with Apron applied as a seed dressing.

ACKNOWLEDGMENT

We express our thanks to Ciba-Geigy for supplying Metalaxyl as a standard, Ridomil, and Apron.

Registry No. Metalaxyl, 57837-19-1.

LITERATURE CITED

Tafuri, F.; Marucchini, C.; Patumi, M.; Businelli, M. *J. Agric. Food Chem.* **1981**, *29*, 1296.

Zazzerini, A.; Marucchini, C.; Patumi, M., 3rd Symposium "Chemistry of Pesticide", Piacenza, Italy, Feb 26–27, 1981, p 42.

Cesare Marucchini*[1]
Maurizio Patumi[1]
Antonio Zazzerini[2]

[1]Centro di Studio sulla Chimica degli Antiparassitari del C.N.R. Istituto di Chimica Agraria dell'Università
06100 Perugia, Italy
[2]Istituto di Patologia Vegetale dell'Università
Perugia, Italy

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Identification of an Important New Flavor Compound in Concord Grape: Ethyl 3-Mercaptopropionate

Ethyl 3-mercaptopropionate was isolated and identified for the first time in Concord grape by combination gas chromatography–mass spectrometry analysis. At low concentration this compound possesses high-quality Concord grape aroma and flavor.

The volatile components of Concord grape (*Vitus labrusca*) have been studied by Holley et al. (1955), Neudoerffer et al. (1965), Stevens et al. (1965), and Stern et al. (1967). One hundred and fourteen compounds have

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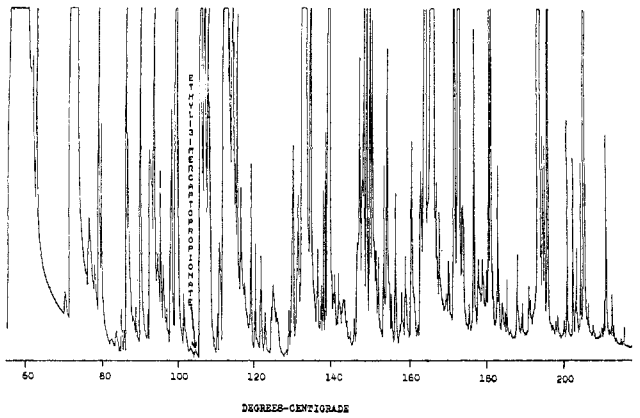


Figure 1. Gas chromatogram of volatile compounds isolated from Concord grape essence.

been identified by GC–MS analysis in the present study of Concord grape volatiles. The most important of these compounds to the distinctive flavor of Concord grape is ethyl 3-mercaptopropionate and the well-known component methyl anthranilate (Power and Chestnut, 1921). Methyl anthranilate plays an important role in Concord grape flavor; however, it is not the full flavor of this fruit (Stern et al., 1967).

Ethyl 3-mercaptopropionate was identified among the volatile components of natural Concord grape essence (250-fold) at a very low level (low-ppm range) and at even lower concentration in fresh Concord grapes. At full strength this potent aroma compound has a strong skunklike aroma; however, in the low-ppm range it takes on a very pleasant fruity and fresh grape quality that is described as crushed Concord grape aroma.

EXPERIMENTAL SECTION

Isolation of Volatiles. Natural Concord grape essence (250-fold) obtained from Interbahm International, Inc., Englewood, NJ, and fresh Concord grapes were used in this study. The essence and the fresh fruit sample were separately placed in a glass washing bottle, and the volatile components were adsorbed on Tenax GC, 60–80 mesh, packed into a 0.3 mm × 12 cm piece of glass tubing by using ultrapure helium flow rate of 20 cm^3 for 24 h. The grape volatiles from the essence and from the fresh grapes were then desorbed from the Tenax by inserting the glass tubing containing Tenax into the heated injection port of the gas chromatograph.

Gas Chromatography–Mass Spectrometry. GC–MS analysis was performed by using a Perkin-Elmer 990 gas chromatograph coupled directly to a Du Pont 21-491 mass spectrometer via a heated all-glass connection. The volatiles were desorbed from the Tenax trap at 250 °C in the injection port and were cryogenically deposited on the front end of a 100 m by 0.01 in. i.d. glass capillary column coated with OV-101 at −40 °C. Separation of the components was achieved by temperature programming the column from −40 to +30 °C at 4 deg/min and then to 200 °C at 1 deg/min at a flow rate of 1 cm^3/min. A gas chromatogram of the volatiles from the grape essence is shown in Figure 1. The gas chromatogram of the volatiles from fresh Concord grapes is similar to Figure 1 but at lower concentration levels.

Chemicals. The ethyl 3-mercaptopropionate used as a reference in this study was obtained from Polysciences, Inc., Warrington, PA.

RESULTS AND DISCUSSION

Thiols often play important roles and are well-known components of many food flavors including meat, fish, cheese, vegetables, coffee, nuts, etc. (Maga and Katz, 1976). On the other hand, thiols have not been reported in red fruit flavor systems including grape except for methanethiol in strawberry (van Straten et al., 1981). The present study demonstrates the importance of ethyl 3-mercaptopropionate to the characteristic flavor of Concord grapes. Ethyl 3-mercaptopropionate was added to a typical artificial Concord grape flavored beverage formulation at about 1 ppm and produced a higher quality, more natural Concord grape flavor. The relatively low concentration of this compound in the total volatile gas chromatogram of Concord grape essence is shown in Figure 1.

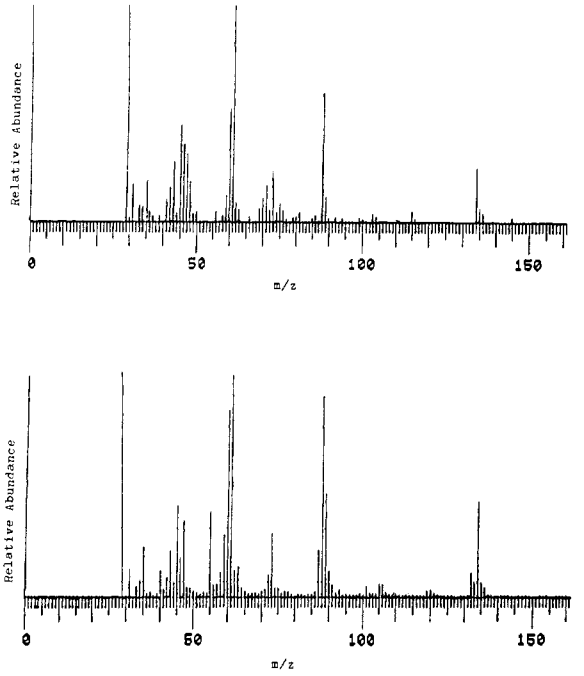


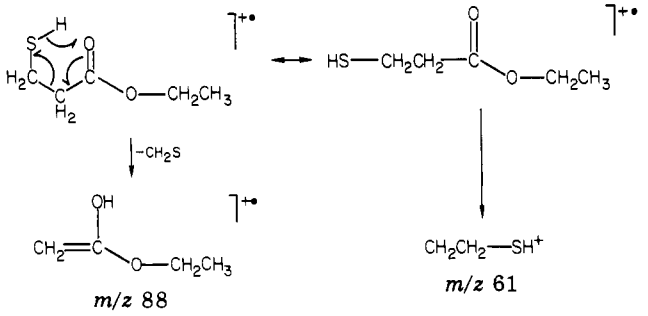
Figure 2. Mass spectra of an unknown compound isolated from Concord grape essence (top) and from a reference sample of ethyl 3-mercaptopropionate (bottom).

Analysis of the mass spectra from this chromatogram showed the presence of a compound at low concentration with a molecular weight of 134 that contained an M + 2 ion at m/z 136 at about 4% relative intensity to the molecular ion. The retention index of this compound (relative to ethyl esters) is 5.8, which matches closely the retention index of 5.9 obtained for pure ethyl 3-mercaptopropionate. Computer-reconstructed specific ion chromatograms of m/z 136, 88, and 61 also showed the presence of this compound in the fresh Concord grape volatile chromatogram at the same retention index.

The mass spectrum of ethyl 3-mercaptopropionate obtained from Polysciences, Inc., and the mass spectrum of the unknown component from Concord grape volatiles are shown in Figure 2. The isotopic M + 2 ion at m/z 136 indicates the presence of sulfur in the molecule. The prominent ion at m/z 88 is typical of ethyl esters resulting from the six-member transition process depicted in Scheme I. The base peak at m/z 61 is produced by cleavage of the $CH_2CH_2SH^+$ group from the molecule.

In the wine industry a flavor note found in many wines made from native American grapes is described as "foxy". Attempts to correlate this "foxy" flavor with methyl anthranilate were unsuccessful and the origin of the foxiness of the aroma in these wines is unclear (Nelson et al., 1977). It is suggested here that ethyl 3-mercaptopropionate at certain levels may be a primary contribution to the "foxy" character of some American wines. It is well recognized in the flavor industry that variations in the concentration

Scheme I



of certain chemicals can have a dramatic effect on their flavor characteristics. Ethyl 3-mercaptopropionate, which has a flavor threshold in water of 0.2 ppm, is a very good example of this phenomenon. At low concentration levels it has a very pleasant, fruity, grapy character, while at higher concentrations its aroma takes a skunky or foxy, animal-like aroma.

Registry No. Ethyl 3-mercaptopropionate, 5466-06-8.

LITERATURE CITED

Holley, R. W.; Stoyla, B.; Holley, A. D. *Food Res.* **1955**, *20* (4), 326.
Maga, J. A.; Katz, I. *CRC Crit. Rev. Food Sci. Nutr.* **1976**, *7*, 147.
Nelson, R. R.; Acree, T. E.; Lee, C. Y.; Butts, R. M. *J. Food Sci.* **1977**, *42*, 57.
Neudoerffer, T. S.; Sandler, S.; Zubeckis, E.; Smith, M. D. *J. Agric. Food Chem.* **1965**, *13*, 584.
Power, F. B.; Chesnut, V. K. *J. Am. Chem. Soc.* **1921**, *43*, 1741.
Stern, D. J.; Lee, A.; McFadden, W. H.; Stevens, K. L. *J. Agric. Food Chem.* **1967**, *15*, 1100.
Stevens, K. L.; Lee, A.; McFadden, W. H.; Teranishi, R. *J. Food Sci.* **1965**, *30*, 1006.
van Straten, S.; de Vrijer, F. L.; de Beauveser, J. C. "Volatile Compounds in Food", 4th ed.; Central Institute for Nutrition and Food Research: Zeist, The Netherlands, 1981.

Michael G. Kolor

General Foods Technical Center
Tarrytown, New York 10591

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Poly(ethylene glycol) Pretreatment Reduces Pyrethroid Adsorption to Glass Surfaces

Pretreatment of glass vials with a solution of high molecular weight poly(ethylene glycol) (M_r 20 000; 4% w/v) reduced the adsorption of pyrethroid insecticides to vessel surfaces. This treatment also reduced the adsorption of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, dieldrin, and insect juvenile hormone III, but it increased the adsorption of trifluralin. Surface treatment may prove effective in maintaining aqueous solutions of known concentrations of pyrethroids and some other lipophilic pesticides for use in in vitro assay procedures.

Studies of the action and fate of lipophilic pesticides in aqueous systems are often complicated by the sorption of the test compound to the walls of the vessels used for such experiments. Previous studies have documented the adsorption of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) (Champion and Olsen, 1971), the pyrethroid insecticide permethrin (Sharom and Solomon, 1981), and the dinitroaniline herbicide trifluralin (Sharom and Solomon, 1981; Strachan and Hess, 1982) from aqueous media to glass and plastic surfaces. During the course of our studies of pyrethroid metabolism and action in isolated biochemical preparations, we found it necessary to identify methods to minimize surface adsorption. We now report a surface treatment method that reduces the adsorption of pyrethroids and some other lipophilic pesticides to glass vessels.

MATERIALS AND METHODS

Surface Treatment Procedures. Three poly(ethylene glycols) were tested: Carbowax 20M (M_r 20 000; Fisher Scientific, Rochester, NY); Carbowax 20M–TPA (M_r 20 000; terminated with terephthalic acid; Applied Science, State College, PA); Carbowax 4000 (M_r 4000; Applied Science). Glass scintillation vials (7 mL) were immersed in dilute (0.1–10%) aqueous solutions of each of the above, drained, oven-dried (110 °C) overnight, and used for adsorption assays. Vials were also silanized after base washing with dimethyldichlorosilane (5% in toluene) or were treated with commercial siliconizing agents (Sigmacote, Sigma Chemical Co., St. Louis, MO; Surfasil, Pierce Chemical Co., Rockford, IL) according to manufacturers' instructions.

Radiolabeled Compounds. The following compounds were available from previous syntheses in this laboratory: NRDC 157-^{14}C [3-phenoxybenzyl (1*R*,*cis*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate; Soderlund, 1979]; NRDC 157-*t* (Soderlund et al., 1983a); NRDC 163-^{14}C (the 1*R*,trans isomer of NRDC 157; Soderlund et al., 1983b). The following compounds were obtained as gifts: *trans*- and *cis*-permethrin-^{14}C (FMC Corp., Middleport, NY); fenvalerate-^{14}C (Shell Development Co., Modesto, CA); deltamethrin-^{14}C [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,*cis*)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate; Roussel-Uclaf-Procida, Romainville, France]; fluvalinate-^{14}C [(*R*,*S*)-α-cyano-3-phenoxybenzyl (*R*,*S*)-2-[2-chloro-4-(trifluoromethyl)-anilino]-3-methylbutyrate; Zoecon Corp., Palo Alto, CA); trifluralin-^{14}C (J. O. Nelson, Department of Entomology, University of Maryland, College Park, MD). The following compounds were purchased: DDT-^{14}C and juvenile hormone III-*t* (New England Nuclear, Boston, MA); Dieldrin-^{14}C (Amersham Corp., Arlington Heights, IL). All compounds were purified by thin-layer chromatography (silica gel 60 F_{254} chromatoplates, 0.25 mm gel thickness;

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