

photodegradable formulations of Mirex can be devised by the incorporation of amines into the baits used for control of the imported fire ants. Also, it is possible that environmental degradation mechanisms may exist that utilize these pathways. These areas and the extension of this reaction to other chlorinated materials are being actively investigated in these laboratories.

LITERATURE CITED

- Alley, E. G., Dollar, D. A., Layton, B. R., Minyard, J. P., Jr., *J. Agr. Food Chem.* **21**, 138 (1973).
 Alley, E. G., Layton, B. R., Minyard, J. P., Jr., *J. Agr. Food Chem.* **22**, 442 (1974).
 Benesi, H. A., Hildebrand, J. H., *J. Amer. Chem. Soc.* **71**, 2703 (1949).
 Dilling, W. L., Braendlin, H. P., McBee, E. T., *Tetrahedron* **23**, 1211 (1967).
 Eaton, P., Carlson, E., Lombardo, P., Yates, P., *J. Org. Chem.* **25**, 1225 (1960).
 Gibson, J. R., Ivie, G. W., Dorough, H. W., *J. Agr. Food Chem.* **20**, 1246 (1972).
 Ivie, G. W., Casida, J. E., *J. Agr. Food Chem.* **19**, 405, 419 (1971).
 Lautenberger, W. J., Jones, E. N., Miller, J. G., *J. Amer. Chem. Soc.* **90**, 1110 (1968).

- McBee, E. T., Roberts, C. W., Idol, J. D., Jr., Earle, R. H., Jr., *J. Amer. Chem. Soc.* **78**, 1511 (1956).
 Miller, L. L., Narang, R. S., *Science* **169**, 368 (1970).
 Miller, L. L., Narang, R. S., Nordblom, G. D., *J. Org. Chem.* **38**, 340 (1973).
 Ohashi, M., Kazuo, T., Kenji, S., *J. Chem. Soc., Chem. Commun.*, 384 (1973).
 Stevenson, D. P., Coppinger, G. M., *J. Amer. Chem. Soc.* **84**, 149 (1962).
 Zipp, D. H., Gerding, H., *Recl. Trav. Chim. Pays-Bas* **77**, 682 (1958).

Earl G. Alley*
 Bobby R. Layton
 James P. Minyard, Jr.

Mississippi State Chemical Laboratory
 Mississippi State, Mississippi 39762

Received for review December 31, 1973. Accepted March 27, 1974. The authors are indebted to the Entomology Research Division of the United States Department of Agriculture for financial support for this research.

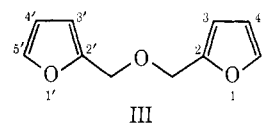
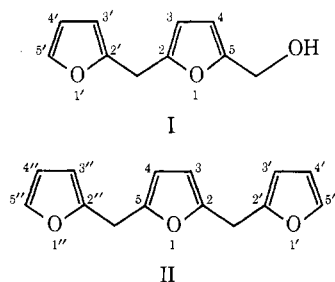
Mass Spectrometry of Three Furanic Compounds Containing Two or Three Furan Nuclei

Low-resolution mass spectra and high-resolution data are presented and discussed for the following compounds: [(5-hydroxymethyl-2-furyl)-(2'-furyl)]methane (I), [2-(2'-furfuryl)-5-(2''-fur-

furyl)]furan (II), and difurfuryl ether (III). Observed metastable ions are indicated as support for the proposed fragmentations.

Mass spectrometry is an important tool for the elucidation of the structure of natural products and of flavor constituents (Kolor, 1972). Furanic compounds from carbohydrate degradation are often found in foods and food-related model systems (Hodge, 1967; Ferretti *et al.*, 1970). Whereas a reasonable amount of published data on electron-impact induced fragmentation of certain classes of furanic compounds is available (Porter and Baldas, 1971), very little correlated mass spectral information exists for compounds containing more than one furan nucleus (Budzikiewicz *et al.*, 1967; Porter and Baldas, 1971). Compounds having two or three furan nuclei have been identified in roasted coffee beans (Stoll *et al.*, 1967; Stofelsma *et al.*, 1968), in popcorn (Walradt *et al.*, 1970), and in heated whey powder (Ferretti and Flanagan, 1971b). We previously reported (Ferretti *et al.*, 1974) mass spectral characteristics of four acyl derivatives of 2,2'-difurfylmethane in the hope that they may be of use to other investigators in identifying such compounds and structural-related ones.

This investigation is the continuation of our previous work, and deals with high-resolution measurements of the following compounds.



These compounds have been identified in a (milk-related) lactose-casein browning system (Ferretti and Flanagan, 1971a). The ether III and the trifuranic compound II have also been found in an *N*^α-formyl-L-lysine-D-lactose model system (Ferretti and Flanagan, 1973) and/or in heated whey powder (Ferretti and Flanagan, 1971b).

EXPERIMENTAL SECTION

For gas chromatography-mass spectrometry an LKB 9000 instrument and the same conditions previously described (Ferretti *et al.*, 1974) were used. The high-resolution mass spectra (resolution *ca.* 10,000) were determined with a CEC 21-110B instrument at 70 eV and an ion source temperature of 150°. Sample introduction, exact mass measurements, and calculations were performed as described previously (Ferretti *et al.*, 1974). The metastable ions were observed in the photographic charts from the LKB spectrometer.

The three compounds were synthesized and purified as reported earlier (Ferretti and Flanagan, 1971a).

RESULTS AND DISCUSSION

The mass spectra and elemental compositions of important ions of the following compounds are shown in Figure 1: [(5-hydroxymethyl-2-furyl)-(2'-furyl)]methane (I), [2-(2'-furfuryl)-5-(2''-furfuryl)]furan (II), and difurfuryl ether (III). Scheme I illustrates the possible fragmentation processes for compounds I and II, and Scheme II illustrates the degradation of III. In both schemes the observed metastable transitions are indicated by asterisks.

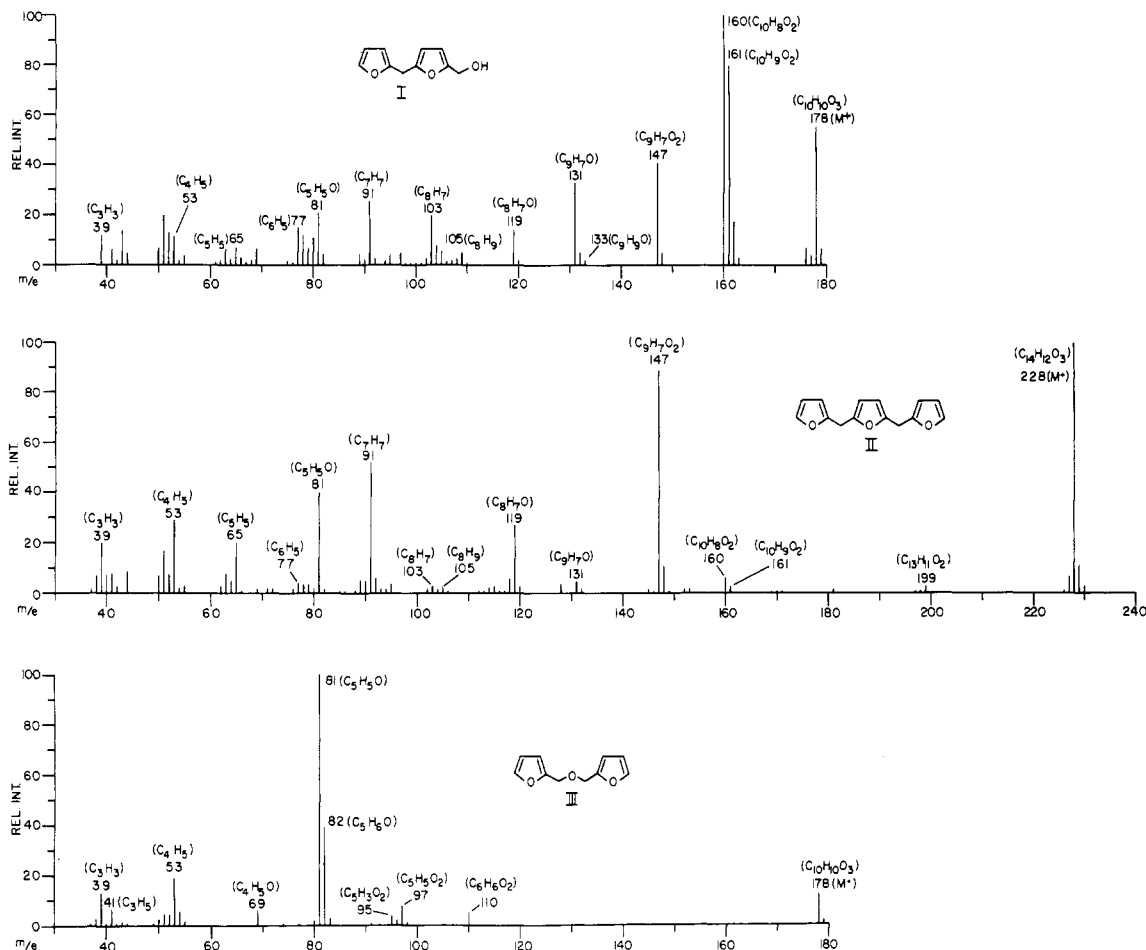
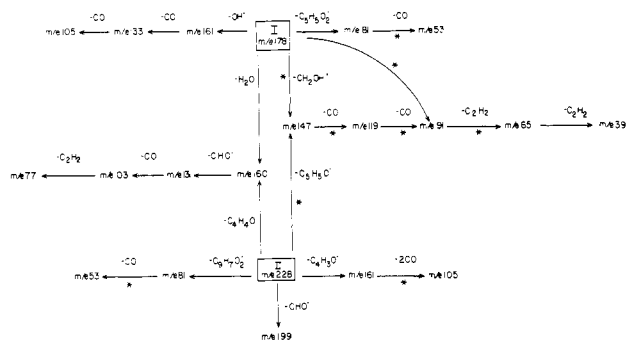
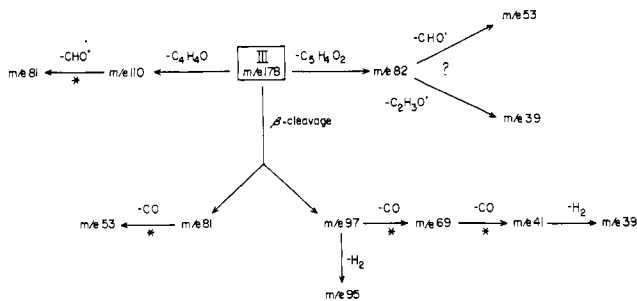


Figure 1. Mass spectra of compounds I, II, and III.

Scheme I. Fragmentation Processes for I and II



Scheme II. Fragmentation Processes for III



The mass spectra of I and II can be compared with those of the acyl derivatives of 2,2'-difurylmethane (Ferretti *et al.*, 1974). Their similarity is remarkable both in terms of the presence of ions at specific m/e values and of mode of fragmentation primarily consisting of successive

eliminations of CO and ethylene. The major fragmentation pathways in I are those initiated by the loss of the hydroxymethyl radical ($M^+ \rightarrow m/e$ 147) and of one molecule of water ($M^+ \rightarrow m/e$ 160). The major fragments in the spectrum of II result from an α cleavage relative to the center furan nucleus with the charge unevenly distributed between the $[C_9H_7O_2]^+$ species (m/e 147) and the m/e 81 fragment which is probably the pyrilium ion (Budzikiewicz *et al.*, 1967). Of the two minor pathways for the fragmentation of II, one is initiated by the loss of a furyl radical ($M^+ \rightarrow m/e$ 161); the other pathway, which results in the rearrangement ion of m/e 160, is triggered by the elimination of the elements of a neutral furan molecule with attendant hydrogen rearrangement. The elimination of CHO \cdot from the molecular ion of II is analogous to the previously observed (Ferretti *et al.*, 1974) elimination of an acetyl radical from [(5-acetyl-2-furyl)-(5'-methyl-2'-furyl)]methane and from [(5-formyl-2-furyl)-(5'-methyl-2'-furyl)]methane involving the furan oxygen.

The mass spectrum of III is characterized by the m/e 81 and 97 fragments probably resulting, at least in part, from simple β cleavage, and by the two rearrangement ions of m/e 82 and 110. The latter results from the molecular ion by elimination of the elements of furan. A similar elimination was observed in the spectrum of II (*vide supra*). One of the plausible explanations for the presence of the ion of m/e 82 in the spectrum of III is the occurrence of a β cleavage with concomitant hydrogen transfer and expulsion of the elements of furfural. This mode of fragmentation is frequently encountered in ethers (Budzikiewicz *et al.*, 1967). If the $[C_5H_6O]^+$ species has the structure of methylfuran, then it can eject a CHO \cdot (m/e 82 \rightarrow m/e 53) or an acetyl radical (m/e 82 \rightarrow m/e 39) as shown in Scheme II.

LITERATURE CITED

- Budzikiewicz, H., Djerassi, C., Williams, D. H., "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.
- Ferretti, A., Flanagan, V. P., *J. Agr. Food Chem.* 19, 245 (1971a).
- Ferretti, A., Flanagan, V. P., *J. Dairy Sci.* 54, 1764 (1971b).
- Ferretti, A., Flanagan, V. P., *J. Agr. Food Chem.* 21, 35 (1973).
- Ferretti, A., Flanagan, V. P., Ruth, J. M., *J. Agr. Food Chem.* 18, 13 (1970).
- Ferretti, A., Flanagan, V. P., Ruth, J. M., *Org. Mass Spectrom.* 8, 403 (1974).
- Hodge, J. E., "Symposium on Foods. Chemistry and Physiology of Flavors," Schultz, H. W., Day, E. A., Libbey, L. M., Ed., Avi Publishing Co., Westport, Conn., 1967, pp 465-491.
- Kolor, M. G., in "Biochemical Applications of Mass Spectrometry," Waller, G. R., Ed., Wiley-Interscience, New York, N. Y., 1972, pp 701-722.
- Porter, Q. N., Baldas, J., "Mass Spectrometry of Heterocyclic Compounds," Wiley-Interscience, New York, N. Y., 1971.
- Stoffelsma, J., Sipma, G., Kettenes, D. K., Pypker, J., *J. Agr. Food Chem.* 16, 1000 (1968).
- Stoll, M., Winter, M., Gautschi, P., Flament, I., Willhalm, B., *Helv. Chim. Acta* 50, 628 (1967).
- Walradt, J. P., Lindsay, R. C., Libbey, L. M., *J. Agr. Food Chem.* 18, 926 (1970).

Aldo Ferretti*¹
 Vincent P. Flanagan¹
 John M. Ruth²

Dairy Products Laboratory
 Eastern Regional Research Center
 Agricultural Research Service
 U. S. Department of Agriculture
 Philadelphia, Pennsylvania 19118
¹ Nutrition Institute
 BARC-East
 Beltsville, Maryland 20705
² Agricultural Environmental Quality Institute
 Agricultural Research Service
 U. S. Department of Agriculture
 Beltsville, Maryland 20705

Received for review January 11, 1974. Accepted May 2, 1974. Research was conducted while the Dairy Products Laboratory was located in Washington, D. C. Trade names are mentioned for identification, implying no endorsement by the Department of Agriculture over others of a similar nature not mentioned.

Residues of Dimethoate and Its Oxygen Analog on and in Citrus Leaves following a Helicopter Treatment of the Trees with Dimethoate Ultra-Low Volume Concentrate and High Volume Spray

Residues of dimethoate and its oxygen analog (a metabolite of dimethoate) on and in citrus leaves were investigated by a gas chromatographic-flame photometric detector (gc-FPD) procedure following treatment of the trees with (1) a dimethoate ultra-low volume (ULV) concentrate and (2) a high volume (HV) spray, both applied by helicopter at a rate of 1.0 lb/acre. Residues detected 1 day following treatment indicated uniform deposition of the insecticide with both types

of application. This was true for all segments of the trees, including the bottom and center sections. The ULV treatment produced higher initial residues than the HV spray, probably due to excessive runoff of the aqueous HV spray solution from the waxy leaf surface. After 14 days weathering, residues on and in leaves from the ULV treated trees were slightly higher than those on leaves from HV sprayed trees.

The insecticide dimethoate, *O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorodithioate [registered as Cygon (American Cyanamid Co.); also known as Rogor (Soc. Montecatini)], is a compound exhibiting both systemic and contact action against certain insect pests attacking plants and animals. Studies by de Pietri-Tonelli and Barontini (1963), Gunther *et al.* (1965), and Woodham *et al.* (1974) and others have shown the importance of this insecticide for the control of citrus pests. However, these tests were performed utilizing conventional ground treatment equipment with an average cost of approximately \$25/acre. Aerial ultra-low volume (ULV) treatment of cotton with dimethoate has been studied by Petty and Bigger (1966). Information is not available concerning helicopter treatment of citrus trees with dimethoate.

This report concerns deposition and disappearance of residues of dimethoate and its oxygen analog on and in citrus leaves following a helicopter treatment of the trees with (1) a Cygon 267 ULV concentrate (35% dimethoate) and (2) a Cygon 267 high-volume (HV) spray. These tests were conducted due to the numerous advantages utilizing this means of application: lower cost (approximately \$8/acre), speed of application, and more uniform coverage of

the leaves due to their constant swirling movement as a result of the helicopter's rotor movement.

EXPERIMENTAL SECTION

Type of Citrus, Application Rates, and Procedure. Mature navel orange trees were selected for this study. A 20-acre block was treated with the ULV concentrate at a rate of 1.0 lb of dimethoate per acre. A 156-acre block was treated with the HV spray (3 pints of Cygon 267 diluted to 5 gal with water) also applied at a rate of 1.0 lb of dimethoate per acre. The insecticide was applied with a Bell 47-G helicopter fitted with a 55-gal capacity spray tank, pump, and boom with 48 standard spray nozzles. Helicopter speed was adjusted to 40 mph for the HV treatment with all 48 spray nozzles operating. Speed was increased to 60 mph for the ULV treatment with only 8 spray nozzles operating. Normal operating pressure of the pump was 40 psi for both treatments.

Random trees were selected from each treated block for leaf sample collections. Five trees were sampled in the HV treatment, four in the ULV treated block (Figure 1). Due to heavy rainfall during the 2-day sample collections, alternate trees were sampled for four of the trees in the HV treatment. This was necessary because of the flooding