were done by Se-Hua Tan at the Research & Productivity Council, Fredericton, NB.

Registry No. 6-DMAQ, 96706-37-5; 6-MAQ, 31679-98-8; 5-DMAQ, 96706-38-6; 5-MAQ, 31679-97-7; aminocarb, 2032-59-9; water, 7732-18-5.

LITERATURE CITED

Abdel-Wahab, A. M.; Kuhr, R. J.; Casida, J. E. *J. Agric. Food Chem.* **1966**, *14*, 290.
Abdel-Wahab, A. M.; Casida, J. E. *J. Agric. Food Chem.* **1967**, *15*, 479.
Addison, J. B.; Silk, P. J.; Unger, I. *Bull. Environ. Contam. Toxicol.* **1974**, *11*, 250.
Balba, M. H.; Saha, J. G. *Bull. Environ. Contam. Toxicol.* **1974**, *11*, 250.
Berger, S. T.; Rieker, A. *Tetrahedron* **1972**, *28*, 3123.
Bowie, J. H.; Cameron, D. W.; Giles, R. G. F.; Williams, D. H. *J. Chem. Soc. B* **1966**, 335.
Coffey, S., Ed. "Rodd's Chemistry of Carbon Compounds", 2nd ed.; Elsevier: New York, 1974; Vol. III, Part B, pp 31–36.
Cool, M.; Jankowski, K. *Eur. J. Mass Spectrom. Biochem. Med. Environ. Res.* **1982**, *2*, 83.
Davidson, J.-G.; Dorais, L. "Pulverisations aeriennes d'insecticides contre la tordeuse des bourgeons de l'épinette en 1981. Chapitre 2 - Identification et Evaluation des Repercussions Environnementales", Quebec, Quebec, March 1981.
Hollenstein, R.; von Philipsborn, W. *Helv. Chim. Acta* **1972**, *55*, 2030.
Krishna, J. C.; Casida, J. E. *J. Agric. Food Chem.* **1966**, *14*, 98.
Maguire, R. J. "Aminocarb, a Review of Its Chemistry"; National Water Research Institute, Environment Canada: Burlington, Ontario, May, 1979.
Mallet, V. N.; Levesque, D. *Int. J. Environ. Anal. Chem.* **1983**, *6*, 43.
National Research Council of Canada (NRCC), publication No. 18979, 1982; p 23.
Norris, R. K.; Sternhell, H. *Aust. J. Chem.* **1966**, *19*, 617.
Patel, N. "The Composition of Technical Matacil"; Mobay Chem. Corp., 1978; Report 67418.
Shaikh, Y. A. *J. Heterocycl. Chem.* **1977**, *14*, 925.
Sundaram, K. M. S.; Szeto, S. Y. *J. Environ. Sci. Health, Part B* **1979**, *B14*, 589.
Sundaram, K. M. S.; Szeto, S. Y.; Hindle, R. *J. Chromatogr.* **1980**, *194*, 100.
Vassilieff, V.; Ecobichon, D. J. *Bull. Environ. Contam. Toxicol.* **1982**, *29*, 366.

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Conformer-Restriction Analysis: Pyrethroids Containing Dibenzofuran Alcohol Moieties

Huai-Tsu Tu, W. T. Brady, and S. J. Norton*

In an undertaking of conformer-restriction analysis, seven pyrethroids have been synthesized in which the alcohol moieties are hydroxymethyl (or the α-cyano derivative) substituted dibenzofurans. The acid moiety of each pyrethroid ester was *d-trans*-chrysanthemic acid. The various dibenzofuran alcohols synthesized represent the two planar conformational extremes associated with both 3-phenoxybenzyl alcohol and 1,1′-biphenyl-3-methanol, both of which are potent pyrethroid alcohols. The new pyrethroid esters were found to have very little or no insecticidal activity against the various species tested. It is concluded that planar conformations of the flexible (or twistable) aromatic alcohol moieties of potent pyrethroids are incompatible with binding to an insect receptor site.

INTRODUCTION

During recent years synthetic pyrethroids have attracted considerable attention as potential replacements for naturally occurring pyrethrins and other types of synthetic insecticides (Elliott, 1977; Wilkerson and Norton, 1981; Sheppard and Norton, 1980). Most of the recent successful studies have been primarily concerned with the synthesis of either photostabilized alcohol moieties or the replacement of the isobutenyl groups of the acid moiety by functions that are resistant to oxidative degradation (Sheppard and Norton, 1980; Soderlund and Casida, 1977).

Other studies involving compositional variations of the cyclopropane ring (e.g., an appropriately substituted aziridine ring) have been less successful in producing potent insecticides (Sheppard and Norton, 1980; Casida and Berteau, 1969). Structural and configurational requirements for both the acid and alcohol moieties of active pyrethroids have been extensively studied, and general guidelines have been given which relate to optimal structure/activity relationships (Elliott, 1977). Conformation/activity relationships among pyrethroids is also an important consideration. Insecticidal action is presently interpreted to involve an ability of the active molecule to adopt a conformation in which the structural components necessary for potency are properly oriented with respect to each other and to a complementary receptor (Elliott, 1970; 1977).

In conformational studies of the pyrethroid, decamethrin, the bond rotations of all pertinent single bonds have been determined by calculation (for the free molecule) and by X-ray analysis (the crystalline form) (Elliott and Janes, 1977). In the bonds associated with the ether linkage of the alcohol moiety, bonds a and b were both calculated to be rotated 90° for the free molecule (best rotation to minimize interdependent interference). On the other hand, the rotational angles are 44° and 19° for bonds a and b, respectively, in the crystalline form. It is not known how significant these bond angle preferences are for insecticidal activity. Sharp NMR signals for pyrethroids in solution indicate that the various conformers are interconverted rapidly. At the site of action the forces of binding undoubtedly influence the conformational status of the pyrethroid as it accommodates itself to the binding site.

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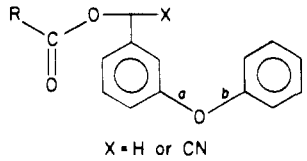


X = H or CN

As a part of our continuing interest in pyrethroid insecticides, we have begun a study of conformer-restriction analysis of the pyrethroid alcohol, 3-phenoxybenzyl alcohol, and its α-cyano derivative. In our initial study, both bond angles a and b (above structure) have been restricted to 0° rotation by a carbon–carbon covalent linkage connecting the two aromatic rings, ortho to the bridging oxygen atom. Thus, a planar relationship between the two aromatic centers of the alcohol is maintained. We wish to report the synthesis of a series of hydroxymethyl-substituted dibenzofurans, along with the corresponding α-cyano derivatives. Upon esterification with chrysanthemic acid, the esters were studied for insecticidal activity.

EXPERIMENTAL SECTION

Infrared spectra were measured on a Perkin-Elmer 1330 spectrometer. Proton nuclear magnetic resonance spectra were obtained on a Hitachi Perkin-Elmer R24-B and a Jeol FX900; data are presented in δ values. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN; analyses are indicated by elemental symbol and were within ±0.4% of the theoretical values. Melting points are uncorrected. For column chromatography, silica gel (60–200 mesh, Fisher Scientific Company) and alumina (neutral aluminum oxide, 80–200 mesh, Fisher Scientific Co.) were used. For thin-layer chromatography, silica gel plates from Eastman Kodak Company were employed.

Synthesis of Dibenzofurancarboxaldehydes. 2-Dibenzofurancarboxaldehyde was synthesized by carbonylation of dibenzofuran employing the method of Hinkel et al. (1937). 2-Dibenzofurancarboxaldehyde: mp 65–67 °C; NMR ($CDCl_3$) 7.3–7.6 (m, 4 ArH), 7.8–8.0 (m, 2 ArH), 8.3–8.4 (m, ArH), 10.0 (s, CHO).

3-Dibenzofurancarboxaldehyde was synthesized from dibenzofuran by a process involving nitration, reduction to the amino group, diazotization of the 3-amino group with replacement by cyanide, and ultimate conversion of the cyanide to the 3-carboxaldehyde substituent (Garmatter and Siegrist, 1974). 3-Dibenzofurancarboxaldehyde: mp 127–129 °C; NMR ($CDCl_3$) 7.2–7.55 (m, 3 ArH), 7.7–8.0 (m, 4 ArH), 10.0 (s, CHO).

4-Dibenzofurancarboxaldehyde was prepared by carbonylation of the dibenzofuran lithium salt by using the method of Gilman et al. (1946). 4-Dibenzofurancarboxaldehyde: mp 96–98 °C; NMR ($CDCl_3$) 7.1–7.53 (m, 4 ArH), 7.65–7.92 (m, 3 ArH), 10.36 (s, CHO).

Synthesis of Dibenzofuranmethanols. 1-Dibenzofuranmethanol was synthesized by reduction of 1-dibenzofurancarboxylate (Ashby and Meth-Cohn, 1974; Tedjamulia et al. 1983). 1-Dibenzofuranmethanol: mp 89–90 °C; NMR ($CDCl_3$) 2.18 (s, OH), 5.19 (s, CH_2), 7.3–7.7 (m, 6 ArH), 8.0–8.15 (m, ArH). 2- and 3-Dibenzofuranmethanols were prepared by the lithium aluminum hydride reduction of the appropriate dibenzofurancarboxaldehyde (Tedjamulia et al., 1983). 2-Dibenzofuranmethanol: mp 111–113 °C; NMR ($CDCl_3$) 2.0 (s, OH), 4.8 (s, CH_2), 7.2–7.6 (m, 4 ArH), 7.75–8.0 (m, 2 ArH), 8.2–8.3 (m, ArH). 3-Dibenzofuranmethanol: mp 120–122 °C; NMR ($CDCl_3$) 2.0 (s, OH), 4.8 (s, CH_2), 7.2–7.6 (m, 5 ArH), 7.7–8.0 (m, 2 ArH).

4-Dibenzofuranmethanol was prepared by reduction of 4-dibenzofurancarboxylate with an excess of lithium aluminum hydride (Tedjamulia et al., 1983). 4-Dibenzofuranmethanol: mp 94–95 °C; NMR ($CDCl_3$) 2.0 (s, OH), 5.0 (s, CH_2), 7.1–7.5 (m, 4 ArH), 7.7–8.0 (m, 3 ArH).

Synthesis of Dibenzofurancyanomethyl Esters of Chrysanthemic Acid. An aqueous solution (10 mL) of 0.5 g of sodium cyanide was added to a solution of 1.0 g of the dibenzofurancarboxaldehyde (0.005 mol) in 10 mL of benzene containing benzyltriethylammonium chloride (0.06 g, 5 mol %).

Chrysanthemic acid chloride (0.95 g) in 2 mL of benzene was then added dropwise with stirring; stirring was continued overnight. The organic layer was then separated and dried and the benzene removed in vacuo. The residue was recrystallized from hexane if solid, or purified by chromatography on silica gel (elution with 0.5% ethyl acetate in hexane) if a liquid. The yields ranged from 38–55% after purification.

2-Dibenzofurancyanomethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate, V: mp 98–100 °C; IR 1735 (ester C=O); NMR ($CDCl_3$) 1.1–1.2 (d, CH_3), 1.25–1.35 (d, CH_3), 1.45–1.55 (d. CH), 1.6–1.75 (d, 2 CH_3), 2.1–2.3 (m, CH), 4.77–5.0 (d, C=CH), 6.59 (s, CH), 7.3–7.6 (m, 5 ArH), 7.8–8.1 (m, 2 ArH); elemental analysis for $C_{24}H_{23}NO_3$, C and H.

3-Dibenzofurancyanomethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)-1-cyclopropanecarboxylate, VI: mp 113–115 °C; IR 1725 (ester C=O); NMR ($CDCl_3$) 1.1–1.2 (d, CH_3), 1.25–1.35 (d, CH_3), 1.45–1.55 (d, CH), 1.65–1.75 (d, 2 CH_3), 2.05–2.25 (m, CH), 4.8–4.95 (d, C=CH), 6.55 (s, CH), 7.25–7.55 (m, 4 ArH), 7.69 (s, ArH), 7.8–7.95 (2 s, 2 ArH); elemental analysis for $C_{24}H_{23}NO_3$, C and H.

4-Dibenzofurancyanomethyl 2,2-dimethyl-3-(2-dimethyl-1-propenyl)-1-cyclopropanecarboxylate, VII: oil; IR 1720 (ester C=O); NMR ($CDCl_3$) 1.0–1.15 (d, CH_3), 1.3–1.4 (d, CH_3), 1.45–1.55 (d, CH), 1.6–1.7 (d, 2 CH_3), 2.0–2.25 (m, CH), 4.85–5.05 (d, C=CH), 6.95 (s, CH), 7.2–7.5 (m, 4 ArH), 7.6–7.9 (m, 3 ArH); elemental analysis for $C_{24}H_{23}NO_3$, C and H.

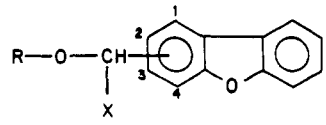
Synthesis of Dibenzofuranmethyl Esters of Chrysanthemic Acid. A solution of chrysanthemic acid chloride (0.95 g, 5.05 mmol) in anhydrous benzene (5 mL) was added dropwise to a stirred solution of the dibenzofuranmethanol (1 g, 5.05 mmol) in anhydrous benzene: pyridine (15 mL/0.41 mL) at room temperature under nitrogen. Stirring was continued overnight. The precipitated pyridine hydrochloride was removed by filtration and the benzene removed in vacuo. The residue was chromatographed on silica gel (0.5% ethyl acetate in hexane) and, if the pure material was a solid, recrystallized from petroleum ether. The yields ranged from 55–72% after purification.

1-Dibenzofuranmethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)-1-cyclopropanecarboxylate, I: oil; IR 1720 (ester C=O); NMR ($CDCl_3$) 1.06 (s, CH_3), 1.31 (s, CH_3), 1.35–1.5 (d, CH), 1.63 (s, $2CH_3$), 1.93–2.18 (m, CH), 4.65–4.8 (d, C=CH), 5.49 (s, CH_2), 7.15–7.55 (m, 6 ArH), 7.7–7.9 (m, ArH); elemental analysis of $C_{23}H_{24}O_3$, C and H.

2-Dibenzofuranmethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)-1-cyclopropanecarboxylate, II: mp 66–68 °C; IR 1720 (ester C=O); NMR ($CDCl_3$) 1.08 (s, CH_3), 1.33 (s, CH_3), 1.45–1.55 (d, CH), 1.65 (s, 2 CH_3), 2.0–2.2 (m, CH), 4.8–4.95 (d, C=CH), 5.2 (s, CH_2), 7.1–7.41 (m, 5 ArH), 7.6–7.8 (m, 2 ArH); elemental analysis for $C_{23}H_{24}O_3$, C and H.

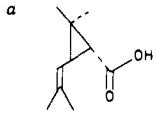
3-Dibenzofuranmethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)-1-cyclopropanecarboxylate, III: mp 81–83 °C; IR 1720 (ester C=O); NMR ($CDCl_3$) 1.07 (s, CH_3), 1.31 (s, CH_3), 1.4–1.55 (d, C=CH), 1.7 (s, 2 CH_3), 2.0–2.2 (m, CH), 4.8–4.95 (d, C=CH), 5.26 (s, CH_2), 7.25–7.6 (m, 5

Table I. Dibenzofuranmethyl and Dibenzofurancyanomethyl Esters of Chrysanthemic Acid



R = *d-trans*-chrysanthemate[a]
X = H or CN

compd no.	X	site of substitution on dibenzofuran
I	H	1
II	H	2
III	H	3
IV	H	4
V	CN	2
VI	CN	3
VII	CN	4

[a] 
d-trans-chrysanthemate

ArH), 7.8–7.95 (m, 2 ArH); elemental analysis for $C_{23}H_{24}O_3$, C and H.

4-Dibenzofuranmethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)-1-cyclopropanecarboxylate, IV: oil; IR 1720 (ester C=O); NMR ($CDCl_3$) 1.07 (s, CH_3), 1.32 (s, CH_3), 1.4–1.55 (d, CH), 1.65 (s, 2 CH_3), 2.0–2.2 (m, CH), 4.7–4.85 (d, C=CH), 5.47 (s, CH_2), 7.0–7.45 (m, 5 ArH), 7.6–7.8 (m, 2 ArH); elemental analysis for $C_{23}H_{24}O_3$, C and H.

Biological Evaluation. All compounds were initially screened for insecticidal activity against the cucumber beetle, *Diabrotica undecimpunctata*, in the adult stage. The compounds were applied topically as acetone solutions to the anesthetized (CO_2) insects at 0.01, 0.1, 1.0, 10, and 100 ppm. Fenvalerate was employed as the control insecticide at 0.01 and 0.1 ppm. None of the pyrethroids synthesized in this investigation exhibited any significant insecticidal activity. Fenvalerate provided 100% mortality at 0.1 ppm and 80% mortality at 0.01 ppm. Additional insecticidal studies with the new compounds were conducted with *Plutella xylostella* (larvae) up to 0.5 ppm, *Megoura viciae* (all stages) up to 0.05 ppm, and *Tetranychus urticae* (active stages) up to 100 ppm. All were found to be much less active than cypermethrin in these studies.

RESULTS AND DISCUSSION

In order to study conformational requirements of the pyrethroid ester alcohols, alcohols and their α-cyano derivatives similar to well-known, potent alcohol moieties, such as 3-phenoxybenzyl alcohol, were synthesized. These alcohols were then condensed with the pyrethroid acid, *d-trans*-chrysanthemic acid, to obtain new esters. The insecticidal properties of the new esters were then compared to those of known pyrethroid esters. The new alcohol moieties chosen were a series of (hydroxymethyl)-dibenzofurans and their α-cyano derivatives (see Table I). These alcohols have essentially the same steric bulk and aromatic characteristics as the two extreme planar conformations of 3-phenoxybenzyl alcohol and its α-cyano derivative, two of the most active pyrethroid alcohols (Figure 1). Among these alcohol analogues, 1- and 3-(hydroxymethyl)dibenzofurans and their α-cyano derivatives are not only two planar conformer analogues, but retain a methyl alcohol (or cyanohydrin) substituent at a position meta to the phenolic ether linkage as found in 3-phenoxybenzyl alcohol. On the other hand, the 2- and 4-(hydroxymethyl)dibenzofurans and their α-cyano derivatives have a methyl alcohol (or cyanohydrin) substituent at a position meta to the biphenyl linkage (Figure 2) as is the case with 1,1′-biphenyl-3-methanol from which insecticidal esters have been recently reported (Plummer and Pincus, 1981). Therefore, it was believed that the dibenzofuran type esters should retain considerable insecticidal activity provided that the planar conformational constraints imposed are consistent with binding to the target site in the insect.

An examination of the literature (Elliott, 1977) indicates that in the most active pyrethroid esters the alcohol portion contains two centers of unsaturation separated by a bridging atom. In allethrin and bioresmethrin this structural feature is the carbon atom of the methylene group, while in biopermethrin and decamethrin the bridging atom is oxygen. The insecticidal activity is very sensitive to chemical and stereochemical changes, indi-

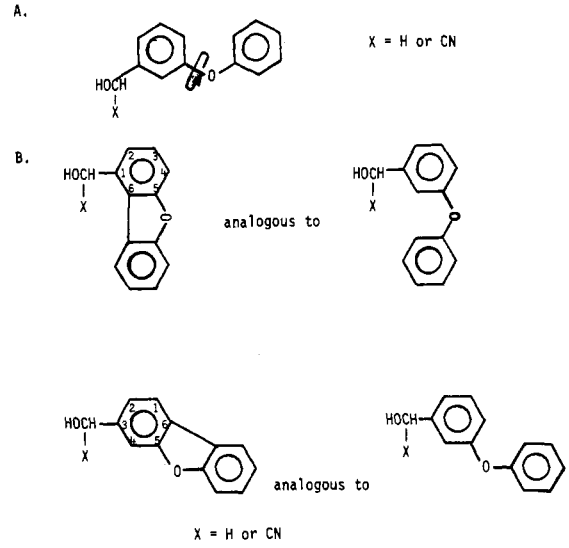


Figure 1. (A) Freely rotated 3-phenoxybenzyl alcohol and its cyano derivative. (B) Two planar conformations of dibenzofuran alcohol moieties and their planar 3-phenoxybenzyl alcohol analogues.

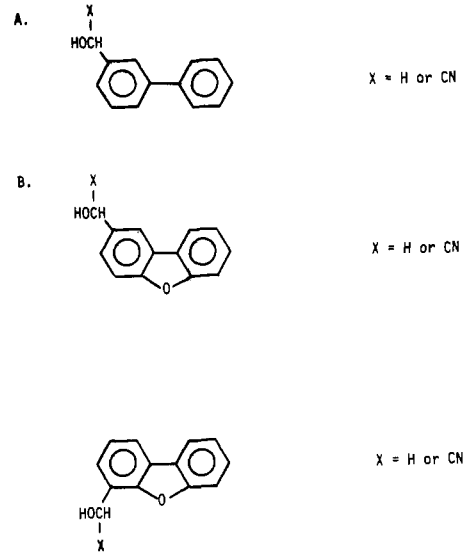


Figure 2. (A) Pyrethroid alcohol, (1,1′-biphenyl)-3-methanol, and its cyano derivative. (B) 2- and 4-(hydroxymethyl)dibenzofurans and the meta relationships between their alcohol substituents and the biphenyl linkage.

cating a strict stereochemical relationship between the receptor site and the pyrethroid for effective insecticidal activity. The active sites probably have a structure, such that upon interaction, pyrethroid molecules must be able to adopt a particular conformation. Another interesting fact is that all known, potent pyrethroid esters have a flexible region in the alcohol moiety.

The results of our study may be interpreted as evidence of whether or not coplanarity between the centers of unsaturation, at two conformational extremes, is consistent with an effective interaction at the pyrethroid binding site. As stated in the biological evaluation section, all of the pyrethroid esters, bearing the "conformational" alcohol moieties synthesized in this study, have no or only very little insecticidal activity. It thus appears that none of the extreme coplanar conformations involving the two aromatic centers of certain pyrethroid alcohols is compatible with the insect binding region.

Recent studies (Plummer and Pincus, 1984) concerned with 2-substituted biphenyl alcohols and 2-substituted heterocyclic analogues of biphenyl pyrethroid alcohols have indicated that insecticidal activity in dependent on the intraring twist angle of the alcohol. More recently (Plummer et al., 1984), studies of pyrethroid insecticides derived from 2,2′-bridged biphenyl-3-ylmethanols indicate that a twist angle of approximately 50° is optimal for biphenyl-related alcohols. These findings suggest that an optimum twist angle exists, and that twist angles less than or more than this angle decrease the insecticidal activity. The study herein supports this proposal in that coplanar aromatic centers (viewed either as linked via a biphenyl linkage or via a phenoxy linkage) are virtually devoid of insecticidal activity. Further studies, in which the two requisite aromatic regions of the alcohol are locked into a rigid framework having defined twist angles, are in progress.

Registry No. I, 96706-39-7; II, 96706-40-0; III, 96706-41-1; IV, 96706-42-2; V, 96706-43-3; VI, 96706-44-4; VII, 96706-45-5; 2-dibenzofurancarboxaldehyde, 5397-82-0; 3-dibenzofurancarboxaldehyde, 51818-91-8; 4-dibenzofurancarboxaldehyde, 96706-46-6; 1-dibenzofuranmethanol, 96706-47-7; 2-dibenzofuranmethanol, 86607-82-1; 3-dibenzofuranmethanol, 96706-48-8; 4-dibenzofuranmethanol, 64102-19-8; dibenzofuran, 132-64-9; dibenzofuran lithium salt, 16669-47-9; 1-dibenzofurancarboxylic acid, 54470-37-0; 4-dibenzofurancarboxylic acid, 2786-05-2; chrysanthemic acid chloride, 14297-81-5; sodium cyanide, 143-33-9; 2-dibenzofurancyanomethanol, 96706-49-9; 3-dibenzofurancyanomethanol, 96706-50-2; 4-dibenzofurancyanomethanol, 96706-51-3.

LITERATURE CITED

Ashby, J.; Ayad, M.; Meth-Cohn, O. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1744.
Casida, J. E.; Berteau, P. E. *J. Agric. Food Chem.* **1969**, *17*, 931.
Elliott, M. *Bull. W. H. O.* **1970**, *44*, 315.
Elliott, M. "Synthetic Pyrethroids"; American Chemical Society: Washington, D.C., 1977; *ACS Symp. Ser.* 42, p 1.
Elliott, M.; Janes, F. J. "Synthetic Pyrethroids"; American Chemical Society: Washington, D.C., 1977; *ACS Symp. Ser.* 42, p 29.
Garmatter, J.; Siegrist, A. E. *Helv. Chim. Acta* **1974**, *57*, 975.
Gilman, H.; Tolman, L.; Yeoman, F.; Woods, L. A.; Shirley, D. A.; Avakian, S., *J. Am. Chem. Soc.* **1946**, *68*, 426.
Hinkel, L. E.; Ayling, E. E.; Beynon, J. H. *J. Chem. Soc.* **1937**, 778.
Plummer, E. L.; Pincus, D. S. *J. Agric. Food Chem.* **1981**, *29*, 1118.
Plummer, E. L.; Seiders, R. P.; Sealye, D. E.; Stewart, R. R. *Pestic. Sci.* **1984**, *15*, 509.
Plummer, E. L.; Stewart, R. R. *J. Agric. Food Chem.* **1984**, *32*, 1116.
Sheppard, R. G.; Norton, S. J. *J. Agric. Food Chem.* **1980**, *28*, 1300.
Soderlund, D. M.; Casida, J. E. "Synthetic Pyrethroids"; American Chemical Society: Washington, D.C., 1977; *ACS Symp. Ser.* 42, p 162.
Tedjamulia, M. L.; Tominaga, Y.; Castle, R. N. *J. Heterocycl. Chem.* **1983**, *20*, 1149.
Wilkerson, M. G.; Norton, S. J. *J. Agric. Food Chem.* **1981**, *29*, 572.

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Residues of Four Pesticides in Alfalfa Seed and Sprouted Alfalfa Seed following Foliar Applications

Jay C. Maitlen* and J. Eric Halfhill

Plots of alfalfa were treated with the registered rates (1X) and twice the registered rates (2X) of demeton, methidathion, oxydemeton-methyl, and trichlorfon applied as foliar sprays with ground equipment. Mature seed was harvested from all plots, cleaned, subdivided, and a portion of each was sprouted. No detectable residues of the pesticides or their metabolites were found in sprouts prepared from seed harvested from the 1X treatments, nor (with the exception of demeton) in sprouts prepared from seed from the 2X treatments. Sprouts from the 2X demeton treatment contained combined average residues of demeton and its metabolites of 0.03 ppm. Seed from the 1X treated alfalfa contained no detectable residues of methidathion (<0.01 ppm), oxydemeton-methyl (<0.02 ppm), or trichlorfon (<0.02 ppm), but seed from the demeton plots contained residues of 0.02 ppm. Also, residues of demeton and its metabolites (0.24 ppm) and trichlorfon (0.05 ppm) were found in seeds from the 2X treated alfalfa, but no residues of methidathion or oxydemeton-methyl were found.

Sprouted alfalfa seeds have become a popular garnish for salads and sandwiches in the past few years. In California alone, in 1979, it was estimated that about 1.5 million pounds of seed were used in the preparation of sprouts, and it is expected that this use will continue to increase (Hesterman and Teuber, 1979). It is obvious that this amount of seed could not all be produced on "organic" farms, therefore, some of this seed may have come from commercial farms involved in the production of alfalfa

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