Chemical and Photochemical Isomerization of Deltamethrin

R. James Maguire

Rivers Research Branch, National Water Research Institute, Department of Environment, Canada Centre for Inland Waters, Burlington, Ontario L7R 4A6, Canada

Chiral high-performance liquid chromatographic analyses have shown that deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] in natural water in the dark is subject to cis/trans isomerization yielding the α-*S*, 1*S* cis isomer 2′-deltamethrin, which is inactive against mice and insects. Sunlight irradiation of deltamethrin as a thin film, on potato leaves, in natural water and in hexane was, however, only a partial detoxification step. Although it produced the inactive 2′ isomer as well as the inactive α-*S*, 1*S* trans isomer 4′-deltamethrin, it did produce in addition the α-*S*, 1*R* trans isomer 3-deltamethrin, which does retain some activity toward mice and insects, albeit less than the parent deltamethrin.

INTRODUCTION

The insecticidal properties of deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate] (Figure 1) were first reported in 1974 (Elliott et al., 1974), and it was developed commercially in France by Roussel Uclaf (Lhoste, 1982). The cis 1*R*,3*R* configuration about the cyclopropane ring and the *S* configuration for the cyano group at the benzylic carbon atom are essential for its high toxicity. In Canada, deltamethrin is marketed by Hoechst Canada Inc. under the trade name DECIS and is registered for use on such crops as tobacco, pears, canola, mustard, potatoes, sunflowers, broccoli, cabbage, wheat, and barley. Contamination of streams and ponds near sprayed fields is undesirable because of the high toxicity of deltamethrin to aquatic organisms (Mulla et al., 1978; Zitko et al., 1979; Bocquet and L'Hotellier, 1985). For this reason buffer zones of 15 and 100 m are commonly used between sprayed areas and water when deltamethrin is sprayed from the ground or air, respectively. Despite these precautions, some deltamethrin may drift to water, and it is necessary to characterize the aquatic persistence and fate of this highly toxic insecticide.

Research on the aquatic environmental dynamics of deltamethrin has shown that the half-life of deltamethrin in water is of the order of hours to days (Tooby et al., 1981; Muir et al., 1985; Maguire et al., 1989). Muir et al. (1985) found that deltamethrin injected below the surfaces of two small ponds rapidly partitioned from water into suspended solids, plants, and sediment, with a half-life of 2–4 h in water, and that major products were *cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DBCA) and 3-phenoxybenzoic acid (PBacid). They found half-lives of 5–14 days for total deltamethrin in sediment and even observed deltamethrin residues up to 306 days posttreatment. Residues of deltamethrin in sediment observed at 306 days were ascribed to release from macrophytes and algae, into which the deltamethrin had partitioned. Maquire et al. (1989) found that major routes of degradation and dissipation of deltamethrin sprayed on a pond were (i) chemical and photochemical conversion to inactive (2+2′)-deltamethrin stereoisomers and (ii) hydrolysis with subsequent oxidation of products. No residues of deltamethrin stereoisomers or any of the four major degradation products sought were found 11 days postspray in water, suspended solids, or sediment. The four products sought were DBCA, PBacid, 3-phenoxybenzyl alcohol (PBalc), and 3-phenoxybenzaldehyde (PBald). In addition, laboratory experiments on the volatilization of deltamethrin formulations from sprayed water as opposed to subsurface-injected water indicated that volatilization from the surface microlayer was a very fast process that could be the major route of dissipation of deltamethrin sprayed on a pond.

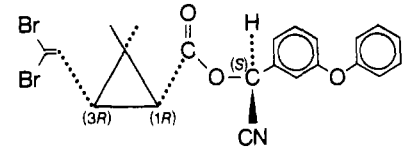

Figure 1. Structure of 1-deltamethrin [(*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate].

In considering the persistence of deltamethrin it is important to distinguish between isomers of differing activity. There are eight possible stereoisomers of deltamethrin. Table I shows the numbering system given by Ruzo et al. (1977) in which the parent deltamethrin is designated 1 and the only other isomer toxic to insects (Tessier, 1982) or mice Ruzo et al., 1977), although to a lesser extent in each case, is designated 3. There appear to be no data on the toxicity of deltamethrin isomers to aquatic organisms. Using pure 1- and 2-deltamethrin and mixtures of the other isomers, Ruzo et al. (1977) have shown that sunlight photolysis of 1-deltamethrin in various solvents results initially in cis/trans isomerization of the acid moiety of deltamethrin, ester cleavage reactions, and loss of bromine. An additional process for dilute solutions in methanol exposed to sunlight involves racemization at the α position in the alcohol moiety by both photochemical and ground-state reactions.

Those few studies of the persistence and fate of deltamethrin in aquatic ecosystems which have been performed to date have not distinguished between individual stereoisomers. Analysis of deltamethrin using an achiral gas chromatographic (GC) stationary phase [e.g., Maguire et al. (1989)] is only capable of distinguishing between four pairs of enantiomers: (1+1′), (2+2′), (3+3′), and (4+4′). Of these, only the (1+1′) and (3+3′) pairs are of insecticidal and mammalian importance since they potentially contain the active 1 and 3 isomers. The achiral analyses conducted heretofore may have overestimated the concentrations of

0021-8561/90/1438-1613$02.50/0 Published 1990 by the American Chemical Society

Table I. Structural Designations of Isomers of Deltamethrin [(*S*)-α-Cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-2,2-Dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate]

isomer	configuration	isomer	configuration
1	α-*S*, 1*R* cis	3	α-*S*, 1*R* trans
1′	α-*R*, 1*S* cis	3′	α-*R*, 1*S* trans
2	α-*R*, 1*R* cis	4	α-*R*, 1*R* trans
2′	α-*S*, 1*S* cis	4′	α-*S*, 1*S* trans

active deltamethrin stereoisomers. A complete description of the environmental dynamics of deltamethrin therefore requires the determination of all eight stereoisomers. This paper reports the chemical and photochemical isomerization of deltamethrin in natural water and on potato leaves monitored by high-performance liquid chromatography (HPLC) with a chiral column. In addition, it extends the work of Ruzo et al. (1977) in determining the time course of the appearance and disappearance of deltamethrin stereoisomers in natural water.

MATERIALS AND METHODS

Materials. Analytical standards of all eight deltamethrin stereoisomers and *cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (DBCA) were provided by Roussel Uclaf, Paris, France. The purity of the isomers was greater than 95% with the exception of the 2′ isomer, which was contaminated with about 15% of the 1′ isomer. DECIS 2.5 EC emulsifiable deltamethrin concentrate in xylenes from Hoechst Canada Inc. (lot DEREHE0101) was bought locally. 3-Phenoxybenzaldehyde (PBald), 3-phenoxybenzyl alcohol (PBalc), and 3-phenoxybenzoic acid (PBacid) were obtained from Aldrich Chemical Co., Milwaukee, WI. Pesticide grade and HPLC grade organic solvents were obtained from Caledon Laboratories, Georgetown, ON, Canada. The HPLC column was a J. T. Baker Bakerbond covalent (*R*)-*N*-[(3,5-dinitrobenzoyl)phenyl]-glycine (DNBPG) chiral column, 4.6 mm × 25 cm, 5-μm spherical particle size (Johns Scientific Inc., Toronto, ON).

The sodium sulfate, silica gel, aluminum foil, and disposable pipets were heated to 500 °C for 24 h before use. All glassware was rinsed with pesticide-grade solvents before use. Organic-free water was distilled water purified by carbon adsorption and reverse osmosis. Analysis of hexane extracts of this water by GC with electron capture detection revealed no contamination, even at 1000-fold concentration.

Analysis. Solutions of deltamethrin isomers in hexane were analyzed with a Waters Associates HPLC and a diode array detector (DAD) set to 220 nm. The sample volume was 25 μL, and the DNBPG column was thermostated to 25 °C. The isocratic method used was a variation of that given by the Collaborative International Pesticides Analytical Council (CIPAC) (1988). The mobile phase used in the CIPAC method was 0.2% 2-propanol in hexane at 1 mL/min. In this work, optimal separation of the eight stereoisomers was achieved with 0.1% 2-propanol in hexane at 0.50 mL/min. Figure 2 shows this optimal separation, and retention times are given in Table II. Resolution of the 2, 2′, 1′, 3, and 3′ isomers was good, but there was substantial overlap between the 4, 4′, and 1 peaks. Other chromatographic conditions tried were less successful. As the concentration of 2-propanol in hexane was increased, peaks 3 and 3′ gradually merged until at 0.2% 2-propanol they were not resolved at any flow rate between 0.3 and 2.0 mL/min. Below 0.1% 2-propanol the isomers did not elute from the column over at least 3 h. At 0.1% 2-propanol, the optimal flow rate was 0.50 mL/min. Below 0.50 mL/min peaks 4′ and 1 began to merge. As the flow rate increased from 0.50 to 1.50 mL/min the overall separation worsened. Gradient chromatography at such low concentrations of 2-propanol in hexane was not possible with the equipment used. Under the conditions described above, the minimum amount of deltamethrin isomer detected was about 75 ng. The DAD was about one-third as sensitive as a conventional ultraviolet–visible detector. The variability in retention time observed with triplicate injections of standards was less than 0.3 min at 75-min retention time.

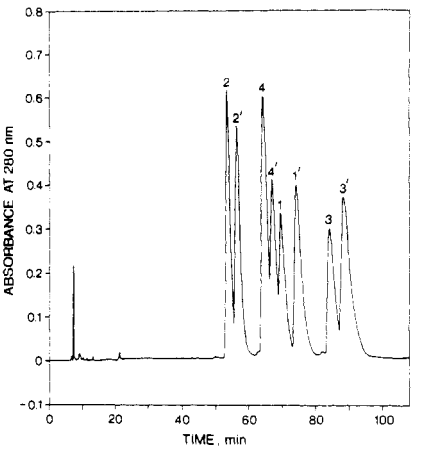

Figure 2. HPLC chromatogram of deltamethrin isomers on covalent DNBPG column with 0.1% 2-propanol in hexane at 0.50 mL/min.

Table II. Retention Times for Deltamethrin Stereoisomers in Figure 1

isomer	retention time, min	isomer	retention time, min
1	69.50	3	84.09
1′	74.09	3′	88.26
2	53.35	4	64.18
2′	56.18	4′	66.92

In earlier work (Maguire et al., 1989) the DECIS emulsifiable deltamethrin concentrate was found to contain only one peak, which was assigned to (1+1′)-deltamethrin since the achiral GC column used could not distinguish between enantiomers. The use of chiral HPLC in this work confirmed that the only compound present was 1-deltamethrin. Furthermore, the DECIS concentrate was stable in the dark at room temperature for at least 3 years.

The HPLC analytical method used in this work was developed specifically for deltamethrin isomers, not for the four degradation products described above. These products do not interfere with the analysis. Under the chromatographic conditions described above, PBald elutes at 36.4 min, and PBalc, PBacid, and DBCA, with injections of 2.5 μg each, were not found. It should be noted that as far as acute toxicity to mice is concerned, none of the common degradation products exhibits significant toxicity relative to deltamethrin (Ruzo et al., 1977).

Chemical and Photochemical Isomerization of Deltamethrin. With the exception of the experiment on deltamethrin sprayed on potato leaves, which was conducted in Prince Edward Island in July 1986, all photolysis experiments were conducted at the laboratory in Burlington, ON, in July 1989.

(*i*) *Thin Film on Glass.* A mixture of deltamethrin stereoisomers was prepared from the 1-deltamethrin analytical standard by the procedure given by Ruzo et al. (1977). 1-Deltamethrin, as a thin film (15 μg/cm²) on glass, was irradiated outdoors with bright summer sunshine for 5 days, and the photoisomers were recovery from the glass with hexane. The volume was reduced to 1 mL, and the deltamethrin isomers were determined as described above. This experiment was conducted in triplicate, and dark controls were employed.

(*ii*) *In Hexane.* One-liter solutions of 1-deltamethrin in hexane (2 μg/L) in Pyrex flasks were exposed to sunlight for periods up to 5 days. At intervals samples were concentrated to 1 mL for analysis. Dark controls were employed. These experiments were conducted in triplicate.

(*iii*) *In Distilled Water and Natural Water.* One-liter solutions of 1-deltamethrin in distilled water at 2 μg/L [the aqueous solubility; Muir et al. (1985)] in Pyrex flasks were exposed to sunlight for periods up to 5 days. As a precaution against precipitation, the experiments were run in 2% acetonitrile, a cosolvent that does not sensitize photolysis (Smith et al., 1977). At

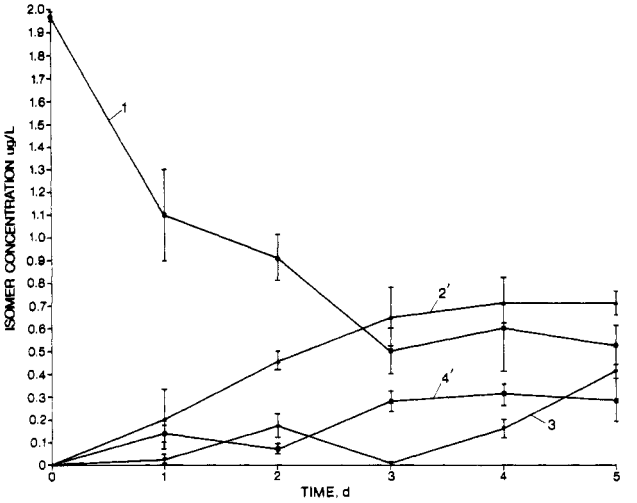

Figure 3. Sunlight isomerization of 1-deltamethrin in hexane.

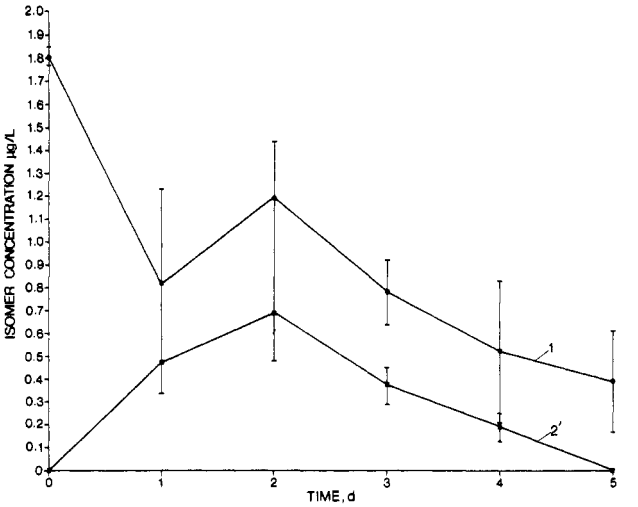

Figure 4. Isomerization of 1-deltamethrin in distilled water in the dark.

intervals samples were concentrated to 1 mL for analysis. Dark controls were employed. The experiment was also conducted in distilled water with 0.005 M mercuric chloride as a microbial inhibitor. Dark controls were again employed. This set of experiments with and without a microbial inhibitor and with dark controls was also conducted with Hamilton Harbour water. All experiments were conducted in triplicate.

(*iv*) *On Potato Leaves.* A potato field in Prince Edward Island was sprayed by aircraft at a rate of 6.2 g of 1-deltamethrin per ha [cf. Maguire et al. (1989)], and samples of potato leaves were collected at random at intervals over a period of 2–3 days postspray. The leaves were frozen immediately for transport to the laboratory. After the leaves were thawed, 10-g samples were extracted in a Soxhlet apparatus with 1/1 (v/v) acetone/hexane for 24 h at 8 cycles/h. The acetone/hexane extracts of 500-mL volume were then diluted with 500 mL of organic-free water, and the hexane layer was separated, dried with sodium sulfate, and concentrated preparatory to cleanup by rotary evaporation to 10 mL and then by a gentle stream of nitrogen to 1 mL. At this point there was usually some precipitation in the test tube, but all the material was transferred to the cleanup column as described below.

The 1-mL hexane extracts were cleaned up on activated silica gel columns of 40-cm length and 2.5-cm diameter, with a layer of sodium sulfate for drying. Three 100-mL fractions were eluted from the columns. Fraction 1 was hexane, fraction 2 was dichloromethane/hexane (20/80 v/v), and fraction 3 was dichloromethane/hexane (60/40 v/v). At each solvent change, a little solvent was used to rinse the test tubes containing the original extract, and in this way even the precipitated material was transferred to the cleanup column. All three fractions were solvent-exchanged with hexane and reduced to 10 mL. When it was found that the deltamethrin isomers eluted in fractions 1–3, all three fractions were combined, and the volume was reduced to 0.1–1 mL for analysis.

RESULTS

Sunlight Photolytic Isomerization of Thin Films and Solutions in Hexane. Ruzo et al. (1977) found that the major photoisomers of 1-deltamethrin in thin films on glass were the (3+4′) isomers, while Hill and Johnson (1987) and Maguire et al. (1989) found (2+2′)-, (3+3′)-, and (4+4′)- in addition to (1+1′)-deltamethrin. This work demonstrated that only three isomers are produced by sunlight irradiation of 1-deltamethrin either as a thin film on glass or in hexane: the 2′, 3, and 4′ isomers. Figure 3 shows the time course of this photolytic isomerization in hexane. At the end of 5 days the sum of the concentrations of the 1, 2′, 3, and 4′ isomers was roughly equal to that of the 1 isomer originally. This finding agrees with the observation of Ruzo et al. (1977) that identified photoproducts formed upon sunlight irradiation in the solid phase and in organic solvents for the most part retain the ester linkage intact. 1-Deltamethrin was recovered quantitatively from dark controls over the 5-day period, indicating no isomerization or degradation in hexane in the dark.

Isomerization in Water in the Dark. Earlier work with achiral analyses had demonstrated that (2+2′)-deltamethrin can be produced from parent 1-deltamethrin by photochemical and dark chemical reactions (Ruzo et al., 1977; Hill and Johnson, 1987; Maguire et al., 1989). From this work it appeared that the 2′ isomer was the only isomer produced in the dark chemical reaction in distilled water and Hamilton Harbour water, with or without the microbial inhibitor mercuric chloride. Figure 4 shows its production in distilled water with added mercuric chloride. The kinetics in Hamilton Harbour water were roughly the same. The persistence of 2′-deltamethrin (i.e., half-life < 5 days) was about the same as had been observed before for (2+2′)-deltamethrin (Maguire et al., 1989). At least seven degradation products were observed during the reaction, eluting between 35 and 45 min under the conditions described above. PBald was the only product identified, and it was a minor product.

Sunlight Isomerization in Water. Sunlight irradiation of 1-deltamethrin in Hamilton Harbour water with or without mercuric chloride produced the 2′, 3, and 4′ isomers, as shown in Figure 5, in addition to small amounts of PBald and several other unidentified products. The half-lives of all isomers were less than 5 days. The kinetics of isomerization and disappearance in sterile and nonsterile solutions were similar. Similar observations were made with 1-deltamethrin in distilled water, but the deltamethrin isomers disappeared somewhat faster than in Hamilton Harbour water, with half-lives of 1–2 days.

Deltamethrin Sprayed on Potato Leaves. Deltamethrin sprayed on potato leaves was presumably subject to both sunlight degradation and metabolism. The 2′, 3, and 4′ isomers were the only isomers found, in addition to the parent 1-deltamethrin and several unidentified products. Table III shows the concentrations of all four isomers found. There was a great deal of variability in the concentrations of the isomers, which was probably the result of variable spray deposition and a light rain between 8 and 10 h after the spray. Interestingly, no 1-deltamethrin was found at 0.1 h after the aircraft spraying despite the fact that the 2′ and 3 isomers were found. In

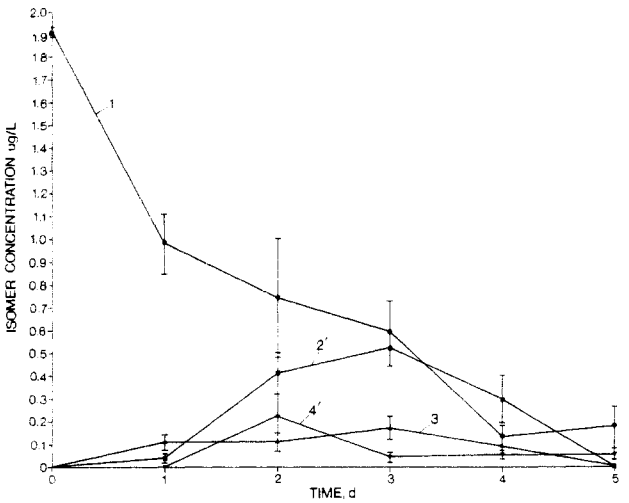

Figure 5. Sunlight irradiation of 1-deltamethrin in Hamilton Harbour water with added mercuric chloride.

Table III. Concentrations (μg/kg Wet Weight) of Deltamethrin Isomers in Potato Leaves after the Spray[a]

time, h	[1]	[2']	[3]	[4']	total
0.1		0.1	0.1		0.2
1.0	0.7	3.1	3.3	0.1	7.2
2.5	0.3	1.5	0.5		2.3
3.1		0.1			0.1
6.5	1.1	0.4	0.9		2.4
8.5	3.2	2.5	1.0		6.7
10.5	0.7	1.6	0.9		3.2
26	0.8	2.7			3.5
34		0.2			0.2
59					

[a] The limit of quantitation for each isomer was 0.1 μg/kg wet weight.

addition, ratios of concentrations of the stereoisomers at the different time intervals exhibited no clear pattern. The first observation may be related to the fact that those isomers which were found were only found at the limit of quantitation, and possibly 1-deltamethrin was present below the limit of quantitation. Both of the above observations may also have been due to variable spray deposition and the sampling of leaves or parts of leaves that may have been shaded by other leaves, resulting in fluctuations in concentrations of photochemically produced stereoisomers. As noted above and elsewhere, the 2' isomer is produced readily in water in a dark chemical reaction, and its appearance 0.1 h after the spray may not have been due to rapid photolysis or metabolism but production from 1-deltamethrin in the airplane spray tanks between the time the pesticide formulation was mixed and the time it was sprayed (Maguire et al., 1989). After 0.1 h its appearance was probably due to sunlight photolysis. The concentration of the isomers declined quickly after 26 h, and no isomer was detected 59 h after the spray.

DISCUSSION

The results of this work supplement those obtained earlier (Maguire et al., 1989). In that work, (2+2')-deltamethrin was identified as the major product of the dark isomerization of parent deltamethrin in water. This work has shown that 2'-deltamethrin is the only product of dark isomerization. Moreover, this work has shown that the 2', 3, and 4' isomers are the only isomers resulting from sunlight irradiation of 1-deltamethrin in thin films or in hexane solutions.

The 2', 3, and 4' isomers of 1-deltamethrin are also produced by sunlight irradiation in water and on potato leaves. This isomerization of 1-deltamethrin is thus only a partial detoxification since 3-deltamethrin retains some toxicity toward insects and mammals. Interestingly, although substantial amounts of (2+2')-deltamethrin were observed in the surface microlayer, subsurface water, and sediment of the sprayed pond in the earlier study employing achiral analyses (Maguire et al., 1989), (3+3')- and (4+4')-deltamethrin were not found. This may have been due to fast degradation in that particular system. The (3+3') and (4+4') pairs have been observed, in addition to (2+2')-deltamethrin, on pasture forage and litter (Hill and Johnson, 1987) and alfalfa (Hill et al., 1989). The results of the present work suggest that the 1, 2', 3, and 4' isomers will be the only ones present whenever achiral analyses reveal the presence of the (1+1'), (2+2'), (3+3') and (4+4') isomers. These isomers can be regarded as products of process A proposed by Ruzo et al. (1977) involving cyclopropane ring opening and cis/trans isomerization.

Although the isomerization of 1-deltamethrin may be viewed as at least a partial detoxification mechanism in mammals and insects, further research is required on the toxicity of deltamethrin isomers to aquatic organisms to make the same statement for aquatic ecosystems.

ACKNOWLEDGMENT

I thank Dr. J. Tessier of Roussel Uclaf, Paris, France, for samples of the stereoisomers of deltamethrin.

LITERATURE CITED

Bocquet, J.-C.; L'Hotellier, M. The Effect of Deltamethrin on the Aquatic Environment. *Pestic. Sci.* **1985**, *16*, 198.

Collaborative International Pesticides Analytical Council. CIPAC Monograph 10, Deltamethrin - 33; CIPAC: 5 Pondwich Road, Herpenden, Herts, England AL5 2H6, 1988; pp 57–66.

Elliott, M.; Farnham, A. W.; Janes, N. F.; Needham, P. H.; Pulman, D. A. Synthetic Insecticide with a New Order of Activity. *Nature* **1974**, *248*, 710–711.

Hill, B. D.; Johnson, D. L. Persistence of Deltamethrin and Its Isomers on Pasture Forage and Litter. *J. Agric. Food Chem.* **1987**, *35*, 373–378.

Hill, B. D.; Inaba, D. J.; Charnetski, W. A. Dissipation of Deltamethrin Applied to Forage Alfalfa. *J. Agric. Food Chem.* **1989**, *37*, 1150–1153.

Lhoste, J., Ed. *Deltamethrin Monograph*; Roussel Uclaf: Paris, 1982; 412 pp.

Maguire, R. J.; Carey, J. H.; Hart, J. H.; Tkacz, R. J.; Lee, H.-B. Persistence and Fate of Deltamethrin Sprayed on a Pond. *J. Agric. Food Chem.* **1989**, *37*, 1153–1159.

Muir, D. C. G.; Rawn, G. P.; Grift, N. P. Fate of the Pyrethroid Insecticide Deltamethrin in Small Ponds: A Mass Balance Study. *J. Agric. Food Chem.* **1985**, *33*, 603–609.

Mulla, M. S.; Navvab-Gojrati, H. A.; Darwazeh, H. A. Toxicity of Mosquito Larvicidal Pyrethroids of Four Species of Freshwater Fishes. *Environ. Entomol.* **1978**, *7*, 428–430.

Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. Pyrethroid Photochemistry: Decamethrin. *J. Agric. Food Chem.* **1977**, *25*, 1385–1394.

Smith, J. H.; Mabey, W. R.; Bohonos, N.; Holt, B. R.; Lee, S. S.; Chou, T.-W.; Bomberger, D. C.; Mill, T. Environmental Pathways of Selected Chemicals in Freshwater Systems. Part I: Background and Experimental Procedures. U.S. Environmental Protection Agency Report EPA-600/7-77-113, U.S. Environmental Protection Agency, Athens, GA 30605, October 1977, 80 pp.

Tessier, J. Structure, Synthesis and Physical-Chemical Properties of Deltamethrin. In *Deltamethrin Monograph*; Lhoste, J., Ed., Roussel Uclaf: Paris, 1982; Chapter 2, pp 37–66.

Tooby, T. E.; Thompson, A. N.; Rycroft, R. O.; Black, I. A.; Hewson, R. T. *A Pond Study to Investigate the Effects on Fish and Aquatic Invertebrates of Deltamethrin Applied Directly to Water*; U.K. Ministry of Agriculture, Fisheries and Food: Burnham-on-Crouch, Essex, England, 1981; 25 pp.

Zitko, V.; McLeese, D. W.; Metcalfe, C. D.; Carson, W. G. Toxicity of Permethrin, Decamethrin and Related Pyrethroids to Salmon and Lobster. *Bull. Environ. Contam. Toxicol.* **1979**, *21*, 338–343.

Received for review November 7, 1989. Accepted March 2, 1990.

Registry No. Isomer 1, 52918-63-5; isomer 2′, 64364-02-9; isomer 3, 52918-63-5; isomer 4′, 52918-63-5.