Coordinating Group for Research on Etiology of Esophageal Cancer in North China, *China Med. J.* 1, 167 (1975).
Forsyth, D. M., Yoshizawa, T., Morooka, N., Tuite, J., *Appl. Environ. Microbiol.* **34**, 547 (1977).
Hesseltine, C. W., Bothast, R. J., *Mycologia* **69**, 328 (1977).
Hidy, P. H., Baldwin, R. S., Greasham, R. L., Keith, C. L., McMullen, J. R., *Adv. Appl. Microbiol.* **22**, 59 (1977).
Ishii, K., Ando, Y., Ueno, Y., *Chem. Pharm. Bull.* **23**, 2162 (1975).
Kellerman, T. S., Marasas, W. F. O., Pienaar, J. G., Naudé, T. W., *Onderstepoort J. Vet. Res.* **39**, 205 (1972).
Kmet, J., Mahboubi, E., *Science* **175**, 846 (1972).
Kotsonis, F. N., Smalley, E. B., Ellison, R. A., Gale, C. M., *Appl. Microbiol.* **30**, 362 (1975).
Kriek, N. P. J., Marasas, W. F. O., Steyn, P. S., Van Rensburg, S. J., Steyn, M., *Food Cosmet. Toxicol.* **15**, 579 (1977).
Lovelace, C. E. A., Nyathi, C. B., *J. Sci. Food Agric.* **28**, 288 (1977).
Marasas, W. F. O., Kriek, N. P. J., Van Rensburg, S. J., Steyn, M., Van Schalkwyk, G. C., *S. Afr. J. Sci.* **73**, 346 (1977).
Marasas, W. F. O., Kriek, N. P. J., Steyn, M., Van Rensburg, S. J., Van Schalkwyk, D. J., *Food Cosmet. Toxicol.* **16**, 39 (1978).
Martin, P. M. D., *S. Afr. Med. J.* **48**, 2374 (1974).
Martin, P. M. D., Keen, P., *Sabouraudia* **16**, 15 (1978).
Mirocha, C. J., Christensen, C. M., in "Mycotoxins", Purchase, I. F. H., Ed., Elsevier, Amsterdam, 1974, pp 129–148.
Mirocha, C. J., Christensen, C. M., Nelson, G. H., *Appl. Microbiol.* **17**, 482 (1969).
Mirocha, C. J., Pathre, S. V., Christensen, C. M., in "Mycotoxins in Human and Animal Health", Rodricks, J. V., Hesseltine, C. W., Mehlman, M. A., Ed., Pathotox Publishers, Park Forest South, 1977, pp 345–364.
Mirocha, C. J., Pathre, S. V., Schauerhamer, B., Christensen, C. M., *Appl. Environ. Microbiol.* **32**, 553 (1976).
Nakano, N., Kunimoto, T., Aibara, K., *Shokuhin Eiseigaku Zasshi* **14**, 56 (1973); *Chem. Abstr.* **80**, 204 (1974).
Rose, E. F., *Med. Biol. Environ.* **4**, 51 (1976).
Rose, E. F., McGlashan, N. D., *Br. J. Cancer* **31**, 197 (1975).
Rubinshtein, Y. I., Kukel, Y. P., Kudinova, G. P., *Vopr. Pitan.* **26**, 57 (1967).
Ruddick, J. A., Scott, P. M., Harwig, J., *Bull. Environ. Contam. Toxicol.* **15**, 678 (1976).
Schoental, R., *Cancer Res.* **34**, 2419 (1974).
Schoental, R., *Cancer* **40**, 1833 (1977).
Schoental, R., Joffe, A. Z., *J. Pathol.* **112**, 37 (1974).
Schoental, R., Joffe, A. Z., Yagen, B., *Br. J. Cancer* **34**, 310 (1976).
Schoental, R., Joffe, A. Z., Yagen, B., *Br. J. Cancer* **38**, 171 (1978).
Steyn, P. S., Vleggaar, R., Rabie, C. J., Kriek, N. P. J., Harington, J. S., *Phytochemistry* **17**, 949 (1978).
Thomas, F., Eppley, R. M., Trucksess, M. W., *J. Assoc. Off. Anal. Chem.* **58**, 114 (1975).
Ueno, Y., Kubota, K., *Cancer Res.* **36**, 445 (1976).
Ueno, Y., Ishii, K., Sato, N., Ohtsubo, K., *Jpn. J. Exptl. Med.* **44**, 123 (1974).
Vesonder, R. F., Ciegler, A., Jensen, A. H., Rohwedder, W. K., Weisleder, D., *Appl. Environ. Microbiol.* **31**, 280 (1976).
Vesonder, R. F., Ciegler, A., Jensen, A. H., *Appl. Environ. Microbiol.* **34**, 105 (1977).
Wehner, F. C., Marasas, W. F. O., Thiel, P. G., *Appl. Environ. Microbiol.* **35**, 659 (1978).
Yoshizawa, T., Morooka, N., *J. Food Hyg. Soc. Jpn.* **15**, 261 (1974).

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Photochemistry of the Potent Knockdown Pyrethroid Kadethrin

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Kadethrin, 5-benzyl-3-furylmethyl (1*R*,*cis E*)-2,2-dimethyl-3-(2′-oxo-3′-thiacyclopentylidenemethyl)-1-cyclopropanecarboxylate, is rapidly photoisomerized to a 1*RS*,cis,trans(*E*,*Z*) mixture, probably via triplet diradicals generated by direct or sensitized photolysis for each of the cyclopropanecarboxylate and vinylcarboxylate isomerizations. A thiolactone lactone is formed by attack of the carbonyl oxygen at C-3 of the cyclopropane ring. Other products originate from hydrolysis of the thiolactone and cyclopropanecarboxylate ester groupings, from oxidation of the furan ring and rearrangement of the intermediate peroxide to a benzyloxylactone derivative, and from oxidation of the alcohol moiety to benzylfuroic acid. Minor photoproducts are (1′*R*,2′*S*)- and (1′*S*,2′*R*)-epoxykadethrin, phenylacetic acid, benzyl alcohol, and benzoic acid. Kadethrin is more toxic to houseflies and mice than isomerized esters and photodecomposed products derived from it. *d*-2-Octyl (1*R*,*trans*)-chrysanthemate undergoes sensitized photoisomerization much slower than *d*-2-octyl pyrethrate, which in turn is slower than the *d*-2-octyl esters of the kadethrin acid moiety and the corresponding lactone.

Kadethrin (Figure 1) (RU 15525), a synthetic pyrethroid exceptionally potent for knockdown (Lhoste and Rauch, 1976; Martel and Buendia, 1974), is a single isomer (of eight possible) and has the 1*R*,3*S*(*E*) or 1*R*,cis(*E*) configuration (Roussel-Uclaf-Procida, 1976).

Environmental instability is desirable in a knockdown insecticide because only brief action is needed and further exposure to toxicants is unnecessary. Studies of the photochemical reactions of related compounds (Holmstead et al., 1977; Ruzo et al., 1977; Ueda et al., 1974) indicate that kadethrin may undergo isomerization at the cyclopropane ring, ester cleavage, and oxidation of the furan group. Kadethrin differs from pyrethroids studied earlier, i.e., the thiolactone ring provides a conjugated double bond system, *E*–*Z* isomerization is possible, and an oxidizable sulfur is present. Thus, photochemical processes and reactivity conferred by the thiolactone are potentially superimposed on other reactions discussed above. Accordingly, the photodecomposition of kadethrin was studied under both laboratory conditions and those relevant to environmental situations.

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MATERIALS AND METHODS

Spectroscopy. Infrared (IR) spectra were determined on a Perkin-Elmer Model 457 grating spectrophotometer using KBr disk, liquid film, or chloroform solution. Nuclear magnetic resonance (NMR) spectra were obtained

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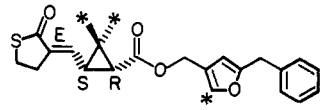


kadethrin [1R, *cis* (E)]

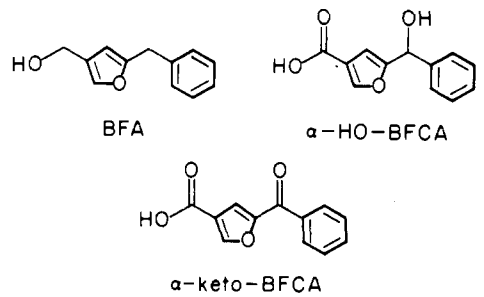
Figure 1. Structure of kadethrin or 5-benzyl-3-furylmethyl (1*R*,*cis*E)-2,2-dimethyl-3-(2′-oxo-3′-thiacyclopentylidenemethyl)-1-cyclopropanecarboxylate. Asterisks designate positions of ^{14}C labels in the acid and alcohol (alc) moieties with specific activities of 54.4 and 43.9 mCi/mmol, respectively.

with the Perkin-Elmer R32B 90-MHz spectrometer using samples dissolved in deuteriochloroform containing 0.5% tetramethylsilane as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and coupling constants (J) are given in hertz (Hz). Chemical-ionization mass spectra (CI-MS) were recorded on the Finnigan Model 1015D mass spectrometer with the System Industries Model 150 control system, using a direct introduction probe and isobutane as the reactant gas at a source pressure of 0.6–1.0 torr.

Thin-Layer and Gas–Liquid Chromatographic Separations and Analyses. Precoated 20 × 20 cm chromatoplates were used as follows: silica gel 60 F-254 (E. Merck, Darmstadt, Germany) with 0.25- and 0.5-mm gel thickness for analysis and preparative isolations, respectively; silica gel GF (Analtech, Inc., Newark, DE) with 1.0- and 2.0-mm gel thickness for preparative isolations. Compounds separated by solvent systems indicated in Table I or described later were detected by their quenching of gel fluorescence under short-wavelength ultraviolet light and recovered by extraction of the gel with acetone or methanol. Epoxides were detected with the 4-(*p*-nitrobenzyl)pyridine reagent (Ueda et al., 1974).

Gas–liquid chromatography (GLC) for analysis of 2-octyl esters utilized 6% QF-1 or 8% DEGS on Chromosorb W (A/W, 80–100 mesh) in stainless steel columns (2 m × 3 mm i.d.) (systems A–C and F referred to later) with a Varian Aerograph Series 1400 gas chromatograph or in glass columns (2 m × 3 mm i.d.) (systems D and E referred to later) with a Hewlett Packard Model 830 gas chromatograph, each equipped with a flame ionization detector. The kadethrin isomers were analyzed with the Aerograph chromatograph using 4% OV-101 in a glass column at 260 °C isothermal and N_2 as the carrier gas at 30 mL/min. The same conditions on OV-101 but with temperature programming from 150–300 °C at 8 °C/min were used to analyze benzyl alcohol, phenylacetic acid, and benzoic acid, which give t_R values of 1.4, 6.5, and 7.1 min, respectively.

Designation of Compounds. Kadethrin derivatives are referred to as shown in Figure 2. The 1*R*,cis(*E*) acid moiety of kadethrin is designated thiolactone-CA and isomers of this acid and of kadethrin as thiolactone-isoCA and isokad, respectively. Hydrolysis of the thiolactone group gives thiolcarboxy derivatives and epoxidation of the propylenic double bond, epoxykad derivatives. The alcohol moiety of kadethrin and some of its oxidized derivatives are abbreviated as follows:



BFA α-HO-BFCA α-keto-BFCA

Table I. Thin-Layer Chromatographic Properties of Kadethrin and Its Isomers and Derivatives

compound	R_f value in indicated solvent system[a] A	B	C
Esters			
kadethrin	*0.46*[b]	*0.62*	0.60
(1*RS*,*cisZ*)-isokad	*0.70*	*0.66*	0.66
(1*RS*,*transE*)-isokad	*0.59*	*0.63*	0.66
(1*RS*,*transZ*)-isokad	*0.48*	*0.62*	0.61
(1′*R*,2′S)- or (1′*S*,2′*R*)-epoxykad	0.11	0.41	0.22
(1′*R*,2′*S*)- or (1′*S*,2′*R*)-epoxykad	0.14	0.52	0.28
(1*R*,*cisE*)-thiolcarboxy-kad	*0.57*[c]	*0.50*[c]	*0.29*
(1*R*,*transE*)-thiolcarboxy-isokad	*0.60*[c]	*0.51*[c]	*0.31*
(1*RS*,*cisE*)-benzyloxylactone	*0.33*	*0.64*	0.49
(1RS,*transE*)-benzyloxylactone	*0.43*	*0.66*	0.55
unknown photoproduct 1	0.31	0.56	
unknown photoproduct 2	0.28	0.53	
Acid Moiety and Related Compounds			
thiolactone-CA		*0.33*	0.25
(1*RS*,*cisZ*)-thiolactone-isoCA		*0.65*	0.29
(1*RS*,*transE*)-thiolactone-isoCA		*0.42*	0.28
(1*RS*,*transZ*)-thiolactone-isoCA		*0.35*	0.26
thiolcarboxy-CA		*0.23*	0.17
thiolactone lactone		*0.32*	0.35
Alcohol Moiety and Related Compounds			
BFA	0.24	0.41	
BFCA	*0.18*	*0.49*	0.25
α-keto-BFCA	0.04	0.31	0.17
α-HO-BFCA	0.04	0.25	0.17
benzoic acid	0.35	0.52	0.37
benzyl alcohol	0.35	0.45	0.44
phenylacetic acid	0.26	0.48	0.38

[a] Tlc solvent systems are as follows: (A) carbon tetrachloride–ether (3:1), two developments; (B) benzene saturated with formic acid–ether (1:3); (C) benzene–ethyl acetate–methanol (15:5:1). In hexane–ether (1:1), the R_f values are 0.43, 0.56, 0.51, and 0.45 for kadethrin, (1*RS*,*cisZ*)-isokad, (1*RS*,*transE*-isokad, and (1*RS*,*transZ*)-isokad, respectively. [b] Italicized numbers designate combinations of compounds and solvent systems used for tentative product identification by cochromatography. [c] As methyl ester.

Chemicals. Roussel-Uclaf-Procida (Paris, France) provided the following standard compounds: kadethrin and its 1*R*,trans(*E*) isomer; [^{14}C]kadethrin preparations (Figure 1); thiolactone-CA and its 1*R*,trans(*E*) isomer; the lactone analogue of thiolactone-CA (i.e., lactone-CA). The 1*R*,trans isomers of chrysanthemic and pyrethric acids were isolated from pyrethrum extract (Elliott and Janes, 1969). BFCA (Figure 2) and three related compounds (BFA, α-HO-BFCA, and α-keto-BFCA) were available from a previous study (Ueda et al., 1975).

Syntheses. Several chemicals were synthesized as described below and characterized by NMR and CI-MS (Table II). Diazomethane in ether–ethanol mixture was used for methylation of carboxylic acids.

Hydrolysis of Kadethrin. Kadethrin (396 mg, 1.0 mmol) was stirred in a solution of KOH (46 mg, 0.82 mmol) in a mixture of ethanol (8 mL) and water (0.8 mL) for 20 min at 60 °C, then water (10 mL) was added and unreacted kadethrin (32%) was recovered by extraction into ether. Acidification (5% HCl) of the aqueous solution and extraction with ether gave thiolactone-CA (12%), (1*R*,*cisE*)-thiolcarboxy-kad (8%) and thiolcarboxy-CA (20%), separated by preparative TLC with solvent system C (Table I) [IR peaks at 2550, 1740, and 1630 cm^{-1} for (1*R*,*cisE*)-thiolcarboxy-kad (liquid film), 1705 and 1680 cm^{-1} for thiolactone-CA (KBr), and 2550 and 1700 cm^{-1} for thiolcarboxy-CA (KBr)]. Hydrolysis of (1*R*,*transE*)-

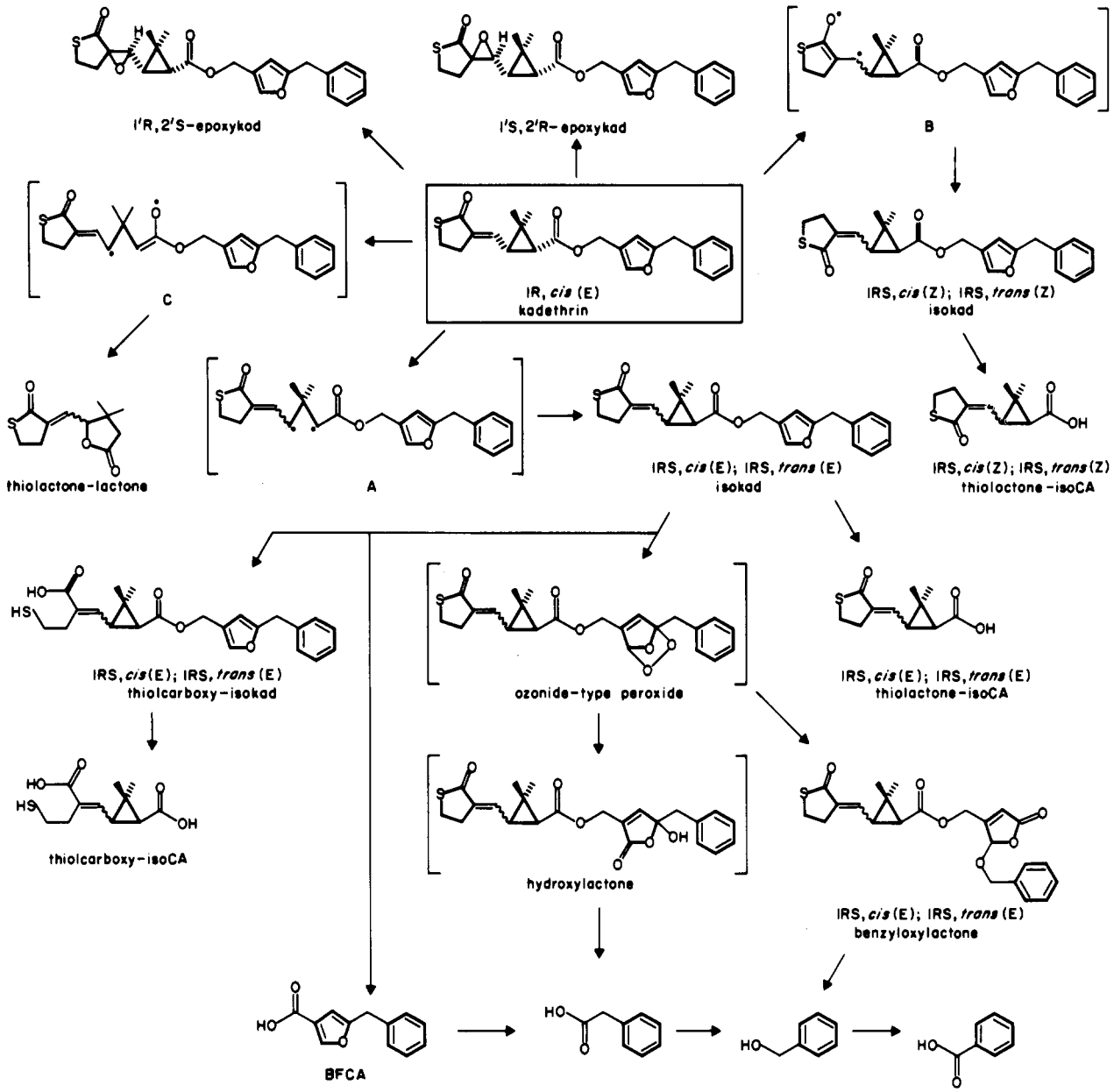


Figure 2. Partial pathways for kadethrin photodecomposition including designations for derivatives. Hypothetical intermediates are shown in brackets.

isokad in the same manner gave (1*R*,*trans*E)-thiolcarboxy-isokad with appropriate spectra.

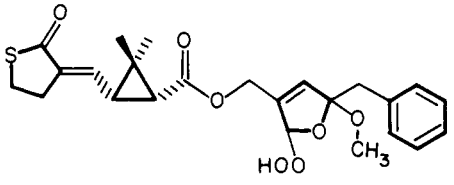
Epoxidation of Kadethrin. Kadethrin (396 mg, 1.0 mmol) was stirred for 2 h at 25 °C with an equimolar mixture of *m*-chloroperbenzoic acid (126 mg, 0.73 mmol) and K_2CO_3 (103 mg, 0.75 mmol) in methylene chloride (2 mL); the mixture was then filtered, the solvent was evaporated, and ether (5 mL) was added to the residue. After washing the ether with 2% aqueous K_2CO_3 solution, the epoxykad isomers were isolated by preparative TLC with chloroform–methanol (8:1) to give two compounds (R_f 0.45, 9.7% yield and R_f 0.60, 1.5% yield). These products lack the cyclopentylidene double bond (IR) and have oxygen incorporated at this position (NMR and MS).

d- and l-2-Octyl Thiolactone-CA and d-2-Octyl Chrysanthemate, Pyrethrate and Lactone-CA. *d-* or *l*-2-Octanol (350 mg) and equimolar dry pyridine in dry benzene (5 mL) were added to the acid chloride, prepared by refluxing thiolactone-CA (600 mg, 2.7 mmol) and 1.5 molar equiv of thionyl chloride (400 mg) in methylene chloride (5 mL) with stirring for 2 h and then concentration in vacuo at 25 °C. After 15 h at 25 °C and filtration, the filtrate was washed with aqueous 2 N HCl solution, water, aqueous $NaHCO_3$ solution and water. After drying (Na_2SO_4) and evaporation in vacuo at 25 °C, the residue was purified by column chromatography on silica gel developed with hexane and ether to obtain the desired ester as a liquid: IR (liquid film) 1740, 1680, 1640 cm^{-1}; NMR (identical for *d-* and *l*-2-octyl esters) δ 0.88 (t, 3 H), 1.16 (s, 3 H), 1.24 (s, 3 H), 1.26 (s, 10 H), 1.34 (s, 3 H), 1.64–2.01 (m, 2 H), 2.88–3.14 (m, 2 H), 3.18–3.41 (m, 2 H), 4.84 (m, 1 H), 6.82 ppm (d, J = 8.5, 1 H).

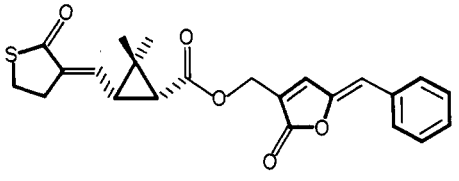
d-2-Octyl esters of chrysanthemic acid, pyrethric acid, and lactone-CA were prepared as above but on a 0.9-mmol scale with product isolation by preparative TLC. Each product of >98% purity (GLC) gave appropriate NMR and mass spectra.

Photodecomposition Procedures. *Rose-Bengal Sensitized Photodecomposition of Kadethrin to Give the Methoxy Hydroperoxide and the Benzylidene Lactone.* A solution of kadethrin (1.0 g, 2.5 mmol) and rose bengal (50 mg) in methanol (200 mL) was irradiated with a 40-W

showcase lamp in a water-cooled immersion apparatus through which oxygen was bubbled for 3 h (cf. Ueda et al., 1974). After removal of solvent (rotary evaporator), ether was added and this solution was dried (Na_2SO_4) and evaporated to give a yellow oil [IR peaks (liquid film) at 3320 (OOH), 1730 (O=CO), 1680 (O=CS), and 1630 (C=C) cm^{-1}]. NMR detected only the methoxy hydroperoxide (88%) in this material but TLC in ether–hexane



methoxy-hydroperoxide



benzylidene-lactone

(3:1) revealed not only this compound (R_f 0.17) but also traces of kadethrin and a few other compounds. The methoxy hydroperoxide liberated iodine from potassium iodide solution. In methanol at 25 °C for 3 days, it gave the benzylidene lactone (quantitative yield); IR (KBr) 1730 (O=CO), 1675 (O=CS), and 1630 (C=C) cm^{-1}.

Ultraviolet Irradiation in Solution. A solution of kadethrin (2.5 mM) and isobutyrophenone (20 mM) in benzene was irradiated (Rayonet reactor, the Southern N.E. Ultraviolet Co., Middletown, CT; 350-nm lamps) in six small borosilicate glass tubes (λ >290 nm) for 3 h. After evaporating the solvent, the product mixture was analyzed by GLC, TLC, and CI-MS. The relative proportion of isomers was determined by comparing the chemical shifts of the vinyl proton.

d- or *l*-2-Octyl thiolactone-CA (0.75 mM) was irradiated as above in benzene containing isobutyrophenone (17 mM). The reaction mixture was analyzed by GLC using peak area ratios where feasible or by TLC and NMR.

Solutions of *d*-2-octyl chrysanthemate, pyrethrate, lactone-CA, and thiolactone-CA were irradiated (λ >290 nm) at 60 μM in acetone or at 30 μM combined with isobutyrophenone (240 μM) in hexane with product analysis by GLC.

Sunlight Irradiation in the Solid Phase. Kadethrin (5 g) on glass (1.3 mg/cm^2) was exposed to bright sunlight for 10 h. The photolyzed mixture (90%), recovered by washing with chloroform and methanol, was fractionated by column chromatography and preparative TLC. The column [80 g of silicic acid (100 mesh, Mallinckrodt Co., St. Louis, MO) packed in hexane] was developed with 300 mL each of hexane, various chloroform in hexane mixtures (v/v, percent, 5, 10, 20, 40, 60, and 80), followed by chloroform (300 mL) and methanol (500 mL). Fractions similar by TLC were combined, further purified by preparative TLC, and analyzed by NMR, CI-MS, and IR.

The [^{14}C]kadethrin preparations as thin films (35 μg/cm^2) on glass (petri dishes) were exposed to sunlight through quartz. The photodecomposition products recovered by washing the glass with chloroform–methanol (3:1) were analyzed by two-dimensional TLC (solvent systems A and B) and liquid scintillation counting and tentatively identified by cochromatography in two dimensions (A and B) or in one dimension (C) (Table I).

Toxicity of Isomers and Photodecomposed Kadethrin. Adult female houseflies (*Musca domestica* L., SCR strain, 15–20 mg each) were treated topically with 1 μL of acetone containing the test compound. Male albino mice (20 g) were treated intraperitoneally (ip) with the pyrethroids in 20 μL of methoxytriglycol. LD_{50} values were determined at 24 h.

RESULTS

Kadethrin Isomers from Irradiation (λ >290 nm) in Benzene Solution with Isobutyrophenone as Sensitizer. Kadethrin irradiated for 3 h gives as major products (>95%) the 1*RS*,cis(*E*)-, 1*RS*,cis(*Z*)-, 1*RS*,-trans(*E*)-, and 1*RS*,trans(*Z*) isomers separable by TLC (Table I) and GLC (t_R values from analysis of individual isolated compounds of 12.2, 9.3, 12.3, and 10.5 min, respectively). The four geometrical isomers were isolated on a silicic acid column as indicated below. Their structures were assigned by NMR and CI-MS (Table II). NMR signals for the 1 and 3 protons are clearly resolved in the trans but not the cis isomer (Bramwell et al., 1969) and the olefinic proton (1′) resonates at lower field in the cis than in the trans and in the E than in the Z isomer (Table II).

Kadethrin Photoproducts from Sunlight Irradiation in the Solid Phase. Twenty–forty percent chloroform in hexane eluted about 50% by weight (2.5 g) of the photodecomposition mixture from the silicic acid column. Further purification of this fraction by TLC with solvent systems A and B and examination by NMR and CI-MS revealed four isomer components eluted from the column in the order: 1*RS*,cis(*Z*), 1*RS*,trans(*E*), 1*RS*,-trans(*Z*), and 1*RS*,cis(*E*). Two minor photoproducts, eluted in the 60% chloroform fraction, were further purified by TLC with solvent system A (R_f 0.33, 3.6 mg and R_f 0.43, 32 mg) and identified by NMR and CI-MS (Table II) as the 1*RS*,cis(*E*)- and 1*RS*,trans(*E*) isomers, respectively, of the benzyloxylactone. IR spectra (chloroform) in each case revealed 1780 (γ-lactone), 1740 (ester), 1680 (thiolactone), and 1650 (C=C) cm^{-1} but no hydroxyl group. Chloroform eluted the thiolactone lactone (2.9 mg) which was further purified by TLC with solvent system C (R_f 0.35) and had appropriate NMR and CI-MS spectra (Table II) and IR (chloroform) peaks [1780 (γ-lactone), 1680 (thiolactone), and 1650 (C=C) cm^{-1}]. Other components eluting with chloroform and separated by TLC with solvent system B were a mixture of benzoic and phenylacetic acids (48 mg, R_f ~0.50) as determined by NMR. Further purification revealed that the upper TLC band (R_f 0.52) was benzoic acid and the lower band (R_f 0.48) was phenylacetic acid, each identified by GLC comparison with an authentic sample and NMR. Acidic compounds were separated by preparative TLC (solvent system B) to yield (1*RS*,trans*E*)-thiolactone-isoCA (R_f 0.42) and thiolactone-CA (R_f 0.33) identified by IR and NMR comparisons with the authentic standards. An additional component (11 mg) isolated by TLC (solvent system B) was identified as benzyl alcohol by GLC comparison with a standard.

The 1′*R*,2′*S*- and 1′*S*,2′*R*-epoxykad isomers are easily detected with the 4-(*p*-nitrobenzyl)pyridine reagent among the photoproducts of kadethrin exposed on silica gel to sunlamp irradiation (method of Ueda et al., 1974); the products cochromatograph with the authentic standards in the chloroform–methanol (8:1) TLC solvent system. The epoxykad isomers are differentiated not only by their TLC properties but also by their NMR spectral features. The epoxide of higher R_f has a larger coupling constant

Table II. Analytical Data for Kadethrin and Its Isomers and Derivatives

designation and mp, °C[a]	NMR chemical shifts (δ) and coupling constants (Hz)							CI-MS (isobutane), *m/e* (rel intens)		
	acid or acid moiety									
	1, d (*J* = 5); 3, dd	1′, d (*J* = 8.5)	$-CH_2S-$, m	$-CH_2-$, m	CH_3-, s	CH_3-, s	other	alcohol moiety[b]	$[M + 1]^+$	other fragments
kadethrin	1.55–2.06	6.77	3.05–3.36	2.68–3.02	1.20	1.28		A	397 (65)	185 (5), 171 (26)
(1*RS*,*cisZ*)-isokad (85–86)	1.56–1.95	6.31	3.00–3.35	2.65–3.00	1.22	1.27		A	397 (13)	171 (6)
(1*RS*,*transE*)-isokad (118–119)	1.79–2.05	6.14	3.05–3.35	2.70–3.05	1.23	1.28		A	397 (100)	171 (33)
(1*RS*,*transZ*)-isokad (82–83)	1.64–1.94	5.56	3.00–3.35	2.67–2.95	1.22	1.28		A	397 (14)	185 (52), 171 (8)
(1′*R*,2′*S*)- or (1′*S*,2′*R*)-epoxykad	1.80–2.01	3.61 (5.7)	3.00–3.31	2.55–3.00	1.20	1.21		A	413 (5)	412 (15), 394 (8)
(1′*R*,2′*S*)- or (1′*S*,2′*R*)-epoxykad	1.79–2.04	3.59 (7.8)	3.31–3.60	2.40–2.92	1.20	1.28		A	413 (9)	412 (24), 394 (8)
thiolcarboxy-kad, methyl ester	1.76–1.95	7.10	2.50–2.68		1.25	1.28	3.70 (CH_3O-)	A	429 (24)	428 (16)
(1*RS*,*cisE*)-benzyloxylactone	1.54–2.32	6.72	3.19–3.48	2.75–3.18	1.22	1.27		B	429 (9)	107 (100)
(1*RS*,*transE*)-benzyloxylactone	1.74–2.05	6.12	3.16–3.44	2.79–3.14	1.22	1.27		B	429 (8)	107 (100)
methoxy hydroperoxide	1.72–2.05	6.73	3.15–3.45	2.80-3.15	1.26	1.31		C		
benzylidene lactone (195–196)	1.55–2.10	6.79	3.19–3.45	2.85–3.16	1.30	1.36		D	411 (5)	289 (8), 241 (3)
thiolactone-CA (161)	1.82–2.05	6.72	3.15–3.40	2.85–3.10	1.20	1.34	10.14 (-OH)		241 (100)[c]	209 (9)
thiolcarboxy-CA, dimethyl ester	1.79–1.95	7.11	2.53–2.65		1.28	1.32	3.62 (CH_3O-) 3.71 (CH_3O-)		273 (35)[c]	272 (18), 241 (100)
thiolactone lactone		6.36	3.20–3.46	2.90–3.20	1.06	1.24	4.72 (-CHO-) (*J* = 7.2) 2.43 ($-CH_2-$)		227 (100)	209 (5)

[a] Crystallized from hexane-ether except thiolactone-CA which was crystallized from benzene. Other compounds are liquids. [b] Alcohol moieties (see Figure 2 and intext figures) give singlet signals as follows: A = 3.90 ($-CH_2C_6H_5$), 4.68 ($-CH_2O-$), 5.96 (-CH=), 7.22 (C_6H_5), 7.32 (=CHO-); B = 4.81 ($-CH_2C_6H_5$), 4.87 ($-CH_2O-$), 5.94 (-OCHO-), 5.98 (-CH=), 7.25 (C_6H_5); C = 3.08 ($-CH_2-$), 3.24 (CH_3O-), 4.54 ($-CH_2O-$), 5.59 (-OCHO-), 5.87 (-CH=), 7.16 (C_6H_5); D = 5.08 ($-CH_2O-$), 6.10 (-CH=), 7.26 (m, C_6H_5), 7.76 ($=CHC_6H_5$). [c] Methyl ester.

Table III. [^{14}C]Kadethrin and Its Photoproducts from Sunlight Irradiation as a Thin Film on Glass

compound	radiocarbon recovery at indicated min, %						
	5	10	20	40	60	240	480
Esters (Average of ^{14}C-acid and ^{14}C-alc)							
kadethrin and isokad							
1*RS,cis*(*E*)	76.0	67.3	49.0	37.7	28.8	8.2	5.2
1*RS,cis*(*Z*)	0.8	1.1	1.6	1.0	1.0	1.0	0.7
1*RS,trans*(*E*)	8.5	12.1	17.4	11.9	12.5	10.1	7.6
1*RS,trans*(*Z*)	0.8	1.7	1.8	0.6	1.5	1.3	1.0
thiolcarboxy-kad and -isokad							
1*RS,cis*(*E*)	<0.1	<0.1	0.5	0.8	0.3	0.5	0.3
1*RS,trans*(*E*)	<0.1	<0.1	0.1	0.7	0.2	0.3	0.2
benzyloxylactone							
1*RS,cis*(*E*)	<0.1	<0.1	<0.1	0.3	<0.1	0.4	0.5
1*RS,trans*(*E*)	<0.1	<0.1	<0.1	<0.1	<0.1	0.6	0.5
unknown product 1	<0.1	<0.1	0.1	0.3	<0.1	0.4	0.4
unknown product 2	0.4	0.5	0.7	0.7	0.6	0.3	0.3
Acid Moiety (^{14}C-acid Only)							
thiolactone-isoCA							
1*RS,cis*(*E*)	0.2	0.8	0.2	1.8	1.1	1.0	1.0
1*RS,cis*(*Z*)	0.1	0.4	0.1	0.7	0.3	0.3	0.3
1*RS,trans*(*E*)	0.1	0.3	0.8	2.9	1.9	1.6	2.3
1*RS,trans*(*Z*)	0.1	<0.1	0.2	0.6	0.7	1.1	1.1
thiolcarboxy-CA	<0.1	0.2	1.1	1.2	1.5	3.5	3.5
thiolactone lactone	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
unknowns[a]	0.4	0.7	2.0	15.9	20.6	31.8	33.6
loss	12.6	14.9	24.4	22.9	29.0	37.6	41.2
Alcohol Moiety (^{14}C-alc Only)							
BFCA	<0.1	<0.1	<0.1	<0.1	0.2	1.1	1.9
unknowns[a]	1.1	1.0	1.4	3.5	4.4	31.7	38.3
loss	12.4	16.3	27.4	42.5	50.5	44.1	43.1

[a] Almost entirely at the origin in TLC solvent systems A and B.

between the 1′ and 3 protons than the epoxide of lower R_f. The available information is not sufficient to assign the 1′*R*,2′*S* and 1′*S*,2′*R* configurations.

[^{14}C]Kadethrin Photoproducts from Sunlight Irradiation as Thin Films on Glass. The principal photoproducts on irradiation of kadethrin for 20 min or less are the isomers discussed above with 1*RS*,trans(*E*) predominating (Table III). Thus, cis–trans isomerization occurs rapidly and in preference to *E*–*Z* isomerization. Small amounts of other photoproducts retained the ester group (detected with both ^{14}C-acid and ^{14}C-alc preparations) and consisted of the thiolcarboxy derivatives from kadethrin hydrolysis and the benzyloxylactone derivatives also found with unlabeled materials as described above. In addition there were two minor unidentified ester photoproducts. Acid moiety fragments include each isomer of kadethrin hydrolyzed at the cyclopropanecarboxylate group (i.e., thiolactone-isoCA), large amounts of thiolcarboxy-CA from thiolactone hydrolysis and trace amounts of thiolactone lactone. Only one alcohol moiety product was identified, BFCA. The benzylidene lactone was not detected as a photoproduct (R_f 0.27 and 0.62 in solvent systems A and B, respectively). Other compounds not found as photoproducts were BFA, α-HO-BFCA and α-keto-BFCA. The loss of labeled products on irradiation is probably due to volatilization as esters or cleavage products and the unknowns were mostly very polar materials remaining at the origin in solvent systems A and B.

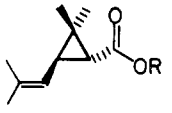
GLC Analysis of Individual Isomeric Components of *d*-2-Octyl Thiolactone-isoCA and Related Esters. The four individual isomeric components of *d*-2-octyl 1*RS,cis,trans*-chrysanthemate are easily separated by GLC on QF-1, giving an order for t_R values of *R* < *S* and *cis* < *trans* (Table IV; Murano, 1972; the same relationship is obtained for the related dichlorovinyl compounds, according to Horiba et al., 1977). The ability to analyze individual isomers of chrysanthemic acid and related compounds as *d*-2-octyl esters provides a convenient method to monitor photoisomerization reactions, providing that each isomer structure can be assigned. This is more difficult with the pyrethrates and the lactone-CA and thiolactone-CA esters than with the chrysanthemates because eight rather than four isomers are involved. These eight isomers are tentatively assigned based on their GLC, TLC, and NMR characteristics and their ratios on approaching a photostationary state. The *d*-2-octyl (1*R*,-*cisE*)-thiolactone-CA and (1*R*,*transE*)-thiolactone-isoCA esters are assigned by standards from synthesis. Four of the isomers are easily related to another set of four isomers on sensitized photoisomerization (isobutyrophenone in benzene) since the 1*R* position is completely racemized, i.e., identical amounts of 1*R* and 1*S* isomers (Table V); this relationship was confirmed for the *d*-2-octyl thiolactone-isoCA components by TLC separation of four 1*RS* racemates (NMR) each of which was then separated by GLC into the 1*R* and 1*S* isomers. The 1*R* isomer of *d*-2-octyl esters gives a smaller t_R value than the 1*S* isomer, and vice versa for the 1-2-octyl esters (Table IV). It remains then only to differentiate the four cis(*Z*) and trans(*Z*) isomers. The cis isomer generally gives a smaller t_R value than the corresponding trans isomer as noted above and this relationship should hold for the thiolactone-isoCA esters. It is valid for the 1*RS*(*Z*)-isokad isomers (t_R values of 9.3 and 10.5 min for the cis and trans isomers, respectively) but is less applicable to the 1*RS*-(*E*)-isokad isomers (12.2 min for cis and 12.3 min for trans). Assignments of the isomeric pyrethrates and *d*-2-octyl lactone-isoCA esters are then based on the analogous *d*-2-octyl thiolactone-isoCA esters, using the same isomer order for t_R values. This is confirmed in part by the product ratios on approaching the photostationary state (Table V).

Photoisomerization of *d*-2-Octyl Thiolactone-CA

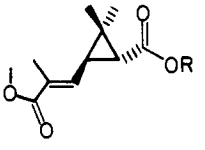
Table IV. Gas–Liquid Chromatographic Properties of Various Isomers of Four *d*-2-Octyl Esters and One *l*-2-Octyl Ester

compound[a]	GLC system[b]	t_R value, min, for indicated isomer							
		cis		trans					
monocarbonyl *d*-2-octyl chrysanthemate	A	1*R* 5.7	1*S* 6.2	1*R* 6.6	1*S* 7.0				
		cis(*Z*)		trans(*Z*)		trans(*E*)		cis(*E*)	
dicarbonyl *d*-2-octyl pyrethrate	B	1*R* 8.4	1*S* 9.0	1*R* 10.4	1*S* 10.8	1*R* 11.3	1*S* 11.8	1*R* 11.8	1*S* 12.3
d-2-octyl lactone-isoCA	C	11.8	12.5	14.8	15.5	16.7	18.0	18.0	18.5
d-2-octyl thiolactone-isoCA	C	10.4	11.0	13.0	13.3	14.1	14.8	14.8	15.4
	D	12.5	14.4	22.6	24.0	26.2	28.2	28.2	30.1
	E	12.5	14.5	26.6	28.3	28.4	31.5	34.6	37.9
l-2-octyl thiolactone-isoCA	F	8.3	7.6	11.1	10.7	12.0	11.8	12.4	12.0

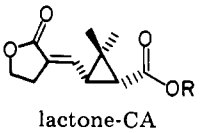
[a] Acid moieties of the starting esters are as follows:



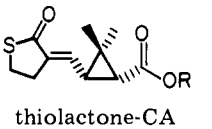
chrysanthemate



pyrethrate



lactone-CA



thiolactone-CA

[b] GLC systems were as follows: A–D and F = 6% QF-1 and E = 8% DEGS; A = 135 °C isothermal, B = 130–180 °C (6 °C/min), C = 150–200 °C (6 °C/min), D = 200 °C isothermal, E = 210 °C isothermal, and F = 180–230 °C (4 °C/min); A–C and F = 20 mL of N_2/min, D = 53 mL of He/min and E = 59 mL of He/min.

Table V. Comparative Sensitized Photoisomerization of Four *d*-2-Octyl Esters and Isomer Ratios of Products on Approaching Equilibrium

measurements	acid moiety of *d*-2-octyl ester: chrysanthemate	pyrethrate	lactone-CA	thiolactone-CA
conversion (μM)[a]				
acetone	2.4	4.2	6	14
isobutyrophenone	9.6	15	18	19
isomer ratio (%) on approaching equilibrium[b]				
1*R*,*cis*(*E*)		19.5	11.5	8.1
1*S*,*cis*(*E*)		11.9	9.4	8.2
1*R*,*cis*(*Z*)		10.3	16.1	13.7
1*S*,*cis*(*Z*)		9.4	15.5	13.4
1*R*,*trans*(*E*)		14.6	15.7	18.4
1*S*,*trans*(*E*)		14.6	15.6	18.5
1*R*,*trans*(*Z*)		10.0	8.2	9.1
1*S*,*trans*(*Z*)		9.7	7.8	9.7

[a] Forty-minute irradiation at (60 μM) ester and (240 μM) isobutyrophenone in hexane. [b] Ninety-minute irradiation for pyrethrate and lactone-CA ester and 150-min irradiation for the thiolactone-CA ester in the isobutyrophenone system as above.

and Related Esters. The reactivity order for the *d*-2-octyl esters on sensitized photodegradation in acetone or combined with isobutyrophenone in hexane is chrysanthemate < pyrethrate < lactone-CA ester < thiolactone-CA ester (Table V). At equilibrium (i.e., 1*R* = 1*S*), the thiolactone-isoCA ester isomer ratio is 2.26:1.66:1.15:1 for trans(*E*):cis(*Z*):trans(*Z*):cis(*E*). Results obtained at preequilibrium conditions (Table V) indicate that this ratio will probably be somewhat different with the pyrethrate and lactone-CA esters.

Toxicity of Kadethrin Isomers and Photoproducts. Kadethrin is more toxic to houseflies and mice than any of its isomers assayed (Table VI). Both insecticidal activity and mouse toxicity are rapidly reduced by exposure to sunlight (Table VI).

Table VI. Toxicity of Kadethrin, Its Isomers, and Photoproducts to Houseflies and Mice

compound	LD_{50}, mg/kg: housefly topical[a]	mouse ip
Kadethrin and Isomers		
isomer kadethrin	2.3	6.8[b]
(1*RS*, *cisE*)-isokad	5.0	13
(1*RS*, *cisZ*)-isokad	21	>500
(1*RS*, *transE*)-isokad	>500	>500
(1*RS*, *transZ*)-isokad		>50
Kadethrin and Photoproducts		
min irradiation		
20	2.4	~14
40	3.2	~18
60	4.3	~25
120	9.3	>125
240	22.1	>125

[a] Values for (1′*R*,2′*S*)- and (1′*S*,2′*R*)-epoxykad are >54 mg/kg. [b] The LD_{50} value is reduced to 1.8 and 2.5 mg/kg, respectively, in mice treated ip with piperonyl butoxide at 150 mg/kg or *S*,*S*,*S*-tributyl phosphorotrithioate at 50 mg/kg at 1 and 6 h, respectively, before kadethrin.

DISCUSSION

The predominant photochemical reactions of kadethrin in the absence of oxygen are isomerizations in the acid moiety to yield eight isomeric compounds as established with the corresponding *d*-2-octyl ester and in part with kadethrin itself (Figures 2 and 3). As with other pyrethroids, these isomerizations occur via the triplet state generated by either direct or sensitized photolysis. Cis–trans isomerization at the cyclopropane ring involves excitation of the carbonyl followed by cleavage of the C1

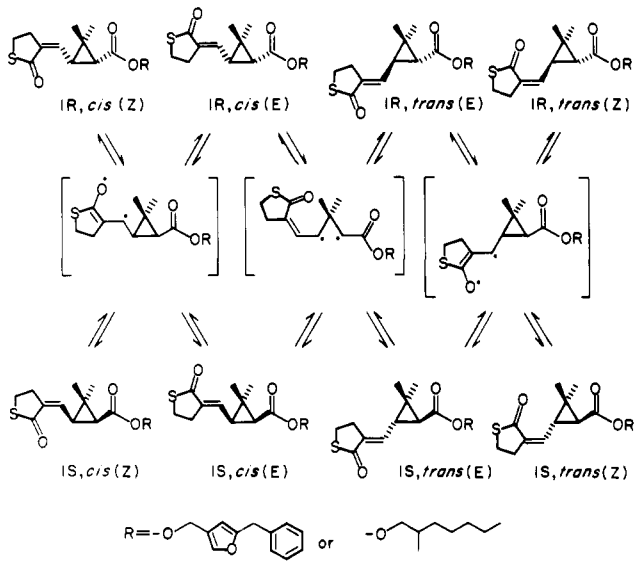
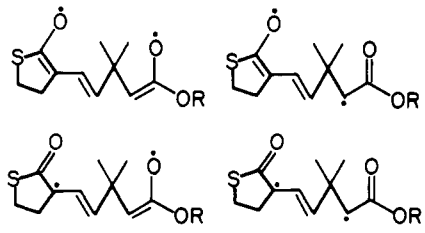


Figure 3. Photoisomerizations at the cyclopropanecarboxylate and vinylcarboxylate substituents of kadethrin or the analogous 2-octyl ester to yield a mixture of eight isomeric esters. All reactions indicated are photochemical processes occurring on direct irradiation or triplet sensitization. Three distinct diradical intermediates are shown but others are also possible (see Discussion).

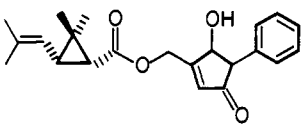
to C3 bond and then recombination of diradical A to a four-isomer mixture with the trans isomers predominating at the photostationary state (Bullivant and Pattenden, 1971; Sasaki et al., 1968; Ueda and Matsui, 1971). *E–Z* isomerization at the side chain is also presumed to involve electronic excitation of the α,β-unsaturated thiolactone carbonyl group to form a diradical intermediate (B) for each cis and trans compound (Coyle, 1978). This allows rotation of the side chain and an *E–Z* isomer mixture is produced on reforming the original conjugated double bond system. While Figure 3 indicates each chromophore reacting separately, it is also possible that both chromophores are involved via diradical structures of the following types:



Although the triplet diradical is probably largely localized as in structures A, B, and C (Figure 2), the resonance states indicated above are also likely to contribute to electron delocalization thus minimizing the preference for cis–trans vs. *E–Z* isomerization reactions. The significant *E*/*Z* ratio differences for the cis and trans compounds probably result from steric preferences in the triplet → ground state decay of the corresponding diradical.

The dicarbonyl compounds (pyrethrate and lactone and thiolactone derivatives) isomerize more rapidly than chrysanthemic acid esters on sensitization with either acetone or isobutyrophenone. This may be due to the dual processes involved, i.e., cyclopropanecarboxylate and vinylcarboxylate isomerizations. It may also result from more efficient energy transfer to a lower energy triplet intermediate stabilized by additional resonance structures as above. Similar isomer ratios are obtained on sensitization with either acetone (Et = 80 kcal/mol) or isobutyrophenone (Et = 73 kcal/mol).

The acid moiety of kadethrin yields products formed by isomerization, rearrangement, oxidation, and hydrolysis or combinations of these reactions (Figure 2). The thiolactone lactone may form via diradical C or the comparable diradical from (1*RS*,cis,trans*E*)-thiolactone-isoCA by attack of the carbonyl oxygen at C-3 of the cyclopropane ring; analogous reactions are known with chrysanthemates (Bullivant and Pattenden, 1971; Sasaki et al., 1970). The thiolactone and cyclopropanecarboxylate ester groups are hydrolyzed to some extent. Epoxidation at the acid side chain yields 1′*R*,2′*S*- and 1′*S*,2′*R*-epoxykad. Several degradation products originate from photodioxygenation of the furan ring to a cyclic ozonide-type peroxide which then decomposes to the benzyloxylactone by migration of the benzyl radical (Ueda et al., 1974). The benzyloxylactone, detected only in the *E* form, decomposes to benzyl alcohol which is then oxidized to benzoic acid. There is a possible difference in the photochemical behavior of the benzylfurylmethyl group in kadethrin and resmethrin. Kadethrin yields no detectable hydroxycyclopentenolone on sunlight irradiation or on rose bengal sensitized photodegradation (in oxygenated methanol followed by $NaBH_4$ treatment; Ueda et al., 1974) whereas with resmethrin the hydroxycyclopentenolone is a major product under both conditions. The reason for this difference was not established. Phenylacetic acid is also formed and it may arise from a hydroxylactone intermediate similar to that obtained from resmethrin (Ueda et al., 1974). BFCA is probably formed by oxidation of BFA liberated on photochemical ester cleavage.



hydroxycyclopentenolone from [1R, cis]-resmethrin

Kadethrin photodecomposes by six major pathways: isomerization of the cyclopropane; isomerization of the side chain of the cyclopropane ring; oxidation of the furan ring to give a cyclic ozonide-type peroxide; epoxidation of the acid side chain; cleavage of the cyclopropanecarboxylate group; cleavage of the thiolactone ring. These processes account for the short residual of kadethrin as an insecticide.

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LITERATURE CITED

Bramwell, A. F.; Crombie, L.; Hemesley, P.; Pattenden, G.; Elliott, M.; Janes, N. F. *Tetrahedron* **1969**, *25*, 1727.
Bullivant, M. J.; Pattenden, G. *Pyrethrum Post* **1971**, *11*, 72.
Coyle, J. D. *Chem. Rev.* **1978**, *78*, 97.
Elliott, M.; Janes, N. F. *Chem. Ind. (London)* **1969**, 270.
Holmstead, R. L.; Casida, J. E.; Ruzo, L. O. *ACS Symp. Ser.* **1977**, *No. 42*, 137.
Horiba, M.; Kobayashi, A.; Murano, A. *Agric. Biol. Chem.* **1977**, *41*, 581.
Lhoste, J.; Rauch, F. *Pestic. Sci.* **1976**, *7*, 247.
Martel, J.; Buendia, J. U.S. Patent 3 842 177, 1974.
Murano, A. *Agric. Biol. Chem.* **1972**, *36*, 2203.

Roussel-Uclaf-Procida, "Kadethrin and Kadethrin 107 Concentrate", Technical Bulletin, Paris, France, Nov 1976.
Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. *J. Agric. Food. Chem.* **1977**, *25*, 1385.
Sasaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1968**, *33*, 676.
Sasaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1970**, *35*, 790.
Ueda, K.; Gaughan, L. C.; Casida, J. E. *J. Agric. Food Chem.* **1974**, *22*, 212.
Ueda, K.; Gaughan, L. C.; Casida, J. E. *J. Agric. Food Chem.* **1975**, *23*, 106.
Ueda, K.; Matsui, M. *Tetrahedron* **1971**, *27*, 2771.

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Studies with 2,4′,5-Trichlorobiphenyl-^{14}C and 2,2′,4,4′,6-Pentachlorobiphenyl-^{14}C in Carrots, Sugar Beets, and Soil

Prannath Moza,* Irene Scheunert, Werner Klein, and Friedhelm Korte

2,4′,5-Trichlorobiphenyl-^{14}C (1.28 kg/ha) and 2,2′,4,4′,6-pentachlorobiphenyl-^{14}C (1.12 kg/ha) were applied each to soil in a lysimeter-type box under outdoor conditions, and carrots were grown. In the following year, sugar beets were grown without retreatment. For the trichlorobiphenyl, only 32.5% of the applied radioactivity was recovered in soil and plants after the first season; 67.5% was lost due to volatilization, uptake by carrot plants was 3.1% of the applied radioactivity. The radioactivity remaining in the soil was partly dispersed to a depth of 40 cm and consisted of 78.7% trichlorobiphenyl, 1.6% soluble conversion products, and 19.7% unextractable residues; in the second year, total recovery as well as the portion of unchanged parent compound decreased. Uptake by sugar beets was only 0.2%. The soluble conversion products in plants and soil were identified as oxygenated metabolites. For the pentachlorobiphenyl, total recovery was 58.5%, and loss due to volatilization 41.5%, uptake by crops 1.4% (after first season), and conversion below 1%; no metabolites were identified.

Polychlorinated biphenyls (PCB's) are still widely distributed pollutants. The fate of these compounds in different ecosystems has attracted much interest. The metabolic conversion of PCB's by various organisms to phenols or their methyl ethers is well known (Block and Cornish, 1959; Hutzinger et al., 1972, 1974; Moza et al., 1973, 1974, 1976a; Herbst et al., 1976; Safe et al., 1974, 1975; Goto et al., 1974a,b; Greb et al., 1975a,b; Lay et al., 1975; Sundström et al., 1975). Some of the phenols are reported to be more toxic than the parent compounds (Yamamoto and Yoshimura, 1973; Yoshimura and Yamamoto, 1973). The accumulation and formation of phenols of a lower chlorinated biphenyl in food crops (Moza et al., 1976b) led us to investigate the total balance of accumulation and the conversion of higher chlorinated isomers in agricultural soil and crops.

The present paper records the balance and conversion of 2,4′,5-trichlorobiphenyl and 2,2′,4,4′,6-pentachlorobiphenyl in carrots (accumulators for lipophilic xenobiotics) in the first year and in the second year sugar beets (a root crop with low oil and high water content).

EXPERIMENTAL SECTION

Apparatus. Packard liquid scintillation counters (Tri-Carb Model 3380 and 3375) with external standardization were used for assaying radioactivity in various extracts. The ^{14}C in insoluble soil and plant residues was determined by liquid scintillation counting after the sample was oxidized to $^{14}CO_2$ in an Oximat (Intertechnique). Radioactive substances were located on TLC plates by scanning, using a scanner supplied by Berthold-Frieseke GmbH, Karlsruhe. An LKB Model 9000 GLC–MS, from LKB Produkter, Bromma, Sweden, was used for mass spectrometry. A 2.0 m × 0.4 cm i.d. glass column packed with 1% OV-1 on Chromosorb W-AW-DMCS 80–100 mesh was used for gas chromatographic separation. The column was programmed from 180 to 240 °C at a rate of 4 °C/min and helium was used as a carrier gas. The mass spectra were recorded at 70 eV.

Reagents. 2,4′,5-Trichlorophenyl-^{14}C (99% pure) and 2,2′,4,4′,6-pentachlorobiphenyl-^{14}C (99.6% pure) synthesized in this laboratory (Sandrock et al., 1978) were uniformly labeled. A scintillation solution based on dioxane was used for assaying various extracts and TLC zones. A toluene based scintillator containing phenethylamine was used for collection and counting $^{14}CO_2$. Thin-layer chromatographic plates were coated with silica gel G (Merck); ready made silica gel plates (Merck, 0.25 mm thick) were also used. For column chromatography silica gel Woelm 0.063–0.2 mm was used. For derivatization of metabolites, diazomethane was prepared from *p*-tolylsulfonylmethylnitrosamide and KOH in diethyl ether.

Procedure. *Plant Growing.* Plants were grown in water-resistant plywood boxes (60 × 60 × 60 cm), one for the experiment with 2,4′,5-trichlorobiphenyl-^{14}C and one for the experiment with 2,2′,4,4′,6-pentachlorobiphenyl-^{14}C. The boxes had perforated bases (to drain the excess water) and were placed in metal trays. They were wrapped with alumina foil to exclude heating by sunlight. About 2.5 cm of washed gravel covered with a layer of well-rotted turf were placed at the bottom of each box. Each box contained 160 kg of soil, 1 cm from the top, and was kept in a large pit with the upper surface at the soil level of the surrounding ground. Air temperature, humidity, and rainfall were recorded during vegetation periods. Table

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