Photodecomposition of Pyrethrin I, Allethrin, Phthalthrin, and Dimethrin

Modifications in the Acid Moiety

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Pyrethrin I, phthalthrin, allethrin, and dimethrin readily decompose when irradiated by a sun lamp, in air, as thin films on glass, the rate of decomposition decreasing in the order listed and each pyrethroid yielding at least 11 products. Hydrolysis does not appear to be a major photochemical reaction for pyrethroids. Work with pyrethrin I and allethrin indicates that the alcohol moiety of pyrethroids suffers photochemical attack, but the chemical reactions involved are not known. The photochemical changes in the acid moiety of each of the four pyrethroids are the same and they involve stepwise oxidation of the *trans*-methyl group of the isobutenyl moiety to the respective alcohol, aldehyde, and carboxylic acid derivatives; oxidation of the isobutenyl double bond to a keto derivative; rupture of this double bond to yield esters of *trans*-caronic acid; and other attacks resulting in at least six additional modifications of the acid moiety.

The insecticidal esters in pyrethrum extract are unstable, converting to noninsecticidal products on exposure to air and sunlight or ultraviolet light. The natural esters and their synthetic analogs, such as allethrin, phthalthrin, and dimethrin, are nonpersistent insecticide chemicals partly as the result of their ease of photodecomposition. It is necessary to understand the photochemistry of pyrethroids to predict conditions for their use, or to devise modifications in structure necessary to achieve an appropriate degree of persistence in insect control. The available chemical information on the photodecomposition of pyrethroids relates primarily to the constituents of pyrethrum extract and in no case identifies the decomposition products. The slow progress in this important area of research is the result of the complex nature of the chemistry involved and the lack of adequate procedures for detecting, separating, and determining the products encountered.

There is some evidence that the photodecomposition of the natural esters in pyrethrum extract involves modification of the acid moieties, but data also exist which support the proposal that the alcohol portions are primarily or importantly involved. These apparent contradictions probably arise from differences in purity of the irradiated materials, the irradiation conditions, the source and spectral range of the light used, the method of determining the degradation products, etc. (Brooke, 1967; Glynne Jones, 1960; Head *et al.*, 1968). Generally, the pyrethroids used were not pure; the conditions of exposure to light varied; and consideration was not always given to the role played by chlorophyll and other impurities in the pyrethrum extract used, in the mechanism of pyrethroid photodecomposition.

The exposure of highly purified pyrethrum concentrate in light petroleum in a closed vessel to direct sunlight, at 30° C. for 3 months, produced resinous material which, after hydrolysis, yielded crystalline chrysanthemumic and chrysanthemumdicarboxylic acids; this finding supports the view that the photodecomposition involves only the cyclopentenolone portion of the esters, the acids not being attacked (Campbell and Mitchell, 1950). When films of pyrethrum oleoresin extract were irradiated with a tungsten light, Brown and Phipers (1955) found that the green-colored material in the extracts catalyzed degradation of the chrysanthemumic acid moiety but not the slower changes taking place in the cyclopentenolone moiety. Freeman (1956) showed that, under ultraviolet light irradiation, the pyrethrins degraded faster than cinerins, allethrin degraded at the slowest rate, and the photodegradation products of the pyrethrins showed infrared spectral changes consistent with chemical modifications occurring only in the side chain of the cyclopentenolone moiety. Irradiation studies with a tungsten lamp showed that pyrethrin I and cinerin I degraded more rapidly than pyrethrin II and cinerin II, that the cinerins were more stable than the pyrethrins, and that the green coloring pigment accelerated the decomposition of the chrysanthemumate moiety (Brown *et al.*, 1957). Exposure of pyrethrin derivatives on Kieselguhr G [as a coating on thin-layer chromatography (TLC) plates] to sunlight or to long-wavelength ultraviolet light, and resolution of the products formed prior to the use of selected chromogenic reagents yielded data showing that the photostability decreases in the order of pyrethrin II, pyrethrin I, isopyrethrin II, and isopyrethrin I; that each of these compounds gives an intermediate product (referred to as "peroxide") detectable with potassium iodide–acetic acid–starch reagent, which converts on longer irradiation to a fluorescent derivative(s) ("lumi" derivative) that does not move from the origin in the solvent system used; and that the photodecomposition products are of greatly reduced insecticidal activity (Stahl, 1960). Gas-liquid chromatography (GLC) analysis of the products formed on exposure of pyrethroids to sunlight, as thin films on glass surfaces, showed that pyrethrins degrade faster than cinerins, the chlorophyll pigments in pyrethrum

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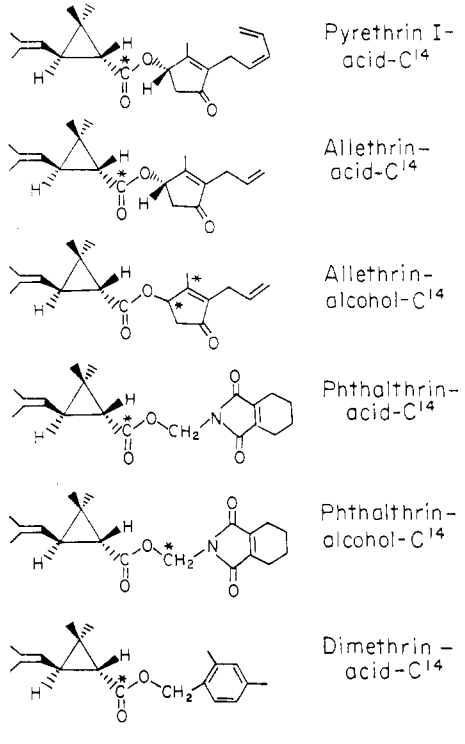
extract catalyze decomposition of the chrysanthemumic acid moiety, and pyrethrin I, cinerin I, jasmolin I, and allethrin give products which separate from their precursors by GLC in a manner suggesting they are formed by degradation of the chrysanthemumate moiety only, the alcohol portion remaining unchanged (Head *et al.*, 1968).

In the quantitative study reported here, use was made of C^{14}-labeled pyrethroids of high stereochemical purity prepared from C^{14}-labeled *d-trans*-chrysanthemumic acid (Nishizawa and Casida, 1965) or from C^{14}-labeled alcohols (Yamamoto and Casida, 1968) and, after exposure of the radioactive pyrethroids as thin films on glass in air to a sun lamp, of TLC methods to resolve the photodecomposition products. This was done directly on the products or on the acids obtained from them by hydrolysis. Pyrethrin I, allethrin, phthalthrin, and dimethrin were intercompared as to their rates of photodecomposition and changes occurring on their acid moieties upon exposure to light. The TLC identification was guided by the use of authentic preparations of unlabeled chrysanthemumic acid derivatives.

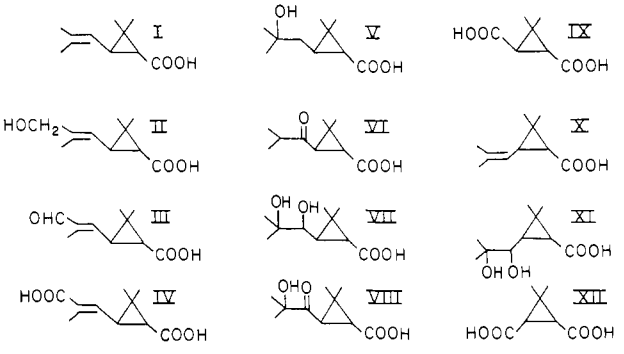
MATERIALS AND METHODS

Experimental Chemicals. The pyrethroids studied in C^{14}-labeled and unlabeled forms, the positions of labeling, and the stereochemistry of the samples utilized, unless specifically indicated otherwise, were as follows:



Six C^{14}-labeled preparations were used: pyrethrin I-acid-C^{14} and allethrin-acid-C^{14}, each of 1.3 mc. per mmole; phthalthrin-acid-C^{14} and dimethrin-acid-C^{14}, each of 0.294 mc. per mmole; allethrin-alcohol-C^{14} prepared from *dl*-allethrolone-C^{14} of 0.162 mc. per mmole; and phthalthrin-alcohol-C^{14} labeled in the *N*-methylene position and of 0.276 mc. per mmole (Yamamoto and Casida, 1968). Each labeled pyrethroid was of greater than 99% radiochemical purity, based on TLC as described later, with the exception of pyrethrin I-acid-C^{14} which was of 94% purity due to partial decomposition during storage in hexane solution. The unlabeled allethrin preparation used was the *α-dl-trans* material (m.p. 49.5° C.; reported 50.5–1° C.) consisting of a mixture of *d*-allethronyl *l-trans*-chrysanthemumate and *l*-allethronyl *d-trans*-chrysanthemumate (Schechter *et al.*, 1951) obtained by recrystallization of technical allethrin (Sumitomo Chemical Co., Osaka, Japan) from hexane. Unlabeled phthalthrin and dimethrin, as the *dl-cis,trans*-chrysanthemumates, were provided as 99% pure materials by Sumitomo Chemical Co. and Benzol Products Co., Newark, N.J., respectively. Unlabeled pyrethrin I, with the configuration of the natural ester, and the mixture of six esters making up natural "pyrethrins" were obtained from Izuru Yamamoto.

The following derivatives of chrysanthemumic acid with the indicated stereochemical configurations and number designations were used as reference standards:



Compounds I to V and X were prepared in this laboratory (Yamamoto *et al.*, 1968) and compounds VI to VIII and XI were obtained from Masanao Matsui (University of Tokyo, Tokyo, Japan). In addition, compound VII was prepared by oxidation of *dl-trans*-chrysanthemumic acid with potassium permanganate in aqueous sodium hydroxide solution according to the procedure of Matsui *et al.* (1956, 1963), yielding a product identical to the sample of compound VII provided by Matsui based on the fact that they both gave the same R_f values on TLC in several solvent systems. [This procedure also produced a second product which had a low R_f value (0.11, solvent system A, see below) but was found to be impure even after repeated recrystallization from nitromethane.] A second preparation of compound VIII was made by oxidation of *dl-trans*-chrysanthemumic acid with potassium permanganate in aqueous sodium hydroxide solution according to the procedure of Matsui *et al.* (1963), yielding a pure product (m.p. and mixed m.p. 142–3° C.; lit. 142–3° C.) (C %, calculated 59.98, found 59.80; H %, calculated 8.05, found 8.09). A third preparation of this same ketol acid (VIII) was made by oxidation of each of *dl-trans*-chrysanthemumic acid and *α-dl-trans*-allethrin with 1.5 times the amount, by weight, of potas-

sium permanganate in acetone solution, yielding a pure product with appropriate melting point, mixed melting point, and elemental analyses. Compounds IX and XII were synthesized by ozonolysis of compound I (m.p. 53.5–4.5° C.) and compound X (m.p. 117° C.) in 44 and 34% yields, respectively, according to the method of Crombie *et al.* (1957). The melting points and elemental analyses of the caronic acids approximated those anticipated: *trans*-isomer (compound IX) (m.p. 218–21° C.; lit. 218–20° C.) (C %, calculated 53.16, found 52.62; H %, calculated 6.37, found 6.08); *meso-cis*-isomer (compound XII) (m.p. 174–6° C.; lit. 178–9° C.) (C %, calculated 53.16, found 53.52; H %, calculated 6.37, found 6.44). A second preparation of compound XI was made by oxidation of *dl-cis*-chrysanthemumic acid with potassium permanganate in aqueous sodium hydroxide solution according to the procedure of Matsui and Yoshioka (1964) (m.p. and mixed m.p. 194–6° C.; lit. 189° C.) (C %, calculated 59.39, found 59.65; H %, calculated 8.97, found 9.38).

Three chrysanthemumdicarboxylates were used for cochromatographic comparisons with certain photodecomposition products. These are referred to by Yamamoto and Casida (1966) as *O*-demethyl allethrin II, *O*-demethyl phthalthrin II, and *O*-demethyl dimethrin II; they have a carboxylic acid group in place of the *trans*-methyl group of the isobutenyl side chain in the chrysanthemumate moiety.

Photodecomposition Procedures and Analytical Methods. Hexane solutions of the pyrethroids were evaporated at 25° C. to form a film on the inside surface (19.6 sq. cm.) of the lower portion of a 5-cm. Petri dish. The amount of deposit was either 50 μg. (2.6 μg. per sq. cm.) of labeled compound alone, or 1 mg. of unlabeled pyrethroid mixed with 50 μg. of the labeled pyrethroid (total of 54 μg. per sq. cm.). These pyrethroid films or coatings were exposed to air in darkness at 25° C. or were irradiated at a distance of 30 cm. below a 275-watt sun lamp (General Electric Co., Cleveland, Ohio) which resulted in elevation of the temperature at the glass surface to approximately 40° C. After various time intervals of exposure, the products were dissolved in methanol-ether mixture (1 to 1) and analyzed by TLC either by spotting directly (as esters) without saponification or by spotting the acid moieties obtained by hydrolysis with 2 ml. of 0.1*N* methanolic sodium hydroxide solution in a 5-ml. sealed glass ampoule for 1 hour in a boiling water bath. The acid moieties were recovered by evaporating the solution to dryness under nitrogen, adding 2 ml. of 5% aqueous sodium hydroxide, extracting the aqueous alkaline solution six times with ether to remove nonacidic compounds partially, adding 2 ml. of 10% hydrochloric acid at 5° C. to acidify the aqueous phase, and extracting the aqueous acid solution 12 times with an equal volume of ether. To this ether extract were added 5 ml. of ether previously saturated with ammonia by shaking with concentrated aqueous ammonium hydroxide solution (to minimize volatilization of the acids during evaporation), and the mixture was concentrated under a mild stream of nitrogen for final quantitative spotting, with repeated ether rinses, onto 20 × 20 cm. silica gel F_{254} precoated plates (Brinkman Instruments, Inc., Westbury, N.Y.). The plates were developed with benzene (saturated with formic acid)-ether mixture (1 to 20) (solvent system A), in the first direction, and with benzene (saturated with formic acid)-ether mixture (10 to 3) (solvent system B), in the second direction. This solvent system was the best of 22 solvent combinations investigated for resolution of the chrysanthemumic acid derivatives; however, saturation of benzene with formic acid was optional in the TLC resolution of the esters. Pyrethroids, photodecomposition products, and chrysanthemumic acid derivatives were detected in 3- to 30-μg. amounts by application of 20% phosphomolybdic acid in absolute ethanol to the TLC plate followed by heating for 10 minutes at 110° C. (Stahl, 1960). *trans*-Caronic acid (IX) was, at times, rendered visible with 0.3% bromocresol green in 80% by volume methanol containing 8 drops of 30% sodium hydroxide per 100 ml. (Kirchner *et al.*, 1951). Radioautography with No-Screen x-ray film was used for location of radioactive products and selected areas of the coating were scraped from the plates into scintillation vials for radioactivity counting. C^{14}-labeled products were tentatively identified by cochromatography with unlabeled authentic reference compounds.

The conditions for these studies were determined in preliminary experiments designed to select the most appropriate photodecomposition, product-separation, and analytical procedures. In the preliminary work, one-dimensional TLC with solvent system B was used.

Toxicity studies were made on unlabeled pyrethroids photodecomposed for 24 hours under the sun lamp as described above, except that the films were of 1.5 mg. per sq. cm. Included in this study were natural "pyrethrins," α-*dl-trans*-allethrin, phthalthrin, and dimethrin. The toxicity comparisons involved these materials with or without the described photodecomposition exposure prior to injecting them in dimethyl sulfoxide solution intraperitoneally into male white mice and applying them topically in acetone solution to female houseflies (*Musca domestica* L., SCR strain) for 24-hour mortality determinations.

RESULTS

Preliminary Studies. The results obtained in the preliminary work indicate that allethrin photodecomposes to give the same qualitative pattern of products when irradiated with either sunlight or the sun lamp and when films of the pyrethroid on glass, filter paper, or the TLC plate are used; there is extensive loss by volatilization of allethrin-acid-C^{14} from the glass surface when the exposure is made for more than 2 hours with films of 2.6 μg. per sq. cm. but not with films of 54 μg. per sq. cm.; the R_f values of the photodecomposition products are always lower than those found for the original pyrethroid and some of the products remain at the origin; the ester group probably does not hydrolyze during photodecomposition because the same pattern of products is obtained for allethrin and phthalthrin with the acid- and the alcohol-labeled preparations; the alcohol

moiety of the alcohol-labeled allethrin suffers modification on irradiation of the pyrethroid on a glass surface for 24 hours, because a mixture of the 2,4-dinitrophenylhydrazones of allethrolone-C^{14} and allethrolone-C^{14} methyl ether can be produced (method of Yamamoto *et al.*, 1968) from allethrin which has not been photodecomposed but not from a photodecomposed sample; the chrysanthemumate moiety of each pyrethroid is modified during a 24-hour irradiation period because saponification of the products from the acid-labeled samples liberates a variety of labeled acids which have the same chromatographic characteristics when derived from any one of the pyrethroids tested, but *trans*-chrysanthemumic acid is not among the liberated products.

Toxicity of Photodecomposition Products. In natural "pyrethrins," *α-dl-trans*-allethrin, phthalthrin, and dimethrin, irradiation for 24 hours under a sun lamp gives a mixture of products that is much less toxic than the original or parent compound. The respective LD_{50} values are increased fourfold or more for "pyrethrins," allethrin, and phthalthrin on intraperitoneal administration to mice and twofold or more for phthalthrin and dimethrin and sevenfold or more for "pyrethrins" and allethrin when applied topically to houseflies.

Relative Rates of Photodecomposition. Each of the four pyrethroids suffers little, if any, loss as a result of volatilization or conversion to other materials when held for up to 32 hours in the dark as a film or thin coating on a glass surface (54 μg. per sq. cm.). On exposure to sun lamp irradiation, they suffer loss by both volatilization and conversion to more polar materials, the rate of transformation varying dramatically with the alcohol moiety—for example, the number of hours of exposure resulting in 90% loss of original compound is approximately 0.2, 8, 4, and 16, respectively, for pyrethrin I, allethrin, phthalthrin, and dimethrin (Figure 1). The increased volatility on exposure to the sun lamp probably results, in part, from the elevated temperature and is greatest with dimethrin and least with phthalthrin. Certain photodecomposition products must volatilize under the conditions of the experiment because, for a given interval after several hours of irradiation, the loss in the total amount of radiocarbon is greater than the amount of the original compound present in the product mixture at the beginning of the interval. Accumulation of photodecomposition products was most prominent with pyrethrin I and phthalthrin, because of their rapid conversion to more polar derivatives which are apparently of low volatility, whereas, with dimethrin, the low rate of photodecomposition and partial volatilization of the products resulted in little accumulation of photodecomposed materials. The photodecomposition products derived from the acid-C^{14}- and alcohol-C^{14}-labeled preparations show a similar persistence pattern with allethrin and phthalthrin, suggesting that the products are esters and not hydrolysis products of the original or modified parent compound and that the ester linkage remains intact (Figure 1). Also, since each of the pyrethroids studied has the same acid moiety and yet the esters vary greatly in stability, it is evident that, at least with pyrethrin I, some portion of the alcohol moiety undergoes rapid photodecomposition during irradiation.

Nature of Photodecomposition Products. Each of the four pyrethroids studied photodecomposes, on exposure as a film or coating (2.6 μg. per sq. cm.) to the sun lamp for 8 hours, to give at least 11 to 15 products, no one of which, other than the material at the origin, represents a major part of the radiocarbon. As shown in Figure 2, the distribution patterns of the photodecomposition products from the acid-C^{14}-labeled preparations are unique for each pyrethroid, suggesting that the products are different with each pyrethroid and, therefore, probably do not arise from hydrolysis of the ester grouping. The TLC distribution patterns obtained after irradiation of the acid-C^{14}- and alcohol-C^{14}-labeled preparations of allethrin and of phthalthrin appear to be the same for each pyrethroid and show no difference in the products formed with either position of labeling, indicating that ester hydrolysis is not a major reaction in the photodecomposition. The radiocarbon unaccounted for in Figure 2 is associated almost entirely with photodecomposition products appearing in TLC regions other than those shown by the spots illustrated; specifically, the loss is: pyrethrin I 36.6%, allethrin 17.7%, phthalthrin 38.9%, and dimethrin 10.6%. Similar studies with varying periods of irradiation indicate that, with each compound, the photodecomposition products of intermediate R_f values predominate at early stages in the photodecomposition while those at the origin predominate at later stages and that only in the case of dimethrin is there little accumulation of products at the origin; apparently, the products of intermediate R_f values are lost both by volatilization and by further decomposition to products remaining at the origin.

The identity of the ester photodecomposition products is not known because none of them cochromatographs with any of the few reference compounds available for this purpose. Thus, none of the products of photodecomposition of allethrin, phthalthrin, or dimethrin cochromatographs with *O*-demethyl allethrin II, *O*-demethyl phthalthrin II, or *O*-demethyl dimethrin II, respectively—i.e., with the products containing a carboxylic acid group in place of the *trans*-methyl group in the isobutenyl side chain of the respective pyrethroid.

Nature of Acid Moieties in Photodecomposed Pyrethroids. Saponification of the mixture of esters obtained from each of the pyrethroids, irradiated as a film or coating (2.6 μg. per sq. cm.) for 8 hours, liberates 16 acids, 12 of which always appear (●, Figure 3) and four of which sometimes appear in small amounts (○, Figure 3). Figure 3 shows the TLC characteristics of these acids and gives the average amounts of the liberated acids recovered, which do not vary in chromatographic characteristics or amount recovered for the four pyrethroids studied. The averages and standard deviations given in Figure 3 are derived from the eight sets of data obtained in two experiments with each of pyrethrin I, allethrin, phthalthrin, and dimethrin, and are calculated in terms of the total radiocarbon applied to the TLC plate. The 19.9% of radiocarbon unaccounted for is due almost entirely to other minor photodecomposition

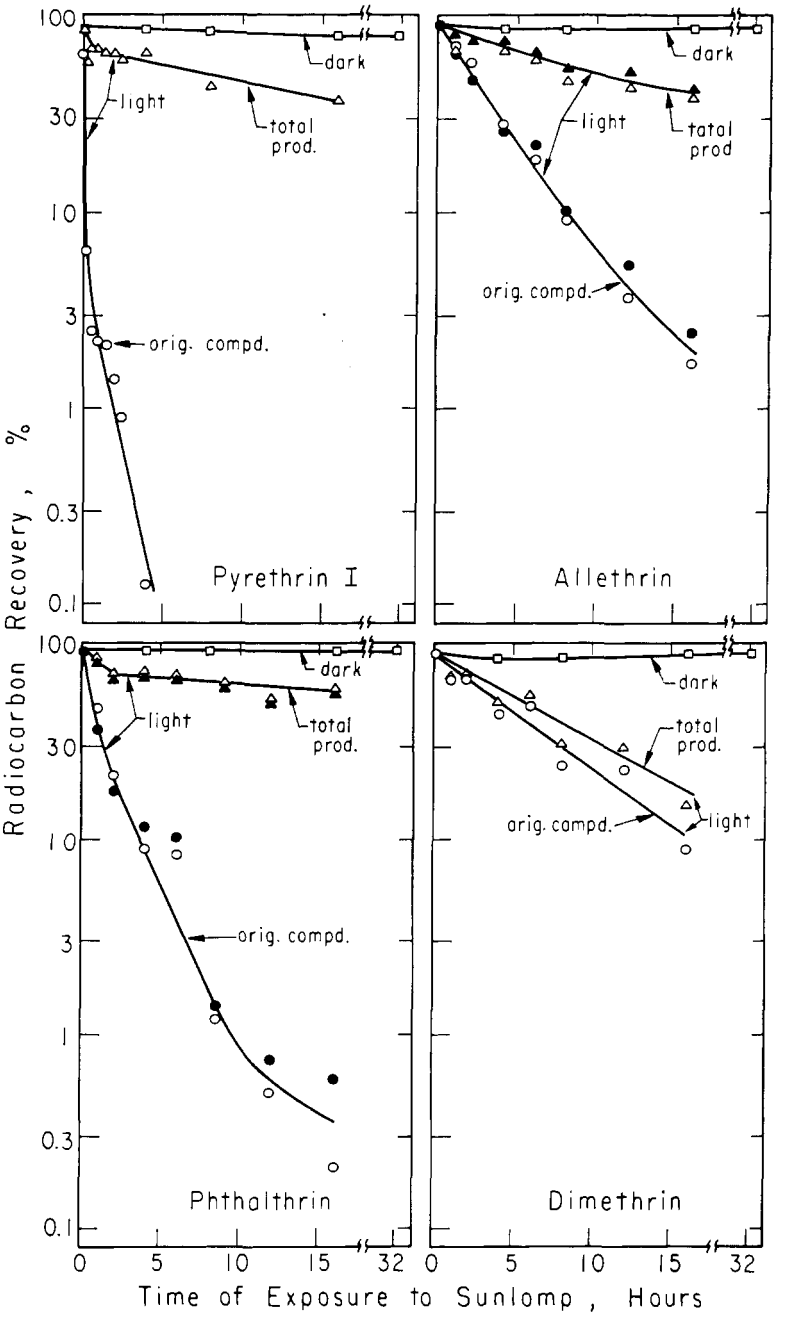


Figure 1. Rate of loss by photodecomposition and volatilization of radiolabeled pyrethrin I, allethrin, phthalthrin, and dimethrin exposed as thin films on a glass surface in the dark or to a sun lamp

□ Dark. Recovery of unmodified pyrethroid with acid-C^{14}-labeled preparations of pyrethrin I and dimethrin or average of data with acid-C^{14}-labeled and alcohol-C^{14}-labeled preparations of allethrin and phthalthrin
Light. Recovery of unmodified pyrethroid plus photodecomposition products with acid-labeled (△) and alcohol-labeled preparations (▲)
Light. Recovery of unmodified pyrethroid with acid-labeled (○) and alcohol-labeled preparations (●)

products (including those indicated by ○) appearing in TLC regions other than those shown by the dark spots (indicated by ●). Only that portion of the acid moiety recovered in ether on extraction of the saponified mixtures, after acidification, is considered and this amount averages 43.5 ± 8.7% of the radiocarbon content of the photodecomposed esters.

Certain known acids (V, VII, VIII, X, XI, and XII; ◌, Figure 3) do not cochromatograph with any major or minor product among the acids recovered from the photodecomposed pyrethroids, while chrysanthemumic acid (I) and five other acids (II, III, IV, VI, and IX) consistently cochromatograph with six of the acids liberated from each pyrethroid. The labeled acid designated

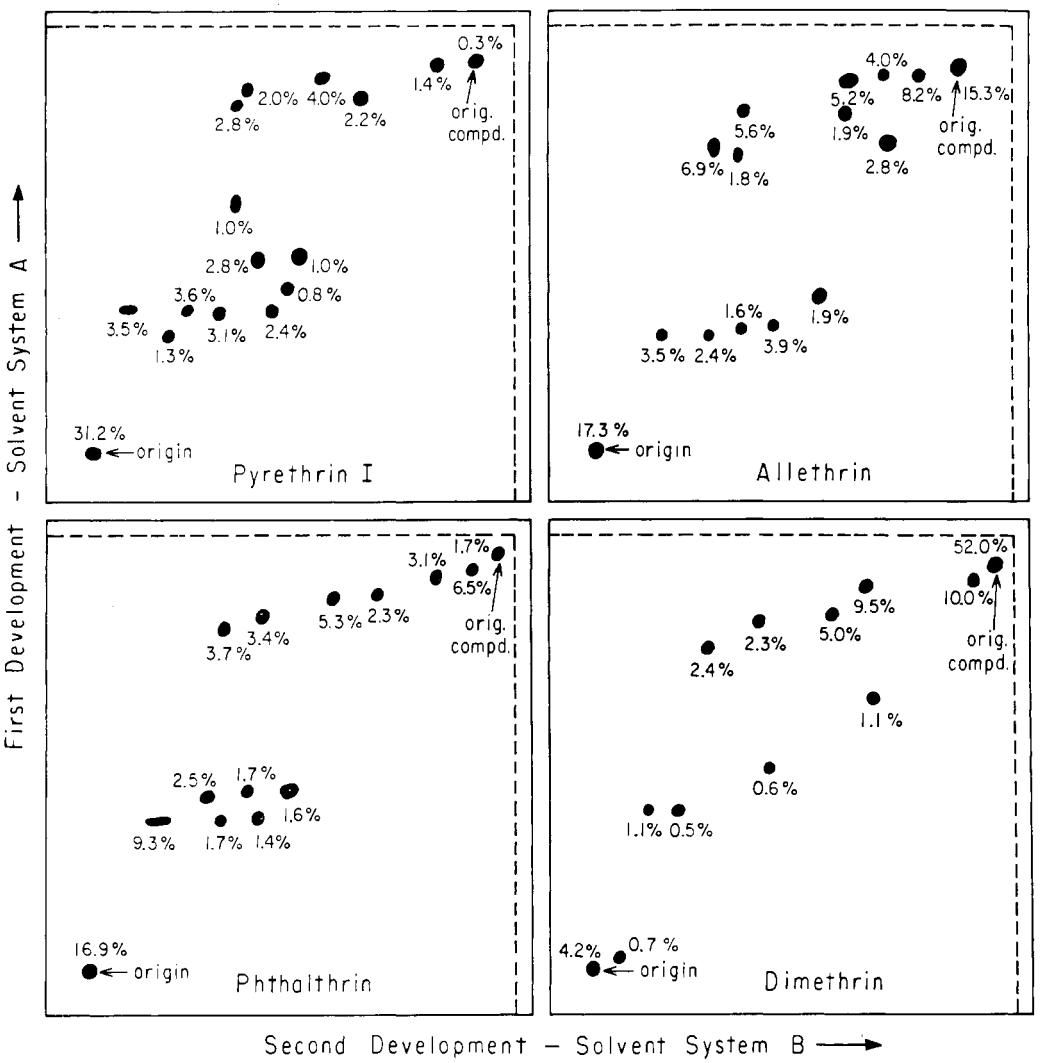


Figure 2. Illustrative chromatograms showing TLC characteristics and yield of products formed from acid-C^{14}-labeled preparations of pyrethrin I, allethrin, phthalthrin, and dimethrin exposed as thin films on a glass surface to a sun lamp for 8 hours

Percentage values relative to total radiocarbon applied to TLC plate

as IX converts, on reaction with diazomethane, to a product that cochromatographs in solvent system B with the product from methylation of *trans*-caronic acid with diazomethane, further confirming the identity of this acid. Thus, only five of the acid moieties are tentatively identified and the others (*a* to *f*) remain of unknown structure. Unknown *b* cochromatographs with the unidentified acid formed on potassium permanganate oxidation of *dl-trans*-chrysanthemumic acid in aqueous sodium hydroxide solution (see above). On irradiation for 24 hours, *trans*-chrysanthemumic acid is no longer present in the acids liberated on saponification. When the material remaining at the origin after TLC of the pyrethroids (which have been irradiated for 8 hours) is recovered from the plate and hydrolyzed, the acids recovered correspond to spots *b*, *d*, IX, II, *f*, and III (Figure 3), the major one being IX. It is clear that esters of *trans*-caronic acid are important constituents of the photodecomposition products of pyrethroids, including those that remain at the origin on chromatography of the products before hydrolysis.

When the photodecomposition products from 2 hours of irradiation of pyrethrin I and allethrin are separated by TLC and then hydrolyzed, more *trans*-chrysanthemumic acid is recovered from the pyrethrin I than from the allethrin; this is probably the result of more rapid conversion to polar products of the pentadienyl than of the allyl side chain during irradiation coupled with the same rate of photodecomposition, in each case, of the rest of the molecule. It is likely that the photodecomposition product chromatographing just below dimethrin in Figure 2 is modified from the dimethrin structure only in having the *trans*-methyl group in the isobutenyl side chain oxidized to an aldehyde group because, on hydrolysis, the acid recovered cochromatographs with compound III.

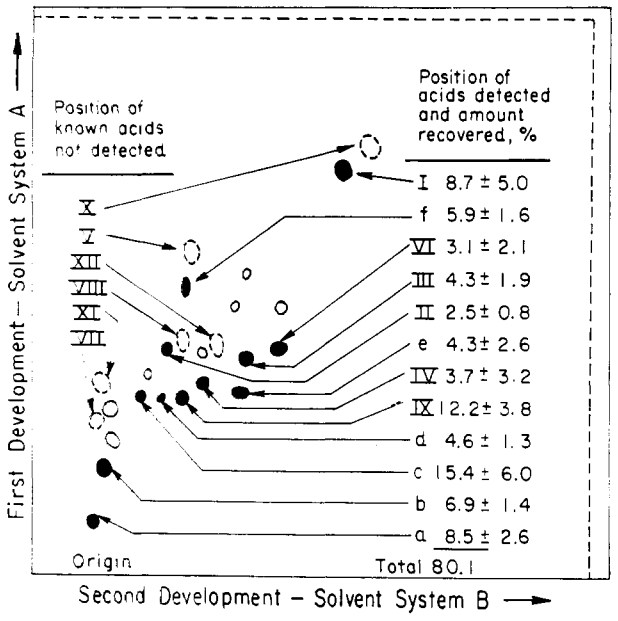


Figure 3. Illustrative chromatogram showing TLC characteristics of unlabeled known acids and C^{14}-labeled acidic products recovered on saponification of samples of acid-C^{14}-labeled preparations of pyrethrin I, allethrin, phthalthrin, and dimethrin exposed as thin films on a glass surface to a sun lamp for 8 hours

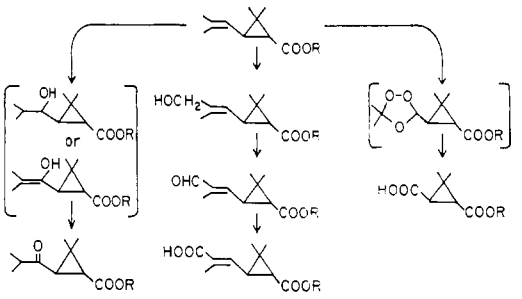


Figure 4. Partial pathways involved in photodecomposition of acid moiety of pyrethroids

R. Alcohol moiety or alcohol moiety modified by photodecomposition

DISCUSSION

In confirmation of previous studies, it is evident that pyrethroid decomposition in air is greatly enhanced by light and markedly influenced by the nature of the alcohol moiety. The photodecomposition reactions are very complex, resulting in formation of a large number of products, most if not all of which probably are esters; the alterations on the chrysanthemumate moiety are independent of the alcohol moiety present; and in the case of certain compounds, such as pyrethrin I, the alcohol moiety is most susceptible to photodecomposition while in others, such as dimethrin, the acid moiety probably photodecomposes most rapidly.

The identity of the photodecomposition products, as such, is not known; however, much is known about the structure of some of the acids released on their saponification. Three of the acids arise in various stages of the oxidation of the *trans*-methyl group in the isobutenyl moiety, having alcohol, aldehyde, or carboxylic acid functions in this position. [These oxidations are similar to those encountered in the biological oxidations of pyrethroids in houseflies (Yamamoto and Casida, 1966; Yamamoto *et al.*, 1968).] Two other acids arise from oxidative attack at the double bond of the isobutenyl moiety, *trans*-caronic acid being the major product of interest from this source.

The nature of the acid moieties identified suggests that the photodecomposition pathways shown in Figure 4 are among those involved in the photodecomposition of pyrethroids. It is known that light catalyzes *cis-trans*-isomerization of methyl *trans*-chrysanthemumate (Sasaki *et al.*, 1968), but there is no evidence that this isomerization occurs in photodecomposition of pyrethroids, *cis*-chrysanthemumic acid (X) and *meso-cis*-caronic acid (XII) not being recovered on hydrolysis of the photodecomposed esters, even after extended irradiation periods (24 hours). However, certain unidentified products might arise from *cis-trans*-isomerization. Photochemical cleavage of the cyclopropane ring occurs with certain chrysanthemumic acid derivatives (Shaffer, 1968); but the degree of involvement of ring cleavage in generating the modified acid moieties from pyrethroids remains unknown. Reactions at two or more sites on the chrysanthemumate moiety may contribute to the large number of products formed.

Photodecomposition reduces or destroys the insecticidal activity of the pyrethroids and also reduces the mammalian toxicity. Although photodecomposition restricts the areas in which pyrethroids are useful in insect control, it also minimizes any potential hazard from toxic residues.

Possibly, the persistence of pyrethroids can be improved by using compounds with groupings which are more stable to photodecomposition. Since the isobutenyl moiety is involved in the photodecomposition to some extent, and is not essential for high insecticidal activity (Berteau *et al.*, 1968; Matsui and Kitahara, 1967), replacement of this grouping by others which photodecompose less rapidly might extend the residual life of pyrethroids. Photodecomposition of the cyclopentenolone esters probably occurs by modifications in the three- to five-carbon aliphatic side chain of the alcohol portion because changes in the nature of this side chain greatly influence the photodecomposition rate. The useful residual life can possibly be prolonged by removal of photosensitizers from pyrethrum extract, by addition of photostabilizers to formulations of pyrethrum or of synthetic pyrethroids, or by modifying the structure of the acid and alcohol moieties of synthetic pyrethroids.

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LITERATURE CITED

Berteau, P. E., Casida, J. E., Narahashi, T., *Science* **161,** 1151 (1968).
Brooke, J. P., *Pyrethrum Post* **9** (1), 18 (1967).
Brown, N. C., Hollinshead, D. T., Phipers, R. F., Wood, M. C., *Soap Chem. Specialities* **33** (9), 87; (10), 91 (1957).
Brown, N. C., Phipers, R. F., *Pyrethrum Post* **3**(4), 23 (1955).
Campbell, A., Mitchell, W., *J. Sci. Food Agr.* **1,** 137 (1950).
Crombie, L., Harper, S. H., Sleep, K. C., *J. Chem. Soc.* **1957,** p. 2743.
Freeman, S. K., *Soap Chem. Specialties* **32** (2), 131; (3), 150 (1956).
Glynne Jones, G. D., *Ann. Appl. Biol.* **48,** 352 (1960).
Head, S. W., Sylvester, N. K., Challinor, S. K., *Pyrethrum Post* **9** (3), 14 (1968).
Kirchner, J. G., Miller, J. M., Keller, G. J., *Anal. Chem.* **23,** 420 (1951).
Matsui, M., Kitahara, T., *Agr. Biol. Chem. (Japan)* **31,** 1143 (1967).
Matsui, M., Uchiyama, M., Yoshioka, H., *Agr. Biol. Chem. (Japan)* **27,** 554 (1963).
Matsui, M., Yamashita, K., Miyano, M., Kitamura, S., Suzuki, Y., Hamuro, M., *Agr. Biol. Chem. (Japan)* **20,** 89 (1956).
Matsui, M., Yoshioka, H., *Agr. Biol. Chem. (Japan)* **28,** 32 (1964).
Nishizawa, Y., Casida, J. E., J. AGR. FOOD CHEM. **13,** 525 (1965).
Sasaki, T., Eguchi, S., Ohno, M., *J. Org. Chem.* **33,** 676 (1968).
Schechter, M. S., LaForge, F. B., Zimmerli, A., Thomas, J. M., *J. Am. Chem. Soc.* **73,** 3541 (1951).
Shaffer, G. W., "Photochemistry of Conjugated Cyclopropyl and Ethylenic Ketones," Ph.D. dissertation, University of California, Berkeley, 1968.
Stahl, E., *Arch. Pharm.* **293/65,** 531 (1960).
Yamamoto, I., Casida, J. E., *Agr. Biol. Chem. (Japan)* **32,** 1382 (1968).
Yamamoto, I., Casida, J. E., *J. Econ. Entomol.* **59,** 1542 (1966).
Yamamoto, I., Kimmel, E. C., Casida, J. E., University of California, Berkeley, unpublished results. 1968.

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