Simultaneous Dermal Exposure to Captan and Benomyl by Strawberry Harvesters

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Ten strawberry harvesters were monitored during working hours for dermal exposure due to captan [3a,4,7,7a-tetrahydro-*N*-[(trichloromethyl)thio]phthalimide] and benomyl [methyl 1-[(butylamino)-carbonyl]-1*H*-benzimidazol-2-ylcarbamate]. The average dermal exposure was found to be 39.01 mg h^{-1} $person^{-1}$ for captan and 5.39 mg h^{-1} $person^{-1}$ for benomyl. The ratio of the dermal concentration of captan and benomyl was found to be similar to the ratio for dislodgeable foliar residues of the same two pesticides from strawberry plants in the same plot. Productivity, as measured by the quantity of fruit picked, and dermal exposure of individuals to benomyl correlate positively. The study was designed to measure left- and right-handed dermal exposure and to determine dextral preference among strawberry pickers.

The determination of dermal exposure to pesticides by harvesters of fruit and field crops forms the basis for establishing reentry intervals. These intervals are designed to permit agricultural field workers to reenter pesticide-treated plots without suffering any ill effects. The regulation of organophosphorus insecticide residues for farm worker protection has been recently discussed by Popendorf and Leffingwell (1982). Most of the previous attempts to correlate dermal human exposure with dislodgeable foliar pesticide residues have dealt with a single pesticide [e.g., Popendorf (1980)]. A field study has now been conducted in which strawberry harvesters were monitored in a plot that had been treated with two fungicides, captan and benomyl, to control mainly botrytis and powdery mildew. The major aim of the experiment was to answer a key question: Does the same proportional relationship exist between two pesticides occurring as dislodgeable foliar residues and dermal deposits?

EXPERIMENTAL SECTION

Description of Field Study. A cooperative strawberry farm located in the Pajaro Valley, near Salinas, CA, was chosen as the site. The date of the study was May 19, 1982. The monitoring was conducted during the morning (0800–1000 h) when the temperature ranged between 53 and 66 °F, and the wind was recorded at less than 7.4 km/h. Ten harvesters who volunteered for this study were provided with light cotton gloves, used in photographic darkrooms, marked with indelible numbers to identify each subject and the letters "R" and "L" to designate the right and left hand. Each volunteer was also provided with dermal dosimeters fastened to the outer side of the forearm, 6 in. above the wrist, with surgical tape. This dosimeter consisted of a 12-ply 3 × 3 in. surgical gauze placed into a slightly larger glossy-paper envelope with a circular 60 mm diameter hole facing the outside (away from the skin) and a piece of polyethylene film placed on the other side of the gauze nearer the skin to serve as a moisture barrier. In this way, 28 cm^2 of the gauze pad was exposed to the environment. The workers were not required to wear any special protective clothing other than those normally worn early in the morning, like slacks and long-sleeve shirts. Subjects were measured for height and weight; age, sex, and manual preference were recorded.

Subjects went about their normal work, picking strawberries in a bending or squatting position. For the comfort of the workers, the gloves and forearm dosimeters were removed from the subjects after about 2 h and stored in plastic bags, packed with "dry ice" during transport, and kept in freezers until the extraction and analyses could be performed. Productivity for each subject was recorded as "number of crates harvested" during the monitoring period.

Forty-eight strawberry leaf disks for dislodgeable residue analyses were taken from different plants diagonally across the strawberry plot with a mechanical leaf punch. This tool is equipped with a 3 cm diameter circular die and attached with a screw cap to a 4-oz widemouth glass jar. Details of this and other sampling techniques are described by Popendorf et al. (1982a).

Information obtained from the commercial pesticide applicator showed that the latest application prior to the study took place on May 15, 1982 (4 days prior to the study) and consisted of the following given as active ingredient (a.i.): 1.5 gal of EC dicofol (2.4 lb of a.i.); 1 lb of benomyl; 4 lb of captan.

Materials and Analytical Instrumentation. Analytical-grade captan, benomyl, and carbendazim (methyl 1*H*-benzimidazol-2-ylcarbamate) were obtained from the EPA Reference Standard Repository, Research Triangle Partk, NC 27711; carbendazim was also obtained from E.I. du Pont de Nemours & Co. All solvents used throughout were HPLC grade ("Baker Analyzed" or equivalent). Water for HPLC solvents was passed through a Milli-Q water purification system. Mobile phases for HPLC were degassed by filtration through Millipore FHUP filters and stirring under a water-pulled vacuum for 30 min.

A Tracor-222 gas chromatography apparatus, equipped with a ^{63}Ni-EC detector and Hewlett-Packard electronic integrator (HP 3390A), was used for captan analysis. The chromatographic column was a 3 ft × 2 mm (i.d.) glass column packed with OV-10 (10%) on Supelcoport (80–100 mesh).

For the analysis of benomyl and carbendazim the following HPLC apparatus was used: Waters Model 6000A solvent delivery system; WISP automatic sample processor; Model 450 variable-wavelength detector; Waters data module; RP-18 Spheri 5 Brownlee Laboratories bonded reversed-phase column (25 cm × 2 mm i.d.). A Bausch & Lomb Spectronic 2000 recording spectrophotometer was employed for confirmatory analysis of benomyl and carbendazim.

Extraction. Gauze patches were individually extracted with 50–60 mL of acetonitrile by placing the sample and solvent into a 125-mL widemouthed LPE bottle fitted with a screw cap and shaking the contents on a mechanical

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platform for 1 h. Gloves were extracted in a similar manner by using 100 mL of solvent and 500-mL plastic bottles. The solvent layer was decanted and passed through a Millipore BD (0.6 μm) filter. Aliquots of the filtrate were analyzed for captan and benomyl by GLC and HPLC, respectively. In order to maintain the linearity of the electron-capture detector for captan analysis, up to 20-fold dilutions of extracts containing high concentrations of this pesticide were necessary.

Dislodgeable foliar pesticide residues and dust were isolated from leaf punches according to methods developed by Gunther et al. (1973, 1974), Iwata et al. (1977), and Popendorf and Leffingwell (1977). Leaf punches were surface-extracted with 100 mL of a 60-ppb aqueous solution of sodium dioctyl sulfosuccinate by agitation on a reciprocal-action mechanical shaker for 30 min. The liquid phase was carefully separated from the plant tissue and extracted 3 times successively with 50 mL each of dichloromethane in a 500-mL separatory funnel. If an emulsion formed, the addition of a few milliliters of saturated aqueous Na_2SO_4 was usually sufficient to separate the phases. The combined organic extracts (bottom phase) were filtered through glass wool and a bed of anhydrous Na_2SO_4 and evaporated in vacuo to complete dryness. The residue was finally taken up in 10.0 mL of acetonitrile. Aliquots of this solution were directly analyzed for captan and benomyl as will be described below.

Leaf dust, originally washed off with the surfactant, remained in the interfacial solvent–water layer in the separatory funnel and was quantitatively transferred after the last solvent extraction to a preweighed glass filter. After being dried at 110 °C overnight, the filter was weighed again, and the weight of the foliar dust was calculated by difference.

Analysis of Captan and Benomyl. One to five microliters of the final extract or appropriate dilutions thereof was analyzed for captan by gas–liquid chromatography. Chromatographic conditions were the following: argon–methane carrier gas flow rate, 65 mL/min; column temperature, 210 °C. Under these conditions, captan eluted as a sharp peak at 1.27 min. No interfering peaks were observed in any of the field samples. Quantification was performed by area integration using an electronic integrator and an external standard calibration curve. Results were reported as μg/sample for patches and gloves and μg/cm² of leaf surface or μg/mg of dust for dislodgeable residues.

The analytical method for benomyl is based on the spontaneous conversion of benomyl to carbendazim in acetonitrile and subsequent analysis of carbendazim by HPLC (Zweig and Gao, 1983). Twenty-five microliters of the final extracts was analyzed by reversed-phase HPLC on a C_{18} bonded column using as mobile phases acetonitrile–water in the proportions of 65:35 or 50:50 v/v and a solvent flow rate of 1.3 or 1.5 mL/min, respectively. Benomyl and carbendazim were detected at 286 nm. The elution time for carbendazim with both mobile phases was found to be 3.4 min. The retention times for benomyl, stabilized by the addition of *n*-butyl isocyanate (Chiba, 1977), were 7.8 and 15.8 min for the two mobile phases, respectively. Quantification was accomplished by an electronic integrator and using the external standard method. The minimum detectable quantity for both compounds as limited by instrumental noise and detector sensitivity was found to be 5 ng. [*Important note*: All extracts must be kept at room temperature for 3 h or 40 °C for 1 h prior to the analysis. The purpose of this waiting period is to permit the quantitative conversion of benomyl to carbendazim in acetonitrile, which is fully discussed by Zweig and Gao (1983).]

Table I. Summary of Recovery Studies for Carbendazim, Benomyl, and Captan

sample	compound	μg added	μg found	% recovery
gauze pad (60 mL)[a]	carbendazim	51.0	49.5	97.0
gloves (100 mL)	carbendazim	102.0	97.5	95.6
gloves (100 mL)	carbendazim	204.0	194.3	95.3
DOSSS[b] (100 mL)	carbendazim	160.0	152.9	95.6
DOSSS (100 mL)	carbendazim	160.0	153.3	95.8
DOSSS (100 mL)	carbendazim	160.0	151.7	94.8
gauze pad (50 mL)	benomyl[c]	127.5	126.6	99.3
gauze pad (50 mL)	benomyl	127.5	125.0	98.0
gauze pad (50 mL)	benomyl	255.0	252.2	98.9
gauze pad (50 mL)	benomyl	255.0	250.0	98.0
gauze pad (60 mL)	captan	27.5	30.2	103.3
gloves (100 mL)	captan	27.5	31.6	108.4
leaf disks no. 1	captan	5.5	5.3	95.6
leaf disks no. 2	captan	2.8	2.7	96.4

[a] Volume of extract. [b] Aqueous solution of 0.06 ppm of sodium dioctyl sulfosuccinate. [c] To a standard solution of benomyl in acetonitrile (50.0 mg/100 mL) was added *n*-butyl isocyanate to a final concentration of 10^3 ppm.

All results are reported as benomyl. If carbendazim was chosen as the external standard, the molecular weight conversion factor of 1.52 was applied.

Estimation of Dermal Exposure. To estimate dermal exposure on the forearm, the following calculations were made: The concentration of pesticide on the patch was multiplied by 645/28, 28 cm² being the exposed surface area of the forearm and 645 cm² the surface area of the forearm of the 50-percentile man (Popendorf and Leffingwell, 1982). This was further corrected for individual body surface differing from that of the 50-percentile man, 1.92 m², by estimating individual body surface from a body weight–height nomograph (Sendroy and Cecchini, 1954). Because gloves cover the entire exposed area of the hands, total manual exposure was estimated without transformations. All exposure data were normalized for an hourly exposure rate.

Recovery Studies for Captan and Benomyl. Control samples of patches, gloves, and strawberry leaves were spiked with known amounts of captan, benomyl, and carbendazim. For recovery purposes, benomyl was stabilized by the addition of excess *n*-butyl isocyanate (Chiba, 1977). Strawberry leaves from a nontreated field were not available when benomyl–carbendazim recovery studies were conducted, and therefore, a dilute aqueous, solution of sodium dioctyl sulfosuccinate served as the surrogate for "dislodgeable foliar residue samples". All spiked samples were processed by the same procedures as described above under Extraction and analyzed by appropriate instrumental methods, GLC or HPLC. As shown in Table I, recoveries were almost quantitative for all compounds studied.

Confirmation of Carbendazim Residues. The identity of suspected carbendazim residues from field samples was confirmed by two independent methods: The solvent extract of a field sample (left-handed glove, subject no. 2) was chromatographed by HPLC and the eluant collected at the previously determined retention time of carbendazim. The UV scan of this solution was identical with the spectrum of authentic carbendazim with characteristic absorption peaks at 286.1 and 280.0 nm and a shoulder at 294.1 nm. The UV spectrum of this solution containing *n*-butyl isocyanate (final concentration 10^3 ppm) was identical with one of authentic benomyl with absorption

Table II. Confirmation of Carbendazim and Benomyl Residues

sample	carbendazim,[a] ng, found	benomyl,[b] ng theory	benomyl,[b] ng found	% recovery
left glove (subject no. 7)	115.2	158.9	162.7	102.6
right glove (subject no. 7)	137.1	189.4	189.0	100.0

[a] Sample extracted with 60 mL of acetonitrile; diluted 1:5 with solvent; 25-μL aliquots were analyzed in duplicate by HPLC. [b] To 20.0 mL of diluted extract 0.2 mL of a 10^4-ppm solution of *n*-butyl isocyanate was added; 25-μL aliquots were analyzed by HPLC in duplicate.

Table III. Hand and Lower Arm Dermal Exposure by Strawberry Harvesters

subject no.	sex	age	productivity, crates/h	exposure, mg/h captan	exposure, mg/h benomyl
1	M	36	7.36	52 (180.9)[a]	15.5
2	M	45	7.36	37.4	12.1
3	M	29	5.45	35.0	4.2
4	M	19	5.38	49.8	2.8
5	F	55	3.00	13.2	1.2
6	M	22	3.40	25.0	1.9
7	M	30	4.00	51.3	4.2
8	M	23	3.25	62.1	4.9
9	F	51	4.65	28.9	2.7
10	F	20	2.96	35.1	4.4
			mean:	39.01	5.39
			rel SD:	38.0	86.4
			captan/benlate = 7.23		

[a] The experimental figure has been deleted as an outlier according to the procedure of Grubbs (1969) and substituted by an estimate of 52 mg/h; see also footnote *a* of Table IV.

Table IV. Left- and Right-Hand and Forearm Exposure to Captan by Strawberry Harvesters

worker no.	dermal exposure, mg h^{-1} $person^{-1}$ forearm left	forearm right	hands left	hands right
1	15.22	4.82	16.14 (144.79)[a]	16.14
2	13.81	4.55	8.96	10.00
3	3.05	2.59	3.39	25.94
4	0.31	1.18	22.69	25.62
5	0.50	3.81	2.75	6.10
6	0.68	0.64	12.14	11.57
7	4.13	3.60	20.32	23.20
8	1.75	2.18	27.32	30.81
9	0.95	0.24	8.67	19.06
10	0.95	2.49	16.67	15.04

[a] This figure is deleted according to the procedure of Grubbs (1969) for outlying observations and is replaced by the value for right-hand exposure, assuming ambidexterity of worker no. 1.

Table V. Left- and Right-Hand and Forearm Exposure to Benomyl by Strawberry Harvesters

worker no.	dermal exposure, mg h^{-1} $person^{-1}$ forearm left	forearm right	hands left	hands right
1	1.25	0.32	6.93	6.96
2	1.16	0.31	5.30	5.23
3	0.42	0.18	1.66	1.94
4	0.0	0.06	1.36	1.38
5	0.0	0.21	0.30	0.67
6	0.07	0.04	0.83	0.97
7	0.28	0.29	1.65	2.00
8	0.19	0.17	2.04	2.46
9	0.07	0.04	0.88	1.67
10	0.09	0.21	1.13	2.94

peaks at 292.6 and 286.1 nm and the absence of the absorption maximum at 280 nm, belonging to carbendazim.

A second confirmatory method involved the demonstration of quantitative conversion of suspected carbendazim to benomyl following the addition of excess *n*-butyl isocyanate. The extracts of two representative field samples (gloves belonging to subject no. 7) were first analyzed for carbendazim by HPLC and, after the addition of *n*-butyl isocyanate, for benomyl. The retention times for carbendazim and converted benomyl from the field samples were identical with those of reference standards. As shown in Table II, quantitative conversion of carbendazim to benomyl had taken place, demonstrating that carbendazim was indeed the compound isolated from field samples.

RESULTS AND DISCUSSION

Dermal Exposure to Benomyl and Captan. The 10 volunteers for this study (7 male and 3 females) were experienced strawberry pickers and ranged in age from 19 to 55 years (Table III). Pickers 1 and 2 were most productive as judged by the numer of crates picked per hour. Each crate consisted of 12 1-pt baskets with a total net weight of fruit of about 5 kg.

Popendorf et al. (1982a,b) and Everhart and Holt (1982) have shown that the major dermal exposure of strawberry harvesters to captan and benomyl occurred on the hands and lower forearms. Dermal body exposure could, therefore, be estimated by monitoring only these two anatomical regions, hands and forearms. This assumption may not be valid for harvesters of other crops, like tree-grown fruits, where Popendorf (1980) observed a more uniform total body exposure. Row crops, like strawberries, are hand-picked from a stooped or squatting position which determines the dermal distribution found by Popendorf (1982a,b) and Everhart and Holt (1982).

Forearm exposure was estimated from the gauze dosimeter placed in a position where greatest exposure from contact with plant foliage would most likely be expected, i.e., the region of the forearm above the wrist. When the concept of the 50-percentile man and the proportional surface allocation for each anatomical region were used, an estimate to that particular region (forearm) was made, notwithstanding the possibility of nonuniform pesticide distribution, leading to possible error in the final estimate.

Table III shows that dermal exposure by the 10 subjects studied ranged from 1.2 to 15.5 mg h^{-1} for benomyl and 13.2 to 51.3 mg h^{-1} for captan. Corresponding means were calculated to be 5.39 mg h^{-1} $person^{-1}$ (86.4%) and 39.01 mg h^{-1} $person^{-1}$ (38.0%), respectively, with the percent relative standard deviations in parentheses. Subject no. 1 exhibited an inexplicably high left-handed captan exposure (see Table IV). However, when Grubbs' (1969) procedure was used, this value could be excluded as an outlier and substituted with the experimental value for the right-handed exposure. Further justification for this adjustment were the equal exposure of benomyl to both hands (Table V) and similar ratios for left and right forearm exposures for captan (3.2) (Table IV) and benomyl (3.9) (Table V).

The higher dermal captan exposure compared benomyl exposure was probably due to the higher rate of captan application (4 and 1 lb/acre, respectively), with both pesticides being applied at the same time. This explanation is further supported by the finding of much higher dislodgeable foliar residue levels for captan than those

Table VI. Dislodgeable Foliar Residues from Strawberry Plants

sample no.	captan μg/cm²	captan μg/mg of dust	benomyl μg/cm²	benomyl μg/mg of dust
1	4.21	10.4	0.73	1.79
2	4.89	13.9	0.78	2.19
mean	4.55	12.2	0.75	1.99
	captan/benomyl = 6.06			

found for benomyl (Table VI).

Benomyl exposures at 4 days postapplication found in this study were similar to those reported by Everhart and Holt (1982). They found an average dermal exposure of 5.9 mg h^{-1} $person^{-1}$ among three strawberry pickers who worked in the field 24 h after the last application of benomyl. Benomyl was at the same rate as that reported for this study (1 lb/acre). According to Baude et al. (1973), foliar benomyl residues appear to be stable over several days after application, e.g., apple leaves were found to retain 91% of the originally applied benomyl 7 days after the last application.

Dislodgeable Foliar Residues. Table VI shows the results from the analysis of dislodgeable foliar residues of captan and benomyl sampled the same day as the study. The ratio of average dislodgeable residues of captan and benomyl is 6.1. The corresponding ratio for dermal exposure is 7.2 (see Table III). These two ratios are similar, suggesting that dislodgeable foliar residues of several pesticides are transferred from foliage in the same proportion to the exposed skin surface of field workers. Popendorf and Leffingwell (1982) and Popendorf et al. (1982,a,b) have already shown that a positive correlation between dislodgeable foliar residues and dermal concentrations of pesticides exists.

When the data from Tables III and VI were used, transfer coefficients (k_d) for captan and benomyl were calculated and found to be 8.5×10^3 and 7.19×10^3 cm^2/h, respectively. K_d is defined as the ratio of dermal concentration to dislodgeable foliar residue and assumes the units of area over time. This constant can be loosely viewed as the product of the surface area contacted per unit time multiplied by the fraction of associated residue transferred. If the transfer were quantitative, one may calculate from the above k_d's that skin contact is 143 and 120 cm^2 of leaf surface/min. In reality, we believe that the surface area is probably much larger, implying that the transfer is less than quantitative. The transfer coefficients from this study are similar to those reported by Popendorf and Leffingwell (1982) for citrus and peach harvesters to organophosphorus insecticides.

In prior studies by this laboratory (Popendorf et al., 1982a,b), surface captan residues of about 1 ppm (or roughly 0.5 μg/cm^2) were found on strawberries, and these residues may, therefore, be a contributory factor of dermal exposure, especially to the hands of fruit harvesters. The relative contribution to dermal exposure from foliar dislodgeable residues and surface residues from fruit remains to be the subject of a future study.

Comparison of Left- and Right-Handed Exposure. Since left- and right-handed gloves were individually analyzed, it was possible, therefore, to compare dermal pesticide exposure of each worker on his left and right hand. At least eight out of these ten workers professed to be right-handed, and the remaining two workers did not express a preference. As may be seen in Tables IV and V, it appears that subject 5 exhibits right-handed preference as shown by the data for both captan and benomyl. In addition, subjects 3, 6, and 10 also showed right-handed preference, based on the data from one of the pesticides. The remaining subjects appear to be ambidextrous in picking strawberries as manifested by hand exposure data. These findings suggest that analyses of chemical exposure on the left and right hand might be a suitable method for conducting time–motion studies of farm workers harvesting row crops.

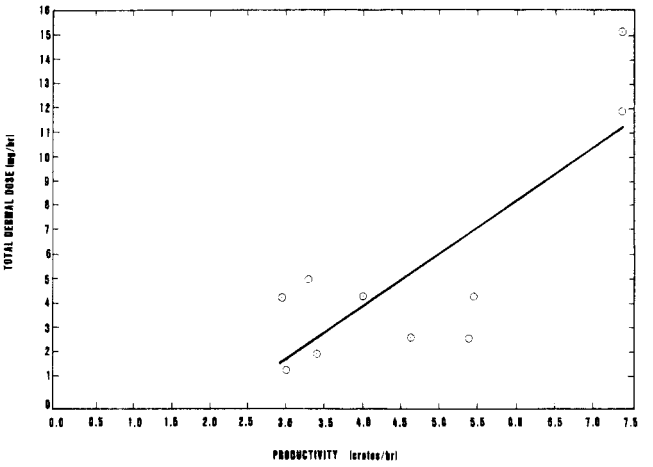

Figure 1. Linear regression curve of "productivity" vs. total dermal dose of benomyl for 10 strawberry harvesters.

Productivity and Exposure. A positive correlation was found between productivity, expressed as crates harvested per hour, and dermal exposure of benomyl per hour (Figure 1) ($r = 0.812$; $p = 0.0043$), which might explain why workers with the greatest productivity (subjects 1 and 2) receive the highest benomyl exposure (Table III). The worker who picks a large amount of fruit may be subject to more skin contact with fruit and foliage bearing dislodgeable pesticide residues than the worker who is less productive. A similar correlation between productivity and dermal exposure to captan was not found.

CONCLUSION

The toxicological consequence of dermal exosure to pesticides by crop harvesters remains uncertain until percutaneous absorption rates for these pesticides have been determined. Although there are few compounds that are quantitatively absorbed through the skin, a conservative estimate of body dose may be made by assuming 100% absorption of the dermal dose. In the absence of the experimentally derived data, this hypothetical dose may serve as a first basis for estimating potential toxicological hazard to crop harvesters.

Another uncertainty, as illustrated by the present study, is the estimation of daily exposure based on a relatively short observation period (less than 2 h). It has been observed in this and previous studies (Popendorf et al., 1982a,b) that gloves became quickly saturated with fruit juice and dew, especially in the early morning hours when most of our observations were made. It seems reasonable to assume that once gloves have become moisture laden, the absorptive capacity of the cotton cloth might be impeded. The techniques for measuring average dermal exposure during a workday may, therefore, not represent actual dermal exposure. This concern has prompted the initiation of a series of studies by this laboratory investigating, comparing, and improving presently used techniques for measuring dermal exposure to pesticides (Noel et al., 1983).

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COMMUNICATIONS

Involvement of Oxygen in the Photoreactions of Cypermethrin and Other Halogenated Pyrethroids

Photolysis of cypermethrin and fenpyrithrin in alcohols, aqueous acetonitrile, and sodium dodecyl sulfate micelles results in isomerization and ester and oxidative cleavage reactions. The nature of the products obtained is dependent on the availability of oxygen and on the solvent used. Similar products are obtained from these pyrethroids and from deltamethrin in alcohol solvents. Oxygen is incorporated into both acid and alcohol moieties upon cleavage. Fenpyrithrin is more photoreactive than cypermethrin in degassed and oxygenated methanol solutions.

Pyrethroid insecticides photodecompose readily in a variety of systems yielding complex mixtures (Ruzo, 1982a; Miyamoto, 1981). The dihalovinylcyclopropanecarboxylates primarily undergo isomerization, reductive dehalogenation, decarboxylation, and especially ester cleavage processes (Ruzo, 1982b), while the chrysanthemates are extensively oxidized (Ruzo, 1982c). Due to their lipophilicity pyrethroids in the environment are generally bound to solid particles (Graham-Bryce, 1980) or combined with organic matter, e.g., on surface slicks of lakes. This report uses two pyrethroids not previously emphasized, cypermethrin (1, Y = C) and fenpyrithrin (1, Y = N) (Figure 1), to consider the origin of 3-phenoxybenzoyl cyanide obtained from deltamethrin (Ruzo et al., 1977) and fenvalerate (Holmstead et al., 1978b), reasons why the characterized mass balance is in general lower for the acid than the alcohol moiety, and the reaction rates and product distribution of *cis*-cypermethrin photolyzed in aqueous acetonitrile vs. micellar solutions.

MATERIALS AND METHODS

Chemicals. Structures and designations of the compounds used are shown in Figure 1. Sources for the pyrethroids and other chemicals are as follows: *cis*- and *trans*-cypermethrin were gifts of Roussel-Uclaf (Paris, France); *cis*- and *trans*-fenpyrithrin were supplied by Dow Chemical Co. (Walnut Creek, CA). Other pyrethroids and degradation products were obtained from sources previously reported (Ruzo and Casida, 1982; Ruzo et al., 1977). Sodium dodecyl sulfate ($NaDodSO_4$, Sigma) was recrystallized from ethanol, while tri-*tert*-butylphenol (TTBP, Aldrich) and dimethylfuran (DMF, Aldrich) were used as received.

Analyses. Thin-layer chromatography (TLC) was carried out as previously reported (Ruzo and Casida, 1982). Gas chromatography–chemical ionization mass spectrometry (GLC–CI-MS) utilized a Finnigan 3200 instrument equipped with 5% OV-101 or OV-25 columns operated with temperature programming (120–240 °C, 6 °C/min) and methane (0.8 torr) as the carrier and ionization gas.

Nuclear magnetic resonance (NMR) was conducted at 250 MHz in benzene-d_6. Fourier-transform infrared spectroscopy (FT-IR) was carried out on KBr micropellets by courtesy of Shell Development Co., Modesto, CA. Ultraviolet spectroscopy utilized a Perkin-Elmer 576 ST spectrophotometer.

Photolysis Procedures. The pyrethroids were irradiated at $\lambda > 290$ nm (Pyrex) in a Rayonette Reactor (The Southern New England Ultraviolet Co., Middletown, CT) equipped with RPR 3000 lamps. Pyrethroid concentra-

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