Photodegradation of Fluvalinate

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The photodegradation of [*trifluoromethyl*-^{14}C]- and [*benzyl*-U-*ring*-^{14}C]fluvalinate (1) was studied in solution (methanol and water) and as thin films (on glass and soil). Fluvalinate has a half-life of about 1 day when an aqueous solution (1 ppb) or thin films (1–4 $\mu g/cm^2$) are exposed to sunlight. Hydrolysis of the cyano moiety in fluvalinate to $CONH_2$ (up to 18% yield) was the only significant modification of the intact ester, a reaction that was nonphotochemical and directly proportional to temperature. 2-Chloro-4-(trifluoromethyl)aniline was the major photoproduct from the acid portion of 1 as a thin film on glass or in aqueous solution (up to 40 and 18% of the applied ^{14}C, respectively). For thin films of 1 on soil, the acid portion was converted mainly to an anilino acid (maximum 24% yield). Under all photochemical conditions 3-phenoxybenzaldehyde and its corresponding acid were major products (40–50% of the applied dose). Other photoproducts of 1 in sunlight recovered in 3–11% yields included a formanilide, an oxamic acid, (3-phenoxyphenyl)acetonitrile, and the cyanohydrin of 3-phenoxybenzaldehyde.

Fluvalinate [1, α-cyano-3-phenoxybenzyl 2-[2-chloro-4-(trifluoromethyl)anilino]-3-methylbutanoate] is an insecticide with pyrethroid-like activity against numerous agricultural pests. We now report the photochemical fate of this compound as a supplement to our previous studies [for the previous report in this series, see Staiger and Quistad (1984)].

The photochemistry of pyrethroids has been investigated extensively in recent years, perhaps more than any other class of pesticides. Numerous reviews are available as predictive models for photodegradation of new pyrethroids (Ruzo, 1982, 1983a,b; Miyamoto, 1981). This study reports the photodegradation of fluvalinate with particular reference to previous investigations with α-cyano-3-phenoxybenzyl pyrethroids (i.e., cypermethrin, fenvalerate, and deltamethrin).

EXPERIMENTAL SECTION

Analytical Methods. Liquid scintillation counting (LSC) was performed with a Packard Model 2425 or 460C spectrometer. Thin-layer chromatography (TLC) utilized silica gel GF plates (Analtech) with radioactive zones located by using a Packard Model 7201 radiochromatogram scanner.

Reversed-phase liquid chromatography (LC) was performed with a Spectra-Physics Model 8000A liquid chromatograph (LiChrosorb RP-8 column, 10 μm, 25 × 0.46 cm; elution at 1.6 mL/min and 35 °C; SP Model 8310 ultraviolet detector, 254 nm). Table I lists the TLC and LC solvent systems used in this work.

Residual radioactivity in soil after extraction was quantified by combustion of aliquots to $^{14}CO_2$ (Harvey OX-300 biological material oxidizer) with collection in Carbon-14 Cocktail (Harvey) followed by LSC.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a Varian T-60 instrument. Mass spectra were obtained with a Hewlett-Packard Model 5985A instrument (GC/MS) in the electron-impact (EI) or chemical-ionization (CI) mode. The ultraviolet spectrum of fluvalinate (99.1% purity) in methanol was recorded with a Perkin-Elmer Model 555 spectrophotometer.

Synthetic Standards. The preparations of [*trifluoromethyl*-^{14}C]fluvalinate and [*benzyl*-U-*ring*-^{14}C]fluvalinate have been described (Quistad et al., 1982; Staiger and Quistad, 1984). Authentic standards of fluvalinate (1), anilino acid **2**, and the haloaniline **3** were synthesized by the Zoecon Chemical Research Department.

Synthetic standards of 3-phenoxybenzoic acid (PBacid, **4**), 3-phenoxybenzaldehyde (PBald, **5**), and the cyanohydrin of PBald (**6**) were available from commercial sources.

The amide analogue of fluvalinate (**7**) was prepared by bubbling HCl gas through fluvalinate (173 mg, 0.34 mmol) in anhydrous ether (20 mL) for 45 min. After the mixture was allowed to stand for 1 h, the ether was evaporated and the crude product was purified by TLC (SS 1) to give **7** in 6% yield (R_f = 0.15).

2-Chloro-4-(trifluoromethyl)formanilide (formanilide **8**) was prepared by treatment of haloaniline **3** with formic acid (10 min, 100 °C). The purified product had the same TLC and NMR characteristics as the photoproduct.

(3-Phenoxyphenyl)acetonitrile (PPAnitrile, **9**) was prepared from 3-phenoxybenzyl bromide and sodium cyanide in ethanol (reflux, 2 h). Following extraction into ether, the product was purified by silica gel chromatography and

Table I. Thin-Layer (TLC) and Liquid Chromatography (LC) Solvent Systems

TLC				
SS 1: hexane–ethyl acetate, 2:1				
SS 2: hexane–ether 1:1				
SS 6: hexane–ethyl acetate–acetic acid, 10:2:0.1				
SS 7: hexane–ethyl acetate, 3:1				
SS 9: hexane–ethyl acetate, 1:1				
SS 11: hexane–ethyl acetate, 4:1				
	LC			
	time, min	methanol	H_2O	1% TFA[a]
SS 3	0	50	40	10
	40	90	0	10
	50	90	0	10
SS 4	0	50	40	10
	15	60	30	10
	30	90	0	10
	40	90	0	10
SS 5	0–25	30	60	10
SS 8	0	60	40	0
	15	70	30	0
	20	80	20	0
	25	90	10	0
	35	90	10	0
SS 10	0	70	30	0
	20	90	10	0
	30	90	10	0

[a] 1% trifluoroacetic acid in H_2O.

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0021-8561/84/1432-1134$01.50/0

the structure confirmed by NMR.

N-[2-Chloro-4-(trifluoromethyl)phenyl]oxamic acid (**10**) was prepared in 58% yield from **3** (0.19 mmol) and oxalyl chloride (1.9 mmol) in CH_2Cl_2 (10 mL) containing pyridine (0.19 mmol). The product was purified by TLC (SS 1, R_f = 0.50) and its structure was verified by NMR and mass spectral analysis.

Authentic diacid **11** was prepared in 85% yield by refluxing anilino acid **2** in 1 M KOH for 6 h: NMR ($CDCl_3$) for **11** as dimethyl ester δ 0.98 (d, 3, J = 3 Hz, CH_3), 1.19 (d, 3, J = 3 Hz, CH_3), 2.10 [m, 1, $(CH_3)_2CH$], 3.71 (s, 3, OCH_3), 3.80 (s, 3, OCH_3) 3.94 (m, 1, CHC=O), 5.18 (d, 1, J = 10 Hz, NH), 6.46 (d, 1, J = 8 Hz, ar), 7.73 (m, 2, ar).

Mercury Lamp Photolysis. Nonradiolabeled fluvalinate (1 g) was dissolved in methanol (1000 mL) for photolytic studies in a quartz immersion cell with a mercury lamp (450-W Hanovia 679A36). After 24 h of continuous irradiation, the solvent was evaporated and numerous photoproducts were isolated by TLC (SS 2). Subsequent purifications by LC allowed characterization of structures by NMR and GC/MS as follows: **4** (as its methyl ester), NMR ($CDCl_3$) δ 3.88 (s, 3, CH_3), 7.21 (m, 9, ar), R_f = 0.74 in SS 2; **6**, NMR ($CDCl_3$) 3.74 (s, 1, OH), 5.36 (s, 1, CHOH), ca. 7.1 (m, 9, ar), R_f = 0.30 in SS 2; CO_2-elimination product **12**, EI mass spectrum m/z (rel intensity) 460 (0.1, M^+ for ^{37}Cl), 458 (0.1, M^+ for ^{35}Cl), 252 (34), 251 (12), 250 (100), 55 (7); CO_2-elimination product **12**, CI (CH_4) mass spectrum m/z (rel intensity) 487 (4, M + 29), 459 (12, M + H), 264 (63), 250 (100), 210 (57), 196 (54), R_f = 0.65 in SS 2; (3-phenoxyphenyl)acetonitrile (**9**), NMR ($CDCl_3$) δ 3.66 (s, 2, CH_2), ca. 7.2 (m, 9, ar), R_f = 0.57 in SS 2.

Thin Film Photochemistry. In order to acquire sufficient masses of photoproducts for spectral characterization, nonradiolabeled fluvalinate (1 g) was coated as a thin film inside four 2–3-L Pyrex Erlenmeyer flasks (treatment rate = 147 $\mu g/cm^2$). The flasks were exposed to sunlight for 7 days at which time photodegradation products were rinsed from the flasks with ether and isolated by preparative TLC (SS 2). The following products were characterized by NMR and mass spectrometry: PBald (**5**), NMR ($CDCl_3$) δ 7.29 (m, 9, ar), 9.45 (s, 1, CHO); 2-chloro-4-(trifluoromethyl)aniline (**3**), k' = 3.1 on LC in SS 3, EI mass spectrum m/z (rel intensity) 197 (34, M^+ for ^{37}Cl), 195 (100, M^+ for ^{35}Cl), 178 (12), 176 (35), 147 (10), 145 (30); (3-phenoxyphenyl)acetonitrile (**9**), EI mass spectrum m/z (rel intensity) 209 (100, M^+), 181 (18), 141 (38), 77 (38), k' = 2.7 for LC in SS 4; 2-chloro-4-(trifluoromethyl)formanilide (**8**), NMR ($CDCl_3$) δ 7.50 (d, 1, J = 8 Hz, ar), 7.59 (s, 1, ar), 7.82 (br s, 1, NH), 8.55 (s, 1, CHO), 8.58 (br s, 1, ar), EI mass spectrum m/z (rel intensity) 225 (12, M^+ for ^{37}Cl, 223 (35, M^+ for ^{35}Cl), 197 (22), 195 (64), 188 (100), 178 (17), 176 (47); oxamic acid **10** (as methyl ester), EI mass spectrum m/z (rel intensity) 283 (10, M^+ for ^{37}Cl), 281 (30, M^+ for ^{35}Cl), 246 (60, M – Cl), 224 (29), 222 (100), 196 (19), 194 (52), CI mass spectrum (CH_4) m/z (rel intensity) 322 (8, M + 41), 310 (17, M + 29), 284 (31, M + H for ^{37}Cl), 282 (100, M + H for ^{35}Cl), 262 (82), R_f = 0.50 in SS 1 for methyl ester, k' = 2.5 in SS 3 for free acid, k' = 13.3 in SS 5 for methyl ester.

The time-dependent dissipation of fluvalinate as a thin film on glass in sunlight was studied according to the following method. Fluvalinate (CF_3 and benzyl labeled) was coated on the inside surfaces of round-bottom flasks by evaporating an acetone solution (10 mL) while rotating the flask to achieve a treatment of 2–4 $\mu g/cm^2$. Immediately following evaporation of the solvent, the flasks were stoppered with polyurethane plugs and placed outdoors for exposure to sunlight. At intervals, the plugs were extracted with methanol and aliquots were quantified by LSC. The flasks were rinsed with methanol and an aliquot was quantified by LSC. Radioactive products in the flask and plug extracts were analyzed directly by coinjection of an aliquot with authentic standards on LC (SS 3 or SS 4).

Due to coelution of PBacid (**4**) and PBald (**5**) on LC, it was necessary to separate these products by TLC (SS 6) prior to LC of the eluted PBald zone (SS 4). Separation of the formanilide **8** from oxamic acid **10** was achieved by TLC (SS 7, R_f = 0.25 for **8** and R_f = 0 for **10**). The formanilide **8** was eluted from the silica gel and shown to coelute with authentic standard on LC (SS 4, k' = 1.6). The methylated oxamic acid (**10**) also coeluted with an authentic standard upon LC (k' = 13.3 in SS 5).

Soil Photochemistry. Sieved sandy loam soil [10 g, 500-μm particle size; for characterization, see Staiger and Quistad (1983)] in Erlenmeyer flasks was autoclaved, cooled, and then treated with an acetone solution of [*trifluoromethyl*-^{14}C]fluvalinate at a rate of 1.3 $\mu g/cm^2$ (0.1 kg/ha, 3–5-mm soil layer thickness). Each flask was stoppered with a polyurethane plug and placed outdoors in natural sunlight. One flask was covered with foil to eliminate sunlight exposure.

At various intervals, the soil was removed and extracted with methanol (~300 mL, Polytron homogenizer) and an aliquot of the extract quantified by LSC. Radioactivity in the dried residual solids was quantified by combustion of aliquots (~0.3 mg) to $^{14}CO_2$. Volatile radioactivity in the plugs was quantified as described previously. The identity of photoproducts in the extracts was investigated by coinjection of an aliquot with authentic standards on LC (SS 8).

Additional soil samples were treated with [*trifluoromethyl*-^{14}C]fluvalinate at a rate of 22 $\mu g/cm^2$ (2 kg/ha) in order to isolate the amide **7** and diacid **11** for structural confirmation. After 2 days of sunlight exposure, the soil was extracted with methanol. The amide analogue (**7**) was isolated by TLC (SS 9, R_f = 0.46) and subsequently purified by LC (SS 10, k' = 9.5) prior to identification by its mass spectrum: EI m/z (rel intensity), 522 (1.0, M^+ for ^{37}Cl), 520 (2.8, M^+ for ^{35}Cl), 252 (35), 251 (13), 250 (100), 227 (37), 198 (22). Likewise, diacid **11** was isolated by exposing treated soil to sunlight for 14 days. Diacid **11** was recovered from the origin zone upon TLC (SS 9). Methylated **11** was purified by LC (k' = 6 in SS 8) and identified from its mass spectra [m/z (rel intensity)]: EI, 301, (5, M^+ for ^{37}Cl), 299 (13, M^+ for ^{35}Cl), 256 (27), 242 (32), 240 (100), 196 (31); CI (CH_4), 340 (2, M + 41), 328 (10, M + 29), 302 (21, M + H for ^{37}Cl), 300 (65, M + H for ^{35}Cl).

The contribution of temperature to the degradation of fluvalinate on soil was analyzed by treating autoclaved soil samples with [*trifluoromethyl*-^{14}C]fluvalinate as above and maintaining them in the dark at four temperatures: 4, 12, 25, and 31 °C. The soil was extracted and analyzed as described previously.

Aqueous Photochemistry. Erlenmeyer flasks containing distilled water (100 mL) and stoppered with polyurethane plugs were sterilized (autoclave) prior to treatment with [*trifluoromethyl*-^{14}C]- or [*benzyl*-^{14}C]fluvalinate. The water samples were shaken gently while introducing an acetone solution of [^{14}C]fluvalinate (40–50 μL, 0.1 μg, 1 ppb). Immediately after treatment, the flasks were placed outdoors in natural sunlight for the duration of the study. One flask was wrapped with foil to eliminate sunlight exposure.

At various intervals individual flasks were removed and radioactivity was quantified in the water and polyurethane

Table II. Photodegradation Products of Fluvalinate under Various Conditions

	maximum % yield (time in days)			
	solution		thin film	
	methanolic (2 mM)	aqueous (1 ppb)	glass (2–4 $\mu g/cm^2$)	soil (1 $\mu g/cm^2$)
anilino acid **2**		3 (1)	1 (4)	24 (1)
haloaniline **3**		17 (2)	40 (2)	3 (10)
PBacid (**4**) + PBald (**5**)	5 (1)	49 (4)	41 (2)	
cyanohydrin **6**	9 (1)	7 (1)	12 (4)	
amide **7**		1 (7)	3 (3)	14 (1)
formanilide **8**		4 (4)	2 (1)	
PPAnitrile (**9**)	4 (1)	8 (7)	2 (2)	
oxamic acid **10**		3 (4)	11 (3)	
diacid **11**				1 (10)
CO_2-elimination adduct **12**	0.8 (1)			

plugs. The water was acidified (2 N HCl) and extracted with ethyl acetate (80 mL, followed by 2 × 50 mL), and aliquots (2 mL) of the extracts were quantified by LSC. Radioactivity in the polyurethane plugs was extracted with methanol, and aliquots were quantified as described previously.

The identity of photoproducts in the extracts was investigated by LC. Aliquots (20 mL) of the ethyl acetate fractions were first reduced in volume prior to coinjection with authentic standards on LC (SS 3 or 4). Volatile products from $^{14}CF_3$-labeled fluvalinate (plug extracts) were analyzed by LC (SS 3) alone or in combination with TLC (R_f = 0.38 in SS 11 for **3**).

RESULTS AND DISCUSSION

Fluvalinate (**1**) absorbs substantial ultraviolet radiation with absorption maxima in methanol at 204 and 254 nm (ϵ = 56 000 and 18 000 M^{-1} cm^{-1}, respectively) due to its several aromatic chromophores. Even at 300 nm, the approximate atmospheric wavelength cutoff for sunlight, fluvalinate absorbs significant energy (ϵ = 2500 M^{-1} cm^{-1}). Accordingly, adequate absorbance renders fluvalinate susceptible to possible photodegradation by sunlight.

Methanolic Solution. Although we are primarily interested in the environmental photodegradation of fluvalinate, we investigated its photochemical fate in organic solvent as a comparison to the work with other pyrethroids and also as a means of acquiring possible photoproduct standards. A methanolic solution of fluvalinate (2 mM) was irradiated for 24 h with a mercury lamp. This lamp emits most of its wattage as visible energy but has significant UV emission at 366 and 313 nm. Only 17% of the total wattage from this lamp is at wavelengths less than 300 nm. The photoproducts from irradiation of a methanolic solution of **1** in a quartz immersion cell are given in Table II. This study utilized nonradiolabeled **1**, and photoproducts were isolated by TLC with yields based on the recovered mass. Relatively volatile photoproducts such as haloaniline **3** could be lost during solvent concentration in this study, which may account for the lack of detectability of **3**. Although a multitude of low-yield products was observed, methanolysis gave PBacid (**4**) and cyanohydrin **6** (5 and 9% yield, respectively). After 24 h of irradiation, 27% of the fluvalinate was recovered intact. Only slightly more fluvalinate was photolyzed with a quartz immersion cell (UV transmission cutoff <200 nm) compared to a Pyrex cell (cutoff ~290 nm). Hence, most photolysis results from wavelengths greater than 290 nm.

Since numerous studies have shown the formation of pyrethroid photoproducts in organic solvent via free radical processes [e.g., Holmstead et al. (1978a,b) and Ruzo et al. (1977)], we specifically looked for such products from **1**. The photoinduced elimination of CO_2 (products analogous to **12**) is a particularly important reaction for fenvalerate irradiation in organic solvents (up to 70% yield; Holmstead et al., 1978b; Reed et al., 1983), but less important for cypermethrin (10% yield; Ruzo, 1983c), deltamethrin (4% yield; Ruzo et al., 1977), and permethrin (negligible formation; Ruzo, 1983b). The photoelimination of CO_2 from esters in organic solvent is a well-known reaction [see Holmstead and Fullmer (1977 and references cited therein)]. The reaction mechanism involves discrete free radicals that, in the case of fenvalerate, have been trapped and observed by ESR (Mikami et al., 1982). Fenvalerate is a particularly good substrate for photoelimination of CO_2 since homolytic scission of bonds results in benzyl radicals from both the acid and alcohol portions of the molecule. The chemical yield of the CO_2-elimination adduct is determined largely by the stability of the evolved free radicals. Thus, fenvalerate (two benzyl radicals) gives a higher yield of the adduct than other pyrethroids with less stable alkyl radicals. The α-cyano moiety also imparts additional stability to the resultant free radicals as evidenced by formation of the adduct from cypermethrin but not permethrin. The low yield (0.8%, Table II) of the CO_2-elimination adduct (i.e., **12**) from fluvalinate probably reflects the reduced stability of the free radical generated from the acid portion of **1**. This observation is reenforced by the apparent lack of other free radical recombination products [e.g., dimerized radicals; cf. Holmstead et al. (1978b)]. Hence, while photoelimination of CO_2 from **1** could be demonstrated, it is a minor process.

The irradiation of **1** in methanol also gave (3-phenoxyphenyl)acetonitrile (PPAnitrile, **9**) in 4–8% yield. This product was also found from solution photochemistry of fenvalerate (1% yield in hexane; Holmstead et al., 1978b; Reed et al., 1983) and deltamethrin (6% yield in methanol; Ruzo et al., 1977). The formation of PPAnitrile from **1** implies that free radicals are present in the methanolic photolysis of fluvalinate, but these radicals are not sufficiently concentrated or stable to efficiently combine with each other.

Thin Film on Glass. Nonradiolabeled fluvalinate was used in a preliminary study to assess the photodegradation of **1** on glass in sunlight. At a dose rate of 147 $\mu g/cm^2$ (15 kg/ha), only 9% of the fluvalinate remained after 7 days in sunlight and a complex mixture of products was observed. Several photoproducts were purified and identified by spectral methods. Although no single photoproduct represented more than 6% of the applied ^{14}C, formanilide **8** was one of the more abundant compounds (4% yield). The mechanism of formation of **8** is unknown, but an analogous formanilide is produced without sunlight from 4-chloroaniline in nutrient medium (Anagnostopoulos et al., 1978). Formanilide **8** could also be formed from the reaction of haloaniline **3** with photochemically generated formic acid, but detection of the latter was not pursued. No evidence was found for diazo adducts from **3**.

The time-dependent photodegradation of fluvalinate was studied by coating a thin film of **1** (2–4 $\mu g/cm^2$) inside Erlenmeyer flasks that were exposed to sunlight for 4 days. The half-life of fluvalinate under these conditions was about 1 day. By using both [*trifluoromethyl*-^{14}C]- and [*benzyl*-^{14}C]fluvalinate, it was possible to follow the fate of both portions of the ester. The major photoproduct from the acid side of **1** was haloaniline **3**. Haloaniline **3** represented up to 40% of the applied dose, but most of the **3** volatilized from the thin film and was trapped by

Table III. Effect of Temperature on Degradation of [*trifluoromethyl*-^{14}C]Fluvalinate as a Thin Film (1 μg/cm^2) on Soil in the Dark for One Week

	% of soil extract		
temp, °C	fluvalinate	amide **7**	anilino acid **2**
4	98	0.3	0
12	90	3.1	6.5
25	60	17	22
31	58	16	26

polyurethane plugs. Nonvolatile photoproducts included amide **7**, anilino acid **2**, formanilide **8**, and oxamic acid **10**, each representing up to 3, 1, 2, and 11% of the applied dose, respectively. The formation of oxamic acid **10** is particularly notable since, in our characterization of **10**, we observed its rather facile decomposition to haloaniline **3** (after acidification or while heating during GC/MS analysis). The oxamic acid **10** may be an important immediate precursor to **3**, the most abundant photoproduct from the acid portion of **1**.

The alcohol moiety of fluvalinate is converted photochemically to products that have been identified previously with other pyrethroids. As with deltamethrin (Ruzo, 1983b), photohydrolysis is the major initial process giving cyanohydrin **6**, which decomposes into hydrogen cyanide and PBald (**5**). Cyanide is converted readily by sunlight to CO_2 (Mikami et al., 1980) while PBald (**5**) is oxidized further to PBacid (**4**). Thus, the major products from alcohol-labeled fluvalinate are a mixture of **4** and **5**. PPAnitrile (**9**) is formed in low yield also (2% of applied ^{14}C) as with fenvalerate (Holmstead et al., 1978b), but the CO_2-elimination product **12** was not found in thin films of **1**, in contrast to the analogous CO_2-elimination products from thin films of fenvalerate (7% yield; Holmstead et al., 1978b) and deltamethrin (4% yield; Ruzo et al., 1977).

Thin Film on Soil. The half-life of [*trifluoromethyl*-^{14}C]fluvalinate on sterilized sandy loam soil was about 1 day. This half-life is shorter than that of fenvalerate (ca. 4 days in summer; Mikami et al., 1980), but the authors of the fenvalerate work found a large dependency of half-life on soil type (2–18-day range). Amide **7** and anilino acid **2** were the major products (up to 14 and 24% of the applied ^{14}C, respectively) when fluvalinate (1 μg/cm^2, 0.1 kg/ha) on sterilized soil was exposed to sunlight for 2 weeks. The actual role of sunlight in the formation of **7** and **2** is somewhat questionable since both were also the major products in a dark control, suggesting that chemically catalyzed hydrolysis or residual microflora may be a more critical determinant of degradation than light. It is notoriously difficult to sterilize soils fully by autoclaving. The thermal degradation of fluvalinate on autoclaved soil after 1 week was investigated at several temperatures (Table III). The formation of amide **7** and anilino acid **2** is clearly temperature dependent, but autoclaving of soils is believed to affect the catalytic properties of the soil. Thus, it is difficult to conclude whether the temperature dependence is due to chemical or biological degradation.

Interestingly, haloaniline **3** is a minor (maximum 3% applied ^{14}C) product of fluvalinate as a thin film on soil in sunlight. This result contrasts with the copious evolution of **3** in the same sandy loam soil when microbially active (Staiger and Quistad, 1983) where about half of the applied [*trifluoromethyl*-^{14}C]fluvalinate was recovered as **3** in the absence of sunlight. This observation, coupled with the high yield of **3** from thin films of **1** on glass in sunlight (Table III), suggests that haloaniline **3** in the presence of soil is photodegraded. The relatively high amount of unextractable ^{14}C in soil after 14 days (35% applied ^{14}C) may reflect the photodegradation and incorporation of **3** into the soil matrix.

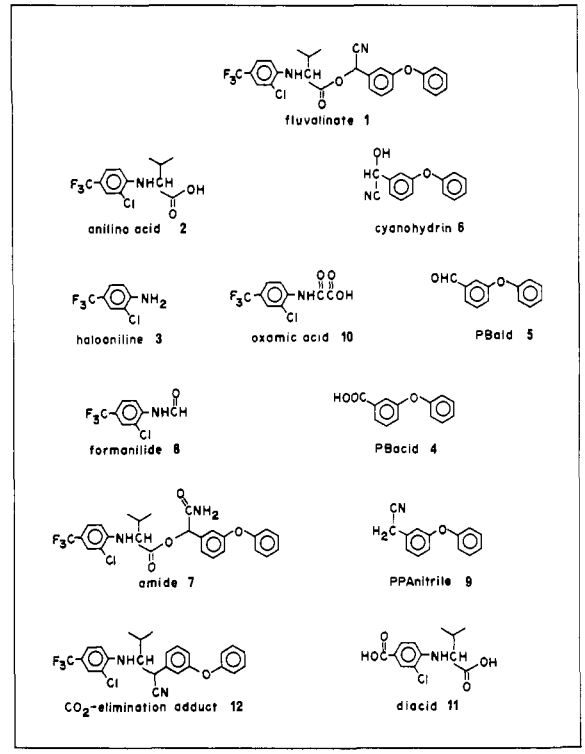

Figure 1. Structures of photodegradation products of fluvalinate.

Diacid **11** was isolated also and identified by GC/MS as its dimethyl ester. This diacid represented about 1% of the applied ^{14}C and has been shown previously by us to form in aqueous solutions as the pH increases.

Although [*benzyl*-^{14}C]fluvalinate was not used in this work, its fate is readily predictable. As with fenvalerate (Mikami et al., 1980), formation of an amide (i.e., **7**) is a high-yield reaction in soil but not for thin films on glass or aqueous solutions of the pyrethroid. In contrast to fenvalerate on soil, we would expect higher yields of PBald and PBacid to complement the higher hydrolysis of fluvalinate [cf. Mikami et al. (1980)].

Aqueous Photochemistry. Fluvalinate is stable in water at neutral pH ($t_{1/2}$ > 30 days at pH 6, 25 °C) but is less stable as the temperature increases ($t_{1/2}$ = ca. 8 days at 42 °C). In this study, 1-ppb solutions of both [*trifluoromethyl*-^{14}C]- and [*benzyl*-^{14}C]fluvalinate were exposed to sunlight for 7 days with water temperatures fluctuating with the daily solar cycle (up to ca. 35 °C in the afternoon sun). Under these natural conditions fluvalinate was stable in the dark ($t_{1/2} \gg 1$ week) but readily decomposed in sunlight ($t_{1/2} < 1$ day).

A dilute aqueous solution of [*trifluoromethyl*-^{14}C]fluvalinate in sunlight gave a multitude of products. The single most abundant product at all times was haloaniline **3** (up to 18% applied dose), which was also present in the dark control but present in higher yield with sunlight. Lower amounts of formanilide **8**, oxamic acid **10**, and anilino acid **2** were also present (up to 4, 3, and 3% of the applied ^{14}C, respectively). The amide **7** represented a maximum of 1% of the applied ^{14}C, and CO_2-elimination adduct **12** was not detected, in contrast to the work of Mikami et al. (1980), who obtained up to 4 and 19% yields of the corresponding photoproducts from aqueous fenvalerate in sunlight.

When [*benzyl*-^{14}C]fluvalinate was exposed to sunlight, the initial hydrolysis product was cyanohydrin **6**, but it never contributed more than 7% of the applied ^{14}C. Further dehydrocyanation of **6** gave PBald (**4**), which along

with its oxidation product [i.e., PBacid (5)] represented the major ^{14}C residues (up to 49% of the applied dose). As with fenvalerate (Mikami et al., 1980), PPAnitrile (9) was a significant aqueous photoproduct (up to an 8% yield).

Conclusions. When fluvalinate is exposed to light in organic solvent, on glass, on soil, or in aqueous solution, it is readily degraded. In natural sunlight, the half-life of fluvalinate is typically 1 day (or less). The alcohol portion of fluvalinate yields most of the same photoproducts (Figure 1) as similar pyrethroids such as cypermethrin, deltamethrin, and fenvalerate although free radical derived photoproducts (e.g., CO_2 elimination adducts like 12) are considerably less abundant from fluvalinate. The acid portion of fluvalinate is converted by sunlight mostly into haloaniline 3 and anilino acid 2 although two previously uncharacterized degradation products from 1 were identified also (formanilide 8 and oxamic acid 10).

ACKNOWLEDGMENT

We thank N. Kerk and L. E. Milligan for laboratory assistance, G. C. Jamieson for mass spectral analysis, and D. A. Schooley for useful suuggestions.

Registry No. 1, 69409-94-5; 2, 76338-73-3; 3, 39885-50-2; 4, 3739-38-6; 5, 39515-51-0; 6, 39515-47-4; 7, 90720-03-9; 8, 90720-03-9; 9, 51632-29-2; 10, 90720-06-2; 11, 85236-41-5; 12, 90720-04-0.

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Received for review March 1, 1984. Accepted May 7, 1984.

Persistence of Aminocarb in Balsam Fir Foliage, Forest Litter, and Soil after Aerial Application of Three Formulations

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One water-based (180 FE) and two oil-based (180 FO and 180 D) aminocarb formulations were applied twice by a fixed-wing aircraft, each at 70 g of a.i./ha, to a coniferous forest near Bathurst, New Brunswick. The highest concentration of aminocarb in foliage was 2.76 ppm (fresh weight), detected 1 h after the second application of formulation 180 D. The residues decreased rapidly within 1 or 2 days after spray application but persisted at lower concentrations thereafter. Twenty-one days after the second spray application, the concentrations of aminocarb in foliage ranged from 0.14 to 0.64 ppm (fresh weight). Only low levels of residue were detected in forest litter and soil. The highest concentrations in litter and in soil were 0.216 ppm (fresh weight) and 0.044 ppm (fresh weight), respectively, detected 2 h after the second application of formulation 180 D. Residues in litter were higher and persisted longer than in soil. There was 0.013 ppm (fresh weight) present in litter 21 days after the second application of formulation 180 D but none were detected in soil after 8 days.

Aminocarb [4-(dimethylamino)-*m*-tolyl *N*-methylcarbamate, Matacil), a broad-spectrum insecticide, was first field tested against spruce budworm [*Choristoneura fumiferana* (Clem.)] in 1970 in New Brunswick and was first used in operational spray programs in 1975. Since then, a total of about one million kg of aminocarb has been applied to the forests of Newfoundland, New Brunswick, Quebec, and Ontario (Nigam, 1980). The formulation Matacil 180 D, which has been used extensively in spray operations, contains by weight 19.5% aminocarb, 30.0% Shell insecticide diluent 585, and 50.5% nonylphenol (National Research Council of Canada, 1982). It has been shown that Matacil 180 D is toxic to juvenile Atlantic salmon, *Salmo salar*, and some species of marine and freshwater invertebrates. The formulation is even more toxic than the pure active ingredient because nonylphenol itself is extremely toxic to these animals (McLeese et al., 1980). In order to minimze the toxicity of the aminocarb formulation, Chemagro Ltd., marketers of Matacil in Canada, has developed a flowable suspension, Matacil 180 F, containing air-milled particles of aminocarb (2–3-μm diameter) suspended in oil, which can be applied either as a water-based (180 FE) or an oil-based (180 FD) for-

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0021-8561/84/1432-1138$01.50/0