was not demonstrated, primarily due to the large experimental variability.

Reaction 6: Conjugates. The acidic metabolites resulting from ester cleavage underwent conjugation with glucuronic acid, sulfate, and glycine, followed by elimination via urinary excretion. Results did not indicate any significant difference between the various isomer preparations.

Based on the data from this and other studies of the metabolism of fenvalerate, there is no apparent qualitative or quantitative difference in the disposition of racemic fenvalerate or its various isomer combinations.

ACKNOWLEDGMENT

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Registry No. 1 (isomer 1), 67890-40-8; 1 (isomer 2), 67890-39-5; 2, 55291-27-5; 5, 97635-01-3; 6 (isomer 1), 97635-02-4; 6 (isomer 2), 97635-06-8; 7, 72061-37-1; 8, 3739-38-6; 9, 35065-12-4; 10 (isomer 1), 97635-03-5; 10 (isomer 2), 97635-07-9; 11, 97635-04-6; 12 (isomer 1), 97644-32-1; 12 (isomer 2), 97635-08-0; 13, 97635-05-7; 14, 50789-43-0; 15, 63987-15-5; *p*-$ClC_6H_4CH(CO_2H)CH(CH_3)CH_2OH$ (isomer 1), 97634-99-6; *p*-$ClC_6H_4CH(CO_2H)CH(CH_3)CH_2OH$ (isomer 2), 97635-00-2.

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Fate of Fenvalerate (Pydrin Insecticide) in the Soil Environment

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The fate of fenvalerate (Pydrin insecticide) in the soil environment was examined. The half-lives of fenvalerate under laboratory aerobic or outdoor conditions in sandy loam and silty clay loam soils are approximately 75–80 days. In addition to degradation products resulting from the cleavage of the ester linkage, $CONH_2$-and 4′-OH-fenvalerate were detected. Further degradation of the soil metabolites was evident by the generation of $^{14}CO_2$ and unextractable residues. The degradation of fenvalerate in the soil environment was primarily by microbial action. Lettuce, beets, and wheat were planted at 30 days, 120 days, and 1 year after the soil was treated with [^{14}C]fenvalerate at a rate equivalent to 2 lb/acre. The crops were harvested at maturity and were found to contain low levels of [*chlorophenyl*-^{14}*C*]- and [*phenoxyphenyl*-^{14}*C*]fenvalerate equivalent residues (below or 1–3 times the limit of detection). Little downward movement of radioactivity was observed in the soil container. It is concluded that under test conditions fenvalerate is relatively nonpersistent in the soil environment. In addition, rotational crops planted at various time intervals after soil treatment contained low, if any, significant residue levels of fenvalerate or its metabolites.

INTRODUCTION

Fenvalerate [1, cyano(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate], known as Pydrin insecticide (Shell Chemical Company), Sumicidin (Sumitomo Chemical Company), and Belmark (Shell International Chemical Company), is an effective broad spectrum synthetic pyrethroid insecticide. In addition to its highly selective insecticidal activities, fenvalerate exhibits improved photolytic stability and an extended field residual activity compared to other commercial pyrethroids. The increased wide use pattern and the longer residual activities of fenvalerate warrant the need of understanding the fate of this compound and its degradation products in the environment. As a part of this comprehensive evaluation, this report summarizes (1) the fate of fenvalerate in the soil environment and (2) the uptake and the accumulation potential of fenvalerate and its metabolites in various agricultural crops (lettuce, beets, and wheat) that occurred under field rotational crop conditions.

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MATERIALS AND METHODS

Test Materials and Reference Standards. Radiolabeled fenvalerate and appropriate reference standards were synthesized by the Biological Sciences Research Center (BSRC), Shell Development Company. Two preparations of [^{14}C]fenvalerate, labeled at the chlorophenyl and the other at the phenoxyphenyl moiety, had a radiochemical purity of greater than 99.5% as determined by thin-layer chromatography (TLC), autoradiography, and liquid scintillation counting (LSC). Authentic standards included CPIA [2, 4-chloro-α-(1-methylethyl)-benzeneacetic acid], 4′-OH-fenvalerate [3, cyano(3-phenoxy-4-hydroxyphenyl)methyl 4-chloro-α-(1-methylethyl)-benzeneacetate], $CONH_2$-fenvalerate [4, (aminocarbonyl)(3-phenoxyphenyl)methyl 4-chloro-α-(1-methylethyl)benzeneacetate], PBacid [5, 3-phenoxybenzoic acid], and 4′-OH-PBacid, [6, 3-(4-hydroxyphenoxy)benzoic acid]. Chemical structures of these compounds are pres-

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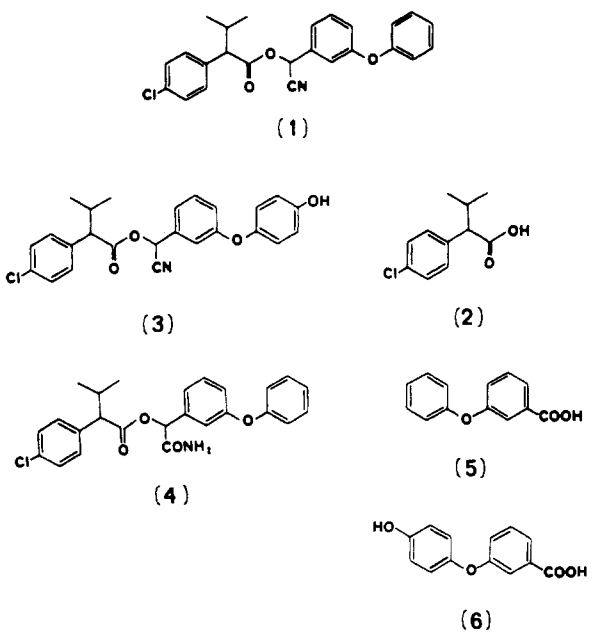

Figure 1. Soil metabolites of fenvalerate.

Table I. Characteristics of Test Soil[a]

	Modesto, CA	W. Burlington, IA
C.E.C., mequiv/100 g	7.5	20.2
field moisture, % ($^1/_3$ bar)	6.7	27.4
bulk density, g/cm^3	1.4	1.1
total nitrogen, %	0.4	0.2
hydrogen, mequiv/100 g	0	6.2
organic matter, %	1.1	2.0
soil pH	7.3	5.3
sand, %	81.6	19.6
silt, %	11.2	62.8
clay, %	7.2	27.6
texture	sandy loam	silty clay loam

[a] Soil samples were analyzed by A&L Midwest Agriculture Laboratories, Inc., Omaha, NE 68144.

ented in Figure 1. Methyl esters of **2** [CPIA-Me, **7**], **5** [PBacid-Me, **8**], and **6** [4′-OH-PBacid-Me, **9**] were prepared by methylation with diazomethane.

Aerobic and Anaerobic Soil Metabolism. Freshly collected Hanford sandy loam (Modesto, CA) and Catlin silty clay loam soils (West Burlington, IA) were used in this study. Air-dried soil samples (24 h at room temperature) were passed through a 2-mm sieve to remove any large debris and were stored at 4 °C prior to use. Physical characteristics of the two test soils are summarized in Table I.

A concentration of 5 ppm of [*chlorophenyl*-^{14}C]fenvalerate (specific activity 14.5 μCi/mg) was established in air-dried test soils (1.2 kg) by applying the appropriate amount of the test material in methanol (6 mg/mL) directly onto the soil surface. After the evaporation of solvent, treated soils were thoroughly mixed and the uniformity was determined by oxygen combustion and LSC of subsamples.

Treated soil samples (100 g each) were transferred to a 500-mL Erlenmeyer flask and the soil moisture level was adjusted to approximately 75% of the field moisture capacity. Soil samples were maintained in the following incubation system which consisted of (1) a gas filter (to remove any CO_2 and gas impurities), (2) a 500-mL gas washing bottle containing water (air humidifier), (3) manifold, (4) treated soil container, (5) a 250-mL gas washing bottle containing 200 mL of ethylene glycol (volatile component trap), and (6) a 250-mL gas washing bottle containing 200 mL of ethanolamine ($^{14}CO_2$ trap). This system could maintain up to eight individual soil containers and allowed for independent air flow control. Gas washing bottles were modified with a sidearm which provided the continuous monitoring of the amount of radioactive volatile components and $^{14}CO_2$ without disturbing the soil container during the entire aerobic and anaerobic incubation periods. The soil metabolism study was conducted in darkness at 23 ± 1 °C.

In the aerobic soil metabolism study, [^{14}C]fenvalerate-treated soils were purged continuously with humidified air (20–30 mL/min). In the anaerobic soil metabolism study, soil samples were initially incubated under aerobic conditions for 30 days prior to establishing anaerobic conditions by water logging the soil container with 200 mL of tap water (2–3 cm above soil surface) followed by the continuous purging of the soil container with humidified nitrogen.

Aliquots (2 mL) of the ethylene glycol and ethanolamine solution were sampled at various time intervals and triplicate subsamples (0.5 mL) were assayed directly by LSC. In order to examine the chemical nature of the soil residues, soil samples were removed at various time intervals (aerobic study immediately after application, 0.5, 1, 2, 3, 6, 9, and 12 months after treatment; anaerobic study 1 and 2 months after maintenance under anaerobic conditions) and extracted three times with 100 mL of methanol ^{14}C residues in the combined methanol extract were concentrated to approximately 25 mL and the residual material was resuspended in saturated sodium chloride solution (50 mL final volume). This aqueous mixture was partitioned three times with equal volumes of chloroform. The combined chloroform extract was dried over anhydrous sodium sulfate, concentrated, and analyzed by two-dimensional TLC. Unextractable soil residues after the methanol extraction was quantitated by LSC after combustion.

In the anaerobic metabolism study, flood water was separated from the soil sample by centrifugation. It was acidified to pH 3 with 6 N hydrochloric acid before partitioning three times with equal volumes of chloroform. ^{14}C residues in the combined chloroform extract were analyzed by two-dimensional TLC. Soil samples were extracted with methanol as described above.

Chromatography and Radioassay. Radioactivity was quantitated in 15 mL of Aquasol-2 scintillation solution (New England Nuclear) with a Packard Model 2660 liquid scintillation system. The radioactive area of the TLC plate, after solvent development and autoradiography, was removed by scraping and analyzed in an Aquasol-2/water (11:4 mL) gel system. ^{14}C residues in the soil sample were analyzed by combusting subsamples (100 mg) in a Packard 306B sample oxidizer. Combustion efficiency was determined by using untreated soil and [^{14}C]fenvalerate solution as the calibration standard. The oxidizer counting solution included a Carbo-Sorb and Permafluor V (10:12 mL) mixture.

^{14}C residues recovered from the soil and aqueous extracts were analyzed by two-dimensional TLC (silica gel F-254, 0.25 mm, E. Merck). The R_f values of fenvalerate and reference standards in several TLC solvent systems are presented in Table II. The distribution pattern of ^{14}C residues on the TLC plate was visualized by autoradiography on Kodak SB-5 single-coated X-ray film.

Capillary gas-liquid chromatography was carried out with a 25 m × 0.37 mm i.d., SE-30, WCOT, glass column in a Varian 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector. Isothermal analysis was carried out at injector, column, and detector temperatures of 280,

Table II. TLC R_f Values and Mass Spectral Data of Fenvalerate and Model Metabolites

	R_f value				
	system 1[a]	system 2[b]	K_{ow}[d]	K_p[e]	mass spectral data, m/z
fenvalerate (1)	0.78	0.72	$>1 \times 10^4$	35	419 (M^+), 225, 181, 169, 167, 154, 152, 127, 125
CPIA (2)	0.70	0.38	48	0.2	212 (M^+), 172, 170, 127, 125
4′-OH-fenvalerate (3)	0.62	0.42	3390	19	435 (M^+), 252, 169, 167, 154, 152, 127, 125, 91, 89
$CONH_2$-fenvalerate (4)[c]	0.54–0.57	0.30–0.35	3849	21	437 (M^+), 421, 419, 395, 393, 252, 198, 169, 167, 154, 152, 127, 125, 91, 89
PBacid (5)	0.49	0.38	543	1.5	214 (M^+), 196, 169, 168, 141, 115, 77
4′-OH-PBacid (6)	0.41	0.16	113	0.5	
CPIA-Me (7)					226 (M^+), 186, 184, 169, 167, 154, 152, 127, 125, 117, 115, 91, 89
PBacid-Me (8)					228 (M^+), 197, 169, 141, 115, 98, 77
4′-OH-PBacid-Me (9)					244 (M^+), 213, 185, 157, 128, 106, 76

[a] Hexane–acetone–acetic acid (25:25:1). [b] Toluene–ether–acetic acid (75:25:1). [c] TLC solvent systems resolved the two corresponding diastereomers. [d] Distribution of radioactivity between octanol and water, log (concentration in octanol/concentration in water). [e] Distribution of radioactivity between soil and water, log (concentration in the sandy loam soil/concentration in water).

Table III. Distribution of Radioactivity Recovered in the Various Fractions from the Sandy Loam Soil Treated with [*chlorophenyl*-^{14}C]Fenvalerate under Aerobic and Anaerobic Conditions

	percent of applied radioactivity									
	aerobic time, months								anaerobic time, months	
	0	0.5	1	2	3	6	9	12	1	2
volatile		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
$^{14}CO_2$		2.1	5.6	11.9	20.2	31.8	47.2	50.5	6.1	4.5
aqueous									8.8	14.5
CPIA (2)									8.4	13.5
methanol extractable	99.6	87.3	80.1	66.1	55.1	31.0	21.8	22.5	73.8	63.5
fenvalerate (1)	98.9	86.5	70.6	54.4	50.0	26.6	17.9	16.6	63.3	57.5
CPIA (2)		0.3	2.2	3.0	1.3	0.4	0.4	2.6	4.2	3.0
4′-OH-fenvalerate (3)		0.4	3.4	4.3	1.9	3.3	1.5	1.1	4.4	1.0
$CONH_2$-fenvalerate (4)			1.4	2.3	1.1	0.3	0.2	1.9	1.1	0.8
bound residues	1.2	6.7	12.9	17.9	22.6	33.2	29.8	26.0	7.2	14.1
total	100.8	96.2	98.7	96.0	98.0	96.1	98.9	99.1	96.0	96.7

245, and 320 °C, respectively. The helium carrier gas and nitrogen make-up gas flow rate through the detector were 3 and 35 mL/min, respectively. On-column split ratio was controlled at 10:1 ratio.

Mass spectral analysis was carried out on the Finnigan 3200 GC–mass spectrometer with a 12 m × 0.3 mm SE-30 WCOT glass column. A summary of the mass spectral data of fenvalerate and model metabolites is also included in Table II.

Rotational Crop Residue Study. Test soils (sandy loam) were packed into a polyethylene container (18-in. diameter, 29-in. high). Two inches of pea gravel were placed in the bottom of the soil containers followed by sandy loam soil to within 3 in. of the top of the container. This rotational crop study was conducted in the outdoor plant growth enclosure area of the Environmental Radioisotope Facility at BSRC. Both [*chlorophenyl*-^{14}C]- and [*phenoxyphenyl*-^{14}C]fenvalerate formulations were prepared in an Atlox–xylene mixture. The final specific activity of the treatment solution was 5 μCi/mg. This level of specific activity allowed for the minimum detection of 0.05 ppm of the total [^{14}C]fenvalerate equivalent residues in the soil and various plant samples. Each soil container was treated with 40 mg of [^{14}C]fenvalerate in the final aqueous application solution of 20 mL and the resulting dose rate was approximately 2 lb/acre.

Seeds of wheat (Anza), table beets (Detroit Red), and leaf lettuce (Prizehead) were planted individually in separate soil containers at 30-day, 120-day, and 1-year intervals after soil application of [^{14}C]fenvalerate. Control crops were also planted individually in the untreated soil containers. To minimize the number of soil containers, radiolabeled test materials required and the amount of crop samples needed to be analyzed, the usage of [*phenoxyphenyl*-^{14}C]fenvalerate was limited to the 120-day rotation interval only. The planting and fertilizing procedures followed acceptable agricultural practices and the watering schedule was based on soil moisture content as determined by tensiometers. This study was conducted between June, 1981 and June, 1983.

Both immature and mature crop samples were analyzed. The leafy portion of the lettuce, the aerial and the root portion of the beets and wheat straw, grain and hulls were radioassayed for the level of total ^{14}C residues. Crop samples were also qualitatively and quantitatively analyzed for [^{14}C]fenvalerate and related degradation products. Samples were homogenized and extracted with hexane, and the organic-extractable and water-soluble conjugates (examined after enzyme hydrolysis with β-glucosidase) were analyzed. Soil core samples collected at the planting and harvest intervals were also examined.

RESULTS AND DISCUSSION

Aerobic and Anaerobic Soil Metabolism. The portion of the applied radioactivity in the ethylene glycol trap, $^{14}CO_2$, solvent extractable, and unextractable fractions under aerobic and anaerobic conditions in the sandy loam and the silty clay loam soils is presented in Tables III and IV. Immediately after soil application, greater than 99% of the applied radioactivity was recovered as [^{14}C]fenvalerate in the methanol extract. A steady decrease of the extractable radioactivity along with a corresponding increase of $^{14}CO_2$ formation and unextractable ^{14}C residues was observed (Figure 2). Radioactivity present in the ethylene glycol trap was negligible thus indicating no radioactive volatile metabolite was generated. The overall recovery of the applied radioactivity throughout this study was consistently greater than 95%.

Autoradiograms of the radioactivity recovered in the methanol extract of the two test soils after 12 months of

Table IV. Distribution of Radioactivity Recovered in the Various Fractions from the Silty Clay Loam Soil Treated with [*chlorophenyl*-^{14}C]Fenvalerate under Aerobic and Anaerobic Conditions

	percent of applied radioactivity									
	aerobic time, months								anaerobic time, months	
	0	0.5	1	2	3	6	9	12	1	2
volatile		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
$^{14}CO_2$		0.5	1.6	3.3	7.7	9.4	12.8	14.3	3.8	3.9
aqueous									4.2	14.5
CPIA (2)									3.7	13.2
methanol extractable	97.5	83.4	79.8	68.4	62.1	39.4	27.9	25.9	73.7	64.4
fenvalerate (1)	97.2	74.2	71.9	55.8	54.6	33.2	21.8	11.8	64.7	56.7
CPIA (2)		1.3	2.5	2.6	1.6	1.2	0.8	1.7	3.8	3.6
4′-OH-fenvalerate (3)		2.5	2.1	2.8	1.1	1.4	0.9	0.2	1.7	1.4
$CONH_2$-fenvalerate (4)		0.4	0.6	0.9	1.1	1.0	1.2	10.0	0.6	0.3
bound residues	2.2	10.9	14.5	16.5	30.5	45.3	48.5	53.4	14.0	13.8
total	99.7	94.8	95.9	88.2	100.3	94.1	89.2	93.6	95.8	96.7

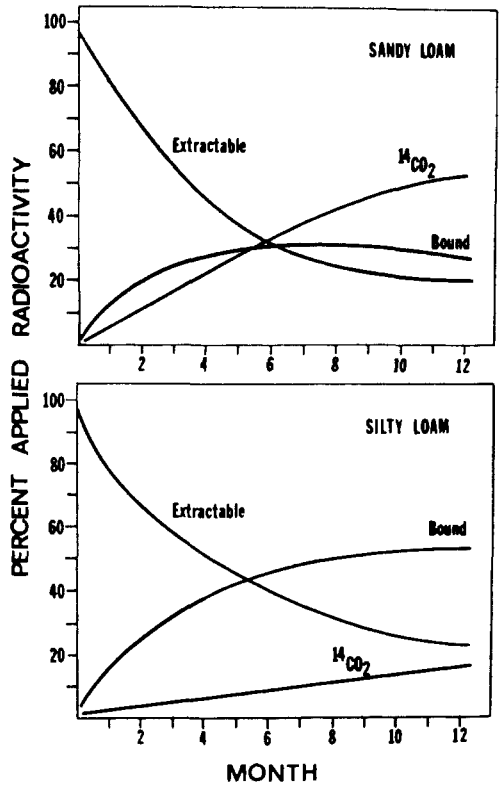

Figure 2. Degradation of [*chlorophenyl*-^{14}C]fenvalerate in the sandy loam and the silty clay loam soils.

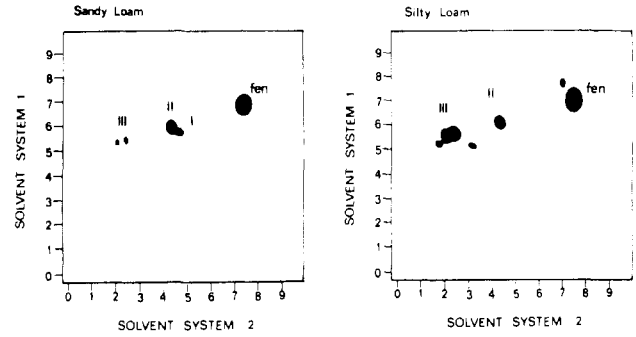

Figure 3. Thin-layer autoradiograms of [*chlorophenyl*-^{14}C]fenvalerate and its metabolites from the sandy loam and the silty clay loam soils after 1 year of aerobic incubation. Metabolites I, II, and III were identified as 4′-OH-fenvalerate (3), CPIA (2), and $CONH_2$-fenvalerate (4), respectively.

aerobic incubation are presented in Figure 3. In addition to the undegraded [^{14}C]fenvalerate, there were at least three primary soil metabolites which were designated as metabolites I, II, and III. These metabolites were separated by preparative TLC prior to chromatographic and spectroscopic analyses. Metabolite I was identified as 4′-OH-fenvalerate (3). Metabolite II, after methylation with diazomethane, was identified as CPIA-Me (7), the methyl ester of CPIA (2). Metabolite III, consisting of two diastereomers, was identified as $CONH_2$-fenvalerate (4). The quantity of these metabolites ranged from 0.2 to 10% of the applied radioactivity. Further degradation of these metabolites was evident by the generation of $^{14}CO_2$ (equivalent to 50% of the applied radioactivity in the sandy loam soil after 12 months) and a significant amount of the applied radioactivity (26%) was recovered as unextractable residues. Continuous aqueous extraction of the unextractable soil residues after the initial methanol extraction resulted in the release of CPIA (2) as the major radiolabeled product. Ether cleavage products, as soil metabolites of fenvalerate (Ohkawa et al., 1978), were not detected in this study.

Several interesting quantitative differences were observed between the sandy loam and the silty clay loam soils under aerobic conditions. In the 12-month sample interval, the level of $^{14}CO_2$ was higher in the sandy loam soil (51 vs. 14%) and the level of unextractable soil bound residues was higher in the silty clay loam soil (53% vs. 26%). A much higher level of $CONH_2$-fenvalerate (4) was also recovered from the silty clay loam soil (10 vs. 2%). Significant qualitative differences in the chemical nature or the metabolite distribution pattern was not observed when the metabolism study was conducted under aerobic or anaerobic conditions.

Radioactivity recovered in the aqueous phase (used for the water logging of the soil chamber) accounted for approximately 13% of the applied radioactivity which was subsequently identified as CPIA (2). The level of unextractable residues was significantly reduced when the sandy loam soil was incubated under anaerobic conditions. The decrease of the unextractable soil bound residues along with the recovery of radioactivity in the water logging fraction suggests that the fenvalerate soil metabolites and bound residues underwent hydrolytic decomposition to yield CPIA (2). No further attempt was made to characterize the chemical nature of the remaining unextractable bound residues.

The dissipation rates ($t_{1/2}$) of [^{14}C]fenvalerate in the sandy loam and the silty clay loam soil under laboratory aerobic conditions are approximately 75–80 days which are somewhat slower than other reported studies ($t_{1/2}$ from 15 days to 3 months, Ohkawa et al., 1978). This is not unexpected since earlier reports showed that variations in the test soil and environment had produced variations in

Table V. Summary of the Distribution of Total [^{14}C]Fenvalerate Equivalent Residues in the Soil, Lettuce, Beets, and Wheat at Various Planting Intervals

	total [^{14}C]fenvalerate equivalent residues, ppm			
	[*chlorophenyl*-^{14}C] after 30 days	[*chlorophenyl*-^{14}C] after 120 days	[*phenoxyphenyl*-^{14}C] after 120 days	[*chlorophenyl*-^{14}C] after 1 year
soil[a] (n = 6)				
0–3 in.	1.99 ± 0.48	1.00 ± 0.27	1.07 ± 0.24	1.31 ± 0.31
3–6 in	0.10 ± 0.05	<0.04[c]	<0.04	<0.04
lettuce	0.02, 0.03[b]	0.01, 0.01	0.01, 0.01	<0.01, 0.01
beets				
leaf	0.18, 0.10	0.02, 0.02	0.02, 0.02	0.03, 0.03
root	0.27, 0.31	0.04, 0.03	0.04, 0.03	0.04, 0.04
wheat				
straw	0.29, 0.33	0.04, 0.05	0.05, <0.04	0.13, 0.15
hull	0.08, 0.07	<0.04	<0.04	<0.04
grain	0.04, <0.04	<0.04	<0.04	<0.04

[a] Initial [^{14}C]fenvalerate concentration in the soil container (2.26 ± 0.44 ppm). [b] Residue data for the crop samples from each of the two soil containers. [c] Residue level below the limit of reliable measurement.

pyrethroid stability (Williams and Brown, 1979; Miyamoto and Mikami, 1983).

An additional study with sterilized sandy loam soil showed the lack of biodegradation of the applied [^{14}C]-fenvalerate or the the formation of unextractable soil bound residues (Lee et al., 1982). Greater than 95% of the applied radioactivity was recovered as the undegraded parent molecule from the sterilized soil after 30 days aerobic incubation. This result indicated the soil degradation of fenvalerate was predominantly by microbial activity. The primary degradation reactions of fenvalerate involved the cleavage of the ester linkage, hydration of the cyano moiety, and the hydroxylation of the phenoxy moiety of the parent molecule.

Rotational Crop Residue Study. A rotational crop study was conducted with [*chlorophenyl*-^{14}C]- and [*phenoxyphenyl*-^{14}C]fenvalerate. The initial concentration of [^{14}C]fenvalerate in the 0–3-in. fraction of the soil container was 2.3 ppm, approximating the 2 lb/acre application rate. Lettuce, beets, and wheat planted 30 days, 120 days, and 1 year after soil application were harvested at various growing stages and at maturity and were analyzed for total ^{14}C residues, parent, and metabolites. A summary of the distribution of the total [^{14}C]fenvalerate equivalent residues (ppm) in the soil and the various crop samples is presented in Table V.

Rapid dissipation of the applied [^{14}C]fenvalerate was observed in the soil containers. The calculated half-life of fenvalerate in the soil containers under outdoor conditions was approximately 60 days. At the 30-day, 120-day, and the 1-year planting time, approximately 75, 40, and 35%, respectively, of the undegraded [^{14}C]fenvalerate was recovered from the 0–3-in. soil depth. $CONH_2$-fenvalerate (**4**) was the major soil degradation product. 4′-OH-fenvalerate (**3**) and CPIA (**2**) were detected as minor soil degradation products of [*chlorophenyl*-^{14}C]fenvalerate. In addition to $CONH_2$-fenvalerate (**4**) and 4′-OH-fenvalerate (**3**), PBacid (**5**) and 4′-OH-PBacid (**6**) were identified as their corresponding methyl esters (**8** and **9**) in the [*phenoxyphenyl*-^{14}C]fenvalerate treated soil containers as minor components. There is no observable qualitative difference when the [^{14}C]fenvalerate treated soil was maintained under outdoor or indoor laboratory conditions.

Monitoring the radioactivity in the various depths of the soil containers indicated [^{14}C]fenvalerate and its degradation products had low soil mobility potential since less than 0.1 ppm of the ^{14}C residues were detected in the 3–6-in. level even two years after application. ^{14}C residues below the 6-in. level were below the limit of detection. This apparent lack of soil mobility was verified by soil column leaching and soil thin-layer chromatography (Reed et al., 1983). By comparing with reference standards of known soil mobility (trichloroacetic acid, 2,4-D, DDT, and atrazine; Helling, 1971), it was found that fenvalerate was immobile in all types of soils tested. Soil degradation products such as CPIA (**2**) and PBacid (**5**) showed low to intermediate mobility in the soil TLC system.

All crop samples contained low levels of ^{14}C residues (<0.05 ppm) from both the [*chlorophenyl*-^{14}C]- or [*phenoxyphenyl*-^{14}C]fenvalerate treated soil containers. Beet roots and wheat straw from the 30-day interval [*chlorophenyl*-^{14}C]fenvalerate treated soil contained the highest level of ^{14}C residue (approximately 0.3 ppm) detected in this study. GLC analysis showed no detectable fenvalerate (<0.01 ppm limit of detection) was recovered from these samples by organic solvent extraction. Approximately 25% of the total ^{14}C residues in these crop samples were identified as the glucoside conjugates of CPIA (**2**). Results from a fractionation experiment (Honeycutt and Adler, 1975) showed a majority of the ^{14}C residues was associated with the unextractable cellulose fraction which accounted for the remaining 75% of the total ^{14}C residues.

CONCLUSION

Results from this and other studies (Ohkawa et al., 1978; Miyamoto and Mikami, 1983) have shown the extensive microbial degradation of fenvalerate in the soil environment. The rate of dissipation is significantly affected by the physicochemical properties and the microbial nature of the test soils. 4′-OH-Fenvalerate (**3**), $CONH_2$-fenvalerate (**4**), CPIA (**2**), PBacid (**5**), and 4′-OH-PBacid (**6**) were identified as principle soil degradation products of fenvalerate. These degradation products had a lesser accumulation potential than the parent molecule as indicated by the lower octanol–water partitioning coefficient (see Table II). The further degradation of the fenvalerate soil metabolites was evident by the generation of $^{14}CO_2$ and the formation of unextractable soil bound residues. The overall metabolic profile of fenvalerate is similar to that reported for other cyano pyrethroids which include fluvalinate (Staiger and Quistad, 1983), cypermethrin (Roberts and Standen, 1977a), deltamethrin (Ruzo and Casida, 1979), and fenpropathrin (Roberts and Standen, 1977b). Relative instability and low mobility of fenvalerate and its metabolites limit the leaching potential of fenvalerate in the soil environment. The rotational crop study showed that very low, if any, residues of fenvalerate and its metabolites occurred in the plants grown in the fenvalerate treated soil.

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Novel Photoreactions of an Insecticidal Nitromethylene Heterocycle

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Tetrahydro-2-(nitromethylene)-2*H*-1,3-thiazine, a remarkably potent insecticide, undergoes facile photoreaction by processes including conversion to the nitrile, reduction to the nitroso derivative and dimerization, oxidative cleavage of the nitromethylene group, and exchange of the vinylic hydrogen in protic solvents. The very efficient exchange reaction is essentially complete before degradation products are evident in the photolysate. Three possible mechanisms for photoexchange at the nitrovinyl group are α,β-addition of the solvent followed by elimination, hydrogen abstraction similar to that in Norrish type II photoreaction, and formation of an excited state with enhanced acidity of the vinylic proton.

The nitromethylene heterocycles are a unique insecticide class including compounds with very high insecticidal activity coupled with low mammalian toxicity (Soloway et al., 1978). Tetrahydro-2-(nitromethylene)-2*H*-1,3-thiazine (1, Shell Development Co.) (Figure 1) is one of the most active compounds but its high photolability is a serious drawback in practical applications. It is therefore of interest and importance to define the principal photoprocesses in the facile decomposition of 1 and the possible involvement of the toxophoric nitromethylene substituent in these reactions.

MATERIALS AND METHODS

Chemicals. Compounds 1, 4, and 5 (Figure 1) were synthetic standards prepared by Shell Development Co. The sensitizers and deuterated solvents were from Aldrich Chemical Co. (Milwaukee, WI).

Photolysis Procedures. 1 at 0.01 M in water, sodium dodecyl sulfate (SDS) (0.03 M) micellar solutions, methanol, dichloromethane, or toluene was irradiated to <10 or ~30% conversion at 360 nm in a Rayonette reactor (The Southern New England Ultraviolet Co., Middletown, CT). Alternatively, for mechanistic studies, 1 at 0.06 M in D_2O or CH_3OD was irradiated to <1% conversion with a low-pressure Hanovia lamp (Pyrex filter) at −80 °C. Benzophenone, biphenyl, and naphthalene were used as sensitizers at 0.1 M in dichloromethane. Solutions were either oxygenated or degassed by flushing (1 h) with oxygen or argon, respectively.

Chromatography and Spectroscopy. Ultraviolet spectra were recorded in hexane, methanol, water, or 0.03 M SDS aqueous micellar solution. Thin-layer chromatography (TLC) employed silica gel F-254 chromatoplates (0.25 mm, EM Reagents) with carbon tetrachloride–ether (3:1) for isolation of 2 and chloroform–methanol (10:1) for other analyses. High performance liquid chromatography (HPLC) utilized a Beckman 344 instrument equipped with a C_{18} μBondapak reverse-phase column eluted with methanol–water gradients. Photoproducts were isolated by combinations of TLC and HPLC, but only 2 was obtained in high purity due to decomposition of others during workup. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker spectrometer at 300 MHz (^{1}H), 47 MHz (^{2}H), and 75.5 MHz (^{13}C). ^{2}H spectra were recorded in the unlocked mode with reference to external deuteriochloroform. Samples were dissolved in protio- or deuteriomethanol, acetone, chloroform, or water as appropriate and chemical shifts are reported as ppm down field from tetramethylsilane.

Mass spectrometry (MS) utilized a Hewlett Packard 5985B system with ionization by electron impact (EI, 70 eV) or chemical ionization (CI, 230 eV) with methane as the reactant gas (0.8 torr). Fast atom (xenon) bombardment (FAB) spectra were obtained on a ZAB-2F mass spectrometer with samples in glycerol matrix. Masses and relative intensities are given for molecular ($M^{+\cdot}$) or quasi-molecular [$(M + 1)^+$] ions and other important fragments. Samples introduced via direct inlet were heated (60–200 °C) as necessary. Benzoic acid from irradiation of 1 in toluene was identified by gas chromatography–mass

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