Original Article

Degradation and Leaching Behavior of the Pyrethroid Insecticide Cypermethrin in Soils

Shinoi SAKATA, Nobuyoshi MIKAMI, Tadashi MATSUDA
and Junshi MIYAMOTO

*Laboratory of Biochemistry and Toxicology, Takarazuka Research Center,
Sumitomo Chemical Co., Ltd., Takatsukasa, Takarazuka 665, Japan*

(Received August 8, 1985)

The degradation of (1*R*,*cis*)- and (1*R*,*trans*)-isomers of cypermethrin [(*RS*)- α -cyano-3-phenoxybenzyl (1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] in two soils was studied under laboratory conditions, using ^{14}C preparations labeled separately in the cyclopropyl and benzyl rings. The half-life of disappearance was 4.1 to 17.6 days for the *trans*-isomer and 12.5 to 56.4 days for the *cis*-isomer. The insecticide was degraded *via* pathways including cleavage of the ester or diphenyl ether bond, hydroxylation at the 4-position of the phenoxy ring, and hydrolysis of the cyano group to the amide and carboxyl groups. The main degradation route was hydrolysis of the ester linkage. The resultant products underwent further degradation to form $^{14}\text{CO}_2$ and bound residues. A larger amount of $^{14}\text{CO}_2$ was evolved in soils treated with the less persistent *trans*-isomer and with the benzyl- ^{14}C preparation. In contrast, a larger amount of bound ^{14}C was formed in soils treated with the *cis*-isomer and with the cyclopropyl- ^{14}C preparation. Although a trace amount of cypermethrin appeared in the effluent from sand containing less than 0.1% organic matter, there was no leaching of cypermethrin with water through other three types of soil columns, when leaching was started immediately after treatment or after a 30-day preincubation of the treated soil columns.

INTRODUCTION

Cypermethrin [(*RS*)- α -cyano-3-phenoxybenzyl (1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] is one of the most potent synthetic pyrethroid insecticides currently used for agriculture. The insecticide has three chiral centers in the molecule, being a mixture of eight isomers. From the viewpoint of environmental safety, metabolism of cypermethrin in soils,^{1,2)} plants³⁾ and rats^{4,5)} as well as its photodegradation^{6,7)} has been studied. The previous studies have shown that the (1*RS*,*cis*)- and (1*RS*,*trans*)-isomers decompose in soils collected in Spain and UK, *via* oxidation and hydrolysis followed by degradation of the resultant products to CO_2 and bound residues.^{1,2)}

The experiments have now been extended, and two types of Japanese soils treated with

the radiolabeled (1*R*,*trans*)- and (1*R*,*cis*)-isomers were analyzed, after a 24-week storage in the laboratory, to obtain more detailed information on the degradation profile. The leaching behavior of cypermethrin in four types of soils were also examined.

MATERIALS AND METHODS

1. Chemicals

Samples of *cis*- and *trans*-cypermethrin labeled with ^{14}C separately at the C-1 position of the cyclopropyl ring, referred to as [cyclopropyl- ^{14}C], and also at the benzyl ring, referred to as [benzyl- ^{14}C], were synthesized by Kana-maru *et al.*⁸⁾ in the Takarazuka Research Center of Sumitomo Chemical Co., Ltd. The specific activity was 22.0 mCi/mmol for the cyclopropyl- ^{14}C and 25.2 mCi/mmol for the benzyl- ^{14}C . The radiochemical purity of all samples was more than 98.2%, as determined by silica

Table 1 Thin-layer chromatographic properties of cypermethrin isomers and their degradation products.

Compound	R _f values with indicated solvent systems ^{a)}				
	A	B	C	D	E
<i>cis</i> -I	0.60 0.56	0.64	0.56	0.67	0.71
<i>trans</i> -I	0.52 0.48	0.63	0.54	0.67	0.69
II	—	0.30	0.28	—	0.48
III	—	0.30	0.23	0.51	0.48
IV	—	0.33	0.17	0.45	0.35 0.30
V	—	0.05	0.04	—	0.20
<i>cis</i> -VI	—	0.49	0.44	0.45	0.58
<i>trans</i> -VI	—	0.46	0.33	0.38	0.53
VII	—	0.39	0.20	0.32	0.51
VIII	—	0.35	0.80	0.66	0.55 0.52
IX	—	0.59 0.45	—	0.53 0.40	—

^{a)} A: hexane/diethyl ether (20/1, 6 times), B: hexane/toluene/acetic acid (3/15/2), C: hexane/acetone (4/1, 2 times), D: toluene/diethyl ether/acetic acid (75/25/1), E: benzene saturated with formic acid/diethyl ether (10/3).

gel thin-layer chromatography (TLC) in solvent system A shown in Table 1.

The unlabeled *cis*- and *trans*-cypermethrin (designated as *cis*- and *trans*-I), along with the following compounds were synthesized in our laboratory for reference purposes¹⁻⁵⁾: (*RS*)- α -cyano-3-hydroxybenzyl (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (II), (*RS*)- α -cyano-3-(4-hydroxyphenoxy)benzyl (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (III), (*RS*)- α -carbamoyl-3-phenoxybenzyl (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (IV), (*RS*)- α -carbamoyl-3-hydroxybenzyl (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (V), (1*R*,3*S*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (VI), 3-phenoxybenzoic acid (VII), (1*R*,3*S*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2-methylcyclopropane-1,2-dicarboxylic acid (VIII), (*RS*)- α -carboxy-3-phenoxybenzyl (1*R*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (IX).

2. Radioassay

Liquid scintillation counting (LSC), combustion analysis and autoradiography were

carried out according to the methods reported previously.⁹⁾

3. Thin-layer Chromatography (TLC)

The precoated silica gel 60F-254 chromatoplates (20×20 cm, 0.25 mm thickness, E. Merck) were used for analytical and preparative purposes. The *R_f* values of *cis*- and *trans*-I and their derivatives by TLC using five solvent systems are shown in Table 1. The solvent systems for two-dimensional development are illustrated, for example, as follows: (B, C) indicates the development in the first direction with solvent system B and in the second direction with solvent system C. The radioactive spots on the TLC plates were detected by autoradiography, and the unlabeled compounds by ultraviolet light.

4. Soils

Two kinds of soils were collected from upland fields in Japan (Kuki in Saitama Pref. and Azuchi in Shiga Pref.) for the metabolism study, and four kinds of upland soils (Sapporo in Hokkaido, Kodaira in Tokyo Metropolis, Muko and Takarazuka in Hyogo Pref.) for the leaching study. Their properties were characterized according to the methods de-

Table 2 Characteristic of soils used in the experiment.

(Dry soil basis)

	Kuki	Azuchi	Sapporo	Kodaira	Muko	Takarazuka
Soil texture	Clay loam	Sandy clay loam	Clay loam	Clay loam	Sand	Sandy loam
Soil particles (%)						
Sand	70.2	62.5	56.0	31.0	99.0	78.0
Silt	22.6	17.0	22.0	40.0	1.0	7.0
Clay	7.2	20.5	22.0	29.0	1.0	14.0
Clay mineral	—	Kaolinite	Allophane	Allophane	—	—
Organic matter content (%)	6.2	0.4	11.0	15.3	0.1	2.3
Cation exchange capacity (me)	34.0	13.2	41.9	53.7	2.3	9.7
pH	5.7	5.5	5.3	5.5	7.8	6.2
Water content (%)	38.3	13.0	29.0	49.3	<0.1	8.9
Maximum water-holding capacity (%)	135.8	63.1	93.0	148.5	33.5	55.9

scribed in a text book,¹⁰⁾ and the results are summarized in Table 2. The soil samples were kept at 0–4°C in the dark and passed through a 2-mm sieve prior to use.

5. Degradation Study in Soils

The soil equivalent to 30 g on an oven-dry weight basis was taken into a 50-ml beaker and the moisture was adjusted to 40% of the maximum water-holding capacity. To the samples, after a 2-week preincubation at $25 \pm 2^\circ\text{C}$ in the dark, the radiolabeled isomers of **I** (30 μg in 100 μl of acetone) were applied. The treated soils were mixed thoroughly to give a concentration of 1.0 ppm, placed in a 3-l glass jar covered with aluminum foil and kept at $25 \pm 2^\circ\text{C}$ for 24 weeks. Each jar was continuously purged with the CO_2 -free air at a flow rate of 25–30 ml/min, and the effluent air was passed in sequence through a polyurethane foam plug¹¹⁾ and a gas washing bottle containing 400 ml of 0.5 N NaOH solution, trapping the volatile ^{14}C including $^{14}\text{CO}_2$. The moisture content of the soils was readjusted periodically to the original value by adding distilled water. The polyurethane foam plugs and the alkaline solution were replaced every two weeks. The polyurethane foam was eluted with methanol (30 ml $\times$ 3) for ^{14}C analysis and the NaOH solution was radioassayed using Aquasol®-2. To determine $^{14}\text{CO}_2$, 1 ml of 1 N BaCl_2 solution was added to 10 ml of the NaOH solution and the

supernatant fraction, separated by centrifugation of the precipitate ($\text{Ba}^{14}\text{CO}_3$), was radioassayed.

At various time intervals, the incubated soils were extracted with methanol (60 ml $\times$ 3) by shaking for 10 min. The methanol extracts, separated by centrifugation at 5000 rpm for 10 min, were combined, radioassayed and concentrated to dryness in a rotary vacuum evaporator. The residues were redissolved in methanol, an aliquot of which was subjected to TLC for analysis of the degradation products. Through extraction, autoradiography and LSC as described above, 96.7–101.0% of the applied **I** isomers were recovered from Kuki and Azuchi soils immediately after the application of cyclopropyl- ^{14}C **I** at a rate of 1 ppm.

The unextracted soil residues were dried, sampled in duplicate (300 mg) and combusted to $^{14}\text{CO}_2$ prior to LSC. Aliquots of the bound ^{14}C were fractionated into fulvic acid, humic acid and humin fractions according to the method described in a previous publication.¹²⁾ The fulvic acid fraction was extracted with ethyl acetate (200 ml $\times$ 3), the organic and aqueous fraction being radiocounted. The organic layer was concentrated and examined by TLC.

6. Leaching Study

Either Sapporo soil (118.2 g on an air-dry weight basis), Kodaira soil (120.6 g), Muko sand (191.9 g) or Takarazuka soil (163.4 g) was

packed uniformly up to 25 cm from the bottom in a glass column 2.5 cm i.d. and 40 cm long. The column was conditioned prior to use by running water at a rate of 6–10 ml/day until the effluent was clear. Onto the column, the soil (23–39 g on an air-dry weight basis) treated with 1 ppm of either cyclopropyl- or benzyl- ^{14}C I (*cis/trans*=1/1 mixture) was placed immediately after mixing or after a 30-day incubation in a stoppered glass flask under aerobic upland conditions at $25 \pm 2^\circ\text{C}$ in the dark. The glass flask was purged with the CO_2 -free air, and $^{14}\text{CO}_2$ evolved during the incubation was trapped in a 0.5 N NaOH solution as described above.

To the top of the treated soil column, 1000 ml of distilled water was applied at a rate of 3 ml/hr for 3 weeks by an automatic dispenser in such a way that no water-layer would build up on the soil. During the percolation the column was covered with aluminum foil, kept at $25 \pm 2^\circ\text{C}$ and the effluxed air was passed through a 0.5 N NaOH solution to trap $^{14}\text{CO}_2$ evolved in the soil column.

After the column had been allowed to drain off, the soil was taken out of the column and divided transversely into 6 fractions (treated soil, 0–5 cm, 5–10 cm, 10–15 cm, 15–20 cm, 20–25 cm downward from the top).

Samples (1 ml) of the column eluate were assayed for a total radiocarbon by LSC. Some effluents containing large amounts of radiocarbon were extracted with ethyl acetate (150 ml $\times$ 3) at pH 1. The ethyl acetate layer was combined, washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated to dryness.

The air-dried soil samples were subjected to combustion analysis to examine the distribution of radiocarbon in the soil column. Some soil sections which contained large amounts of radioactivity were extracted twice with a mixture of 1 N HCl (40 ml) and ethyl acetate (60 ml) by blending for 10 min. The ethyl acetate layers separated by centrifugation at 5000 rpm for 10 min were combined, concentrated to dryness and analyzed by TLC.

RESULTS

1. Degradation in Soils

The degradation curves of *cis*- and *trans*-I in two soils are shown in Fig. 1. The initial half-life ($T_{1/2}$) of disappearance was determined according to the following equations: $\ln Y = A - BX$, $T_{1/2} = (\ln 2)/B$. The calculation was based on the residue data of 0–8 weeks for *cis*-I in Azuchi soil, of 0–4 weeks for *cis*-I in Kuki soil and *trans*-I in Azuchi soil, and of 0–2 weeks for *trans*-I in Kuki soil. As a result, the half-lives were estimated to be 12.5 and 56.4 days for *cis*-I in Kuki and Azuchi soils, and 4.1 and 17.6 days for *trans*-I, respectively. The correlation coefficients (r^2) were more than 0.96 in each case. After 168 days the concentrations of *cis*-I decreased to 0.06 ppm and 0.32 ppm, and those of *trans*-I to 0.03 ppm and 0.09 ppm in Kuki and Azuchi soils, respectively.

2. Degradation Products in Soils

The analysis by TLC showed that there were at least 9 degradation products in the extracts of the soils treated with either cyclopropyl- or phenyl- ^{14}C I isomers. The products, separated by preparative TLC in solvent systems B, C, D and E, were identified by one- or two-dimensional TLC cochromatography with synthesized compounds in the following solvent systems: *cis*- and *trans*-I (A); IV, V and VII (B, E); II and III (B, C); *cis*- and *trans*-VI (B, D). In addition, two minor products with the R_f values of 0.00 and 0.44–0.54 (tailing) in solvent system C were detected. Although

Fig. 1 The concentrations of cypermethrin in soils under aerobic upland conditions.

—, *trans*-isomers; ----, *cis*-isomers; ●, Kuki soil; ▲, Azuchi soil.

Table 3 The concentrations of *cis*- or *trans*-cypermethrin and its degradation products in Kuki soil stored for 14, 56, and 168 days under aerobic upland conditions.

	% of the applied ^{14}C											
	<i>cis</i> -Cypermethrin						<i>trans</i> -Cypermethrin					
	Cyclopropyl- ^{14}C			Benzyl- ^{14}C			Cyclopropyl- ^{14}C			Benzyl- ^{14}C		
	14	56	168	14	56	168	14	56	168	14	56	168
Volatile ^{14}C	3.1	16.5	28.4	10.2	34.3	46.9	7.9	35.2	48.1	21.0	46.1	57.1
Polyurethane plug	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NaOH solution	3.1	16.5	28.4	10.2	34.3	46.9	7.9	35.2	48.1	21.0	46.1	57.1
$^{14}\text{CO}_2$	3.1	16.5	28.4	10.2	34.1	46.7	7.9	35.1	47.9	21.0	45.9	56.8
Others	<0.1	<0.1	<0.1	<0.1	0.2	0.2	<0.1	0.1	0.2	<0.1	0.2	0.3
Extract ^{14}C	58.0	21.5	9.0	47.9	18.1	7.3	19.9	6.9	3.3	15.6	6.0	3.1
<i>cis</i> - I	45.0	11.6	5.6	36.4	12.7	5.0	—	—	—	—	—	—
<i>trans</i> - I	—	—	—	—	—	—	14.6	5.0	2.5	12.3	4.5	2.5
II	1.5	0.9	0.3	1.7	0.9	0.4	0.3	<0.1	<0.1	0.3	0.1	0.2
III	6.4	2.1	0.8	7.0	2.2	0.7	0.8	0.3	0.1	0.8	0.2	0.1
IV	0.7	0.4	0.2	0.7	0.4	0.2	0.2	0.1	<0.1	0.2	0.1	0.1
V	0.2	0.5	0.2	0.3	0.5	0.2	0.1	0.1	<0.1	0.2	0.1	<0.1
<i>cis</i> - VI	1.0	1.5	0.2	—	—	—	—	—	—	—	—	—
<i>trans</i> - VI	—	—	—	—	—	—	2.4	0.2	0.1	—	—	—
VII	—	—	—	0.3	0.3	0.1	—	—	—	0.7	0.1	<0.1
Others	3.2	4.5	1.7	1.5	1.1	0.7	1.5	1.2	0.6	1.1	0.9	0.2
Bound ^{14}C	33.8	57.6	57.1	31.2	41.0	40.3	62.7	49.8	45.1	55.2	41.3	37.7
Fulvic acid	2.0	6.7	6.2	7.4	13.2	13.2	3.8	7.5	7.6	8.7	12.8	11.5
Humic acid	6.1	5.0	6.6	13.1	14.2	14.6	10.9	9.9	9.7	25.5	13.1	13.5
Humin	25.7	45.9	44.3	10.7	13.6	12.5	48.0	32.4	27.8	21.0	15.4	12.7
Total ^{14}C	94.9	95.6	94.5	89.3	93.4	94.5	90.5	91.9	96.5	91.8	93.4	97.9

they were not identified, they amounted in total to 0.2–5.3% of the applied ^{14}C . It was found that they were neither of **VIII**, **IX**, 3-phenoxybenzyl alcohol, 3-phenoxybenzaldehyde nor the hydroxy derivative oxydized at the 2-position of the phenoxy group of **I**. No *cis/trans* isomerization occurred in soils, which was evidenced the recovery of *cis*-**VI** and *trans*-**VI** from the soils treated with *cis*-**I** and *trans*-**I**, respectively.

The amount of degradation products in Kuki and Azuchi soils was listed in Tables 3 and 4. Although all of the identified products were common to both *cis*- and *trans*-**I**, there was a considerable variation in amount of degradation products between the two isomers. In soils treated with the *trans*-isomer, the ester cleavage products such as *trans*-**VI** and/or **VII** were of more importance than **II** and **III**. *Trans*-**VI** and **VII** amounted to 2.4–8.1% and

0.7–2.9% of the applied ^{14}C after 14 days, but rapidly decreased thereafter. In contrast, the degradation products retaining the ester linkage like **II** and **III** were more predominantly formed in soils treated with *cis*-**I**. After 14–56 days **II** and **III** amounted to 7.4% and 7.0% of the applied ^{14}C , respectively, and then both gradually decreased. Thus, these degradation products were not persistent in soils for a longer period of time. Meanwhile, **IV** and **V** amounted to less than 1% of the initial dose in all samples examined during the incubation period.

The extractable ^{14}C decreased steadily with a concomitant increase of the volatile and unextractable bound ^{14}C . A large proportion of the volatile ^{14}C was trapped in the NaOH solution, with less than 0.1% of the applied ^{14}C in the polyurethane plug. The radiocarbon trapped in the alkaline solution was considered to be all $^{14}\text{CO}_2$, since 96.2 to 99.9% of the radio-

Table 4 The concentrations of *cis*- or *trans*-cypermethrin and its degradation products in Azuchi soil stored for 14, 56, and 168 days under aerobic upland conditions.

	% of the applied ^{14}C											
	<i>cis</i> -Cypermethrin						<i>trans</i> -Cypermethrin					
	Cyclopropyl- ^{14}C			Benzyl- ^{14}C			Cyclopropyl- ^{14}C			Benzyl- ^{14}C		
	14	56	168	14	56	168	14	56	168	14	56	168
Volatile ^{14}C	2.8	13.1	21.4	6.3	21.0	35.4	10.8	38.1	52.2	21.1	48.0	61.0
Polyurethane plug	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
NaOH solution	2.7	13.0	21.3	6.3	21.0	35.4	10.8	38.1	52.2	21.1	48.0	61.0
$^{14}\text{CO}_2$	2.7	12.7	20.5	6.3	20.9	35.2	10.8	37.9	51.5	21.1	47.9	60.8
Others	<0.1	0.3	0.8	<0.1	0.1	0.2	<0.1	0.2	0.7	<0.1	0.1	0.2
Extract ^{14}C	89.5	68.2	51.4	84.9	65.1	39.2	64.3	25.2	12.9	57.8	23.0	9.1
<i>cis</i> - I	78.4	51.4	34.9	76.3	52.6	30.0	—	—	—	—	—	—
<i>trans</i> - I	—	—	—	—	—	—	50.1	18.7	8.7	48.8	18.4	7.1
II	4.3	7.4	6.1	4.5	7.0	5.5	2.1	1.3	0.6	2.3	1.4	0.7
III	1.3	1.3	1.2	1.3	1.3	1.0	0.7	0.6	0.3	1.3	0.6	0.3
IV	0.3	0.6	0.6	0.2	0.3	0.3	0.6	0.8	0.1	0.1	0.1	0.1
V	0.1	0.3	0.3	0.2	0.2	0.3	0.1	0.2	0.1	0.3	0.2	<0.1
<i>cis</i> - VI	2.1	1.9	3.2	—	—	—	—	—	—	—	—	—
<i>trans</i> - VI	—	—	—	—	—	—	8.1	1.7	1.1	—	—	—
VII	—	—	—	0.7	0.6	0.3	—	—	—	2.9	1.2	0.3
Others	3.0	5.3	5.1	1.7	3.1	1.8	2.6	1.9	2.0	2.1	1.1	0.6
Bound ^{14}C	7.9	18.0	24.3	7.7	14.2	21.2	22.4	31.5	28.9	19.0	23.5	26.5
Fulvic acid	0.6	4.0	5.0	1.6	5.1	7.5	1.9	7.9	7.2	4.2	8.8	9.0
Humic acid	2.3	2.9	3.6	3.2	4.8	6.6	5.6	6.1	6.1	7.8	7.2	9.2
Humin	5.0	11.1	15.7	2.9	4.3	7.1	14.9	17.5	15.6	7.0	7.5	8.3
Total ^{14}C	100.2	99.3	97.1	98.9	100.3	95.8	97.5	94.8	94.0	97.9	94.5	96.6

carbon was precipitated as $\text{Ba}^{14}\text{CO}_3$. After 168 days $^{14}\text{CO}_2$ amounted to 28.4–56.8% and 20.5–60.8% of the applied ^{14}C in Kuki and Azuchi soils, respectively. A larger amount of $^{14}\text{CO}_2$ was evolved from the soils treated with *trans*-**I** and the benzyl- ^{14}C preparation (Fig. 2).

The bound ^{14}C in Kuki and Azuchi soils amounted to 37.7–62.7% and 19.0–31.5% of the applied ^{14}C for *trans*-**I**, and 31.2–57.6% and 7.7–24.3% for *cis*-**I**. It was formed in larger amounts when the soils were treated with the cyclopropyl- ^{14}C preparation than with the benzyl- ^{14}C preparation (Fig. 3). The bound ^{14}C originating from *cis*-**I** in both soils gradually increased with time, whereas the one from *trans*-**I** in Kuki soil reached the maximum amount 14 days after treatment, and then gradually decreased.

Fractionation of the unextracted soil residues showed that more of the unextracted radio-

activity was associated with the humin fraction in case of the cyclopropyl- ^{14}C preparation. In contrast, the bound ^{14}C was distributed in three fractions of fulvic acid, humic acid and humin in case of the benzyl- ^{14}C preparation. Thus, there was some difference in the distribution profile of the bound radiocarbon between the cyclopropyl- and benzyl- ^{14}C preparations. These evidences suggest that the bound ^{14}C residues mainly originate from the hydrolysis products. Approximately 40–50% of the ^{14}C in the fulvic acid fraction were extracted with ethyl acetate. **I**, **VII** and **VI** were detected in the extracts only in small amounts.

3. Leaching

The distribution of radiocarbon in the soil column and the eluate is shown in Table 5. The results are presented as percentages of the applied radiocarbon. When either the soil

Fig. 2 The evolution of $^{14}\text{CO}_2$ from Kuki and Azuchi soils treated with (1*R*,*trans*)- and (1*R*,*cis*)- ^{14}C -cypermethrin.

▲, Cyclopropyl- ^{14}C ; ■, Benzyl- ^{14}C ; —, *trans*-isomers; ----, *cis*-isomers.

Fig. 3 The amounts of bound ^{14}C in Kuki and Azuchi soils treated with (1*R*,*trans*)- and (1*R*,*cis*)- ^{14}C -cypermethrin.

▲, Cyclopropyl- ^{14}C ; ■, Benzyl- ^{14}C ; —, *trans*-isomers; ----, *cis*-isomers.

Table 5 Total radioactivity of soil sections from columns treated with ^{14}C -cypermethrin.

	% of the applied ^{14}C									
	Sapporo soil				Kodaira soil				Muko sand	
	Unstored ^{a)} Alc ^{c)}	Acid ^{b)}	Stored ^{b)} Alc	Acid	Unstored	Alc	Acid	Stored	Unstored	Alc
Volatile ^{14}C ^{e)}	1.1	1.0	0.8	2.8	0.1	<0.1	15.1	14.3	2.5	<0.1
Soil	84.3	82.8	73.8	65.8	86.9	88.6	64.0	68.5	68.9	77.7
Treated portion	79.3	69.6	64.5	49.4	84.9	78.5	61.3	60.4	51.4	29.8
0-5 cm	2.2	5.5	5.5	3.5	1.3	5.9	1.0	4.6	7.8	19.4
5-10 cm	0.2	3.5	1.3	2.3	0.1	2.8	0.2	0.9	1.4	4.8
10-15 cm	0.1	0.9	0.3	2.0	0.1	0.5	0.1	0.3	0.9	0.8
15-20 cm	0.1	0.3	0.2	1.8	0.1	0.1	0.1	0.2	0.9	0.4
20-25 cm	0.1	0.2	0.1	1.7	0.1	0.1	0.1	0.2	0.5	0.4
Effluent	2.3	2.8	1.9	5.1	0.3	0.7	1.2	1.9	6.0	22.1
Total ^{14}C	85.4	83.8	74.6	68.6	87.0	88.6	79.1	82.8	71.4	77.7
									93.0	93.3
									82.0	83.6

^{a)} Soil columns not incubated.

^{b)} Soil columns incubated for 30 days.

^{c)} Benzyl- ^{14}C cypermethrin.

^{d)} Cyclopropyl- ^{14}C cypermethrin. ^{e)} More than 99% of the volatile ^{14}C was determined to be $^{14}\text{CO}_2$.

columns had been incubated (stored) or not incubated (unstored) before the leaching experiments, less than 5.1% of the applied ^{14}C appeared in the effluent from Kodaira and Sapporo soils containing relatively more organic matter, compared with 1.5 to 31.3% in the effluent from Takarazuka and Muko soils with less organic matter. ^{14}C was eluted in larger amounts from the soil columns treated with the cyclopropyl- ^{14}C preparations than from the ones treated with the benzyl- ^{14}C preparations. The major degradation products in the effluent were **VI** from the alcohol moiety and **VII** from the acid moiety, which amounted to 2.8–4.4% and 7.0–22.1% of the applied ^{14}C , respectively. It appears that **VI** is more readily degraded further or bound to soils than **VII** during the leaching. In fact, bound ^{14}C amounted to 12.3–30% of the applied ^{14}C in Takarazuka soil treated with the benzyl-label, compared with 5.1–18.1% in the one treated with the cyclopropyl-label. **II**, **IV**, **VIII** and **IX** were detected in the effluent only in small amounts. The unchanged **I** amounted to less than 0.3% of the applied radiocarbon.

The major part of the radiocarbon resided in the treated portion of each soil column. The exception was the Muko soil column, in which 5.1 to 19.4% of the applied ^{14}C appeared in the 0–5 cm fraction. The TLC analysis of each soil column showed the presence of a large amount of unchanged **I** together with a relatively small amount of **II**, **IV**, **VI**, **VII** and **VIII**.

During the percolation $^{14}\text{CO}_2$ was evolved from the soil columns, amounting to 0.1 to 2.5% under unstored conditions, and 0.8 to 17.6% under stored conditions (Table 5).

DISCUSSION

The half-life of disappearance in soils was 4.1 to 17.6 days for (1*R*, *trans*)-cypermethrin and 12.5 to 56.4 days for the (1*R*, *cis*)-isomer under aerobic upland conditions. As estimated from the half-life values, the *trans*-isomer was degraded about 3 to 4 times more rapidly than the *cis*-isomer. The results were in accord with the previous observations,^{1,2)} in which 50% of the (1*R*, *trans*)- and (1*R*, *cis*)-isomers applied to soils were degraded in 2 weeks and 4 weeks, respectively.

Fig. 4 Proposed degradation pathways for cypermethrin in soils.

[]: Degradation products of cypermethrin detected only in the leaching study.

Based upon the identified products, the proposed degradation pathways for **I** in soils are shown in Fig. 4. The insecticide underwent cleavage of the ester or diphenyl ether bond, hydroxylation at the 4-position of the phenoxy ring, and hydrolysis of the cyano group to the amide and carboxyl groups. The product unique to this experiment was **II**, which was considered to be formed at least in part *via* oxidation at the 2-position of the phenoxy ring followed by spontaneous cleavage of the diphenyl ether linkage.^{16,19)} In contrast, the dicarboxylic acid (**VIII**) oxidized at one of the *gem*-dimethyl groups of **VI** was not detected in the soil extracts. However, a trace amount of **VIII** appeared in the effluent from the soil columns. Their degradation profiles were very similar to those of other pyrethroids, namely permethrin,^{13,14)} fenprothrin,¹⁵⁾ fenvalerate¹⁶⁾ and deltamethrin.¹⁷⁾ The main degradation route was hydrolysis of the ester linkage leading to the formation of **VI** and **VII**. The hydrolysis products were further degraded to $^{14}\text{CO}_2$ and/or bound to soils. Generally, $^{14}\text{CO}_2$ and bound ^{14}C residues were formed in large amounts in soils treated with the less persist-

ent *trans*-isomer, whereas oxidation products retaining the ester linkage such as **II** and **III** were of more importance in soils treated with the *cis*-isomer. Although the previous study¹⁾ showed that soils treated with *cis*-isomer of **I** contained both *cis*- and *trans*-isomers of **VI**, no *cis/trans* isomerization was observed in this experiment. It appears that **VI** is less susceptible to further degradation than **VII**, since the former was detected in soils of higher concentrations than the latter, and more rapid evolution of ¹⁴CO₂ occurred in soils treated with the benzyl-¹⁴C preparation. In contrast, somewhat a greater amount of bound ¹⁴C was formed in soils treated with the cyclopropyl-¹⁴C preparation. There was a considerable variation in the distribution profiles of bound ¹⁴C residues in the fulvic acid, humic acid and humin between the benzyl- and cyclopropyl-¹⁴C preparations. It appears that the bound ¹⁴C stems mainly from the hydrolysis products. The bound ¹⁴C residues arising from the *trans*-isomer of **I** in Kuki soils decreased with time, probably due to further degradation to carbon dioxide. Roberts and Standen²⁾ reported that the bound residues arising in soils from *cis*- and *trans*-isomers of **I** were further degraded to ¹⁴CO₂ when mixed with fresh untreated soils.

As with other pyrethroids,^{16,18)} leaching of cypermethrin in soils was limited, because of its quite low water solubility and rapid adsorption onto soil particles.

REFERENCES

- 1) T. R. Roberts & M. E. Standen: *Pestic. Sci.* **8**, 305 (1977)
- 2) T. R. Roberts & M. E. Standen: *Pestic. Sci.* **12**, 285 (1981)
- 3) A. N. Wright, T. R. Roberts, A. J. Dutton & M. V. Doig: *Pestic. Biochem. Physiol.* **13**, 71 (1980)
- 4) M. J. Crawford, A. Croucher & D. H. Hutson: *J. Agric. Food Chem.* **29**, 130 (1981)
- 5) M. J. Crawford, A. Croucher & D. H. Hutson: *Pestic. Sci.* **12**, 399 (1981)
- 6) L. O. Ruzo: *J. Agric. Food Chem.* **31**, 1115 (1983)
- 7) N. Takahashi, N. Mikami, T. Matsuda & J. Miyamoto: *J. Pesticide Sci.* **10**, 629 (1985)
- 8) H. Kanamaru, M. Okuno, K. Kawahara, I. Nakatsuka & A. Yoshitake: *Abstr. Annu. Meet. Agric. Biol. Chem.*, Tokyo, p. 324, 1984
- 9) N. Mikami, N. Takahashi, K. Hayashi & J. Miyamoto: *J. Pesticide Sci.* **5**, 225 (1980)
- 10) Anonymous: "Experiments in Agricultural Chemistry," ed. by Department of Agricultural Chemistry, Faculty of Agriculture, Kyoto University, Vol. I, Sangyo Tosho Publishing Co., Ltd., Kyoto, 1968 (in Japanese)
- 11) P. C. Kearney & A. Konston: *J. Agric. Food Chem.* **24**, 424 (1976)
- 12) *Fed. Regist.* **40**, 26893 (1975)
- 13) H. Kaneko, H. Ohkawa & J. Miyamoto: *J. Pesticide Sci.* **3**, 43 (1978)
- 14) D. D. Kaufman, S. C. Hayes, E. G. Jordon & A. J. Kayser: *ACS Symp. Ser.* **42**, 147 (1977)
- 15) T. R. Roberts & M. E. Standen: *Pestic. Sci.* **8**, 600 (1977)
- 16) H. Ohkawa, K. Nambu, H. Inui & J. Miyamoto: *J. Pesticide Sci.* **3**, 129 (1978)
- 17) L.-Z. Zhang, S. U. Khan, M. H. Akhtar & K. C. Iverson: *J. Agric. Food Chem.* **32**, 1207 (1984)
- 18) D. D. Kaufman, B. A. Russel, C. S. Helling & A. J. Kayser: *J. Agric. Food Chem.* **29**, 239 (1981)
- 19) L. C. Gougham, T. Unai & J. E. Casida: *J. Agric. Food Chem.* **25**, 9 (1977)

要 約

ピレスロイド系殺虫剤サイパーメスリンの土壌中での分解と溶脱

坂田信以, 三上信可, 松田 正, 宮本純之

ピレスロイド系殺虫剤サイパーメスリンのシスおよびトランス異性体のシクロプロパン環もしくはベンジルフェニル環を¹⁴Cで標識した化合物を用いて、土壌中での分解と溶脱について検討した。トランスおよびシス異性体を2種類の土壌に1ppmの割合で添加して好氣的畑地条件に保つと、消失半減期がそれぞれ4.1~17.6日、12.5~56.4日の速度で分解した。主な分解経路はエステル結合の加水分解で、ほかにジフェニルエーテル結合の開裂、フェニル環の水酸化、シアノ基の加水分解をうけ、生成した分解物はさらにCO₂まで分解したりbound¹⁴Cを形成した。¹⁴CO₂は、シス異性体より分解の速いトランス異性体から、またシクロプロパン環¹⁴C標識体よりフェニル環¹⁴C標識体からより多く生成した。一方、bound¹⁴Cはシス異性体およびシクロプロパン環¹⁴C標識体からより多く生成した。有機物含量が0.1%以下で粘土含量が1%以下の武庫砂の場合には、処理直後に溶脱を行なうと溶出液に微量のサイパーメスリンが検出されたが、他の土壌の場合には、処理直後および30日間インキュベート後にかかわらず、溶出液中にはサイパーメスリンは検出されなかった。