Permethrin異性体の土壌中における分解と移行

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Degradation and Movement of Permethrin Isomers in Soil

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Degradation and movement of (+)-*trans* and (+)-*cis* isomers of permethrin [3-phenoxybenzyl (±)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] in soil were studied under laboratory conditions. When (+)-*trans* and (+)-*cis* isomers of permethrin labeled with ^{14}C in the alcohol or acid moiety were applied to two types of soil (Kodaira and Azuchi) at the rate of 1.0 ppm and held at 25°C in the dark under upland conditions, both isomers were rapidly decomposed with the half-lives of 6 to 12 days. The degradation rate of (+)-*trans* isomer was slightly faster than that of (+)-*cis* isomer in both soils. Major degradation products from both isomers were 3-(4′-hydroxyphenoxy)benzyl-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, 3-phenoxybenzyl alcohol, 3-phenoxybenzoic acid, 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid, and its hydroxylation derivatives.

Although both (+)-*trans* and (+)-*cis*-permethrin hardly moved through the soil with water, the degradation products such as 3-phenoxybenzoic acid, 3-(4′-hydroxyphenoxy) benzyl-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate were slightly eluted with water.

INTRODUCTION

Permethrin [3-phenoxybenzyl (±)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] has great potential as an agricultural insecticide, because it combines high insecticidal activity, low mammalian toxicity and adequate stability in air and light.[1]

It was reported that permethrin was rapidly metabolized in rats, and both acid and alcohol moieties were almost completely eliminated from the body. The insecticide was also readily metabolized in cows. The majority of the metabolites appeared in the urine with rats and in the feces with cows. More extensive ester cleavage or conjugation of metabolites occurred with *trans*-permethrin than with *cis*-permethrin in both rat and cow.[2,3]

Permethrin was rapidly degraded in bean plants and cotton leaves.[4,5] The half-life was about 7 to 9 days in bean plants. In bean plants, the *trans* isomer of permethrin was more rapidly metabolized than the *cis* isomer.

This report is concerned with degradation of the permethrin isomers in two types of soil under upland conditions and their leaching ability from soil columns.

MATERIALS AND METHODS

1. *Thin-layer Chromatography (tlc)*

Precoated silica gel 60F-254 chromatoplates (20×20 cm, 0.25 mm layer thickness, E. Merck) were used for both preparative and analytical purposes. The solvent systems used were; A) toluene, B) *n*-hexane/acetone=4/1(v/v), C) benzene saturated with formic acid/ether=10/3 (v/v), D) *n*-hexane/toluene/acetic acid=3/15/2 (v/v), E) *n*-hexane/ether =1/5(v/v), F) chloroform/ether=19/1(v/v), G) *n*-hexane/toluene=3/15(v/v), H) chloroform saturated with formic acid/methanol=9/1 (v/v). The *Rf* values for authentic standards and metabolites in these solvent systems are shown in Table 1. The solvent systems for two-dimensional *tlc* are shown for example as follows; (F×2, E) indicates development in the first direction twice with solvent system

Table 1 Thin-layer chromatographic properties of *t*– and *c*–permethrin and their derivatives.

Compound	*Rf* values with indicated solvent systems							
	A	B	C	D	E	F×2	G	H
t–Permethrin	0.44	0.47	0.69	0.65	0.75			
c–Permethrin	0.47	0.52	0.69	0.68	0.75			
4′–OH–*t*–Permethrin			0.50	0.21				
4′–OCH_3–*t*–Permethrin	0.39	0.39						
4′–OH–*c*–Permethrin			0.50	0.24				
4′–OCH_3–*c*–Permethrin	0.41	0.43						
PBalc					0.43	0.46		
PBacid			0.39	0.32				0.64
PBacid–Me	0.31						0.42	
t–Cl_2CA			0.43	0.38				
t–Cl_2CA–Me	0.38						0.47	
c–Cl_2CA			0.05	0.39				
c–Cl_2CA–Me	0.46						0.53	
t–OH–*t*–Cl_2CA			0.09	0.09				
t–OH–*t*–Cl_2CA–Me			0.22	0.16				
c–OH–*t*–Cl_2CA			0.04	0.06				
t–OH–*c*–Cl_2CA			0.12	0.09				
t–OH–*c*–Cl_2CA–Me			0.22	0.16				
c–OH–*c*–Cl_2CA			0.06	0.07				
c–OH–*t*–Cl_2CA–lactone			0.39	0.23				
c–OH–*c*–Cl_2CA–lactone			0.41	0.25				

F and in the second direction with solvent system E. For cochromatography of ^{14}C metabolites or their derivatives, the spots of the unlabeled standards were detected by ultraviolet fluorescence quenching and then were compared with the radioactive spots detected by radioautography.

2. *Chemicals*

(+)–*trans* and (+)–*cis*–Permethrin labeled with ^{14}C in the acid or alcohol moieties were synthesized by Nakatsuka *et al.*[6] The structure and labeling position of both isomers are shown in Fig. 1. (+)–*trans* and (+)–*cis*–Permethrin were designated as *t*–permethrin and *c*–permethrin, respectively. The labeling with ^{14}C in the acid and alcohol moieties were represented as *acid* and *alc*, respectively. The specific radioactivity of the four permethrin preparations was; 5.15 mCi/mmol for ^{14}C–*alc*–*t*–permethrin, 4.68 mCi/mmol for ^{14}C–*alc*–*c*–permethrin, 3.83 mCi/mmol for ^{14}C–*acid*–*t*–permethrin and 4.29 mCi/mmol for ^{14}C–*acid*–*c*–permethrin. The radiochemical purity was determined by *tlc* in toluene; 99.2% for ^{14}C–*alc*–*t*–permethrin, 98.4% for ^{14}C–*alc*–*c*–permethrin, 98.3% for ^{14}C–*acid*–*t*–permethrin and 99.0% for ^{14}C–*acid*–*c*–permethrin. The following authentic standards were synthesized as described previously[5]; 3–(4′–methoxyphenoxy) benzyl (+)–*trans*–3–(2,2–dichlorovinyl)–2,2–dimethylcyclopropanecarboxylate (4′–OCH_3–*t*–permethrin), 3–(4′–methoxyphenoxy)benzyl (+)–*cis*–3–(2,2–dichlorovinyl)–2,2–dimethylcyclopropanecarboxylate(4′–OCH_3–*c*–permethrin), 3–phenoxybenzyl alcohol(PBalc), 3–phenoxybenzoic acid(PBacid), methyl 3–phenoxybenzoate(PBacid–Me), (+)–*trans*–3–(2,2–dichlorovinyl)–2,2–dimethylcyclopropanecarboxylic acid (*t*–Cl_2CA), (+)–*cis*–3–(2,

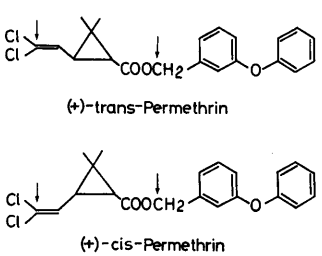

Fig. 1 The structure and labeling position of (+)–*trans* and (+)–*cis*–permethrin. The arrows show the labeling positions.

2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (*c*-Cl_2CA), methyl (+)-*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate(*t*-Cl_2CA-Me), methyl (+)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate(*c*-Cl_2CA-Me). Four metabolites which were hydroxylated at the *gem*-dimethyl group of *t*-Cl_2CA and *c*-Cl_2CA were each isolated from the urine of rats dosed orally with ^{14}C-*acid*-*t*- or *c*-permethrin according to Gaughan *et al.*[3] Those were each methylated with diazomethane in ether for 6 hr at room temperature. On methylation, (+)-*trans*-3-(2,2-dichlorovinyl)-2-methyl-2-*cis*-hydroxymethylcyclopropanecarboxylic acid(*c*-OH-*t*-Cl_2CA) and (+)-*cis*-3-(2,2-dichlorovinyl)-2-methyl-2-*cis*-hydroxymethylcyclopropanecarboxylic acid(*c*-OH-*c*-Cl_2CA) were each converted to the corresponding lactones(*c*-OH-*t*-Cl_2CA-lactone and *c*-OH-*c*-Cl_2CA-lactone). The methylated products and lactones were purified by repeated preparative *tlc* and then identified by chemical ionization mass spectra (CI-MS) or electron impact mass spectra (EI-MS). CI-MS were obtained on a Shimadzu-LKB 9000 combined gas chromatograph-mass spectrometer using methane as a reagent gas at about 1 Torr. The gas chromatographic inlet system was equipped with a 2.0 m × 3 mm glass column, packed with 10% SE-30 on Chromosorb W(AW-DMCS) 60/80 mesh. Column temperature was 150°C and a flow rate of carrier gas (He) was 30 ml/min. The helium separator and the ion source were maintained at 200°C and 290°C, respectively. Accelerating voltage, ionization potential and ionizing current were 3,500 V, 500 eV and 259 μA, respectively. EI-MS were obtained on a Shimadzu-LKB 9000 mass spectrometer at 12 and 70 eV. *c*-OH-*t*-Cl_2CA-lactone and *c*-OH-*c*-Cl_2CA-lactone gave the same CI-MS; *m/e* 249, 247, 237, 235, 209, 207 (M+1, base peak), 201, 189. The molecular ion of methyl (+)-*trans*-3-(2,2-dichlorovinyl)-2-methyl-2-*trans*-hydroxymethylcyclopropanecarboxylate (*t*-OH-*t*-Cl_2CA-Me) and methyl (+)-*cis*-3-(2,2-dichlorovinyl)-2-methyl-2-*trans*-hydroxymethylcyclopropanecarboxylate (*t*-OH-*c*-Cl_2CA-Me) was not detected with CI-MS; *m/e* 223, 221 (M+1-H_2O, base peak), 209, 207, 191, 189. The EI-MS of *t*-OH-*t*-Cl_2CA-Me and *t*-OH-*c*-Cl_2CA-Me were as follows; *m/e* 240 (M+2), 238 (M), 209, 207, 183, 181 (base peak).

3. Radioassay and Radioautography

The content of radiocarbon in organo-soluble fractions from soils was determined with a Packard Model 3385 Tri-Carb liquid scintillation spectrometer equipped with an automatic external standard in low potassium glass vials using 15 ml of a dioxane scintillation fluid (5.0 g of 2,5-diphenyloxazole and 100 g of naphthalene in 1 liter of dioxane). The conditions for liquid scintillation counting (*lsc*) were as follows; back ground, 30-40 dpm, counting efficiency, more than 85%. Un-extractable soil residues were dried over P_2O_5 in a vacuum desiccator and then about 200 mg of each sample was combusted in a Packard Model 306 sample oxidizer prior to *lsc*. For radioautography, developed *tlc* plates were placed under X-ray film (Industrial X-ray film 150, Fuji Photo Film Co., Ltd, Tokyo, Japan) and held at 0 to 4°C for several days depending on the radioactivity. Quantitation of radiocarbon on *tlc* plates was conducted by scraping the appropriate gel regions into scintillation vials and counting them.

4. Degradation in Soil

The soil samples were collected from the arable layer of upland fields in Kodaira, Tokyo and Azuchi, Shiga, from August to October, 1975 and stored at 0 to 4°C in the dark. The characteristics of these two soils were as follows; Kodaira light clay soil with sand, silt, clay and organic matter contents of 31, 40, 29% and 15.3%, resepctively, cation exchange capacity 53.7 me/100 g, pH (H_2O) 5.5; Azuchi sandy clay loam soil with sand, silt, clay and organic matter contents of 64, 17, 19% and 2.5%, respectively, cation exchange capacity 13.5 me/100 g, pH(H_2O) 6.3. The soils were grained and passed through a 3 mm sieve before use. Thirty grams of the soil (on air-dry weight basis) were placed in a 100 ml beaker, wetted with distilled water to 50% of the maximum water holding capacity and then preincubated in the dark at 25±2°C for a week. Thirty micrograms of ^{14}C-*t*- and *c*-permethrin in 0.1 ml of methanol

corresponding to 1.0 ppm on an air-dry soil weight basis were added to the soil samples by a microsyringe (the approximate concentration that would result if recommended quantity of the insecticide was reached or incorporated into the surface 10 cm of soil). The treated soils were incubated in the dark at 25±2°C for up to 60 days. At intervals, the soil samples were extracted three times with 70 ml of methanol in a Waring blendor (methanol extract), followed by three extractions with 70 ml of 7% hydrochloric acid in methanol (HCl–methanol extract). The HCl–methanol extracts were concentrated, dissolved in water and then reextracted with benzene. An equal volume of 12 N hydrochloric acid was added to the remaining aqueous layer and the solution was heated at 100°C for 30 min. ^{14}C–Degradation products were extracted three times with benzene. Both methanol extracts and combined benzene extracts were each concentrated and analyzed by *tlc*. The residual soils after extraction were dried and assayed for radiocarbon. All experiments were carried out in duplication.

When permethrin isomers were analyzed by the combination of methanol extraction, *tlc*, radioautography and *lsc* immediately after application of ^{14}C–*alc*–*t*– and *c*–permethrin to two types of soil at 0.1 ppm, the recovery was more than 96.0%.

5. Identification of Degradation Products

Certain degradation products with carboxyl and/or phenol groups were converted to the corresponding methyl esters or methyl ethers by treatment with diazomethane in ether. The methylated products were identified by two-dimentional *tlc* cochromatography with the authentic standards. The following solvent systems were used; (A, B) for 4′–OCH_3–permethrin, (A, G) for PBacid–Me, *t*–Cl_2CA–Me and *c*–Cl_2CA–Me, (F×2, E) for PBalc. For identification of *t*–OH–*t*–Cl_2CA, *c*–OH–*t*–Cl_2CA, *t*–OH–*c*–Cl_2CA, *c*–OH–*c*–Cl_2CA, *c*–OH–*t*–Cl_2CA–lactone and *c*–OH–*c*–Cl_2CA–lactone, one-dimensional *tlc* cochromatography was carried out in both solvent systems C and D. Polar metabolites remaining at the origin of *tlc* plate developed with solvent system D were scraped from the *tlc* plate, extracted with methanol and hydrolyzed in 6 N HCl at 100°C for 30 min. After extraction with ether, ^{14}C–products in the hydrolyzate were identified by *tlc* cochromatography as mentioned above.

6. Leaching Test

Each air-dry soil was packed uniformly to a depth of 20 cm in a glass column of 2.5 cm i.d. Then, the soil incubated with 1.0 ppm of ^{14}C–*alc*–*t*– or *c*–permethrin for 0 day or for 21 days was applied to the top of the soil column in height of 5 cm. The column was percolated with about 300 ml of water at a flow rate of 6–30 ml/hour, and effluents were collected. After percolation, the soil in the column was removed, sectioned 5 cm lengths. The sectioned soils and effluents were analyzed for radiocarbon. Effluents were further freeze-dried, and the residue was extracted with methanol and analyzed for degradation products by *tlc*.

RESULTS

1. Degradation of t– and c–Permethrin in Soil under Upland Conditions

Figure 2 (A, B, C and D) shows the results of the time course study on dissipation of the radiocarbon following application of ^{14}C–permethrin isomers to two types of soil. Both *t*– and *c*– permethrin were applied at the rate of 1.0 ppm and held under upland conditions.

In the case of ^{14}C–*alc*–*t*–permethrin, the radiocarbon in organosoluble fractions (methanol extracts plus HCl–methanol extracts) rapidly decreased with time in two types of soil, and 13 to 14% of the applied radiocarbon were recovered 60 days after treatment. On the other hand, the radiocarbon bound to the soil increased for up to 10 days and then reached nearly the constant level. With ^{14}C–*alc*–*c*–permethrin, the decrease of organosoluble radiocarbon was more gradual and the amount of bound ^{14}C after 60 days was larger. With both isomers, two types of soil showed more or less similar tendency in dissipation and distribution of the radiocarbon in organosoluble fractions and soil residues. The recovery of the radiocarbon was greater with *cis*-isomer than with *trans*-isomer. The bound residues were hardly removed

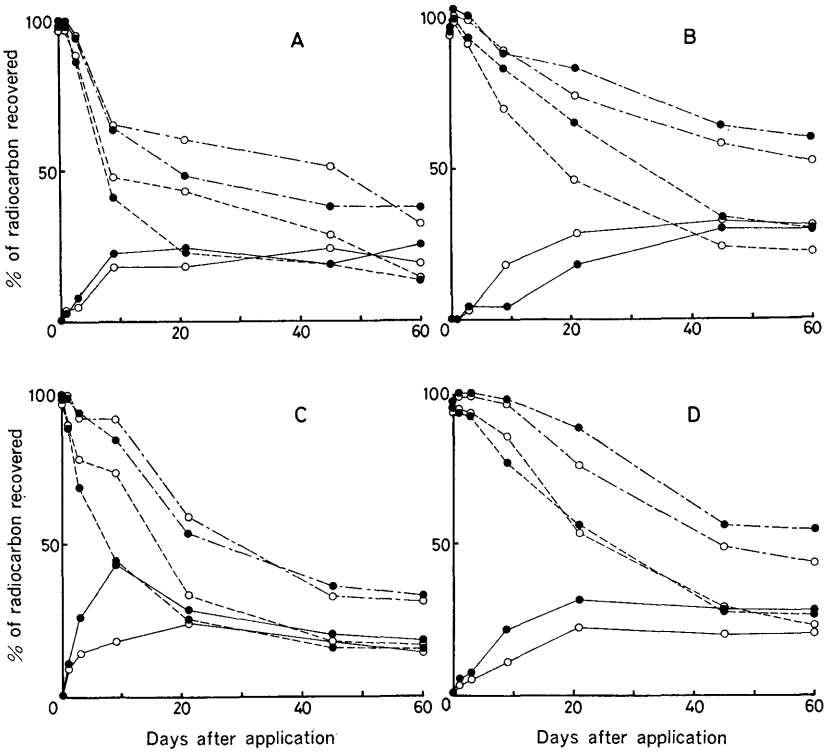

Fig. 2 Dissipation and distribution of the radiocarbon after application of ^{14}C-labeled permethrin preparations to the upland soils at the rate of 1.0 ppm.
Kodaira soil -—●—-: total ^{14}C, --●--: organosoluble, —●—: soil residues.
Azuchi soil -—○—-: total ^{14}C, --○--: organosoluble, —○—: soil residues.
A: ^{14}C-*alc*-*t*-permethrin, B: ^{14}C-*alc*-*c*-permethrin.
C: ^{14}C-*acid*-*t*-permethrin, D: ^{14}C-*acid*-*c*-permethrin.

from both soils by further extraction with 0.5 N NaOH solution. The volatile radiocarbon was tried to trap both in a polyurethane plug and 0.5 N NaOH solution for up to 21 days after application of ^{14}C-*alc*-*t*- and *c*-permethrin according to Kearney and Kontson.[7] Any detectable radiocarbon was hardly found in the polyurethane plug, but a fairly larger amount of the radiocarbon was trapped in 0.5 N NaOH trap. Thus, the loss of the radiocarbon from the soil appears to be due in part to degradation to volatile products such as CO_2.

With ^{14}C-acid-permethrin isomers (Fig. 2C and 2D) the radiocarbon in organosoluble fractions rapidly decreased in two types of soil, similarly well to the alcohol labeled preparation. A larger amount of total radiocarbon was recovered with *c*-permethrin than with *t*-permethrin, as with the alcohol labeled preparations. The patterns of dissipation and

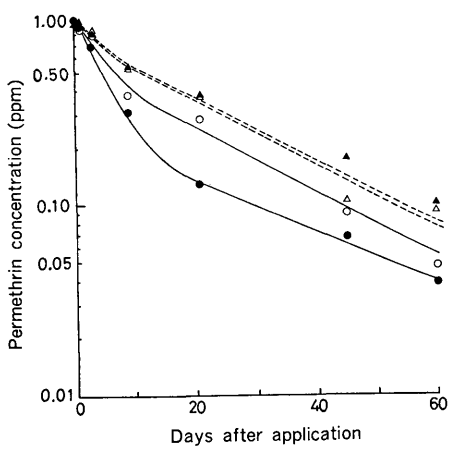

Fig. 3 The degradation rate of *t*- and *c*-permethrin in two types of soil under upland conditions.
t-permethrin —●—: Kodaira soil, —○—: Azuchi soil.
c-permethrin ---▲---: Kodaira soil, ---△---: Azuchi soil.

distribution of the radiocarbon from both acid and alcohol moieties of permethrin were nearly the same in two types of soil under upland conditions.

The recovery rates of *t*– and *c*–permethrin in two types of soil under upland conditions are presented in Fig. 3. *t*–Permethrin was degraded at faster rates than *c*–permethrin in both Kodaira and Azuchi soils. The half-lives were approximately 6 to 9 days and 12 days for *t*–and *c*–permethrin, respectively. After 60 days, the residue level was 0.040 to 0.048 ppm for *t*–permethrin and 0.101 to 0.096 ppm for *c*–permethrin.

2. Degradation Products

Table 2 shows the relative amounts of the degradation products obtained from both isomers of ^{14}C–*alc*– and ^{14}C–*acid*–permethrin 21 and 60 days after application to the upland soils. From ^{14}C–*alc*–preparations, 4′–OH–permethrin, PBalc and PBacid were obtained. 4′–OH–Permethrin was obtained in a larger amount from *c*–permethrin than from *t*–permethrin and in Kodaira soil as compared with Azuchi soil. A larger amount of PBacid was obtained with *t*–permethrin than with *c*–permethrin. A small amount of PBalc was found with both *t*– and *c*–permethrin. These degradation products are unlikely to accumulate in the soil, because the amounts of these products were smaller in 60 days soils than 21 days soils. Most of the radiocarbon presented as others in the table was not extracted from aqueous layer with acidic benzene and they contained more than 5 unidentified spots separated by *tlc* in solvent systems C and D. These unidentified products are unlikely to retain the ester linkage, based on *tlc* comparison of ^{14}C–*alc*– and *acid*–permethrin preparations. 3–(4′–Hydroxyphenoxy) benzyl alcohol and 3–(4′–hydroxyphenoxy)

Table 2 Relative amounts of permethrin metabolites 21 and 60 days after application of ^{14}C–labeled *t*– and *c*–permethrin to two types of soil under upland conditions.

^{14}C compound	% of radiocarbon recovered as indicated products							
	21 days				60 days			
	t–Permethrin		*c*–Permethrin		*t*–Permethrin		*c*–Permethrin	
	Kodaira	Azuchi	Kodaira	Azuchi	Kodaira	Azuchi	Kodaira	Azuchi
	^{14}C–alcohol labeled permethrin							
Organosoluble								
Permethrin	13.3	28.9	37.9	29.8	4.0	4.8	10.1	9.6
4′–OH–Permethrin	1.2	1.2	10.8	4.3	0.4	0.3	4.0	1.6
PBalc	0.2	0.2	0.3	0.2	0.1	0.1	0.2	0.1
PBacid	2.6	3.3	0.7	0.4	0.9	0.5	0.7	0.5
Others	5.7	9.2	16.1	11.2	7.3	7.8	14.9	10.4
Subtotal	22.7	42.8	65.8	46.0	12.6	13.5	29.9	22.0
Soil residues	24.3	17.6	17.5	28.1	25.4	18.2	30.1	29.3
Total ^{14}C	47.0	60.4	83.3	74.1	38.0	31.7	60.0	51.3
	^{14}C–acid labeled permethrin							
Organosoluble								
Permethrin	6.4	14.7	19.8	24.6	2.0	5.4	4.1	8.8
4′–OH–Permethrin	1.0	0.5	10.9	4.4	0.3	0.2	2.8	1.4
Cl_2CA	2.5	4.9	5.8	6.2	1.5	0.8	4.7	2.5
c–OH–Cl_2CA	0.4	0.4	0.7	0.6	0.2	0.2	0.3	0.2
t–OH–Cl_2CA	0.4	0.3	0.7	0.4	0.1	0.2	0.2	0.2
Lactones[a)]	0.6	1.5	2.3	1.4	0.6	1.1	1.0	0.6
Others	14.1	12.4	16.0	16.2	10.3	9.8	15.5	9.3
Subtotal	25.4	34.7	56.2	53.8	15.0	16.7	28.4	23.0
Soil residues	27.6	24.5	32.4	22.3	17.8	14.2	27.2	20.7
Total ^{14}C	53.0	59.2	88.6	76.1	32.8	30.9	55.6	43.7

[a)] *c*–OH–*t*–Cl_2CA– and *c*–OH–*c*–Cl_2CA–lactone

Table 3 Leaching of radiocarbon from soil columns treated with ^{14}C–*alc*–*t*– and *c*–permethrin.

Fraction		% of radiocarbon recovered			
		t–Permethrin		*c*–Permethrin	
		Kodaira	Azuchi	Kodaira	Azuchi
		Immediately after treatment of soil with ^{14}C–alcohol labeled permethrin			
Treated soil		98.0	96.7	99.0	97.6
Soil layer	0– 5 cm	1.6	1.9	0.8	2.0
	5–10 cm	0.3	0.8	0.2	0.2
	10–15 cm	0.1	0.4	0.0	0.1
	15–20 cm	0.0	0.2	0.0	0.1
Effluent		0.0	0.0	0.0	0.0
		21 days after incubation of soils with ^{14}C–alcohol labeled permethrin			
Treated soil		88.5	82.8	83.0	92.9
Soil layer	0–5 cm	2.8	10.8	6.2	2.8
	5–10 cm	2.0	3.7	2.7	2.2
	10–15 cm	2.0	1.3	2.5	0.9
	15–20 cm	2.9	1.1	2.1	0.7
Effluent		1.8	0.3	2.6	0.5

benzoic acid were not positively identified.

From ^{14}C–*acid*–permethrin preparations, 4′–OH–permethrin, Cl_2CA, and its hydroxylation derivatives were obtained. The amount of Cl_2CA was slightly larger with *c*–permethrin than with *t*–permethrin. *t*–OH–*t*–Cl_2CA and *t*–OH–*c*–Cl_2CA were found in small amounts. In addition, small amounts of *c*–OH–*t*–Cl_2CA–lactone and *c*–OH–*c*–Cl_2CA–lactone were detected. These lactones seem to be derived from *c*–OH–*t*–Cl_2CA and *c*–OH–*c*–Cl_2CA during the course of purification and *tlc* development in acidic solvent systems as mentioned by Gaughan *et al.*,[3] Cl_2CA and its hydroxylation products were found to somewhat greater extents in 21 days soils as compared with 60 days soils. Most of the radiocarbon presented as others in the table were not extracted from aqueous layer with acidic benzene and they contained more than 9 unidentified spots separated by *tlc* in solvent systems C and D. These unidentified products are unlikely to retain the ester linkage, based on *tlc* comparison of ^{14}C–degradation products from ^{14}C–*alc*– and *acid*–permethrin preparations.

3. Leaching Test

Table 3 shows the degree of leaching of permethrin and its degradation products through soil columns. When *t*– and *c*–permethrin mixed with soils were directly applied to soil columns, both isomers hardly moved through the columns of two types of soil with water. Only 1.0 to 3.3% of the radiocarbon was found in lower soil layers, but no radiocarbon was detected in effluents. On the other hand, when the soil preincubated with 1.0 ppm of ^{14}C–*alc*–permethrin for 21 days was placed onto the top of soil columns, the radiocarbon ranging from 7.9 to 17.2% of the recovered moved to lower soil layers, and 0.3 to 2.6% was found in effluents. On analysis of the column soil, 4′–OH–permethrin and PBacid were found in lower layers of Kodaira soil treated with *c*–permethrin and in the lower layers of Azuchi soil treated with *t*–permethrin, respectively. These findings indicate that *t*– and *c*–permethrin hardly moved through the soil with water, whereas the degradation products such as 4′–OH–permethrin and PBacid were slightly eluted with water. With ^{14}C–*acid* labeled permethrin, leaching test was not carried out.

DISCUSSION

t– and *c*–Permethrin were rapidly degraded in the soil under upland conditions with the half-lives of approximately 6 to 12 days.

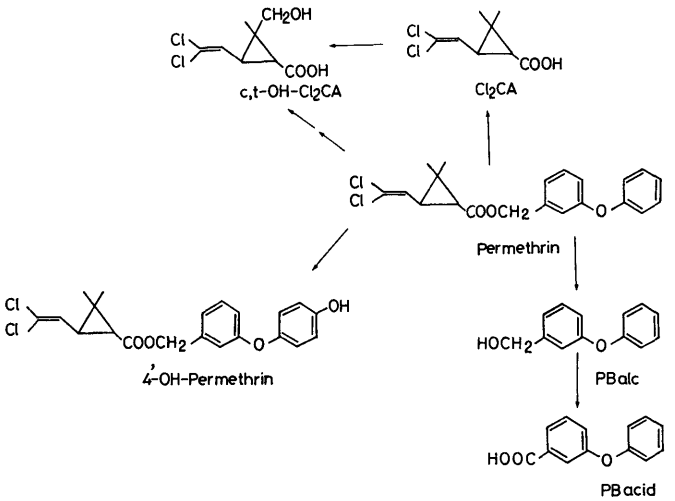

Fig. 4 Degradation pathways for permethrin in the soil.

The time required for disappearance of 90% of the applied insecticide was 30 to 50 days for *t*–permethrin and 40 to 60 days for *c*–permethrin.

Figure 4 shows the degradation pathways for permethrin isomers in the soil. Both isomers underwent mainly hydroxylation both at the phenoxy group of the alcohol moiety and at the *gem*-dimethyl group of the acid moiety, cleavage of the ester linkage, and oxidation of benzyl alcohol to benzoic acid. A larger amount of 4'–OH–permethrin was produced with *c*–permethrin than with *t*–permethrin. Cl_2CA was also obtained in somewhat larger amounts with *c*–permethrin than with *t*–permethrin. On the other hand, PBacid was obtained in a larger amount from *t*–permethrin than from *c*–permethrin. The sum of these identified degradation products was somewhat larger with *c*–permethrin than with *t*–permethrin, although the degradation of *t*–permethrin was slightly faster than *c*–permethrin. Since the recovery of the total radiocarbon was lower with *t*–permethrin than *c*–permethrin, the products derived from *t*–permethrin appears to be more easily degraded to volatile products than from *c*–permethrin.

There was a remarkable difference in organic matter contents between Kodaira and Azuchi soils. However, the degradation rate of permethrin isomers and the amount of bound ^{14}C were not clearly distinguishable. Only a small difference in the amount of 4'–OH–permethrin derived from *c*–permethrin was found between two types of soil.

In bean plants,[5] permethrin was also rapidly metabolized with the half-life of approximately 7 to 9 days for *t*– and *c*–permethrin, respectively. The major metabolic reactions were hydroxylation both at the phenoxy ring (2'– and 4'–position) and at the *gem*–dimethyl group, and cleavage of the ester linkage. Most of the metabolites retaining carboxyl and phenol groups were conjugated with glucose. In addition, permethrin and its metabolites hardly translocated from the treated sites to the other parts of bean plants. These results suggest that *t*– and *c*–permethrin undergo similar primary degradation reactions except for the conjugation reactions, although hydroxylation at the 2'–position of phenoxy ring and the *cis-trans* isomerization occurring on the leaf surface of bean plants were not recognized in the soil.

When applied to the field, permethrin is likely to stay mainly at the application sites and not to move to the other parts of plants and soils. The chemical appears to be easily degraded in soils and plants as well as by sunlight.[8,9] Therefore, permethrin is considered neither to persist nor to disperse widely in the environment.

要　　約

Permethrin [3-phenoxybenzyl (±)-*cis*, *trans* 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate) の (+)-*trans* 体もしくは (+)-*cis* 体を畑地条件下で2種類の土壌（小平，安土）に 1.0 ppm の割合で添加すると，いずれも速やかに消失し，半減期はそれぞれ約6–9日と約12日であった．処理60日後の permethrin の残留量は，(+)-*trans* 体では約 0.05 ppm (+)-*cis* 体では約 0.1 ppm で，(+)-*trans* 体は (+)-*cis* 体よりも土壌中で早く分解された．土壌中で permethrin は *cis* 体，*trans* 体ともにエステル結合の開裂，アルコール側のフェノキシ基と酸側のジメチル基の水酸化，benzyl alcohol から benzoic acid への酸化を経て分解される．主分解物は 3-phenoxybenzyl alcohol, 3-phenoxybenzoic acid, 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid およびそれの水酸化体と permethrin の水酸化体であった．

Permethrin は土壌から容易に溶脱されないが，3-phenoxybenzoic acid や permethrin の水酸化体のような分解物は水により若干溶脱された．

REFERENCES

1) M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, D. A. Pulman & J. H. Stevenson: *Nature* **246**, 169 (1973)
2) M. Elliott, N. F. Janes, D. A. Pulman, L. C. Gaughan, T. Unai & J. E. Casida: *J. Agric. Food Chem.* **24**, 270 (1976)
3) L. C. Gaughan, T. Unai & J. E. Casida: *J. Agric. Food Chem.* **25**, 9 (1977)
4) L. C. Gaughan, T. Unai & J. E. Casida: *ACS. Symp. Ser.* **42**, 186 (1977)
5) H. Ohkawa, H. Kaneko & J. Miyamoto: *J. Pesticide. Sci.* **2**, 67 (1977)
6) I. Nakatsuka, F. Shono & A. Yoshitake: *J. Labelled Comp.* **13**, (4), 561 (1977)
7) P. C. Kearney & A. Kontson: *J. Agric. Food Chem.* **24** (2), 424 (1976)
8) M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, D. A. Pulman & J. H. Stevenson: Proceeding 7th British Insecticide and Fungicide Conference, 721 (1973)
9) R. L. Holmstead, J. E. Casida & L. O. Ruzo: *ACS. Symp. Ser.* **42**, 137 (1977)