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Original Articles

Metabolic Fate of Fenvalerate (Sumicidin®) in Bean Plants

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Metabolic fate of fenvalerate [α–cyano–3–phenoxybenzyl–2–(4–chlorophenyl)isovalerate] and the [*S*]–acid ester isomer in bean plants was studied under laboratory conditions. When fenvalerate and the [*S*]–acid isomer were each applied to the leaf surface of bean plants at a rate of 10 μg per leaf, both compounds similarly disappeared from the treated leaves with half-lives of approximately 14 days. On and/or in the plants, fenvalerate and the [*S*]–acid isomer underwent decarboxylation, ester cleavage, hydrolysis of the CN group to $CONH_2$ and COOH groups, hydroxylation at 2′– and 4′–phenoxy positions, conversion of the alcohol moiety to 3–phenoxybenzyl alcohol and 3–phenoxybenzoic acid, and conjugation of the resulting carboxylic acids and alcohols with sugars. Very little of ^{14}C was transferred to other parts of the bean plants. When bean plant seedlings were planted for 30 days in Kodaira light clay and Katano sandy loam soils treated with 1.0 ppm of ^{14}C–fenvalerate, roots retained fairly large amounts of ^{14}C, shoots, pods and seeds contained very little ^{14}C. No parent compound was detected in shoots.

INTRODUCTION

Fenvalerate [Sumicidin®, α–cyano–3–phenoxybenzyl–2–(4–chlorophenyl)isovalerate] is one of the most potent pyrethroid insecticides, controlling various insect pests of cotton and other crops.[1,2] In connection with practical use, it is important to evaluate the fate of this insecticide in the environment. The metabolism of fenvalerate in soils,[3] an aquatic model ecosystem[4] and rats,[5] and its photodegradation[6,7] were already established.

Fenvalerate possesses two asymmetric carbon atoms, αC of the α–cyano–3–phenoxybenzyl alcohol moiety and C2 of the acid moiety, and the [2*S*] isomers are more insecticidally potent than the [2*R*] isomers.[8] The present study deals with the metabolic fate in bean plants of fenvalerate and the [2*S*, α*RS*] isomer labled with ^{14}C at the benzylic carbon (Cα), cyano group (CN) and carbonyl group (CO).

MATERIALS AND METHODS

1. Chemicals

Fenvalerate is designated as 2*RS*–fenvalerate, when distinguished from the isomers. The ester derived from [*RS*]–α–cyano–3–phenoxybenzyl alcohol and [*S*]–2–(4–chlorophenyl)isovaleric acid is designated as 2*S*–fenvalerate or the [*S*]–acid isomer.

The following ^{14}C–labeled preparations were used: 2*RS*–fenvalerate labeled at the cyano (^{14}CO) group; 2*S*–fenvalerate labeled at the cyano (^{14}CN) group, the carbonyl (^{14}CO) group of the acid moiety and the benzylic carbon ($^{14}C\alpha$) of the alcohol moiety. These labeled compounds were prepared by Nakatsuka *et al.*[9] of Sumitomo Chemical Co., Ltd. The specific activity was in the following (mCi/mmol): ^{14}CN–[2*RS*, α*RS*]–Fenvalerate, 4,4; ^{14}CN–[2*S*, α*RS*]–Fenvalerate, 15.7; ^{14}CO–[2*S*, α*RS*]–Fenvalerate, 5.0; $^{14}C\alpha$–[2*S*, α*RS*]–Fenvalerate, 20.0. [2*RS*, α*RS*] and [2*S*, α*RS*] are designated as 2*RS* and 2*S*, respectively, in the text. The radiochemical purity of these

preparations was determined as greater than 99% by silica gel thin-layer chromatography (*tlc*) in the following solvent systems: *n*–hexane–toluene–acetic acid (3 : 15 : 2), *Rf*=0.61; *n*–hexane–benzene (1 : 1), *Rf*=0.18; *n*–hexane–ether (4 : 1), *Rf*=0.63.

The following unlabeled standard compounds were prepared in this department:[3,4,5,15] 2*RS*–fenvalerate, 2–(3–phenoxyphenyl)–3–(4–chlorophenyl)–4–methylpentanenitrile[decarboxyl fenvalerate], α–carbamoyl–3–phenoxybenzyl–2–(4–chlorophenyl)isovalerate[$CONH_2$–fenvalerate], α–carboxy–3–phenoxybenzyl–2–(4–chlorophenyl)isovalerate [COOH–fenvalerate], 2–(4–chlorophenyl)isovaleric acid[Cl–Vacid], 3–phenoxybenzaldehyde [PBald], 3–phenoxybenzyl alcohol [PBalc], 3–phenoxybenzoic acid [PBacid], 3–phenoxymandelic acid [PBalc–COOH], 3–(2′–hydroxyphenoxy)benzoic acid [2′–HO–PBacid], 3–(4′–hydroxyphenoxy)benzoic acid [4′–HO–PBacid], α–cyano–3–hydroxybenzyl–2–(4–chlorophenyl)isovalerate [desphenyl fenvalerate] and α–cyano–3–(4′–hydroxyphenyl)–benzyl–2–(4–chlorophenyl)isovalerate[4′–HO–fenvalerate].

β–Glucosidase (almond) and cellulase (*Aspergillus niger*) were purchased from Sigma Chemical Co., St. Louis, Mo.

2. *Radioanalysis and Radioautography*

Liquid scintillation counting (*lsc*), combustion analysis and radioautography were conducted as reported previously.[5,10] The following scintillation fluids were used for *lsc*: a dioxane scintillation fluid (5 g of 2,5–diphenyloxazole and 100 g of naphthalene in 1 liter of dioxane) for organosoluble fractions and gel regions on *tlc* plates; Aquasol–2® (New England Nuclear) for aqueous fractions; a 9 : 15 mixture of Oxisolb–CO_2® and Oxiprep® (New England Nuclear) for combustion analysis.

Industrial X-ray films (No. 150, Fuji Photo Film Co., Tokyo, Japan) were used for radioautography.

3. *Tlc*

Precoated silica gel 60F–254 chromatoplates (20×20 cm, 0.25 mm thickness, E. Merck) were used for analysis and preparation of degradation products. The solvent systems used, *Rf* values for fenvalerate and its degradation products are listed in Table 1. Solvent systems for two-dimensional development are illustrated for example as follows: (A, B) indicates development in the first direction with solvent system A and in the second direction with solvent system B. Unlabeled standard chemicals were visualized under ultraviolet light. Radioactive spots were detected by radioautography and quantitatively analyzed as reported previously[5].

Table 1 *Tlc Rf* values for fenvalerate and its metabolites.

Compound	*Rf* values with indicated solvent systems[a]		
	A	B	C
Fenvalerate	0.61	0.72	0.51, 0.34
Decarboxyl Fenvalerate	0.59	0.72	0.47, 0.42
$CONH_2$–Fenvalerate	0.30, 0.27	0.30, 0.25	
COOH–Fenvalerate	0.32	0.60	
4′–HO–Fenvalerate	0.27	0.57	
Desphenyl Fenvalerate	0.27	0.57	
Cl–Vacid	0.42	0.57	
PBald	0.49	0.67	
PBalc	0.28	0.40	
PBacid	0.39	0.52	
2′–HO–PBacid	0.25	0.36	
4′–HO–PBacid	0.15	0.28	
PBalc–COOH	0.06	0.15	

a) A, *n*–hexane–toluene–acetic acid (3/15/2, v/v); B, benzene saturated with formic acid-ether (10/3); C, *n*–hexane–ether (20/1), 8 developments.

4. Foliar Treatment and Analysis of Plants

Kidneybean plants (*Phaseolus vulgaris* L.) were held in a greenhouse at 25±2°C before and after treatment. Each of ^{14}CN–2*RS*–, ^{14}CO–2*S*–, and ^{14}Cα–2*S*–fenvalerate preparations was evenly applied to the upper surface of two primordial leaves of 14-day old seedlings at a rate of 10 μg in 100 μl methanol per 20 cm^2 by a microsyringe on October 14, 1977. Then, buds were removed off every two weeks to prevent the treated leaves from defoliation. The removed buds were kept at −20°C until analyzed. In a separate experiment, the treated seedlings were grown for 60 days without removing buds off for investigating distribution and movement of radioactivity to edible portions (pods and seeds). Although about 80% of the treated leaves were defoliated after 60 days in this experiment, seedlings with the treated leaves were subjected to analysis.

At various time intervals, two bean seedlings were harvested and sectioned into three parts: treated leaves, shoots and roots except the treated leaves, and edible portions. The treated leaves, and shoots and roots were immediately frozen in liquid nitrogen, ground to a fine powder with a mortar and pestle, and then extracted with methanol (5 ml/g) by homogenization with a Waring blender (Nihon Seiki Co., Tokyo, Japan). The homogenate was filtered and the residue was extracted two additional times in the same manner. The methanol-insoluble residues of treated leaves were further extracted three times with water–methanol (1 : 1) (5 ml/g) by homogenization with a Polytron (Type PT 10–35, Kinematica GmbH, Luzern, Steinhofhalde, Switzerland). The combined methanol and water–methanol extracts of plants were analyzed for ^{14}C. The edible portions were dried over P_2O_5 in a vacuum desiccator and then combusted for quantitation of the total radiocarbon. The extracts from the treated leaf, and shoot and root fractions were each concentrated and subjected to *tlc* in solvent systems A, B and C. By the combination of extraction, *tlc*, radioautography and *lsc*, 96.9% of fenvalerate was recovered from bean leaves immediately after application of ^{14}CN–2*RS*–fenvalerate at a rate of 10 μg per leaf.

5. Uptake of Soil Residues into Bean Plants

Characteristics of soil used for this study are in the following: Kodaira light clay soil with sand, silt, clay and organic matter contents of 31, 40, 29% and 15.3%, respectively, cation exchange capacity 53.7 meq/100 g dry soil, pH (H_2O) 5.5; Katano sandy loam soil with sand, clay and organic matter contents of 80, 12, 8% and 1.8%, respectively, cation exchange capacity 9.3 meq/100 g dry soil, pH (H_2O) 5.8. Detailed characteristics of these soils were reported previously.[3] On March 3, 1978, ^{14}CN–2*S*– or ^{14}Cα–2*S*–fenvalerate (0.1 mg/ml acetone) was applied to soils at a rate of 1.0 ppm on a dry weight basis, and the soil was mixed well, and then 300 g soil was placed into a plastic pot (11 cm i.d.×7 cm height). The treated soils were incubated for 14 days at 25±2°C in the dark. Then, 14-day old seedlings of kidneybean plants were each transplanted into the pots and held in a greenhouse at 25±2°C. About 30–50 ml of water was applied to each pot every day. After 30 days, the plants were carefully pulled out of soils and the roots were thoroughly washed with 200 ml of water. The harvested seedlings were sectioned into roots, shoots and edible portions, and each part was analyzed as mentioned above. The soil was extracted three times with methanol (3 ml/g) by homogenization and centrifugation, and the combined extracts were analyzed for ^{14}C and degradation products.

6. Characterization of Metabolites

Extracts from the treated leaves of bean plants were each subjected to preparative *tlc* in solvent system A. Radioactive gel regions were divided into several fractions and individual fractions were extracted with methanol. Then, the recovered products were each identified by one- or two-dimensional *tlc* cochromatography with authentic standards. The fraction retained at the origin of the plates developed with solvent system A was designated as polar metabolites. The fraction of polar metabolites was dissolved in 2 ml of 0.2 M acetate buffer, pH 5.0, and incubated with either β–glucosidase (6 mg), cellulase (6 mg) or a mixture of β–glucosidase (6 mg) and cellulase (6 mg) at 37°C for 48 hr. Then, the

incubation mixtures were adjusted to pH 1 to 2 with conc. hydrochloric acid and extracted with ether (8 ml×3). The combined ether extracts were analyzed by *tlc* in solvent systems A and B. Unextractable residues of the treated leaves were also subjected to enzyme hydrolysis. About 400 mg of the dried residues dissolved in 10 ml of 0.2 M acetate buffer, pH 5.0, was incubated with a mixture of *β*-glucosidase (30 mg) and cellulase (30 mg) at 37°C for 48 hr. Then, the incubation mixture was separated into supernatant and residue fractions by centrifugation. The supernatant was extracted and analyzed as described above.

Direct *tlc* comparison of metabolites from three labeled preparations was used to distinguish products retaining the ester linkage from hydrolysis products. Metabolites retaining the ester linkage are commonly detected with three ^{14}C-labeled compounds, while hydrolysis products from the alcohol moiety are detected with $^{14}C\alpha$– and ^{14}CN–preparations, but not with ^{14}CO–preparation.

RESULTS

1. *^{14}C Distribution*

After foliar application of each of three ^{14}C–labeled fenvalerate preparations to bean plants at a rate of 10 *μg* per leaf, the recovery of total radiocarbon gradually decreased with time, as shown in Fig. 1. After 60 days, 85 to 86% of the applied radiocarbon was recovered from the plants treated with ^{14}CO–2*S*– and $^{14}C\alpha$–2*S*–fenvalerate, while 67% was recovered from the plants treated with ^{14}CN–2*RS*–fenvalerate. Most of the recovered radiocarbon was present in the treated leaves, and only 2 to 6% of the applied radiocarbon was found in other parts of the plants. A whole-body radioautogram of bean plant harvested at 30 days after treatment showed that most of the applied ^{14}C remained at the treated leaf (Fig. 2). *Tlc* analysis of the extracts from the plants indicated that no fenvalerate was present in shoots and roots except the treated leaves.

In a separate study, movement of radiocarbon from the treated leaves to edible portions was determined as shown in Table 2. The radiocarbon equivalent to 0.001 to 0.024 ppm and 0.002 to 0.009 ppm of fenvalerate was detected in pods and seeds, respectively, and shoots and roots contained 0.008 to 0.028 ppm 60 days after treatment. These findings indicate that very little ^{14}C moved from the application site to other parts of bean plants.

2. *Residue Levels of Fenvalerate*

As shown in Fig. 3 and Table 3, fenvalerate

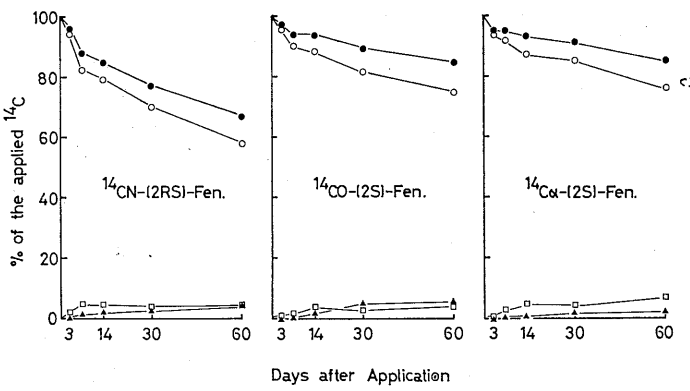

Fig. 1 Dissipation and distribution of ^{14}C in bean plants after foliar treatment with ^{14}CN–2*RS*–, ^{14}CO–2*S*– and $^{14}C\alpha$–2*S*– fenvalerate preparations at a rate of 10 *μg* per leaf.
● Total ^{14}C, ○ Extractable ^{14}C of the treated leaves, □ Extract residues of the treated leaves, ▲ Shoots and roots except the treated leaves.

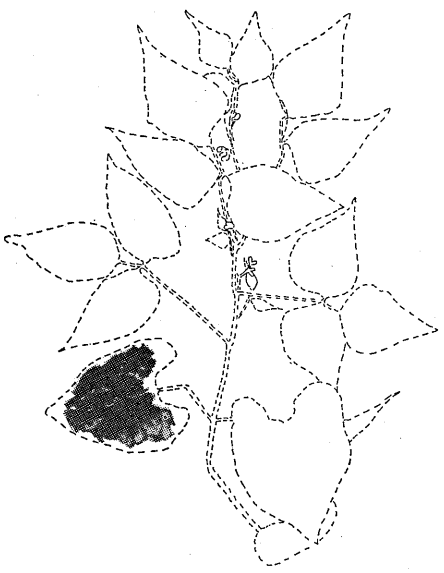

Fig. 2 A Whole-body radioautogram of bean seedling harvested at 30 days after foliar treatment with ^{14}CN–2*RS*–fenvalerate.

Table 2 Distribution of ^{14}C in bean plants 60 days after foliar application of each of three ^{14}C–fenvalerate preparations at the rate of 10 μg per leaf.

	^{14}C, ppm fenvalerate equivalent		
	^{14}CN–[2*RS*]–Fen.	^{14}CO–[2*S*]–Fen.	$^{14}C\alpha$–[2*S*]–Fen.
0 day treated leaves	3.89*	3.76*	4.26*
60 days treated leaves			
^{14}C	2.47	2.86	3.53
Fenvalerate	1.88	1.85	2.27
Shoots and Roots	0.019	0.028	0.008
Pods	0.012	0.024	0.001
Seeds	0.009	0.009	0.002

* Applied dose (μg)/weight of 60 days treated leaves (g).

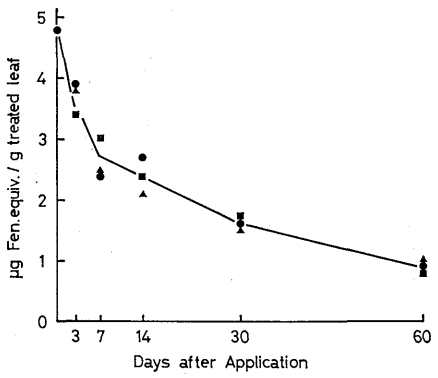

Fig. 3 Residual behavior of fenvalerate in the treated leaves of bean plants after foliar treatment with ^{14}C–labeled fenvalerate preparations at a rate of 10 μg per leaf. ● ^{14}CN–[2*RS*]–fen., ▲ ^{14}CO–[2*S*]–fen., ■ $^{14}C\alpha$–[2*S*]–fen.

readily disappeared with time from the treated leaves of bean plants, and 43 to 48% of the applied was recovered 60 days after treatment. The half-life of fenvalerate in the treated leaves of bean plants was approximately 14 days, and the residue level of fenvalerate after 60 days was 0.8 to 1.0 ppm. There seems to be no difference in the degradation rate in bean plants between 2*RS*– and 2*S*–fenvalerate.

3. *Metabolites in Bean Plants*

The organosoluble fractions from the treated leaves were analyzed for fenvalerate metabolites. Two ester metabolites were found with three ^{14}C–labeled fenvalerate preparations. These were tentatively identified as $CONH_2$–fenvalerate and COOH–fenvalerate by two-dimensional *tlc* cochromatography in solvent system (A, B) with the authentic standards. Decarboxyl fenvalerate was also identified by *tlc* cochromatography with the authentic standard. This product was obtained with ^{14}CN– and $^{14}C\alpha$–fenvalerate, but not with the ^{14}CO–labeled compound. The *Rf* value of the product was nearly the same as that of fenvalerate in solvent systems A and B, but apparently different from fenvalerate in solvent system C (Table 2). Cl–Vacid was produced from the ^{14}CO–compound, and PBacid was produced from the $^{14}C\alpha$–compound. These two metabolites were each identified by two-dimensional *tlc* cochromatography in solvent system (A, B) with the authentic standards. As shown in Table 4, each of these identified metabolites accounted for less than 2% of the applied radiocarbon 30 and 60 days after treatment.

The amount of ^{14}C in the fraction of polar metabolites gradually increased with time. The fraction was subjected to β–glucosidase and/or cellulase hydrolysis. Cellulase, and a mixture of β–glucosidase and cellulase were similarly effective in hydrolysis of conjugates, and released large amounts of aglycons as compared with β–glucosidase alone. Most of aglycons released by cellulase or β–glucosidase–cellulase hydrolysis were identified by cochromatography with authentic standards in solvent systems A and B. The following aglycons were recognized: PBalc–COOH from the ^{14}CN–preparation; Cl–Vacid from the ^{14}CO–preparation; PBalc, PBald, PBacid, 2′–HO–PBacid, 4′–HO–PBacid and PBalc–COOH

Table 3 Amounts of fenvalerate and its metabolites in bean plants 30 and 60 days after foliar application of ^{14}C–labeled compounds at the rate of 10 μg per leaf.

	% of the applied ^{14}C					
	^{14}CN–[2*RS*]–Fen.		^{14}CO–[2*S*]–Fen.		^{14}Cα–[2*S*]–Fen.	
	Days after application					
	30	60	30	60	30	60
Treated leaves	73.3	62.3	84.0	79.1	89.2	83.1
Extractable ^{14}C	69.6	57.7	81.3	74.5	85.1	76.4
Fenvalerate	55.0	42.8	56.5	47.8	52.5	44.0
Decarboxyl Fen.	1.3	1.1	—	—	1.6	1.9
$CONH_2$–Fen.	0.3	0.3	0.4	0.3	0.3	0.3
COOH–Fen.	0.3	0.2	0.4	0.1	0.3	0.5
Cl–Vacid	—	—	<0.1	0.2	—	—
PBacid	—	—	—	—	0.5	0.5
Cl–Vacid-conj.	—	—	8.2	4.6	—	—
PBalc–CN–conj.	2.8	2.8	—	—	5.5	4.8
PBalc–COOH–conj.	0.6	0.5	—	—	0.9	0.7
PBalc–conj.	—	—	—	—	3.7	1.9
PBacid–conj.	—	—	—	—	1.5	1.2
2′–HO–PBacid–conj.	—	—	—	—	2.5	1.9
4′–HO–PBacid–conj.	—	—	—	—	4.5	3.1
Other conjugates	0.5	0.6	0.2	0.2	1.4	0.6
Other products	8.8	9.4	15.6	21.3	9.9	15.0
Bound ^{14}C	3.7[a)]	4.6	2.7[a)]	4.6	4.1[a)]	6.7
Cl–Vacid–conj.		—		0.4		—
PBalc–conj.		—		—		0.1
PBacid–conj.		—		—		0.1
2′–HO–PBacid–conj.		—		—		0.1
4′–HO–PBacid–conj.		—		—		0.3
Shoots and roots except the treated leaves	3.8	4.8	4.7	5.7	1.7	2.4
Extractable ^{14}C	1.1	1.6	3.7[b)]	4.6[b)]	1.3[b)]	2.0[b)]
Bound ^{14}C	2.7	3.2	1.0	1.1	0.4	0.4
Total ^{14}C	77.1	67.1	88.7	84.8	90.9	85.5

a) Not characterized.
b) No fenvalerate was detected.

from the $^{14}C\alpha$–preparation. Direct hydrolysis of fenvalerate appears to give α–cyano–3–phenoxybenzyl alcohol [PBalc–CN], which is quite unstable even under physiological conditions and on *tlc* plates, and easily decomposed to PBald and HCN. Therefore, it appears that on enzymatic hydrolysis of conjugates, release of PBald from the $^{14}C\alpha$–labeled and loss of the radiocarbon from the ^{14}CN–labeled compound during extraction and analysis suggest the presence of PBalc–CN–conjugates. Among the conjugates cleaved by enzymatic hydrolysis, the major products were conjugates of Cl–Vacid and perhaps PBalc–CN which accounted for 5 to 8% of the applied ^{14}C. The fraction of "other products" in Table 4 included a number of minor metabolites and polar metabolites which were not cleaved by enzymatic hydrolysis. 2′–HO–fenvalerate, 4′–HO–fenvalerate and 3–phenoxybenzyl cyanide were not detected in any fractions.

Unextractable residues (bound ^{14}C in Table

3) also released several aglycons including Cl–Vacid, PBalc, PBacid, 2′–HO–PBacid and 4′–HO–PBacid in very small amounts on hydrolysis with a mixture of β–glucosidase and cellulase.

4. Uptake of Soil Residues into Bean Plants

After 30 days cultivation of bean plant seedlings in soils treated with 1.0 ppm of each of ^{14}CN–2*S*– and ^{14}Cα–2*S*–fenvalerate, amounts of the radiocarbon in pods and seeds, shoots and roots were determined (Fig. 4). The ^{14}C content in roots and shoots of the plants grown in Kodaira light clay soil was 140 to 200 ppb and 14 to 23 ppb, respectively. The roots and shoots planted in Katano sandy loam soil contained 340 to 360 ppb and 14 to 17 ppb, respectively. Most of the radiocarbon found in roots appears to be due in part to direct contamination with the compounds. The ^{14}C content in pods and seeds was 3 to 8 ppb and much less than that in shoots. The parent compound was not detected in shoots. The pods and seeds were not analyzed for the parent compound, because of their very small content of ^{14}C.

These findings indicate that very little fenvalerate residues in soils were taken up into bean plants, and translocated from roots to shoots and edible portions.

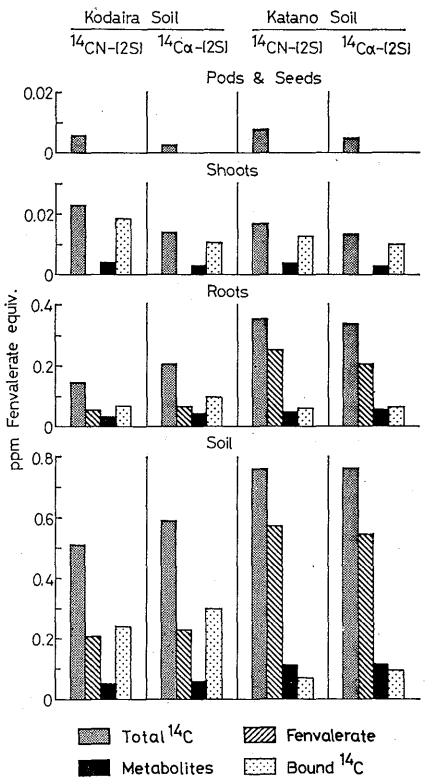

Fig. 4 Uptake and distribution of ^{14}C in bean plants 30 days after transplantation to soils treated with ^{14}CN–2*S*– and ^{14}Cα–2*S*–fenvalerate preparations at the rate of 1.0 ppm.

The fraction of metabolites includes 4′–HO–fenvalerate, desphenyl fenvalerate, $CONH_2$–fenvalerate, PBacid and polar products with soils and roots of plants, and polar products with shoots.

DISCUSSION

After foliar treatment, fenvalerate and its [*S*]–acid isomer similarly disappeared from the treated leaves of bean plants with half-lives of approximately 2 weeks under laboratory conditions. The degradation rate of some pyrethroids with 3–phenoxybenzyl moiety was also determined under greenhouse conditions. The half-life was less than one day for phenothrin in bean and rice plants,[10] 8 days for decamethrin in cotton,[11] 7–9 days[12] and 1–2 weeks[13] for permethrin in bean plants. Based on these findings, the degradation of fenvalerate appears to be somewhat slower than that of the other pyrethroids in plants. However, fenvalerate disappeared much more rapidly under field conditions, and the half-life was less than one day in cabbage[14] and about 2 days in cotton.[7]

Fenvalerate was degraded via photochemical reactions as well as via various biochemical reactions in bean plants. Figure 5 shows the proposed metabolic pathways for fenvalerate. The insecticide underwent decarboxylation, hydrolysis of the CN group to $CONH_2$ and COOH groups, hydroxylation at 2′– and 4′–positions of the phenoxy group and cleavage of the ester linkage. Decarboxyl fenvalerate was considered to be a photoproduct.[6,7,15] $CONH_2$– and COOH–fenvalerate also appear to be produced in part via photochemical[15] and/or physicochemical reactions.[8] These products further underwent ester cleavage. 2′–HO– and 4′–HO–PBacid appear to be produced following hydroxylation at 2′– and 4′–positions of the phenoxy moiety and cleav-

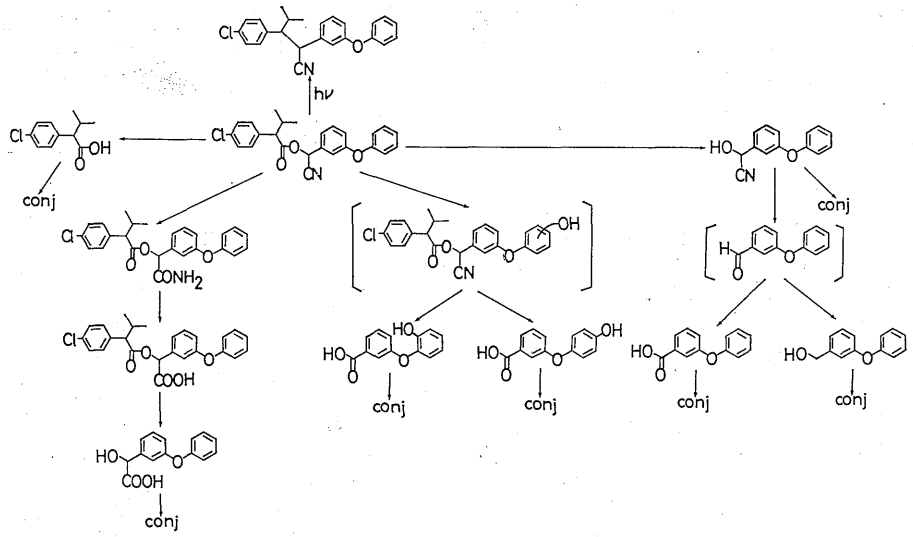

Fig. 5 Proposed metabolic pathways for fenvalerate on and/or in bean plants.

age of the ester linkage as reported with permethrin[12,13] and decamethrin.[11] Cleavage of the ester linkage of fenvalerate produced Cl–Vacid and PBalc–CN which were in part conjugated with sugars. PBalc–CN also appears to decompose to HCN and PBald as reported with decamethrin.[11] PBald was further oxidized to PBacid and reduced to PBalc. Although HCN was not determined in this study, it may be easily transformed to CO_2 by the action of sunlight.[15] Most of the resulted carboxylic acids and alcohols were conjugated with sugars including glucose. The conjugates in bean plants were much more efficiently cleaved by cellulase as compared with β–glucosidase. There seem to be three different types of conjugates: (1), glucosides which were hydrolyzed by β–glucosidase; (2), conjugates with polysaccharides which were cleaved by cellulase but not by β–glucosidase; and (3), conjugates with other unidentified fragments which were not cleaved by both enzymes. More *et al.*[16] showed that PBacid forms conjugates with glucose, glucosylarabinose and glucosylxylose in vine, cotton and other plants.

The identified fenvalerate metabolites in bean plants were analogous to those in mammals except for the nature of the conjugating moieties[5] and the photoproducts. PBalc–CN was probably conjugated with sugars in bean plants, whereas PBalc–CN and its conjugate were not found as mammalian metabolites.[5] Although a few photoproducts were produced on bean plants in very small amounts, these were equally or less toxic on an acute basis to mice than the parent compound itself.[7] Other major constituents of the residues in bean plants were unextractable bound residues, which were cleaved to very small extents by β–glucosidase–cellulase hydrolysis. Therefore, these are considered to be of little toxicological importance because of the limited bioavailability, as illustrated by carbamate insecticides.[17]

Very little of fenvalerate residues in soils were taken up into bean plants and transferred from roots to shoots and edible portions. This appears to relate to the fact that fenvalerate is tightly adsorbed on to soil particles and hardly eluted with water.[3] Therefore, the soil residues seem to have little effects on rotational crops in the field.

REFERENCES

1) N. Ohno, K. Fujimoto, Y. Okuno, M. Hirano, N. Itaya, T. Honda & H. Yoshioka: *Pestic. Sci.* **7**, 241 (1976)
2) N. Ohno, N. Itaya, M. Hirano, I. Ohno, K. Aketa & H. Yoshioka: *J. Pesticide Sci.* **2**, 533 (1977)
3) H. Ohkawa, K. Nambu, H. Inui & J. Miyamoto:

J. Pesticide Sci. **3**, 129 (1978)
4) H. Ohkawa, R. Kikuchi & J. Miyamoto: *J. Pesticide Sci.* **5**, 11 (1980)
5) H. Ohkawa, H. Kaneko, H. Tsuji & J. Miyamoto: *J. Pesticide Sci.* **4**, 143 (1979)
6) R. L. Holmstead & D. G. Fullmer: *J. Agric. Food Chem.* **25**, 56 (1977)
7) R. L. Holmstead, D. G. Fullmer & L. O. Ruzo: *J. Agric. Food Chem.* **26**, 954 (1978)
8) I. Nakayama, N. Ohno, K. Aketa, Y. Suzuki, T. Kato & H. Yoshioka: "Advances in Pesticide Science," ed. by H. Geisbühler, Part 2, Pergamon Press, New York, p. 174, 1979
9) I. Nakatsuka, F. Shono, H. Ohkawa & A. Yoshitake: Abstracts of Papers, 2nd Annual Meeting of the Pesticide Science Society, Tokyo, No. 107, 1977
10) K. Nambu, H. Ohkawa & J. Miyamoto: *J. Pesticide Sci.* **5**, 177 (1980)
11) L. O. Ruzo & J. E. Casida: *J. Agric. Food Chem.* **27**, 572 (1979)
12) H. Ohkawa, H. Kaneko & J. Miyamoto: *J. Pesticide Sci.* **2**, 67 (1977)
13) L. C. Gaughan & J. E. Casida: *J. Agric. Food Chem.* **26**, 525 (1978)
14) N. S. Talekar: *J. Assoc. Off. Anal. Chem.* **60**, 908 (1977)
15) N. Mikami, N. Takahashi, K. Hayashi & J. Miyamoto: *J. Pesticide Sci.* **5**, 225 (1980)
16) J. E. More, T. R. Roberts & A. N. Wright: *Pestic. Biochem. Physiol.* **9**, 268 (1978)
17) T. C. Marshall & H. W. Dorough: *J. Agric. Food Chem.* **25**, 1003 (1977)

要　　約

フェンバレレート（スミサイジン®）のマメ幼苗における代謝分解

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Fenvalerate と〔*S*〕-酸エステル異性体のインゲンマメ幼苗における代謝分解性を実験室条件下で検討した．

^{14}C 標識の fenvalerate (CN) と〔*S*〕-酸異性体 (CO, Cα, CN) をマメの葉面に 10 μg/20 cm^2 の割合で塗布すると，両化合物は同様に半減期約2週間の速度で処理葉より減少した．^{14}C の処理葉から他の部位への移行はわずかであった．マメ葉における代謝分解は脱炭酸，エステル加水分解，CN 基の $CONH_2$ と COOH 基への変換，フェノキシ基の 2′ と 4′ 位での水酸化，アルコール部分の 3-phenoxybenzyl alcohol と 3-phenoxybenzoic acid への変換，生成したカルボン酸やアルコール類の糖との抱合を経て進行した．

1.0 ppm の ^{14}C 標識 Fenvalerate で処理した2種の土壌にインゲンマメの苗を移植して，30 日後には，かなりの ^{14}C が根に取り込まれた．しかし，地上部，可食部における ^{14}C はごくわずかで，親化合物は検出されなかった．