

殺虫剤ピラクロホスのキャベツにおける代謝

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Original Article

Metabolic Fate of Insecticide Pyraclofos in Cabbage Plants

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Metabolic fate of pyraclofos, 1-(4-chlorophenyl)pyrazol-4-yl ethyl S-propyl phosphorothiolate (Voltage), in cabbage plants was studied under laboratory conditions using ^{14}C -pyraclofos labeled at the benzene ring. When ^{14}C -pyraclofos was applied to the leaf surface of the plants at the rate of $2\text{ }\mu\text{g}/\text{cm}^2$, pyraclofos disappeared from the treated leaf with a half-life of approximately one week. Thirty days after foliar application, most of ^{14}C -radioactive carbon (^{14}C) was found in the treated site of the leaves, however, ^{14}C translocated to the nontreated portions was a small extent. Major metabolic pathways of pyraclofos in cabbage leaves were cleavage of P-O-aryl bond to yield 1-(4-chlorophenyl)-4-hydroxypyrazole, and followed by conjugation with sugars such as glucopyranoside or malonylglucopyranoside. A small amount of the parent compound was detected in the treated site, but not in the nontreated portions of the leaves. When cabbage plants were cultivated for 30 days using soils treated with ^{14}C -pyraclofos at the rate of 10 ppm, most of the ^{14}C was found in the treated soil. A small amount of ^{14}C was translocated to the plants, and most of it was in the roots. On the other hand, ^{14}C detected from the edible portion, leaf and stem was very small extent, and no parent compound was determined.

INTRODUCTION

Pyraclofos,* 1-(4-chlorophenyl)pyrazol-4-yl ethyl S-propyl phosphorothiolate (Voltage), has widely been used for agricultural pest control, and shows a potent insecticidal activity against a wide range of pest insects, especially, larvae of *Lepidoptera* such as *Plutella* spp., *Spodoptera* spp., *Pieris* spp. and *Heliothis* spp.¹⁻⁹⁾ As to the mode of action of pyraclofos in insects, oxidative activation in the central nervous system of *Spodoptera* larvae and degradation by aliesterases were already established by Kono *et al.*¹⁾ The metabolism of pyraclofos in rats has also been reported by

Tashiro *et al.*⁴⁾ The present study deals with metabolic fate in cabbage plants of ^{14}C -pyraclofos.

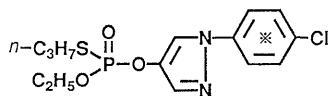
MATERIALS AND METHODS

1. Chemicals

^{14}C -pyraclofos labeled uniformly at benzene ring was synthesized by Daiichi Pure Chemical Co., Ltd. according to the method prepared by our research laboratories (Fig. 1). The specific radioactivity was 185.7 MBq (5.02 mCi)/mmol, and radiochemical purity was more than 99% by silica gel thin-layer chromatography. The following authentic compounds were prepared in our laboratories: pyraclofos, 1-(4-chlorophenyl)-4-hydroxypyrazole (CHP), 1-(4-chlorophenyl)pyrazol-4-yl ethyl hydrogen phosphate (CHP-EHP), 1-(4-chlorophenyl)pyrazol-4-yl ethyl methyl phosphate (CHP-EHP-Me),

* Pyraclofos (IUPAC name): (R,S)-[O-1-(4-chlorophenyl)pyrazol-4-yl O-ethyl S-propyl phosphorothioate], Voltage.

1-(4-chlorophenyl)pyrazol-4-yl *S*-propyl hydrogen phosphorothiolate (CHP-SHP), 1-(4-chlorophenyl)pyrazol-4-yl methyl *S*-propyl



※: ^{14}C labeled position

Fig. 1 Chemical structure of pyraclofos.

phosphorothiolate (CHP-SHP-Me), ethyl *S*-propyl hydrogen phosphorothiolate (ESP), ethyl methyl *S*-propyl phosphorothiolate (ESP-Me), ethyl dihydrogen phosphate (EHP), dimethyl ethyl phosphate (EHP-Me), *S*-propyl dihydrogen phosphorothiolate (SHP), dimethyl *S*-propyl phosphorothiolate (SHP-Me) and trimethyl phosphate (PA-Me) (Tables 1 and 2). 2,3,4,6-Tetra-*O*-acetyl- α -D-glucopyranosyl bromide, α -glucosidase (E.C. 3.2.1. 20, Yeast, Type III) and β -glucosidase (E.C. 3.2.1. 21,

Table 1 *R_f* values of authentic compounds by TLC.

$\text{R} = \text{O} - \text{C}_5\text{H}_4\text{N}_2$ Chemical	<i>R_f</i> value			
	Solvent system ^{a)}			
	A	B	C	D
EtO(PrS)P(O)(R) [Pyraclofos]	0.88	0.64	0.32	
H(R) [CHP]	0.88	0.38	0.16	
C ₆ H ₁₀ O ₅ (R) [CHPG]	0.69	0.08	0.05	
malonyl-C ₆ H ₁₀ O ₅ (R) [CHPMG]	0.16	0.05	0.0	
HO(PrS)P(O)(R) [CHP-SHP]	0.14	0.05	0.0	
HO(EtO)P(O)(R) [CHP-EHP]	0.11	0.05	0.0	
EtO(PrS)P(O)OH [ESP]	0.0	0.0	0.0	0.65
PrSP(O)(OH) ₂ [SHP]	0.0	0.0	0.0	0.53
EtOP(O)(OH) ₂ [EHP]	0.0	0.0	0.0	0.48

^{a)} Solvent system: A, ethyl acetate-methanol (2:1, v/v); B, toluene-ethyl acetate (4:1, v/v); C, hexane-ethyl acetate (2:1, v/v); D, *n*-propanol-water-ammonia water (10:5:1, v/v/v).

Abbreviations: Et, ethyl; Pr, *n*-propyl.

Table 2 Characterization of authentic compounds by GC-MS.

$\text{R} = \text{O} - \text{C}_5\text{H}_4\text{N}_2$ Chemical	GC-MS ^{a)}		
	<i>R_t</i> (min)	C.T. (°C)	<i>m/z</i>
EtO(PrS)P(O)(R) [Pyraclofos]	14.1	(200) ^{b)}	362, 360 (M ⁺), 318, 196, 194, 139
H(R) [CHP] ^{c)}			196, 194 (M ⁺), 139
C ₆ H ₁₀ O ₅ (R) [CHPG] ^{c)}			356 (M ⁺), 194, 138
malonyl-C ₆ H ₁₀ O ₅ (R) [CHPMG] ^{c)}			398 (M ⁺ - CO ₂), 247, 229, 205, 194
[CHPMG] ^{d)}			443 (M ⁺ + 1)
CH ₃ O(PrS)P(O)(R) [CHP-SHP-Me]	12.2	(200) ^{b)}	348, 346 (M ⁺), 196, 194, 138
EtO(CH ₃ O)P(O)(R) [CHP-EHP-Me]	9.4	(200) ^{b)}	318, 316 (M ⁺), 196, 194, 138
EtO(PrS)P(O)OCH ₃ [ESP-Me]	7.6	(150) ^{c)}	198 (M ⁺), 183, 156
PrSP(O)(OCH ₃) ₂ [SHP-Me]	6.8	(150) ^{c)}	184 (M ⁺), 170, 153, 110
EtOP(O)(OCH ₃) ₂ [EHP-Me]	4.0	(150) ^{c)}	153 (M ⁺), 139, 127, 110
OP(OCH ₃) ₃ [PA-Me]	3.1	(150) ^{c)}	141 (M ⁺), 127, 110

^{a)} Carrier gas: He, 30 ml/min, analyzed at 70 eV. ^{b)} Column: OV-17 (EI-MS). ^{c)} Direct insertion (EI-MS). ^{d)} Direct insertion (SI-MS). ^{e)} Column: 5% PEG-20M Gas Chrom Q (EI-MS).

Abbreviations: Et, ethyl; Pr, *n*-propyl; C.T., column temp.; EI, electron impact; SI, selected ion; MS, mass spectrometry.

Almond, Type II) were purchased from Sigma Chemical Co., U.S.A. Liquid scintillation cocktail was purchased from Wako Pure Chemical Industries, Ltd., Japan. All other chemicals were reagent grade unless otherwise noted in this paper.

2. Synthesis of 1-(4-Chlorophenyl)pyrazol-4-yl β -D-glucopyranoside

2,3,4,6-Tetra-*O*-acetyl- α -D-glucopyranosyl bromide in acetone was added to CHP dissolved in 1 N NaOH aq. solution with stirring for 3 hr at room temperature, followed by concentration under reduced pressure. CHP- β -D-glucopyranosyl tetra acetate was obtained by filtration, and refluxed in anhydrous methanol containing 0.003 N sodium methoxide at 70°C for 10 min for deacetylation. The reaction mixture was dissolved in water. CHP- β -D-glucopyranoside was extracted with ethyl acetate, and recrystallized from acetone as white flaky crystals. $^1\text{H NMR}$ $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ ppm: 3.7–4.2 (5H, m, glucose-2, 3, 4, 6-H), 4.8 (1H, d, $J=7$ Hz, glucose-1-H), 7.5 (2H, d, $J=9$ Hz, phenyl-2, 6-H), 7.6 (1H, s, pyrazole-3-H), 7.8 (2H, d, $J=9$ Hz, phenyl-3,5-H) and 8.1 (1H, s, pyrazole-5-H). $[\alpha]_D^{20} -36.0^\circ$ ($c=0.72$, CHCl_3).

3. Synthesis of 1-(4-Chlorophenyl)pyrazol-4-yl 6-*O*-malonyl β -D-glucopyranoside

Dicyclohexyldicarboimide was added to a mixture of CHPG and malonic acid in dioxane with stirring for 4 hr at room temperature. Insoluble materials were removed by filtration after addition of water to the reaction mixture. The filtrate was concentrated under reduced pressure, and the residue was subjected on an ion exchange resin (Dowex 1 $\times$ 4: CH_3COO^-) column chromatography. 1-(4-Chlorophenyl)pyrazol-4-yl 6-*O*-malonyl β -D-glucopyranoside was eluted with 4 N acetic acid-methanol (1:1, v/v), and purified by TLC and HPLC.

$^1\text{H NMR}$ $\delta_{\text{TMS}}^{\text{acetone-d}_6}$ ppm: 4.0–4.5 (2H, m, glucose-2, 3-H), 4.7 (1H, d, $J=7$ Hz, glucose-1-H), 7.5 (2H, d, $J=9$ Hz, phenyl-2,6-H), 7.6 (1H, s, pyrazole-3-H), 7.9 (2H, d, $J=9$ Hz, phenyl-3,5-H) and 8.2 (1H, s, pyrazole-5-H). $[\alpha]_D^{20} -36.7^\circ$ ($c=1.0$, CH_3OH).

4. Foliar Treatment

Two-month old cabbage plants (*Brassica oleracea*, cv. Shoshu) after sowing were used through this study. To upper surface of four leaves which are not formed into a round in each plant, ^{14}C -pyraclofos dissolved in methanol was evenly treated at a rate of 2 $\mu\text{g}/\text{cm}^2$ (52 $\mu\text{g}/\text{leaf}$) using a microsyringe. Three treated plants were held in a plant growth chamber [NS-280 FH, Takayama Co., Ltd.] for 30 days [photoperiod, 25,000 lux at 25°C for 12 hr; dark period, at 18°C for 12 hr per day]. On day 5, 10, 20 and 30, one leaf was sampled from each plant to determine pyraclofos, its metabolites and distribution levels of ^{14}C in the leaf.

In a separate experiment, one leaf which was not formed into a round was treated with ^{14}C -pyraclofos in each plant by almost the same manner described above. Three treated plants were grown for 30 days without removing leaves off for investigating distribution of ^{14}C to the edible portion which is formed into a round. The plants were harvested and sectioned into five portions such as edible, treated and nontreated leaves, stem and root. ^{14}C levels of the soils in a Wagner pot (11 cm i.d. $\times$ 12 cm) were also examined. Each sample was kept in a deep freezer at -25°C until analysis.

For the identification of dearylated phosphorus-containing metabolites in leaves, the plant was treated with nonlabeled pyraclofos at the rate of 4 $\mu\text{g}/\text{cm}^2$, and grown in a greenhouse for 30 days.

5. Uptake of ^{14}C into the Plants from Soils Treated with ^{14}C -Pyraclofos

One hundred grams of soil were screened through a 2 mm-mesh prior to treatment of ^{14}C -pyraclofos at a rate of 10 ppm on wet weight basis for each plant. The treated soils maintained at a soil moisture content of 75% of 0.33 bar moisture content were incubated at 25°C for 24 hr in dark room, and placed evenly on the top layer of soils in the Wagner pot. After 30 days, three plants were carefully pulled out of the soils, and roots were thoroughly washed with water. Each plant was sectioned into four portions such as the edible, leaf, stem and root, and the soil in

the pot was also fractionated into the treated (100 g) and nontreated layers (1120 g).

6. Characterization of Metabolites

Three treated leaves sampled were cut into fine pieces, and extracted twice with 50% aqueous methanol solution (50 ml/15 g wet tissue weight) followed by extracting twice with methanol using a Biomixer (BM-1, Nihon Seiki Co., Ltd.). The extracts were combined, and concentrated to remove methanol under reduced pressure. The residue was extracted three times with ethyl acetate (50 ml) by the addition of the same volume of water. ^{14}C in ethyl acetate, water and non-extractable fractions was radioassayed by combustion analysis and/or LSC. The ethyl acetate extractable fraction was also analysed by TLC and HPLC cochromatographies, and mass spectrometry (MS) in comparison with the authentic compounds.

The leaves treated with nonlabeled pyraclofos were extracted with the same manner described above to identify phosphorus-containing polar metabolites. The water fraction obtained was passed through Diaion HP-20 column, and subjected on to Amberlite IRA-410 (OH^-) column chromatography, followed by elution of 1 N HCl solution. Polar metabolites isolated were treated with diazomethane to determine by GC and GC-MS with the authentic compounds.

7. Hydrolysis of Metabolite

α -Glucosidase or β -glucosidase dissolved in 0.1 M acetic acid buffer solution (pH 4) was preincubated at 37°C for 30 min prior to the addition of ^{14}C -metabolite, and shaken for 2 hr. In the separate experiment, the metabolite was subjected with 2 N HCl solution at 100°C for 1 hr. The aglycone liberated in the mixture was extracted with ethyl acetate, and analyzed by TLC, HPLC and MS with the authentic compound.

8. Silica Gel Thin-Layer Chromatography (TLC)

Precoated silica gel 60 F₂₅₄ chromatoplate (20×20 cm, 0.25 mm thickness, E. Merck) was used for isolation and identification of metabolites. *R_f* values of authentic compounds

are shown in Table 1. Nonlabeled phosphorus-containing metabolites on TLC plate were detected under UV light or by color reaction. The reagents are as follows: a, 1% palladium chloride; b, conc. sulfuric acid; c, ammonium molybdate [60% perchloric acid (5 ml), 1 N HCl (10 ml), 4% ammonium molybdate (25 ml), H_2O (40 ml)]; d, naphthoresorcine [2% naphthoresorcine in ethanol-20% sulfuric acid (7/1, v/v)].

9. Autoradiography and Radioanalysis

TLC autoradiography (ARG), liquid scintillation counting (LSC) and combustion analysis were described in the previous report.⁴⁾ Radioactive spots on TLCs were detected using a TLC chromalyzer (JTC-601, Aloka) and/or by ARG using an X-ray film (IX Type 150, Fuji Photo Film Co., Ltd.).

10. High Performance Liquid Chromatography (HPLC)

HPLC analysis was conducted with a Shimadzu LC-3A system equipped with a UV detector (SPD-6A). Analytical conditions for the parent compound and CHP were as follows: column, Nucleosil C₁₈ (4.0 mm i.d. × 250 mm, GL Science); mobile phase, acetonitrile-water (6/4, v/v); UV wave length, 254 nm, and for CHPG and CHPMG: column, Radial Pak C₁₈ (8 mm i.d. × 100 mm); mobile phase, acetonitrile-water (6/4, v/v); UV wave length, 254 nm.

11. Spectroscopy

Electron impact mass spectrum (EI-MS) was recorded on a Shimadzu QP-1000 mass spectrometer. ^1H NMR was recorded on a EM-390 Varian spectrometer (90 MHz). GC was conducted with a Shimadzu GC-7A system, and analytical conditions for metabolites were described in the previous report.⁴⁾

RESULTS AND DISCUSSION

1. Translocation of ^{14}C in Plants by Foliar Treatment

As shown in Fig. 2, when ^{14}C -pyraclofos was applied on the leaf surface of cabbage plants at the rate of 2 $\mu\text{g}/\text{cm}^2$ (52 $\mu\text{g}/\text{leaf}$), most of ^{14}C was found in the treated leaf, particularly, in the treated site, and a small amount of ^{14}C

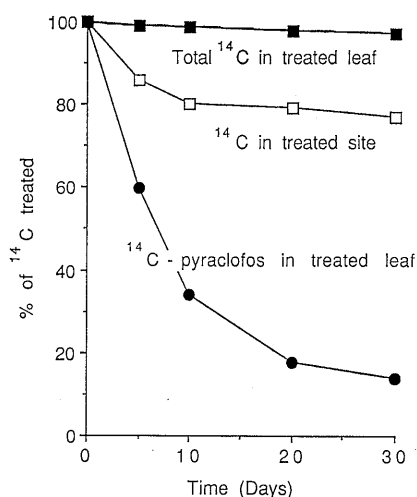


Fig. 2 Residual behavior of pyraclofos in the treated leaves of cabbage plants 10, 20 and 30 days after foliar application with ^{14}C -pyraclofos at the rate of $2\ \mu\text{g}/\text{cm}^2$ ($52\ \mu\text{g}/\text{leaf}$).

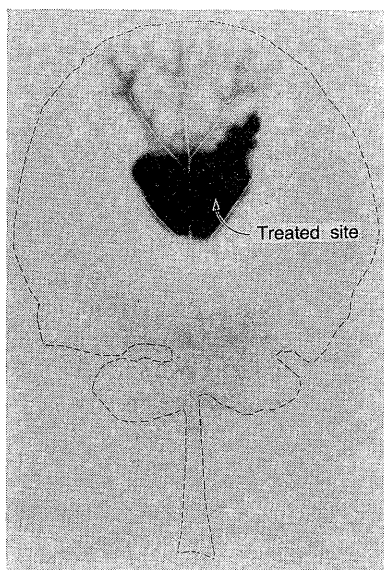


Fig. 3 Autoradiogram of cabbage leaf harvested 30 days after foliar application with ^{14}C -pyraclofos at the rate of $2\ \mu\text{g}/\text{cm}^2$ ($52\ \mu\text{g}/\text{leaf}$).

was translocated to the nontreated sites of the plants. The total ^{14}C recovered from the leaves also gradually decreased with time, and showed 97.2% on day 30. Pyraclofos in the treated leaves decreased with a half-life of

Table 3 Distribution of ^{14}C in cabbage plants 30 days after foliar treatment with ^{14}C -pyraclofos.

Portion	Wet weight (g)	Concentration ^{a)} ($\mu\text{g}/\text{g}$)	% of ^{14}C treated
Treated leaf (treated site)	46	1.10 ± 0.03	97.2
(nontreated site)			(77.0) ^{b)}
Nontreated leaf	85	<0.01	(20.2)
Edible	208	<0.01	0.7
Stem	29	0.01 ± 0.002	0.1
Root	24	<0.01	0.3
Soil	1110	<0.01	<0.1
Total			98.6

^{a)} The values are indicated the mean and S.D. of three plants as pyraclofos equivalent $\mu\text{g}/\text{g}$ wet tissue.

^{b)} The values in the parentheses are expressed details of ^{14}C in the treated leaf.

approximately one week under laboratory conditions. A typical autoradiogram of the treated leaf 30 days after foliar treatment is shown in Fig. 3. Most of ^{14}C treated in the plant was detected in the treated site, and about 20% of ^{14}C treated were translocated to the nontreated site of the leaf, and a small amount of ^{14}C was in the other portions of the plants such as edible, stem and root, and soils (Table 3). Thus, it was likely that pyraclofos and its ^{14}C -metabolites were hardly translocated from the treated site to the other nontreated portions of the plants.

2. Metabolites in Leaf

Parent compound was detected in the treated site of the leaf, but not in the nontreated portions of the plants. Amount of the sugar conjugates increased with time, and CHPG and CHPMG were identified as a major metabolite of the plants (Table 4). CHPG was subjected to α -, β -glucosidase or HCl hydrolysis. There seems to be no difference in hydrolysis behavior by both β -glucosidase and HCl, and CHPG gave the same aglycone in the reaction mixture. The released aglycone was identified as CHP by TLC, HPLC and EI-MS. On the other hand, no hydrolyzate of CHPG was given by α -glucosidase. These findings suggested that CHPG was formed as β -glucoside. Four unknown metabolites (I-IV)

Table 4 Amounts of pyraclofos and its metabolites in cabbage plants 5, 10, 20 and 30 days after foliar treatment with ^{14}C -pyraclofos.

Fraction	Metabolite	<i>Rf</i> value ^{b)}	% of ¹⁴ C treated ^{a)}			
			Days after treatment			
			5	10	20	30
In ethyl acetate						
	Pyraclofos	0.88	59.7	34.1	17.7	13.7 (13.7) ^{c)}
	CHP	0.88	—	—	—	1.1 (1.1)
	Unknown I	0.73	—	—	—	— (1.0)
	CHPG	0.69	10.6	7.2	10.9	11.9 (57.5)
	Unknown II	0.49	—	2.5	2.1	1.3 (1.5)
	CHPMG	0.16	25.0	46.6	49.8	51.3 (7.3)
	Unknown III	0.04	—	2.0	5.9	5.7 (1.5)
	Unknown IV	0.00	—	1.2	2.6	1.7 (3.1)
	[Subtotal]		[95.3]	[93.6]	[89.0]	[86.7] [86.7]
In water			1.3	2.1	4.2	4.9 (4.9)
In nonextractable			2.4	3.1	4.7	5.6 (5.6)
Total			99.0	98.8	97.9	97.2 (97.2)

^{a)} Data are expressed as percent of pyraclofos equivalent.

^{b)} Solvent system: ethyl acetate-methanol (2: 1, v/v).

^{c)} Values in parentheses indicated percent of metabolites when the extract in ethyl acetate was allowed to stand at room temperature for 10 days after extraction.

—, not determined.

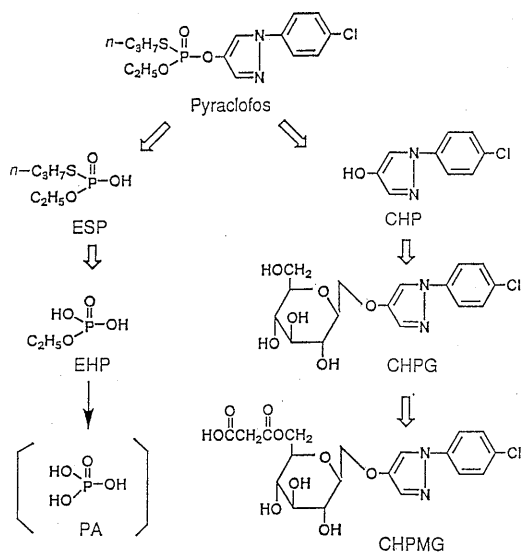


Fig. 4 Proposed metabolic pathways for pyraclofos in cabbage plants.

in ethyl acetate extractable fraction failed to characterize, because each metabolite was a small extent (Table 4). The proposed metab-

olic pathways of pyraclofos in cabbage plants are shown in Fig. 4. CHP and ESP formed were mainly the result of hydrolysis of P-O-aryl bond of pyraclofos in the leaves. CHP yielded predominantly seemed to be conjugated with sugars, because CHP was hardly detected in the leaves for a period of 20 days after foliar application, and a very small amount of it was detected on day 30.

Many studies have been made on the sugar conjugation of xenobiotic in plants.⁵⁻¹³⁾ Schmitt *et al.*⁵⁾ reported that phenolic hydroxyl group was easily conjugated with glucose and/or malonylglucose in wheat and soybean plants. Furthermore, Mikami *et al.*⁶⁾ reported that malonylglucoside conjugate as pyrethroid metabolite was found in several kinds of plants. Relatively larger amount of malonylglucoside conjugate was found in cabbage when compared with other plants examined. When the ethyl acetate extractable fraction prepared from the leaf 30 days after application was allowed to stand at room temperature for 10 days, CHPMG in ethyl acetate was rapidly

Table 5 Distribution of ^{14}C in cabbage plants 30 days after soil treatment with ^{14}C -pyraclofos.

Portion	Wet weight (g)	Concentration ^{a)} ($\mu\text{g/g}$)	% of ^{14}C treated
Edible	128	<0.01	0.1
Leaf	182	<0.01	0.1
Stem	36	0.01 ± 0.01	<0.1
Root	27	0.48 ± 0.06	1.3
Soil ^{b)}			
(treated layer)	100	8.40 ± 0.38	84.0
(nontreated layer)	1120	0.11 ± 0.13	12.3
Total			97.8

^{a)} The values are indicated the mean and S.D. of three plants as pyraclofos equivalent $\mu\text{g/g}$ wet tissue.

^{b)} Soils were treated with ^{14}C -pyraclofos at concentration of 10 ppm.

decreased with time, that is, decreasing of CHPMG was accompanied by increasing CHPG as shown in Table 4. The malonylated conjugate, therefore, seemed to be relatively stable in leaves, but not stable in organic solvent. It appears likewise well possible that the most of present CHPG is generated as an artifact from CHPMG. Matern *et al.*⁷⁾ and Köster *et al.*⁸⁾ also reported that malonic ester bonds may easily be degraded during isolation process and/or in some organic solvents, so that many reported β -D-glucopyranoside conjugates could originally have been malonylated.

Based on the results of this study, it was found that the malonylglucopyranoside conjugation was more predominant in cabbage plants, as judged from larger amount of CHPMG than that of CHPG. It seems likely that the dearylation, followed by malonylglucopyranoside conjugation, is the major metabolic pathways of pyraclofos. In plants conjugation may determine the nature of the terminal residues since elimination is not a significant factor. Conjugation probably plays an important role in pyraclofos detoxication in plants.

Although ^{14}C in the water fraction prepared by foliar application of ^{14}C -pyraclofos was not put into further analysis for the identification of ^{14}C -metabolites due to a very small extent, some dearylated phosphorus-containing me-

tabolites were characterized using the water fraction obtained from the leaf treated with nonlabeled pyraclofos. ESP and EHP were identified by GC and EI-MS as the major metabolites, and a small amount of phosphoric acid (PA) was determined. The concentrations of ESP, EHP and PA in the treated leaf were 0.05, 0.01 and 0.002 ppm, respectively. Furthermore, efforts were made to examine the metabolites of dealkylation such as CHP-EHP and CHP-SHP by HPLC, TLC and/or GC-MS analyses using the authentic standards, because EHP was found in the leaves. However, no such metabolite was detected in the extracts of the plants analyses. Therefore EHP was given with time by the cleavage of S-P bond of ESP in the leaves, followed by PA. PA was likely to incorporate as a constituent of the plant tissues as the terminal metabolite.

3. Translocation of ^{14}C into Plants by Soil Treatment

A small amount of ^{14}C was detected in the plants 30 days after soil treatment with pyraclofos. Most of ^{14}C treated were found in the soils, and 84.0 and 12.3% were in the treated soil and nontreated soil layers, respectively, and very small amount of ^{14}C was translocated from the roots to the stems, leaves and/or edible portions of cabbage plants. ^{14}C detected in the root appeared to be due in part to direct contamination of the treated soils. ^{14}C found in stems and roots was less than 0.1 and 1.3%, respectively, and 0.1% in both the edible portion and leaves (Table 5). The parent compound was not detected in the plants except the roots.

Those findings suggested that pyraclofos was tightly adsorbed on to the treated soil particles, and hardly eluted by ground water and rain. Therefore, the soil residues seem to have little effects on rotational crops in the field.

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要 約

殺虫剤ピラクロホスのキャベツにおける代謝

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ピラクロホス (ボルテージ) のベンゼン環 ^{14}C -標識体を用いて, キャベツにおける吸収, 移行性および代謝分解性を実験室条件下で検討した. キャベツの葉面上に $2\text{ }\mu\text{g}/\text{cm}^2$ の割合で ^{14}C -ピラクロホスを塗布処理すると, ピラクロホスは半減期約1週間の速度で減少した. 葉面塗布処理30日後の ^{14}C -放射活性 (^{14}C) の大部分は処理部位から検出され, 非処理部へ移行した量は少なかった. 葉部中におけるピラクロホスの主要代謝経路は P-O-aryl 結合の開裂による 1-(4-chlorophenyl)-4-hydroxypyrazole (CHP) の生成, および CHP とグルコースあるいはマロニルグルコースとの抱合体の生成であった. 親化合物は葉部の処理部位にわずかに認められたが, 非処理部からは検出されなかった. ^{14}C -ピラクロホスを濃度 10ppm の割合で混和処理した土壌を用いてキャベツを30日間栽培したとき, 処理した ^{14}C の大部分は処理土壌中に認められた. 植物体へ移行した ^{14}C はわずかであり, そのほとんどは根部中に認められた. 一方, 地上部中へ移行した ^{14}C はごくわずかであり, 親化合物は検出されなかった.