

## Original Article

## Metabolism of Cycloprothrin in Rice Plants

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Absorption, translocation and metabolism of an insecticide, cycloprothrin [(*RS*)- $\alpha$ -cyano-3-phenoxybenzyl (*RS*)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropane carboxylate], were examined in rice plants under laboratory conditions. When  $^{14}\text{C}$ -cycloprothrin was applied to simulated paddy water, the radioactivity in the rice plants in the 3.5-leaf stage increased with time to reach a maximum concentration within 7 days, and this level was retained to the mature stage. At the mature stage, the rice shoots and the hulled grains contained 0.161 and 0.157 ppm  $^{14}\text{C}$ -cycloprothrin equivalents, respectively. A small amount of unchanged cycloprothrin was found in the shoots but not in the grains.  $^{14}\text{C}$ -Cycloprothrin topically applied on the leaf surface was not readily translocated to other untreated parts, and 98% of the applied radioactivity was recovered from the treated parts even after 28 days. When an emulsion of  $^{14}\text{C}$ -cycloprothrin was applied to rice plants in the heading stage, it adhered to the foliage at 9.33 ppm and the level hardly lowered during the progression to the mature stage. Unchanged cycloprothrin remained in the shoots and hulled grains at 9.452 and <0.001 ppm, respectively. The relative amount of optical isomers of cycloprothrin did not change in the mature shoots after foliar application. Cycloprothrin was metabolized *via* ester cleavage, hydroxylation at the 4-ethoxy position, decarboxylation, hydrolysis of the CN group to  $\text{CONH}_2$  and  $\text{COOH}$  groups and conjugation.

## INTRODUCTION

Cycloprothrin [Cyclosaal® (*RS*)- $\alpha$ -cyano-3-phenoxybenzyl (*RS*)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropane carboxylate] is a new type of insecticide with a combined DDT-pyrethroid structure, which is used for control of insect pests on paddy rice plants, vegetables and fruit trees. In connection with the practical use of this insecticide, it is important to evaluate its metabolic fate in mammals and in the environment. The metabolism study on cycloprothrin in rats has already been done,<sup>1)</sup> and this time we studied the absorption, translocation and metabolic fate of cycloprothrin in rice plants. This paper reports the results.

## MATERIALS AND METHODS

## 1. Chemicals

$^{14}\text{C}$ -Cycloprothrin labeled at the C-3 position of the 2,2-dichlorocyclopropane ring in the acid moiety with a specific radioactivity of 455 MBq/mmol and a radiochemical purity of more than 99% was used in the experiments.<sup>1)</sup> Authentic compounds to identify cycloprothrin metabolites were synthesized in our laboratory. The *R<sub>f</sub>* values on silica-gel 60F<sub>254</sub> chromatoplates (20×20 cm, 0.25 mm thick, Merck, Germany) with several solvent systems and the names or abbreviations of the chemicals are shown in Table 1.

## 2. Radioassay

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

Table 1 Cycloprothrin and its metabolites in rice plants.

Designation or Abbreviation	Chemical name	<i>R<sub>f</sub></i> values in solvent systems <sup>a)</sup>			
		A	B	C	D
Cycloprothrin	( <i>RS</i> )- $\alpha$ -cyano-3-phenoxybenzyl ( <i>RS</i> )-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate	0.45	0.89	0.76	0.53
HO-Cycloprothrin	( <i>RS</i> )- $\alpha$ -cyano-3-phenoxybenzyl ( <i>RS</i> )-2,2-dichloro-1-(4-hydroxyphenyl)cyclopropanecarboxylate	0.21	0.72	0.50	0.20
CONH <sub>2</sub> -Cycloprothrin	( <i>RS</i> )- $\alpha$ -aminocarbonyl-3-phenoxybenzyl ( <i>RS</i> )-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate	0.16	0.49	0.37	0.07
COOH-Cycloprothrin	( <i>RS</i> )- $\alpha$ -hydroxycarbonyl-3-phenoxybenzyl 2,2-dichloro-1-( <i>RS</i> )-(4-ethoxyphenyl)cyclopropanecarboxylate	0.09	0.40	0.38	0.11
HO-phenoxybenzyl Cycloprothrin	( <i>RS</i> )- $\alpha$ -cyano-3-(4-hydroxyphenoxy)benzyl ( <i>RS</i> )-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate	0.21	0.71	0.49	0.17
HO-phenyl-Cycloprothrin	( <i>RS</i> )- $\alpha$ -cyano-3-hydroxybenzyl ( <i>RS</i> )-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate	0.23	0.71	0.54	0.22
De-CO <sub>2</sub> -Cycloprothrin	( <i>RS</i> )-1-[( <i>RS</i> )- $\alpha$ -cyano-3-phenoxybenzyl] 2,2-dichloro-1-(4-ethoxyphenyl)cyclopropane	0.57 0.47	0.89	0.82 0.77	0.62 0.53
C <sub>2</sub> H <sub>5</sub> O-Acid	( <i>RS</i> )-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylic acid	0.24	0.52	0.52	0.29
HO-Acid	( <i>RS</i> )-2,2-dichloro-1-(4-hydroxyphenyl)cyclopropanecarboxylic acid	0.10	0.37	0.38	0.12
HOC <sub>2</sub> H <sub>4</sub> O-Acid	( <i>RS</i> )-2,2-dichloro-1-[4-(2-hydroxyethoxy)phenyl]-cyclopropanecarboxylic acid	0.04	0.17	0.19	0.05

<sup>a)</sup> Solvent systems: A, hexane: acetone (3: 1); B, hexane: benzene: ethyl acetate: 2-propanol: acetic acid (100: 60: 40: 10: 1); C, hexane: isopropyl ether: acetone: acetic acid (40: 40: 20: 1); D, hexane: ethyl ether: acetic acid (40: 20: 1).

carried out according to the methods reported previously.<sup>1)</sup>

### 3. Rice Plants

Rice plants (*Oryza sativa* L.) of the Japanese variety "Nihon-bare" were cultivated in Wagner pots (1/5000 a) filled with Ageo soil (clay loam) in a greenhouse in our laboratory. Seedlings in the 3.5-leaf and heading stages were used in the experiments.

## 4. Treatment with <sup>14</sup>C-Cycloprothrin

### 4.1 Submerged application

Rice plants in the 3.5-leaf stage in Wagner pots (1/5000 a) were selected for the experiment. Granules containing 0.4% <sup>14</sup>C-cycloprothrin were prepared and applied to paddy water 4 cm deep at a rate of 200 mg (925 kBq) per pot. The plants were harvested at intervals and divided into roots and shoots. The mature plants were divided into hulled grains,

hulls, roots and shoots.

### 4.2 Topical application

An aliquot of 1000 ppm water emulsion of <sup>14</sup>C-cycloprothrin was applied to the center of the third leaf at the 3.5-leaf stage with a microsyringe at a rate of 1.5  $\mu$ g/cm<sup>2</sup> (1.48 kBq/cm<sup>2</sup>). At intervals, plants were harvested and divided into the applied part and others.

### 4.3 Foliar application

Ten milliliters of 160 ppm water emulsion of <sup>14</sup>C-cycloprothrin was sprayed onto rice plants in the heading stage in Wagner pots (1/5000 a). This dose was calculated from the practical application rate of 80 g of active ingredient/ha in the field. The plants were harvested at intervals.

## 5. Treatment of Soils

Aichi clay loam and Chiba sandy clay loam soils were used. Each soil equivalent to 39.2

g on a dry weight basis was placed in a 200 ml Erlenmeyer flask and water was added up to 2 cm from the bottom to simulate a flooded condition. The soils were incubated at 30°C in the dark for a week. After the preincubation, 39.2  $\mu$ g of  $^{14}$ C-cycloprothrin (37 kBq) in 0.1 ml of acetonitrile was added to each soil. The dose corresponded to 1 ppm cycloprothrin on a dry soil basis. The treated soils were incubated at 30°C in the dark. The evolved  $^{14}$ CO<sub>2</sub> was collected in 10% NaOH solution (50 ml) after purging the flask with CO<sub>2</sub>-free air. At intervals, a sample of each treated soil was extracted with acetonitrile. The extracts were concentrated *in vacuo* and then partitioned into ethyl acetate.

#### 6. Fractionation of the Radioactivity

Plant samples were cut into small pieces and homogenized in acetonitrile with a Polytron® (Kinematica, Switzerland). The homogenate was extracted with acetonitrile and acetonitrile-water (2:1). The extracts were combined, concentrated *in vacuo* and partitioned between ethyl acetate and water (pH 3). The amount of radioactivity in the ethyl acetate layer, the aqueous layer and the residues was measured. The ethyl acetate layer was concentrated and separated by TLC. A part of the aqueous layer was lyophilized to dryness. The residues and the origin of the TLC plates (silica-gel 60F<sub>254</sub>, 0.25 mm thick, Merck) were extracted with methanol. The methanol extract was treated with  $\beta$ -glucosidase (Sigma) and cellulase (Sigma) in 0.1 M sodium acetate buffer (pH 4.8).<sup>2)</sup> After incubation at 37°C for 24 hr, the reaction mixture was adjusted to pH 3 with HCl and extracted with ethyl acetate. Radioactive metabolites in the extracts were detected and identified by co-chromatography with authentic samples on TLC, and the radioactivity was measured with a liquid scintillation counter.

#### 7. Determination of Optical Isomers of Cycloprothrin

The ethyl acetate extract from the shoots was mixed with unlabeled cycloprothrin as a carrier and poured onto a silica-gel column for cleanup. A mixture of radioactive and non-radioactive cycloprothrin was eluted with

hexane-ethyl acetate (9:1) from the column. The effluent was treated with *l*-menthol in HCl by heating and converted into  $\alpha$ -1-menthylloxycarbonyl-3-phenoxybenzyl (*RS*)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropane carboxylate according to the method of Horiba *et al.*<sup>3)</sup> The obtained diastereoisomeric mixture was analyzed by high-performance liquid chromatography on an instrument (Shimadzu LC-6A) equipped with an ultraviolet detector operating at 254 nm and a radio analyzer (Aloka RLC-551) (A. Kurozumi: unpublished data). The operating conditions: column, RADIAL-PAC(A) Silica pressurized with Z-type Pressurized Module (RCSS, Waters Co.); mobile phase, hexane-isopropyl ether-ethyl acetate (100:3:1, v/v); flow rate, 1.5 ml/min.

### RESULTS

#### 1. Absorption and Translocation of $^{14}$ C-Cycloprothrin in Rice Plants

When  $^{14}$ C-cycloprothrin was topically applied to the third leaves of rice plants in the 3.5-leaf stage, the recovery of total radio-carbon decreased only slightly with time, as shown in Table 2. After 28 days, 98.7% of the applied radioactivity was recovered from the plants. Most of the recovered radioactivity was present in the treated leaves, only 0.08% of the applied radioactivity in the other parts.

Table 2 Translocation of radioactivity in rice plants after topical application on the leaf surface.

Plant parts			% of applied radioactivity		
			Days after application		
			7	14	28
Treated leaf (Third leaf)	Applied	part	102	104	98.4
	Upper	part	0.02	0.05	0.15
	Lower	part	0.02	0.03	0.09
Untreated leaves	Fifth leaf			0.01	0.02
	Fourth leaf		<0.01	0.01	0.01
	Second leaf		<0.01	<0.01	0.01
Sheath			0.01	0.01	0.04
Total			102	104	98.7

Table 3 Absorption and translocation of radioactivity in rice plants after submerged application.

Plant parts	Fractions	$\mu\text{g } ^{14}\text{C-cycloprothrin Eq/g (undried weight)}$				
		Days after application				
		7	14	28	56	132
Shoot	Cycloprothrin	0.102	0.057	0.035	0.008	0.049
	Others	0.007	0.008	0.028	0.024	0.028
	Unextractable residues	0.004	0.007	0.023	0.062	0.084
	Total	0.113	0.072	0.086	0.092	0.161
Root	Cycloprothrin	0.131	0.291	0.066	0.076	0.274
	Others	0.003	0.047	0.026	0.052	0.193
	Unextractable residues	0.003	0.063	0.042	0.089	0.421
	Total	0.137	0.401	0.134	0.217	0.888

Table 4 Amount of residual radioactivity in whole rice plants after foliar application at the heading stage.

Fractions	Days after application			
	0	7	14	51
	$\mu\text{g/g}^{\text{a)}} (\mu\text{g/p})^{\text{b)}})$	$\mu\text{g/g} (\mu\text{g/p})$	$\mu\text{g/g} (\mu\text{g/p})$	$\mu\text{g/g} (\mu\text{g/p})$
Cycloprothrin	9.33 (377 )	7.22 (333 )	5.82 (299 )	7.09 (296 )
Others	0.14 ( 5.65)	0.30 ( 13.8 )	0.36 ( 18.5 )	0.83 ( 34.6)
Unextractable residues	0.02 ( 0.81)	0.03 ( 1.38)	0.04 ( 2.05)	0.30 ( 12.5)
Total	9.49 (383 )	7.55 (348 )	6.22 (320 )	8.22 (343 )

a)  $\mu\text{g } ^{14}\text{C-cycloprothrin Eq/g (undried weight)}$ .b)  $\mu\text{g } ^{14}\text{C-cycloprothrin Eq/whole plant}$ .

By submerged application, the radioactivity was absorbed into the stems and the roots, and translocated to the upper parts of the plants. Table 3 shows the absorption and translocation patterns of the radioactivity derived from  $^{14}\text{C-cycloprothrin}$  applied to the paddy water. Radioactivity concentration in the shoots reached a plateau within 7 days after treatment and tended to decrease slightly thereafter. Radioactivity levels in the shoots were 0.113 and 0.092 ppm cycloprothrin equivalent 7 and 56 days after treatment, respectively. At the mature stage, 0.157, 0.417 and 0.161 ppm cycloprothrin equivalents of radioactivity were present in the hulled grains, hull and the shoots, respectively. The ratios of  $^{14}\text{C-cycloprothrin}$  to total radioactivity in the shoots

after 7 and 56 days were 90 and 9%, respectively. The acetonitrile-water extractable metabolites reached a maximum 28 days after treatment and remained almost constant thereafter. The bound radioactivity, however, increased at the mature stage. Radio-carbon concentration in roots was relatively high (0.888 ppm) at the mature stage. The radioactivity ratio in the roots was 31% for  $^{14}\text{C-cycloprothrin}$  and 47% for unextractable residues.

## 2. Persistence of $^{14}\text{C-Cycloprothrin}$ in Rice Plants

Changes in the levels of  $^{14}\text{C-cycloprothrin}$  and its metabolites residues in rice plants after foliar application at the heading stage are

Table 5 Distribution of radioactivity in mature rice plant after submerged or foliar application.

Plant parts	Fraction	Submerged application		Foliar application	
		$\mu\text{g/g}^{\text{a)}$	% $^{\text{b)}$	$\mu\text{g/g}$	%
Hulled grain	Cycloprothrin	<0.001		<0.001	
	Others	0.004		0.005	
	Unextractable residues	0.152		0.026	
	Total	0.157	6.30	0.031	0.07
Hull	Cycloprothrin			3.773	
	Others			0.647	
	Unextractable residues			0.397	
	Total	0.417	2.19	4.817	5.11
Shoot	Cycloprothrin	0.049		9.452	
	Others	0.028		1.078	
	Unextractable residues	0.084		0.359	
	Total	0.161	30.0	10.89	94.8
Root	Cycloprothrin	0.274			
	Others	0.193			
	Unextractable residues	0.421			
	Total	0.888	61.0		

<sup>a)</sup> Values are expressed by  $\mu\text{g } ^{14}\text{C-cycloprothrin Eq/g}$  (undried weight).

<sup>b)</sup> Values are expressed as % of radioactivity of each part with respect to total radioactivity in the plant.

Table 6 Proportions of the four optical isomers in applied and residual cycloprothrin.

	Isomer ratios (%)			
	A	B	C	D
Applied cycloprothrin	25.8	22.5	27.1	24.6
Residual cycloprothrin	27.7	25.1	25.1	22.1

shown in Table 4. When a 160 ppm water emulsion of  $^{14}\text{C-cycloprothrin}$  was sprayed on rice plants,  $^{14}\text{C-cycloprothrin}$  remained at 9.33 ppm in the whole plants. During the following 2 weeks, the residual concentration decreased to 79% of the initial levels, but did not decrease further towards the mature stage. Nearly 95% of the radioactivity in the plants in the mature stage was located in the shoots as shown in Table 5. The remaining radioactivity was 5.11% in the hulls and 0.07% in hulled grains.

### 3. Analysis of Cycloprothrin Stereoisomers in Rice Plants

Optically active derivatives of the four isomers were completely separated by HPLC within 20 minutes and eluted in the order shown in Fig. 1. Table 6 shows the proportions of the four optical isomers in the applied and residual cycloprothrin in the shoots 51 days after foliar application. The relative amounts of cycloprothrin isomers A, B, C, and D prior to the treatment were 25.8%, 22.5%, 27.1% and 24.6%, respectively. Fifty-one days after foliar application, the amount of residual  $^{14}\text{C-cycloprothrin}$  in the shoots decreased to 78%, but there was no change in the abundance ratio.

### 4. Metabolism of $^{14}\text{C-Cycloprothrin}$ in Rice Plants

Plant metabolites at the mature stage were analyzed. The metabolites identified by two-dimensional co-TLC and their abundance in the

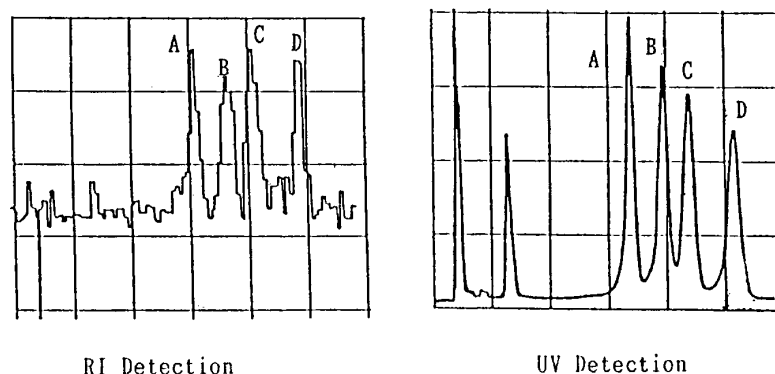


Fig. 1 HPLC chromatogram of *l*-menthyl ester derivative of racemic cycloprothrin.

A: (*R*)- $\alpha$ -cyano-3-phenoxybenzyl (*S*)-2,2-dichloro-1-(4-ethoxyphenyl) cyclopropanecarboxylate.  
 B: (*R*)- $\alpha$ -cyano-3-phenoxybenzyl (*R*)-2,2-dichloro-1-(4-ethoxyphenyl) cyclopropanecarboxylate.  
 C: (*S*)- $\alpha$ -cyano-3-phenoxybenzyl (*R*)-2,2-dichloro-1-(4-ethoxyphenyl) cyclopropanecarboxylate.  
 D: (*S*)- $\alpha$ -cyano-3-phenoxybenzyl (*S*)-2,2-dichloro-1-(4-ethoxyphenyl) cyclopropanecarboxylate.  
 HPLC conditions: column, RADIACL-PAC(A) Silica; mobile phase, hexane-isopropyl ether-ethyl acetate (100: 3: 1, v/v) at a flow rate of 1.5 ml/min; ultraviolet detection wavelength, 254 nm.

Table 7 Cycloprothrin and its metabolites in rice plants after submerged or foliar application.

Cycloprothrin and metabolites		$\mu\text{g } ^{14}\text{C-cycloprothrin Eq/g (undried weight)}$			
		28 days after Submerged application		51 days after Foliar application	
		Shoot <sup>a)</sup>	Grain <sup>a)</sup>	Hull <sup>a)</sup>	Shoot
Cycloprothrin		0.035		3.773	9.452
HO-Cycloprothrin		0.001		0.040	0.118
CONH <sub>2</sub> -Cycloprothrin					0.032
COOH-Cycloprothrin					0.014
De-CO <sub>2</sub> Cycloprothrin					0.078
C <sub>2</sub> H <sub>5</sub> O-Acid		0.008		0.220	0.286
HO-Acid	Free	0.003			0.082
	Conj.				0.197
HOC <sub>2</sub> H <sub>4</sub> O-Acid	Free				0.008
	Conj.				0.006
Others		0.016	0.005	0.387	0.267
Unextractable residues		0.023	0.026	0.397	0.359

<sup>a)</sup> Untreated enzyme.

extracts are shown in Table 7. On the 51st day after rice plants were treated with <sup>14</sup>C-cycloprothrin on the leaves, seven metabolites, (*RS*)- $\alpha$ -cyano-3-phenoxybenzyl (*RS*)-2,2-dichloro-1-(4-hydroxyphenyl)cyclopropanecarboxylate (HO-cycloprothrin), (*RS*)- $\alpha$ -aminocarbonyl-3-phenoxybenzyl (*RS*)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate (CONH<sub>2</sub>-cycloprothrin), (*RS*)- $\alpha$ -hydroxycarbonyl-3-phenoxybenzyl (*RS*)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate

(COOH-cycloprothrin), (*RS*)-1-[(*RS*)- $\alpha$ -cyano-3-phenoxybenzyl] 2,2-dichloro-1-(4-ethoxyphenyl)cyclopropane (De-CO<sub>2</sub>-cycloprothrin), (*RS*)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylic acid (C<sub>2</sub>H<sub>5</sub>O-acid), (*RS*)-2,2-dichloro-1-(4-hydroxyphenyl)cyclopropanecarboxylic acid (HO-acid) and (*RS*)-2,2-dichloro-1-[4-(2-hydroxyethoxy)phenyl]cyclopropanecarboxylic acid (HOC<sub>2</sub>H<sub>4</sub>O-acid), were found in the shoots, but only two, HO-cycloprothrin and C<sub>2</sub>H<sub>5</sub>O-acid, in the hulls. These metabolites

could not be confirmed in the hulled grains owing to their small amount. In the shoots, 86.7% of the radioactivity was present as parent compound, 7.5% being identified metabolites, 2.5% extractable unknown metabolites and 3.3% unextractable residues. The major metabolites in the shoots were  $C_2H_5O$ -acid and conjugated HO-acid.

On the 28th day after the submerged application of  $^{14}C$ -cycloprothrin to rice plants, the shoots contained radioactivity equivalent to 0.086 ppm cycloprothrin.  $^{14}C$ -Cycloprothrin accounted for 40.7% of the radioactivity in the shoots. The other radioactivity in the shoots was 14.0% in the ethyl acetate extract fraction, 18.6% in the water-soluble fraction and 26.7% in the unextractable residues. The ethyl acetate extract fraction contained HO-cycloprothrin,  $C_2H_5O$ -acid and HO-acid.

#### 5. Degradation of $^{14}C$ -Cycloprothrin in Flooded Soils

The degradation of  $^{14}C$ -cycloprothrin in flooded soils is shown in Table 8.  $^{14}C$ -Cycloprothrin degraded in flooded soil with an initial half-life of about 61 days in Aichi soil and about 33 days in Chiba soil. In contrast, the amounts of  $^{14}CO_2$  evolved and bound radioactivity increased with time. After 24 weeks,  $^{14}CO_2$  evolved from the Aichi and Chiba soils amounted to 25.0% and 43.7% of the applied

radioactivity, respectively. The bound radioactivity in the Chiba soil reached its maximum amount after 16 weeks. At least seven degradation products were identified in the flooded soils. There was no difference in degradation pattern between the Aichi and Chiba soils. The major degradation product in the soils was  $C_2H_5O$ -acid, which amounted to 19.9% of the applied radioactivity after 16 weeks in the Aichi soil and 29.8% after 4 weeks in the Chiba soil.  $C_2H_5O$ -Acid subsequently degraded further.

#### DISCUSSION

When  $^{14}C$ -cycloprothrin was applied into paddy water, radioactivity concentration in rice shoots reached a plateau within 7 days after treatment and tended to decrease slightly thereafter. The ratio of  $^{14}C$ -cycloprothrin to total radioactivity in the shoots decreased after 7 days. The bound radioactivity increased at the mature stage, however. In soils under flooded conditions,  $^{14}C$ -cycloprothrin was relatively stable and more than 50% of the parent compound still remained on the 28th day after treatment. This suggests that most of the radioactivity detected in the shoots was due to the movement of  $^{14}C$ -cycloprothrin on the shoot surface by capillary action and the absorption of radioactivity still dissolved in the paddy water. Furthermore,

Table 8 Degradation of cycloprothrin in flooded soils.

	% of the applied radioactivity					
	Aichi soil			Chiba soil		
	Weeks after application			Weeks after application		
	4	16	24	4	16	24
Cycloprothrin	67.3	36.4	24.2	51.7	20.6	13.8
CONH <sub>2</sub> -Cycloprothrin	1.6	2.7	2.8	0.8	0.8	0.7
COOH-Cycloprothrin	0.1	0.8	0.4	0.1	0.1	0.1
$C_2H_5O$ -Acid	14.0	19.9	8.1	29.8	4.0	0.6
HO-Acid	0.7		1.8	0.6		
Mixtures	1.0	0.8	0.5	0.7	0.7	0.5
Others	3.5	7.0	5.8	3.0	4.9	1.3
Unextractable residues	5.5	14.2	27.7	4.0	28.2	28.3
CO <sub>2</sub>	2.2	18.0	25.0	5.0	27.2	43.7
Total	95.9	99.8	96.3	95.7	86.5	89.0

Mixture: HO-cycloprothrin + HO-phenoxybenzylcycloprothrin + HO-phenylcycloprothrin.

availability to rice plants of  $^{14}\text{C}$ -cycloprothrin adsorbed on soil particles was very poor, and the transport of  $^{14}\text{C}$ -cycloprothrin and/or its metabolites from the roots to the shoots and the grains was limited. As a result, radioactivity concentration in the grains was low.

After foliar treatment, disappearance of  $^{14}\text{C}$ -cycloprothrin from the rice plants was very slow. Seventy-eight percent of the administered  $^{14}\text{C}$ -cycloprothrin was recovered unchanged from the mature whole rice plants (51 days after treatment). On topical application of  $^{14}\text{C}$ -cycloprothrin to the leaf surface, the translocation of radioactivity to the untreated parts was very slight. Under greenhouse conditions, phenothrin disappeared from

rice plants with a half-life of less than one day.<sup>4)</sup> Ethofenprox decreased to 10% of the applied radioactivity in about 20 days on rice leaves.<sup>5)</sup> Cycloprothrin appears to degrade in rice plants more slowly than other pyrethroids with a 3-phenoxybenzyl moiety. However, under field conditions, disappearance of cycloprothrin from rice plants may be accelerated by such physicochemical factors as wind, sunlight and rainfall.

The metabolic behavior of cycloprothrin in the rice plants after foliar or submerged application is summarized in Fig. 2. Seven different metabolites were identified. Main metabolites were  $\text{C}_2\text{H}_5\text{O}$ -acid,  $\text{HO}$ -acid and  $\text{HO}$ -cycloprothrin. They were also main me-

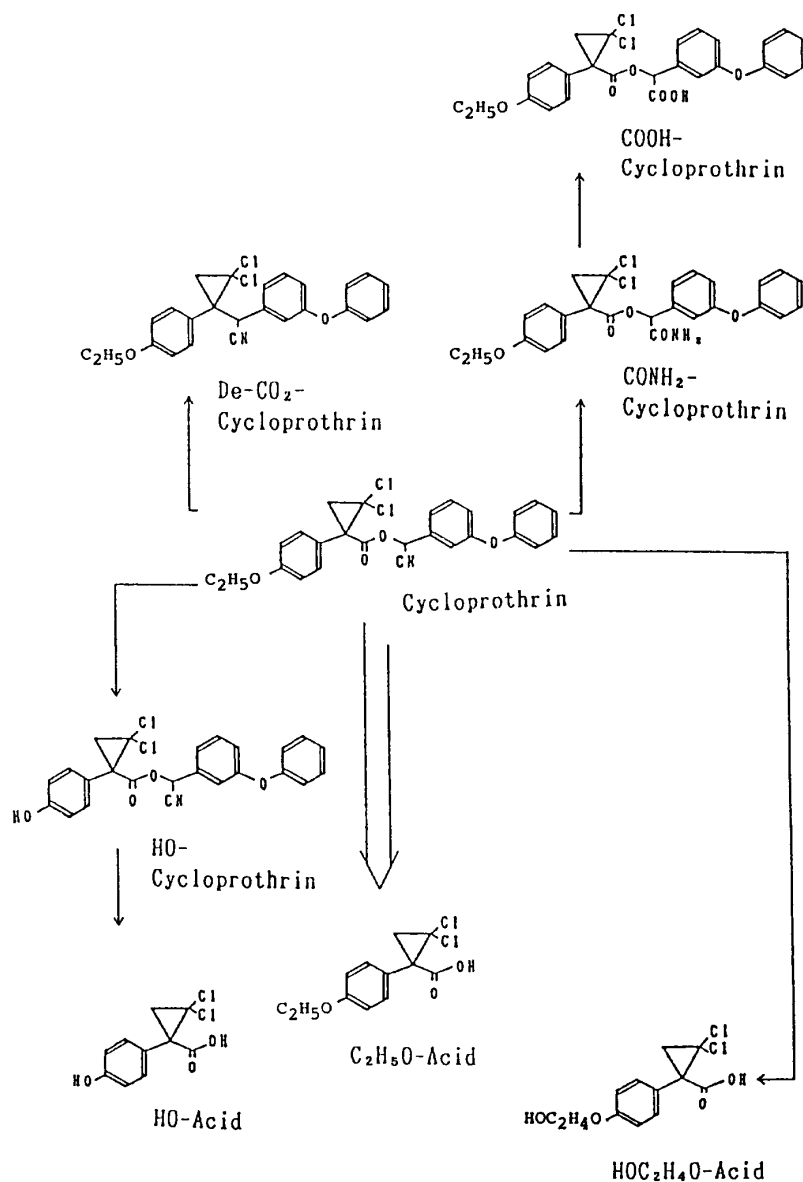


Fig. 2 Proposed metabolic pathways for cycloprothrin in rice plants.

tabolites in rats.<sup>1)</sup> This therefore suggested that major metabolic pathways of cycloprothrin are hydrolysis and oxidation in plants as well. On the other hand, De-CO<sub>2</sub>-, CONH<sub>2</sub>- and COOH-cycloprothrin were minor metabolites, which were not identified in rats. CONH<sub>2</sub>- and COOH-cycloprothrin were also found in soils under flooded conditions. De-CO<sub>2</sub>-cycloprothrin was considered to be a product of photodecomposition on the leaf surface. CONH<sub>2</sub>- and COOH-cycloprothrin appear to be produced in part *via* photochemical and/or other physicochemical reactions. Such decarboxylation and hydrolysis of the CN group to CONH<sub>2</sub> and COOH groups were also observed with fenvalerate.<sup>6)</sup> The hulled grains contained a small amount of radioactivity, but neither cycloprothrin nor its metabolites were identified.

Cycloprothrin is a mixture of four stereoisomeric esters; it has two asymmetric carbons in the acid and alcohol moieties. In the experiment to determine optical isomers, the total amount of unmetabolized cycloprothrin in the shoots decreased by 22%, but the abundance ratio did not change. This suggests that there is no stereospecificity in the metabolism of cycloprothrin in rice plants.

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#### 要 約

#### シクロプロトリンのイネにおける代謝

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シクロプロトリンは水稻, 野菜, 果樹等の害虫を防除するために開発された殺虫剤である. Cyclopropane 環の 3 位を <sup>14</sup>C で標識したシクロプロトリンを用いて, イネにおける吸収移行および代謝について検討した. <sup>14</sup>C-シクロプロトリンを水面処理すると, 3.5 葉期におけるイネ体の放射能濃度は 7 日まで経時的に増加し, 以後ほぼ同濃度で推移した. 処理 132 日後の茎葉と玄米には <sup>14</sup>C-シクロプロトリン換算で 0.161 ppm と 0.157 ppm 相当の放射能が移行残留した. 茎葉から未変化のシクロプロトリンが微量検出されたが, 玄米からは検出されなかった. イネの葉面に塗布した <sup>14</sup>C-シクロプロトリンはほとんど浸透移行せず, 塗布 28 日後においても処理放射能の 98% が塗布部位に残留した. 出穂期のイネに茎葉散布した <sup>14</sup>C-シクロプロトリンも同様な挙動を示し, 玄米への放射能の移行は非常に少なかった. 散布直後植物体全体に 9.33 ppm の <sup>14</sup>C-シクロプロトリンが付着した. 51 日後の収穫時, 茎葉に残留した <sup>14</sup>C-シクロプロトリンは 9.454 ppm であり, 玄米は 0.001 ppm 以下であった. 散布 51 日後茎葉に残留したシクロプロトリンの 4 種立体異性体の存在比に変化は認められなかった. イネ体から 7 種の代謝物が検出され, 主代謝物は (RS)-2, 2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylic acid, (RS)-2, 2-dichloro-1-(4-hydroxyphenyl)cyclopropanecarboxylic acid, (RS)-α-cyano-3-phenoxybenzyl(RS)-2, 2-dichloro-1-(4-hydroxyphenyl)cyclopropanecarboxylate および (RS)-1-[(RS)-α-cyano-3-phenoxybenzyl]2, 2-dichloro-1-(4-ethoxyphenyl)cyclopropane であった.