Original Article

Photodegradation of the Pyrethroid Insecticide Cypermethrin in Water and on Soil Surface

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Photodegradation of (1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-isomers of cypermethrin [(*RS*)- α -cyano-3-phenoxybenzyl (1*RS*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] in water and on soil surface was studied, using ^{14}C preparations labeled separately at the cyclopropyl C-1, cyano or benzyl ring. The *cis*-isomer was photodecomposed 1.4–1.7 times faster in sunlight than the *trans*-isomer in water. The half-life of the *cis*-isomer was 2.3–2.6 days in distilled water and 1 ppm humic acid aqueous solution, and 0.6–0.7 day in natural river and sea water, and <0.5 day in 2% aqueous acetone. A triplet photosensitizer acetone together with the naturally occurring substances in river and sea water enhanced the photodegradation of both isomers. On three kinds of soil surface, both isomers were rapidly photodegraded with the initial half-life of 0.6–1.9 days. The photoreactions involved were: 1*R*/1*S* and *cis*/*trans* isomerization of the cyclopropane ring, cleavage of the ester or diphenyl ether linkage, oxidation of the CHO group to the COOH group, hydration of the CN group to the CONH₂ group, hydrolysis of the CONH₂ group to the COOH group, oxidative cleavage of the halogenated side chain, dehalogenation, intramolecular cyclization to form γ - or δ -lactone, and photomineralization of the cyclopropyl C-1, cyano and benzyl ring to $^{14}\text{CO}_2$.

INTRODUCTION

Cypermethrin [NRDC 149, (*RS*)- α -cyano-3-phenoxybenzyl (1*RS*)-*cis*, *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate], (*PI*), is a mixture of eight isomers owing to three chiral centers at the cyclopropyl C-1 and C-3, and the benzyl methine carbon atom. The insecticide has proved to be effective for the control of insect pests in cotton, top fruits and vegetable crops.¹⁾ Cypermethrin is two to three times more active toward houseflies than permethrin,¹⁻³⁾ and the (1*RS*)-*cis*-isomers are more active than the corresponding (1*RS*)-*trans*-isomers by a factor of two.⁴⁾ From the viewpoint of environmental safety, studies on metabolism of *PI* in plants,⁵⁻⁷⁾ soils,⁸⁻¹¹⁾ rats¹²⁻¹⁴⁾ and mice^{15,16)} have already been performed.

This paper deals with photodegradation of the (1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-isomers in water and soil surface in natural sunlight, using six kinds of ^{14}C -labeled preparations.

MATERIALS AND METHODS

1. Radioactive Chemicals

The (1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-*PI* labeled with ^{14}C separately at the cyclopropyl C-1 (referred to as cyclopropyl- ^{14}C), cyano (^{14}CN) or benzyl ring (uniform labeling, benzyl- ^{14}C) were synthesized at the Takarazuka Research Center, Sumitomo Chemical Co., Ltd.¹⁷⁾ The specific activities were as follows: cyclopropyl- ^{14}C -*PI*; 22.0 mCi/mmol, ^{14}CN -*PI*; 28.0 mCi/mmol, benzyl- ^{14}C -*PI*; 25.2 mCi/mmol. Each preparation had more than 99% radiochemical purity as determined by thin-layer

Table 1 Designation and chemical name of cypermethrin (*P1*) and its derivatives.

Designation	Chemical name
<i>P1</i>	(<i>RS</i>)- α -Cyano-3-phenoxybenzyl (1 <i>R</i>)- <i>cis,trans</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
<i>P2</i>	(<i>RS</i>)- α -Carbamoyl-3-phenoxybenzyl (1 <i>R</i>)- <i>cis,trans</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
<i>P3</i>	(<i>RS</i>)- α -Carboxy-3-phenoxybenzyl (1 <i>R</i>)- <i>cis,trans</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
<i>P4</i>	(<i>RS</i>)- α -Cyano-3-hydroxybenzyl (1 <i>R</i>)- <i>cis,trans</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
<i>P5</i>	(<i>RS</i>)- α -Carbamoyl-3-hydroxybenzyl (1 <i>R</i>)- <i>cis</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
<i>P6</i>	(1 <i>R</i>)- <i>cis,trans</i> -3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid
<i>P7</i>	3,3-Dimethylcyclopropane-1,2-dicarboxylic acid
<i>P8</i>	3,3-Dimethylcyclopropane-1,2-dicarboxylic acid anhydride
<i>P9</i>	6,6-Dichloro-3,3-dimethyl-4-hydroxy-5-hexenoic acid γ -lactone
<i>P10</i>	6-Chloro-3,3-dimethyl-4-hydroxy-5-hexenoic acid γ -lactone
<i>P11</i>	3-(2-Chloro-2-hydroxyvinyl)-2,2-dimethylcyclopropanecarboxylic acid δ -lactone
<i>P12</i>	3-Hydroxybenzoic acid
<i>P13</i>	3-Phenoxybenzaldehyde
<i>P14</i>	3-Phenoxybenzoic acid
<i>P15</i>	3-(2-Hydroxyphenoxy)benzoic acid
<i>P16</i>	3-(4-Hydroxyphenoxy)benzoic acid
<i>P17</i>	3-Phenoxybenzyl cyanide
<i>P18</i>	3-Phenoxybenzylacetamide
<i>P19</i>	3-Phenoxybenzylacetic acid
<i>P20</i>	1,2-Bis(3-phenoxyphenyl)-1,2-dicyanoethane
<i>P21</i>	α -Cyano-3-phenoxybenzyl alcohol
<i>P22</i>	α -Carbamoyl-3-phenoxybenzyl alcohol
<i>P23</i>	α -Carboxy-3-phenoxybenzyl alcohol

chromatography (TLC) on solvent systems A, B, C and D, followed by autoradiography and liquid scintillation counting (LSC).

2. Unlabeled Chemicals

Unlabeled chemicals, shown in Table 1, were synthesized for reference standards at the Takarazuka Research Center, Sumitomo Chemical Co., Ltd.⁵⁾ *P9*, *P10* and *P11* were prepared by irradiation of *cis-P6* in 50% aqueous acetonitrile with UV light (>300 nm) from a 450 W high pressure mercury vapor lamp for 5 hr. The reaction mixture was fractionated on a column of silica gel with hexane/ethyl acetate (3/1), and the photoproducts were purified by repetitive preparative TLC with several solvent systems. *P9*: NMR (CDCl₃) δ 5.94 (1 H, d, $J=9.5$ Hz), 4.87 (1 H, d, $J=9.5$ Hz), 2.40 (2 H, s), 1.22 (3 H, s), 1.07 (3 H, s) ppm; EI-MS (m/z) 212 (M+4), 210 (M+2), 208 (M), 173, 133, 131, 129, 125, 113, 56; IR (direct)

2950, 2910, 1780, 1620, 1460, 1280, 1220, 1190, 990, 914 cm⁻¹. *P10*: NMR (CDCl₃) δ 6.25 (1 H, dd, $J=1, 7$ Hz), 5.79 (1 H, dd, $J=7, 9$ Hz), 5.11 (1 H, dd, $J=1, 9$ Hz), 2.51 (1 H, d, $J=17$ Hz), 2.31 (1 H, d, $J=17$ Hz), 1.23 (3 H, s), 1.05 (3 H, s) ppm; EI-MS (m/z) 176 (M+2), 174 (M), 149, 107, 105, 93, 85, 83, 43; IR (KBr) 2950, 2920, 1775, 1625, 1460, 1380, 1280, 1135, 990 cm⁻¹. *P11*: NMR (CDCl₃) δ 5.38 (1 H, s), 2.62 (1 H, d, $J=4.3$ Hz), 2.31 (1 H, d, $J=4.3$ Hz), 1.21 (3 H, s), 1.19 (3 H, s) ppm; EI-MS (m/z) 174 (M+2), 172 (M), 159, 157, 137, 129, 131, 109, 95, 93, 55, 53; IR (direct) 3090, 2960, 2920, 1800, 1680, 1450, 1185, 1125, 980, 940, 805 cm⁻¹.

3. Chromatography

Precoated silica gel 60 F₂₅₄ chromatoplates (20×20 cm, a layer 0.25 mm thick, E. Merck) were used for analytical and preparative purposes. The solvent systems used, and the *R_f*

Table 2 TLC *R_f* values of cypermethrin (*PI*) and its degradation products.

Chemical	<i>R_f</i> values			
	A	B	C	D
(1 <i>RS</i> , <i>cis</i> , α <i>RS</i>)- <i>PI</i>	0.43, 0.48	0.84	0.67	0.68
(1 <i>RS</i> , <i>trans</i> , α <i>RS</i>)- <i>PI</i>	0.36, 0.40	0.84	0.67	0.68
<i>cis</i> - <i>P2</i>	0.0	0.28, 0.31	0.25, 0.28	0.14, 0.16
<i>trans</i> - <i>P2</i>	0.0	0.27, 0.29	0.23, 0.26	0.13, 0.15
<i>cis</i> - <i>P3</i>	0.0	0.34, 0.37	0.57	0.17, 0.20
<i>trans</i> - <i>P3</i>	0.0	0.33, 0.34	0.54	0.17, 0.19
<i>cis</i> - <i>P4</i>	0.0	0.31, 0.34	0.50	0.43, 0.45
<i>trans</i> - <i>P4</i>	0.0	0.30, 0.32	0.50	0.43, 0.45
<i>P5</i>	0.0	0.05	0.16	0.04
<i>cis</i> - <i>P6</i>	0.02	0.26	0.57	0.45
<i>trans</i> - <i>P6</i>	0.01	0.26	0.57	0.38
<i>P7</i>	0.0	0.26	0.20	0.15
<i>P8</i>	0.02	0.48	0.42	0.39
<i>P9</i>	0.09	0.47	0.44	0.44
<i>P10</i>	0.07	0.44	0.41	0.42
<i>P11</i>	0.13	0.56	0.51	0.49
<i>P12</i>	0.0	0.15	0.31	0.18
<i>P13</i>	0.43	0.45	0.69	0.61
<i>P14</i>	0.0	0.29	0.52	0.32
<i>P15</i>	0.0	0.28	0.34	0.17
<i>P16</i>	0.0	0.16	0.30	0.09
<i>P17</i>	0.18	0.66	0.61	0.52
<i>P18</i>	0.0	0.18	0.19	0.04
<i>P19</i>	0.0	0.42	0.46	0.19
<i>P20</i>	0.02	0.65	0.59	0.60
<i>P21</i>	0.02	0.28	0.49	0.38
<i>P22</i>	0.0	0.06	0.14	0.02
<i>P23</i>	0.0	0.07	0.20	0.02

A: hexane/diethyl ether (20/1), B: hexane/toluene/acetic acid (3/15/2), C: benzene saturated with formic acid/diethyl ether (10/3), D: toluene/diethyl ether/acetic acid (75/25/1).

values of *PI* and its degradation products are listed in Table 2. The resolved radioactive spots were detected by autoradiography and the non-radioactive compounds were visualized by UV fluorescence quenching or exposing to iodine vapor.

High-performance liquid chromatography (HPLC) was carried out by using a Shimadzu LC-4A instrument equipped with a Shimadzu SPD-2AS UV detector (230 nm), with a pre-packed SUMIPAX-OA 2000 column containing a chiral adsorbent (Sumika Analytical Center Co., Ltd., 250 mm $\times$ 4 mm i.d.), using hexane/1,2-dichloroethane/2-propanol (500/30/0.15) as a mobile phase (1 ml/min). The retention time of the eight isomers of *PI* is listed in Table 3. The radioactive *PI* in acetone, which would

Table 3 Separation of the eight isomers of cypermethrin (*PI*) by HPLC.

Optical isomer	Retention time (min)
(1 <i>R</i> , <i>cis</i> , α <i>R</i>)- <i>PI</i>	19.6
(1 <i>R</i> , <i>cis</i> , α <i>S</i>)- <i>PI</i>	25.8
(1 <i>S</i> , <i>cis</i> , α <i>R</i>)- <i>PI</i>	27.8
(1 <i>S</i> , <i>cis</i> , α <i>S</i>)- <i>PI</i>	20.6
(1 <i>R</i> , <i>trans</i> , α <i>R</i>)- <i>PI</i>	23.3
(1 <i>R</i> , <i>trans</i> , α <i>S</i>)- <i>PI</i>	31.8
(1 <i>S</i> , <i>trans</i> , α <i>R</i>)- <i>PI</i>	33.4
(1 <i>S</i> , <i>trans</i> , α <i>S</i>)- <i>PI</i>	24.1

Column: SUMIPAX-OA 2000 (4 mm i.d. $\times$ 250 mm), Mobile phase: hexane/1,2-dichloroethane/2-propanol (500/30/0.15), Flow rate: 1 ml/min.

contain the eight isomers, was obtained by scraping the corresponding gel region of developed TLC plates with solvent system A, eluted with acetone, and analyzed by HPLC. Quantitation of the eight isomers was carried out by directly collecting of the eluates into vials at 15-sec intervals prior to LSC.

4. Spectroscopy

Infrared (IR) spectra were recorded on a Hitachi 285 IR Spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained by a Hitachi R-40 (90 MHz) or JEOL-JNM-FX-100 (100 MHz) spectrometer in deuteriochloroform containing 1% tetramethylsilane as an internal standard. Electron impact mass (EI-MS) spectra were recorded on a Hitachi M-80 Gas Chromatograph/Mass Spectrometer (GC-MS) equipped with a M-003 data system at 70 eV using a direct insertion technique.

5. Radioassay

Liquid scintillation counting (LSC), combustion analysis and autoradiography were carried out according to the procedures reported previously.¹⁸⁾

6. Photolysis Experiments

6.1 Photolysis in water

In addition to distilled water, 2% aqueous acetone and aqueous humic acid (1 ppm) solution as well as natural water from a river and the sea were utilized in the photolysis experiments. The aqueous humic acid solution was prepared as follows: 0.1 N NaOH (1 ml) containing 5 mg of humic acid (Aldrich Chemical Co., Ltd.) was added to distilled water (5 l) and stirred for 2 hr. The solution was adjusted to pH 6.3 with 0.1 N HCl. Water was collected at the Muko River (pH 8.7) or the seaside in Nishinomiya (pH 8.3), Hyogo Prefecture, Japan. The water samples were sterilized through 0.1 μ m filter paper (No. 85 SB, 60 mm in diameter, Toyo Roshi Co., Ltd.) immediately before use.

Because of a rapid disappearance of *P1* in water even at below its water solubility (8.9 ppb at 25°C), probably due to sticking to the glass wall, more stable suspensions of *P1* were prepared at 50 ppb, using Tween 85 (a surfactant, Wako Pure Chemical Co., Ltd.) which

absorbs no UV above 290 nm.

The ¹⁴C-*P1* suspension was prepared as follows: ¹⁴C-*P1* (400 g) and Tween 85 (20 mg) were dissolved in chloroform (10 ml) and 1 ml of the solution was taken into a 1-liter quartz flask. After evaporating the solvent under reduced pressure, water (800 ml) was added and then shaken for 1 hr by a mechanical shaker to attain a level of 50 ppb. More than 95% of the radioactivity remained in the aqueous layer after standing for 10 days without stirring. Each flask was exposed to natural sunlight for 10 days (*ca.* 8 hr per day in September in 1983). The sunlight intensity with wavelengths between 300 and 400 nm was approximately 290, 1180 and 239 μ W/cm² at the beginning, middle and end of the day, respectively. While exposed to sunlight, each test tube covered with aluminum foil containing 10 N NaOH solution (10 ml) was kept in a 1-liter quartz flask in order to trap the volatile ¹⁴C including ¹⁴CO₂ and H¹⁴CN. No significant pH change was observed in the aqueous suspensions except 2% aqueous acetone, in which the pH decreased from 5.4 to 3.7 after 1-day exposure. A dark control experiment was also conducted by covering the flask with aluminum foil to ensure that a given product was derived through photochemical processes.

6.2 Photolysis on soil surfaces

The following soils were used in the experiments: Kodaira light clay (Tokyo Metropolis), Katano sandy loam (Hyogo Pref.) and Azuchi sandy clay loam (Shiga Pref.). The physicochemical characteristics are shown in Table 4. Soil thin-layer plates (10×10 cm, 500 μ m thickness) were prepared with fine soil particles passed through a 2 mm sieve according to the method used by Helling *et al.*¹⁹⁾ Onto the soil TLC plate, ¹⁴C-*P1* in diethyl ether (1 ml) was evenly applied with a brush at a rate of 1.1 μ g/cm² and then exposed to natural sunlight during August 1983 in Takarazuka, Hyogo, Japan. Sunlight intensity with wavelengths between 300 and 400 nm was approximately 1010, 1640 and 270 μ W/cm² at the beginning, middle and end of the day, respectively. During the photolysis, the water contents of Kodaira, Katano and Azuchi soil TLC plates changed from 12.1, 1.4 and 2.1% to 9.2, 0.7 and 1.5%, respectively. A dark control ex-

Table 4 Physico-chemical characteristics of soil used in the experiments.

Sampling site	Soil texture	pH	Soil separate (%)			Clay mineral	O.M. ^{a)}	C.E.C. ^{b)}	Maximum water-holding capacity ^{c)}
			Sand	Silt	Clay				
Kodaira	Light clay	5.5	31	40	29	Kaolinite	15.3	53.7	148.5
Katano	Sandy loam	4.6	90	2	8	Kaolinite	1.9	9.3	79.6
Azuchi	Sandy clay loam	6.3	65	18	17	Allophane	2.5	13.5	88.7

^{a)} Organic matter contents (%).

^{b)} Cation exchange capacity (meq/100 g dry soil).

^{c)} g/100 g dry soil.

periment was conducted with by keeping the soil TLC plates in the dark.

7. Extraction and Analysis

7.1 Aqueous suspensions

At specified intervals after exposed to sunlight, 130 ml of the suspension was taken into a gas-washing bottle and acidified to pH 1 with 2 N H₂SO₄ to determine the amount of ¹⁴CO₂ and/or H¹⁴CN prior to being subjected to extraction with a twofold volume of ethyl acetate. By bubbling of N₂ gas into the acidified suspension at *ca.* 1500 ml/min for 30 min, ¹⁴CO₂ and/or H¹⁴CN were introduced into a 0.6 N NaOH solution (200 ml). Recovery of each product exceeded 90%. Following the precipitation of ¹⁴CO₂ in the alkaline solution as Ba¹⁴CO₃ by adding 2 N BaCl₂, the solution was centrifuged at 5000 rpm for 5 min to separate the supernatant from Ba¹⁴CO₃. The supernatant was acidified to pH 3 with H₂SO₄. Through the process He gas was bubbled at *ca.* 100 ml/min for 6 hr to trap the liberated H¹⁴CN in a glass tube in liquid nitrogen. The H¹⁴CN trapped in a glass tube was dissolved in 0.1 N NaOH (0.6 ml) and 0.5 ml of the solution was subjected to the colorimetric analysis (560 nm) using *o*-dinitrobenzene and *p*-nitrobenzaldehyde.²⁰⁾ More than 80% of HCN with its amount ranging from 6 ng to 150 ng was recovered by the procedure described above. ¹⁴CO₂ and/or H¹⁴CN in the alkaline traps kept in a 1-liter quartz flask were analyzed by the same procedures.

The combined ethyl acetate extract from the aqueous suspension was radioassayed by LSC and the remainder was evaporated and analyzed by TLC and HPLC.

7.2 Extraction of soil

The soil thin-layer was scraped off and extracted with acetone/distilled water (1/5, 30 ml×3) by shaking for 10 min. The mixture was centrifuged at 3000 rpm for 5 min to separate the supernatant from the soil residue. The combined extract was assayed for ¹⁴C, evaporated and analyzed by TLC and HPLC. An aliquot of the unextractable soil residue was combusted prior to LSC and the remainder was fractionated into the fulvic acid, humic acid and humins according to the general procedures.²¹⁾

8. Determination of Quantum Yield

The quantum yields of (1*R*, *cis*)- and (1*R*, *trans*)-*P1*, *cis*- and *trans*-*P6*, and *P14* were determined by comparing the photolysis rate with that of parathion as a reference compound at 313 nm using a merry-go-round type photochemical apparatus which was reported previously.¹⁸⁾ The aqueous solutions of radiolabeled (1*R*, *cis*)- and (1*R*, *trans*)-*P1* (50 ppb), *cis*- and *trans*-*P6* (1 ppm), *P14* (1 ppm) and parathion (0.2 ppm) were placed into a quartz tube and irradiated for up to 24 hr.

RESULTS

1. Photolysis in Water

The photodegradation rates of (1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-*P1* in water by natural sunlight decreased in the following order: 2% aqueous acetone > river and sea water > humic acid aqueous solution = distilled water (Fig. 1). The *cis*-isomer was photodecomposed 1.4–1.7 times faster than the *trans*-isomer in solutions except 2% aqueous acetone, in which no significant difference was observed in the

Table 5 Half-life values of (1*R*, *cis*, α *RS*)- and (1*R*, *trans* α *RS*)-cypermethrin (*PI*) in sunlight and darkness.

	Half-life (days)			
	(1 <i>R</i> , <i>cis</i> , α <i>RS</i>)- <i>PI</i>		(1 <i>R</i> , <i>trans</i> , α <i>RS</i>)- <i>PI</i>	
	Sunlight	Dark	Sunlight	Dark
Water				
Distilled water	2.6	> 10 (95.6) ^{a)}	3.6	> 10 (94.4) ^{a)}
Aqueous humic acid	2.3	> 10 (95.8) ^{a)}	3.4	> 10 (95.2) ^{a)}
River water	0.6	> 10 (88.7) ^{a)}	1.0	> 10 (55.3) ^{a)}
Sea water	0.7	> 10 (83.9) ^{a)}	1.0	> 10 (59.6) ^{a)}
2% Aqueous acetone	<0.5	> 10 (97.4) ^{a)}	<0.5	> 10 (95.0) ^{a)}
Soil				
Kodaira	0.6	> 7 (84.2) ^{b)}	0.7	> 7 (84.0) ^{b)}
Azuchi	1.5	> 7 (80.8) ^{b)}	1.3	> 7 (81.8) ^{b)}
Katano	1.9	> 7 (94.2) ^{b)}	1.7	> 7 (91.4) ^{b)}

a) Recovery (%) of *PI* after 10 days in darkness.

b) Recovery (%) of *PI* after 7 days in darkness.

Fig. 1 Degradation of ¹⁴C-(1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-cypermethrin (*PI*) in various kinds of aqueous suspensions in sunlight and darkness.

—: Sunlight,: Darkness.

photolysis rate. The half-life of disappearance ranged from <0.5 day to 3.6 days (Table 5). As estimated from the half-life values, the photodegradation of both isomers in river and sea water was *ca.* 3–4 times as rapid as that in distilled water, suggesting that a triplet photosensitizer acetone together with naturally occurring substances in river and sea water

enhanced the photodegradation of both isomers. In darkness, both isomers were fairly stable in the solutions tested, but in slightly basic media such as river and sea water both isomers were gradually degraded. After 7 days, the recovered *PI* amounted to 53.3–59.6 and 83.9–88.7% of the applied ¹⁴C, respectively.

Both isomers underwent rapid and extensive

Table 6 The amount of (1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-cypermethrin (*PI*) and their photoproducts in distilled water and 2% aqueous acetone in sunlight.

	% of the applied ¹⁴ C											
	Distilled water						2% Aqueous acetone					
	(1 <i>R</i> , <i>cis</i> , α <i>RS</i>)- <i>P1</i>			(1 <i>R</i> , <i>trans</i> , α <i>RS</i>)- <i>P1</i>			(1 <i>R</i> , <i>cis</i> , α <i>RS</i>)- <i>P1</i>			(1 <i>R</i> , <i>trans</i> , α <i>RS</i>)- <i>P1</i>		
	Exposure period (days)											
	10			10			0.5			0.5		
	Cy ^{a)}	CN ^{b)}	Bz ^{c)}	Cy	CN	Bz	Cy	CN	Bz	Cy	CN	Bz
Volatile ¹⁴ C	0.6	39.0	2.2	0.6	36.6	1.1	1.0	8.9	0.6	1.1	8.9	0.9
¹⁴ CO ₂	0.3	34.6	2.0	0.4	34.1	1.0	0.8	6.8	0.4	0.6	6.7	0.7
H ¹⁴ CN	—	<0.1	—	—	<0.1	—	—	<0.1	—	—	<0.1	—
Others	0.3	4.4	0.2	0.2	2.5	0.1	0.2	2.1	0.2	0.5	2.2	0.2
Extractable ¹⁴ C	90.9	42.2	80.2	80.3	40.6	86.5	82.6	74.6	87.7	82.3	76.5	88.6
(1 <i>R</i> , <i>cis</i> , α <i>R</i>)- <i>P1</i>	5.5	4.7	5.2	3.1	2.7	4.7	0.8	0.9	0.9	0.1	0.1	0.2
(1 <i>R</i> , <i>cis</i> , α <i>S</i>)- <i>P1</i>	4.2	3.4	4.0	2.8	2.3	3.6	0.9	0.8	0.7	0.1	0.1	0.2
(1 <i>S</i> , <i>cis</i> , α <i>R</i>)- <i>P1</i>	3.3	3.9	1.5	2.5	2.1	3.5	0.2	0.2	0.2	0.1	0.1	0.2
(1 <i>S</i> , <i>cis</i> , α <i>S</i>)- <i>P1</i>	3.1	3.5	2.1	2.0	2.0	3.7	0.2	0.1	0.2	0.1	0.1	0.2
(1 <i>R</i> , <i>trans</i> , α <i>R</i>)- <i>P1</i>	3.9	4.7	2.8	9.3	6.6	9.7	0.3	0.3	0.3	0.6	0.9	1.0
(1 <i>R</i> , <i>trans</i> , α <i>S</i>)- <i>P1</i>	4.5	5.3	3.5	10.1	7.2	9.3	0.2	0.2	0.2	0.6	1.0	1.1
(1 <i>S</i> , <i>trans</i> , α <i>R</i>)- <i>P1</i>	3.9	3.1	2.4	3.4	2.9	4.8	0.2	0.2	0.2	0.1	0.1	0.2
(1 <i>S</i> , <i>trans</i> , α <i>S</i>)- <i>P1</i>	3.6	3.7	2.5	2.9	2.2	3.4	0.3	0.3	0.3	0.1	0.2	0.2
<i>P2</i>	2.4	0.8	1.1	5.1	0.7	1.5	1.1	0.5	0.4	1.6	0.5	0.8
<i>P3</i>	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	0.2	<0.1	<0.1
<i>P4</i>	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.7	<0.1	0.4	0.2	<0.1	0.4
<i>P5</i>	<0.1	<0.1	0.1	0.3	0.4	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<i>cis</i> - <i>P6</i>	20.4	—	—	1.4	—	—	1.9	—	—	3.8	—	—
<i>trans</i> - <i>P6</i>	18.9	—	—	13.1	—	—	5.9	—	—	6.5	—	—
<i>P7</i>	<0.1	—	—	<0.1	—	—	0.5	—	—	0.8	—	—
<i>P8</i>	<0.1	—	—	<0.1	—	—	0.3	—	—	0.2	—	—
<i>P9</i>	<0.1	—	—	<0.1	—	—	0.6	—	—	1.6	—	—
<i>P10</i>	<0.1	—	—	<0.1	—	—	0.5	—	—	2.3	—	—
<i>P11</i>	<0.1	—	—	<0.1	—	—	0.2	—	—	0.8	—	—
<i>P12</i>	—	—	0.2	—	—	0.3	—	—	<0.1	—	—	0.1
<i>P13</i>	—	—	8.4	—	—	6.5	—	—	6.4	—	—	6.3
<i>P14</i>	—	—	25.6	—	—	17.9	—	—	8.4	—	—	9.5
<i>P15</i>	—	—	<0.1	—	—	<0.1	—	—	0.4	—	—	0.6
<i>P16</i>	—	—	0.2	—	—	0.4	—	—	0.2	—	—	0.2
<i>P17</i>	—	0.3	2.5	—	<0.1	1.3	—	0.3	0.4	—	0.5	0.3
<i>P18</i>	—	0.2	0.2	—	0.1	<0.1	—	0.4	0.4	—	0.8	1.0
<i>P19</i>	—	0.2	0.2	—	<0.1	<0.1	—	6.4	5.3	—	6.8	4.3
<i>P20</i>	—	<0.1	<0.1	—	<0.1	<0.1	—	3.4	2.5	—	2.3	1.3
<i>P21</i>	—	<0.1	0.1	—	<0.1	0.3	—	0.7	2.5	—	4.0	3.3
<i>P22</i>	—	0.4	0.5	—	0.3	1.0	—	<0.1	<0.1	—	0.6	0.5
<i>P23</i>	—	<0.1	<0.1	—	<0.1	0.2	—	0.1	0.1	—	0.2	0.1
Others	17.2	8.0	17.1	24.2	11.1	14.2	67.6	59.8	57.3	62.5	58.2	56.6
Aqueous ¹⁴ C	3.8	1.3	5.0	5.8	1.1	2.9	5.6	1.2	1.1	4.7	1.2	1.1
Total ¹⁴ C	95.3	82.5	87.4	86.7	78.3	90.5	89.2	84.7	89.4	88.1	86.6	90.6

a) Cyclopropyl-¹⁴C.b) ¹⁴CN.c) Benzyl-¹⁴C.

Table 7 The amount of (1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-cypermethrin (*PI*) and their photoproducts in river water and 1 ppm humic acid aqueous solution in sunlight.

	% of the applied ¹⁴ C											
	River water						Humic acid aqueous solution					
	(1 <i>R</i> , <i>cis</i> , α <i>RS</i>)- <i>PI</i>			(1 <i>R</i> , <i>trans</i> , α <i>RS</i>)- <i>PI</i>			(1 <i>R</i> , <i>cis</i> , α <i>RS</i>)- <i>PI</i>			(1 <i>R</i> , <i>trans</i> , α <i>RS</i>)- <i>PI</i>		
	Exposure period (days)											
	10			10			10			10		
	Cy ^{a)}	CN ^{b)}	Bz ^{c)}	Cy	CN	Bz	Cy	CN	Bz	Cy	CN	Bz
Volatile ¹⁴ C	2.8	67.8	6.5	1.4	62.7	5.2	1.0	27.0	2.1	2.0	34.2	1.2
¹⁴ CO ₂	2.6	63.1	6.2	1.3	59.9	5.0	0.5	25.0	1.7	1.7	30.5	0.7
H ¹⁴ CN	—	<0.1	—	—	<0.1	—	—	<0.1	—	—	<0.1	—
Others	0.2	4.7	0.3	0.1	2.8	0.2	0.5	2.0	0.4	0.3	3.7	0.5
Extractable ¹⁴ C	86.7	10.8	76.1	91.8	12.3	80.7	90.7	58.8	91.8	86.8	50.2	89.3
(1 <i>R</i> , <i>cis</i> , α <i>R</i>)- <i>PI</i>	0.1	0.5	0.1	0.2	0.3	0.1	2.6	6.2	5.2	3.5	3.4	3.9
(1 <i>R</i> , <i>cis</i> , α <i>S</i>)- <i>PI</i>	0.1	0.4	0.1	0.2	0.3	<0.1	2.1	5.7	3.4	3.8	3.1	3.7
(1 <i>S</i> , <i>cis</i> , α <i>R</i>)- <i>PI</i>	<0.1	0.2	0.2	0.2	0.4	<0.1	1.8	5.1	3.9	3.2	3.6	3.2
(1 <i>S</i> , <i>cis</i> , α <i>S</i>)- <i>PI</i>	<0.1	0.2	0.2	0.2	0.4	<0.1	2.0	5.8	4.1	4.1	3.2	3.9
(1 <i>R</i> , <i>trans</i> , α <i>R</i>)- <i>PI</i>	0.1	0.3	0.1	0.2	0.3	0.1	2.1	6.7	5.1	10.9	10.1	8.8
(1 <i>R</i> , <i>trans</i> , α <i>S</i>)- <i>PI</i>	0.2	0.2	0.2	0.3	0.3	0.1	2.5	7.1	4.7	10.0	9.7	8.5
(1 <i>S</i> , <i>trans</i> , α <i>R</i>)- <i>PI</i>	<0.1	0.3	0.2	0.2	0.3	0.1	2.4	6.5	4.2	2.7	3.3	3.1
(1 <i>S</i> , <i>trans</i> , α <i>S</i>)- <i>PI</i>	0.1	0.2	0.1	0.2	0.3	<0.1	2.2	6.9	5.2	3.9	2.9	3.4
<i>P2</i>	0.8	0.4	0.5	0.6	0.7	0.2	0.2	0.3	1.0	2.5	0.7	0.7
<i>P3</i>	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<i>P4</i>	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<i>P5</i>	0.1	<0.1	0.6	<0.1	<0.1	0.1	<0.1	0.1	0.2	0.2	0.2	0.1
<i>cis</i> - <i>P6</i>	30.7	—	—	24.1	—	—	26.1	—	—	2.3	—	—
<i>trans</i> - <i>P6</i>	46.2	—	—	58.6	—	—	22.0	—	—	17.4	—	—
<i>P7</i>	<0.1	—	—	<0.1	—	—	<0.1	—	—	<0.1	—	—
<i>P8</i>	<0.1	—	—	<0.1	—	—	<0.1	—	—	<0.1	—	—
<i>P9</i>	<0.1	—	—	<0.1	—	—	<0.1	—	—	<0.1	—	—
<i>P10</i>	<0.1	—	—	<0.1	—	—	<0.1	—	—	<0.1	—	—
<i>P11</i>	<0.1	—	—	<0.1	—	—	<0.1	—	—	<0.1	—	—
<i>P12</i>	—	—	0.2	—	—	0.2	—	—	0.3	—	—	0.3
<i>P13</i>	—	—	0.2	—	—	0.1	—	—	6.4	—	—	4.7
<i>P14</i>	—	—	59.2	—	—	67.8	—	—	29.8	—	—	29.3
<i>P15</i>	—	—	1.9	—	—	1.1	—	—	0.3	—	—	0.2
<i>P16</i>	—	—	0.6	—	—	0.4	—	—	0.4	—	—	0.3
<i>P17</i>	—	0.4	<0.1	—	0.4	0.2	—	0.4	1.5	—	0.5	1.0
<i>P18</i>	—	0.1	0.1	—	0.1	<0.1	—	0.1	0.1	—	0.1	0.1
<i>P19</i>	—	0.2	0.2	—	0.1	0.1	—	<0.1	0.2	—	<0.1	<0.1
<i>P20</i>	—	<0.1	<0.1	—	<0.1	<0.1	—	<0.1	<0.1	—	<0.1	<0.1
<i>P21</i>	—	0.2	<0.1	—	<0.1	0.2	—	0.6	0.8	—	0.5	0.6
<i>P22</i>	—	1.7	2.3	—	3.1	2.4	—	0.2	0.7	—	0.3	0.4
<i>P23</i>	—	0.3	0.2	—	0.2	0.2	—	0.1	0.2	—	0.1	0.1
Others	8.3	5.0	9.0	6.9	5.2	7.3	24.7	7.4	14.4	22.3	8.5	13.1
Aqueous ¹⁴ C	5.2	4.8	7.4	2.6	4.7	7.2	5.6	0.9	3.9	3.7	0.9	2.9
Total ¹⁴ C	94.7	83.4	90.0	95.8	79.7	93.1	97.3	86.7	97.8	92.5	85.3	93.5

a) Cyclopropyl- ^{14}C .b) ^{14}CN .c) Benzyl- ^{14}C .

Fig. 2 Relative isomerization rates leading to equilibrium *cis/trans* mixtures of (1*R*, *cis*, α RS)- or (1*R*, *trans*, α RS)-cypermethrin (P1) in water. —: (1*R*, *cis*, α RS)-P1, ----: (1*R*, *trans*, α RS)-P1. $\blacktriangle$, Distilled water; $\triangle$, 1 ppm humic acid; $\bullet$, River and sea water; $\blacksquare$, 2% Aqueous acetone.

isomerization of the cyclopropane ring, *i.e.* interconversion of the *trans*- and *cis*-isomers, the reaction occurring most rapidly in the presence of acetone and declining, in order, in river and sea water, humic acid aqueous solution and distilled water (Fig. 2). This indicated that acetone, together with naturally occurring substances in river and sea water such as humic acids, enhanced the photoisomerization of both isomers. The *cis*-isomer underwent isomerization more rapidly than the *trans*-isomer in any water tested. Isomerization of the cyclopropane ring reached an equilibrium within 10 days except in distilled water and humic acid aqueous solution. At equilibrium, the more thermodynamically stable *trans*-isomer constituted 51–59% of the isomer mixture.

Tables 6 and 7 show the amount of the *cis*- and *trans*-isomers and their photodegradation products in water. The *cis/trans* and 1*R*/1*S* isomerization products and ester cleavage products (P6, P14) were common major photoproducts, with a relatively large amount of P13 in distilled water and P13 and P19 in 2% aqueous acetone. The evolution of $^{14}\text{CO}_2$ from the ^{14}CN label was more significant than that from the cyclopropyl- and benzyl- ^{14}C labels

Fig. 3 Comparison of UV spectra of (1*R*, *cis*, α RS)- and (1*R*, *trans*, α RS)-cypermethrin (P1) with solar irradiance.

in any water tested. However, H^{14}CN remained below the detection limit (0.1% of the applied ^{14}C). The distribution of the photoproducts in sea water was almost the same as that in river water. The ester cleavage and isomerization of the cyclopropane ring were slightly enhanced in humic acid aqueous solution but not in distilled water. Both P6 and P14 were of more importance than the isomerization products in river water, humic acid aqueous solution and 2% aqueous acetone, although they were formed as much as the isomerization products in distilled water. These evidences indicated that the ester bond cleavage following subsequent photomineralization of the CN fragment to CO_2 was accelerated by acetone and natural substances in river and sea water which contained humic acids. The photoproducts unique in 2% aqueous acetone were P7, P8, P9, P10 and P11 which amounted to 0.2–2.3% of the applied ^{14}C after one day, showing no tendency to increase with time. The other products such as P2, P3, P4, P5, P12, P15, P16, P17, P18, P20, P21, P22 and P23 were of minor importance in any water tested.

2. Direct Photolysis Rate

The direct photolysis half-lives of the (1*R*, *cis*)- and (1*R*, *trans*)-P1 and other major photoproducts such as *cis*- and *trans*-P6 and P14 in distilled water near the surface were calculated according to the equation of $T_{1/2} = 0.693/(\phi k_a)$

Table 8 Half-life of disappearance of (1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-cypermethrin (*P1*) and their major photoproducts in distilled water in natural sunlight in fall at 40° North Latitude.

Compound	$\phi^a)$	Half-life (days)	
		Calcd. ^{b)}	Found
(1 <i>R</i> , <i>cis</i> , α <i>RS</i>)- <i>P1</i>	0.16	2.8	2.6
(1 <i>R</i> , <i>trans</i> , α <i>RS</i>)- <i>P1</i>	0.097	3.7	3.6
<i>cis</i> - <i>P6</i>	0.035	22.3	—
<i>trans</i> - <i>P6</i>	0.017	32.9	—
<i>P14</i>	0.00047	183.0	—

^{a)} Disappearance quantum yield.

^{b)} Calculated half-life according to the equation of $T_{1/2} = 0.693/(\phi k_a)$.

in fall at 40°N (Table 8). The quantum yield (ϕ ; three replicate measurements in distilled water at 313 nm) and the rate of specific sunlight absorption (k_a) were determined according to the method reported previously (Fig. 3).¹⁸⁾ The quantum yield of the *cis*-isomers of both *P1* and *P6* were 1.6–2.1 times higher than that of the *trans*-isomers. The calculated half-life of *P1* was in good accord with that observed in the outdoor experiments. Estimates based on the calculated half-lives, seem to show that *P6* and *P14* gradually undergo further photodegradation in water by natural sunlight.

3. Photolysis on Soil Surfaces

As shown in Fig. 4 and Table 5, sunlight had a significant effect on the degradation of (1*R*, *cis*)- and (1*R*, *trans*)-*P1* on three types of soils used for the experiments. The half-lives of disappearance of both isomers were 0.6–0.7, 1.3–1.5 and 1.7–1.9 days on the Kodaira, Azuchi and Katano soils, respectively. No significant difference was observed in two isomers' degradation rate.

After 7 days more than 60% of the applied ¹⁴C was recovered from the soil and the remaining ¹⁴C was lost probably due to evaporation (Table 9). More of the radiocarbon was lost from the Azuchi and Katano soils treated with the cyclopropyl-¹⁴C and ¹⁴CN labels than those treated with the benzyl-¹⁴C label. By contrast, there was no significant loss of radioactivity in the dark.

Major degradation products were *P2* in the Kodaira soil and *P2* and *P14* in the Azuchi and Katano soils. The amide analog (*P2*) gradually increased with time. Although *P2* was also formed in darkness, sunlight significantly accelerated the transformation of *P1* to *P2* on soil surfaces. As compared with the photolysis in water, the *cis/trans* or 1*R*/1*S* isomerization products were of minor importance, which amounted to less than 3% of the applied ¹⁴C after 7 days in any soil tested. The other products such as *P2*, *P3*, *P4*, *P5*, *P12*, *P13*,

Fig. 4 Degradation of ¹⁴CN-(1*R*, *cis*, α *RS*)-cypermethrin (*P1*) on soil surfaces in sunlight and darkness.

Table 9 The amount of (1*R*, *cis*, α *RS*)-cypermethrin (*PI*) and their photodegradation products in three kinds of soils in sunlight or darkness after 7 days.

	% of the applied ¹⁴ C											
	Kodaira				Azuchi				Katano			
	Sunlight			Dark	Sunlight			Dark	Sunlight			Dark
	Cy ^{a)}	CN ^{b)}	Bz ^{c)}	Bz	Cy	CN	Bz	Bz	Cy	CN	Bz	Bz
Extract ¹⁴ C	37.3	35.9	40.2	101.2	65.6	68.9	76.0	87.7	57.7	54.0	70.1	97.1
(1 <i>R</i> , <i>cis</i> , α <i>R</i>)- <i>PI</i>	1.0	4.9	5.3	72.4	31.2	27.7	29.2	84.7	35.2	30.2	33.4	95.9
(1 <i>R</i> , <i>cis</i> , α <i>S</i>)- <i>PI</i>	1.1	0.9	1.1	44.0	10.2	10.6	9.0	37.8	16.2	15.7	12.5	45.7
(1 <i>S</i> , <i>cis</i> , α <i>R</i>)- <i>PI</i>	0.1	0.1	<0.1	0.1	0.3	0.3	0.2	0.3	0.6	0.5	0.5	0.4
(1 <i>S</i> , <i>cis</i> , α <i>S</i>)- <i>PI</i>	0.1	0.1	<0.1	0.1	0.2	0.3	0.3	0.1	0.3	0.3	0.3	0.3
(1 <i>R</i> , <i>trans</i> , α <i>R</i>)- <i>PI</i>	0.1	0.1	0.1	0.1	0.3	0.2	0.2	0.2	0.4	0.5	0.4	0.3
(1 <i>R</i> , <i>trans</i> , α <i>S</i>)- <i>PI</i>	0.1	<0.1	<0.1	0.2	0.2	0.2	0.2	0.3	0.4	0.4	0.4	0.2
(1 <i>S</i> , <i>trans</i> , α <i>S</i>)- <i>PI</i>	<0.1	<0.1	<0.1	0.1	0.1	0.3	0.2	0.3	0.5	0.4	0.4	0.3
(1 <i>S</i> , <i>trans</i> , α <i>S</i>)- <i>PI</i>	0.1	0.1	<0.1	0.2	0.2	0.2	0.3	0.2	0.4	0.4	0.6	0.2
<i>P2</i>	25.1	24.0	23.4	9.5	31.2	32.6	31.7	5.8	4.8	5.3	4.4	1.1
<i>P3</i>	1.0	1.0	0.9	0.1	<0.1	<0.1	<0.1	0.4	0.1	0.1	<0.1	<0.1
<i>P4</i>	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	0.3	0.9	<0.1
<i>P5</i>	0.2	0.4	0.5	<0.1	0.4	0.3	0.6	<0.1	0.4	0.2	0.2	<0.1
<i>P6</i>	<0.1	—	—	—	<0.1	—	—	—	<0.1	—	—	—
<i>P12</i>	—	—	0.2	<0.1	—	—	0.8	<0.1	—	—	1.8	<0.1
<i>P13</i>	—	—	<0.1	<0.1	—	—	0.1	<0.1	—	—	0.2	<0.1
<i>P14</i>	—	—	2.6	0.4	—	—	6.8	0.3	—	—	11.7	0.4
<i>P16</i>	—	—	<0.1	<0.1	—	—	0.1	0.4	—	—	0.4	<0.1
<i>P17</i>	—	<0.1	<0.1	<0.1	—	<0.1	0.2	0.2	—	0.5	0.5	0.2
<i>P18</i>	—	<0.1	<0.1	<0.1	—	<0.1	<0.1	<0.1	—	<0.1	<0.1	<0.1
<i>P21</i>	—	<0.1	<0.1	0.3	—	0.1	0.3	0.2	—	0.8	1.1	0.3
<i>P22</i>	—	2.5	3.0	<0.1	—	1.9	2.1	<0.1	—	0.7	0.6	<0.1
<i>P23</i>	—	0.3	0.2	<0.1	—	0.1	0.1	<0.1	—	<0.1	0.1	<0.1
Others	8.4	5.5	7.2	1.0	14.2	11.5	14.0	2.0	20.1	12.8	20.4	1.9
Bound ¹⁴ C	47.3	45.6	45.4	2.1	11.3	7.9	9.8	0.5	11.6	7.6	12.9	0.4
Humic acid	5.0	7.9	8.0	* ^{d)}	1.4	1.1	1.7	*	2.1	1.5	3.4	*
Humic acid	19.3	26.7	26.1	*	1.8	1.4	2.7	*	1.4	0.8	2.8	*
Fulvic acid	23.0	11.0	11.3	*	8.1	5.4	5.4	*	8.1	5.3	6.7	*
Total ¹⁴ C	84.6	81.5	85.6	103.3	76.9	76.8	85.8	88.2	69.3	61.6	83.0	97.5

^{a)} Cyclopropyl-¹⁴C.^{b)} ¹⁴CN.^{c)} Benzyl-¹⁴C.^{d)} Not determined.

P16, *P17*, *P18*, *P19*, *P21*, *P22* and *P23* were also of minor importance.

DISCUSSION

(1*R*, *cis*, α *RS*)- and (1*R*, *trans*, α *RS*)-cypermethrin (*PI*) have their absorption maxima significantly below 290 nm but have measurable absorption tails above the base line in their absorption spectra at wavelengths greater than 290 nm. The UV spectra of the *cis*- and

trans-isomers in acetonitrile/water (1/1) exhibit 198-nm (ϵ 29,200) and 196-nm (ϵ 41,200) bands, respectively, for the allowed π - π^* transition of the phenyl rings and 273-nm (ϵ 1100) and 272-nm (ϵ 1900) bands, respectively, which are essentially n - π^* in character, resulting from the combined transitions of the carbonyl group and the lower energy band of the aromatic rings. These π - π^* and n - π^* transitions can lead to the production of either singlet or

triplet excited state, so no unique excited state can be invoked to explain the variety of photochemical reactions. The energy levels of singlet and triplet excited states of the *cis*-isomer were determined to be 89.3 and 59.6 kcal/mole, respectively, by measuring the fluorescence and phosphorescence spectra in acetonitrile.²²⁾

The half-lives of disappearance of the *cis*- and *trans*-isomers in water and on soil surface in natural sunlight or darkness are summarized in Table 5. Natural substances in river and sea water appear to accelerate the photodegradation of both isomers. It has been reported that humic acids, tryptophan and tyrosine in natural water act as photosensitizers towards some kind of pesticides in the environment.²³⁻²⁵⁾ At least humic acids accelerated the *cis/trans* isomerization of both isomers of cypermethrin in water. In the dark the *trans*-isomer was degraded more rapidly than the *cis*-isomer in slightly basic media. The hydrolysis study revealed that the *trans*-isomer was hydrolyzed 1.2-1.7 times more rapidly than the *cis*-isomer between pH 3 and pH 12.²⁶⁾ Although photodegradation of both isomers was also significant on soil surfaces, no distinct difference in the photolysis rate was observed, which was not the case with the photolysis in water. The photodegradation rate on soil surface was closely correlated with the contents of organic matter in soil, with the correlation coefficients being 0.94 to 0.97.

The comparative photolysis study of synthetic pyrethroids in distilled water has shown that the photodegradation rate decreased in the order of deltamethrin > cypermethrin > permethrin > fenvalerate, with the half-lives of 1.4 to 10 days.²⁷⁾ The photostability of cypermethrin, compared with that of deltamethrin, is attributed to the lower quantum yield and the lower rate of specific sunlight absorption.²⁷⁾

Based upon the identified products, the proposed photodegradation pathways of *PI* are shown in Fig. 5. The *cis*- and *trans-PI* were decomposed *via* pathways including 1*R*/1*S* and *cis/trans* isomerization of the cyclopropane ring, cleaving of the ester or diphenyl ether linkage, oxidation of the CHO group to the COOH group, hydration of the CN group to

the CONH₂ group, hydrolysis of the CONH₂ group to the COOH group, oxidative cleaving of the halogenated side chain, dehalogenation, and intramolecular cyclization to form γ - or δ -lactone. The product distribution depended upon a phase in which the reaction developed. The identified photoproducts in water were produced predominantly through 1*R*/1*S* or *cis/trans* isomerization and/or ester-cleaving reactions. At equilibrium, although the more thermodynamically stable *trans*-isomer was more predominant than the *cis*-isomer, the ratio of 1*R*/1*S* of isomerized photoproducts was close to unity. It seems that *cis/trans* or 1*R*/1*S* isomerization occurs through re-combination of the biradical which was formed *via* cleavage of the C-1-C-3 bond.²⁸⁾ The isomerization appears to proceed in part *via* a triplet excited state, since the reaction was considerably enhanced in the presence of acetone ($E_t=78$ kcal/mol) and benzophenone ($E_t=69$ kcal/mol), and efficiently quenched by 1,3-cyclohexadiene ($E_t=50$ kcal/mol) and molecular oxygen²²⁾ and so does the photolysis of deltamethrin.²⁸⁾ In the photolysis of deltamethrin, the $\alpha R/\alpha S$ epimerization has also been observed. In the present study the $\alpha R/\alpha S$ epimerization was not pursued because of the usage of a racemic mixture at the benzylic carbon atom. The photo-induced isomerization products were further degraded to *P6* and *PI4* by the scission of the acyl-oxygen bond. There existed more ester cleavage products in natural river and sea water than in distilled water. H¹⁴CN released on scission of the acyl-oxygen bond was promptly transformed at least in part to ¹⁴CO₂ by natural sunlight and hardly detected in water.

The photoproducts unique in 2% aqueous acetone were *P7*, *P8*, *P9*, *P10*, *P11* and *P20*. It appears that the former two photoproducts arise from oxidation of the halogenated side chain. *P9* and *P10* are formed *via* C-1-C-3 bond cleavage of the cyclopropane ring with subsequent rearrangement to the enol radical followed by intramolecular re-combination. These photochemical reactions were also observed in the photolysis of other pyrethroids such as pyrethrin I, allethrin, phthalthrin, dimethrin²⁹⁾ and vaporthrin.³⁰⁾ *P11* is formed by intramolecular cyclization of the dechlorinated

Fig. 5 Proposed photodegradation pathways of cypermethrin (P1).

■, Cyclopropyl- ^{14}C ; ▲, ^{14}CN ; ★, Benzyl- ^{14}C .

radical with the carboxyl group. P20 is formed *via* self-coupling of the α -cyano-3-phenoxybenzyl radicals which were derived by cleavages of the ester oxygen-benzyl carbon bond.³¹⁾

On soil surfaces the *cis/trans* or 1*R*/1*S* isomerization hardly occurred, and neither did the photolysis of permethrin.³²⁾ Probably, other reactions proceeded in preference to the isomerization in the solid phase.³³⁾

In contrast to the reductive dehalogenation of deltamethrin,²⁸⁾ the photo-induced dechlorination of cypermethrin and permethrin³²⁾ was quite limited. The chlorine-carbon bond of these pyrethroids appears to be relatively rigid, compared with the bromine-carbon bond.

The identified major photoproducts in water and on soil were also detected among the metabolites of P1 in plants,⁵⁻⁷⁾ soils,⁸⁻¹¹⁾

rats¹²⁻¹⁴⁾ and mice.^{15,16)} Major photoproducts such as P6 and P14 were biodegradable in nature and less toxic than P1 to killifish with 48 hr LC_{50} values of more than 10 ppm.³⁴⁾

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要 約

ピレスロイド系殺虫剤サイパーメスリンの水中および土壌表面における光分解

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水中の (1*R*, *cis*, α *RS*)- および (1*R*, *trans*, α *RS*)-サイパーメスリンに太陽光を照射すると, *cis* 異性体は *trans* 異性体に比べ約 1.4~1.7 倍速く分解し, *cis* 異性体の光分解半減期は蒸留水および 1 ppm 腐植酸水中で 2.3~2.6 日, 河川および海水中で 0.6~0.7 日, 2% アセトン水中で 0.5 日以内であった。土壌表面におけるサイパーメスリンの光分解速度は両異性体間で有意な差はなく, 3 種類の土壌における光分解半減期は 0.6~1.9 日であった。サイパーメスリンは太陽光照射条件下でも, シクロプロパン環の 1*R*/1*S* および *cis*/*trans* 異性化, エステルおよびジフェニルエーテル結合の開裂, CHO 基の COOH 基への酸化, CN 基の CONH₂ 基への水和, CONH₂ 基の COOH 基への加水分解, ハロゲン化側鎖の酸化的開裂, 脱ハロゲン化, 分子内環化および光無機化により分解された。