Photodecomposition of Sumithion® [O,O-Dimethyl-O-(3-methyl-4-nitrophenyl)-phosphorothioate]

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When Sumithion solutions in various solvents in air or deposits on silica gel chromatoplates were irradiated with UV light or sunlight, the following products were obtained; carboxysumithion, sumioxon, carboxysumioxon, 3-methyl-4-nitrophenol, 3-carboxy-4-nitrophenol and methyl parathion (solutions). A trace amount of sumithion S-isomer was found in aqueous methanol solution irradiated with UV light in nitrogen and water solution exposed to sunlight. The same photoproducts in almost same proportions were formed on both chromatoplates and leaf surfaces of bean plants. Two major products, carboxysumithion and sumioxon, and 3-methyl-4-nitrophenol were further degraded into more polar products, and finally into polymeric humic acids. Certain of carbamate and pyrethroid insecticides slightly accelerated the photodecomposition of Sumithion.

Sumithion is of low toxicity to mammals and quite biodegradable. It is revealed that Sumithion undergoes rapid metabolism in mammals,^{1~4)} insects,^{1,5)} plants^{1,6,7)} and micro-organisms,^{8,9)} through dealkylation, hydrolysis, oxidation and reduction.

In the field, the chemical applied will exist as deposits on soil particles, foliage or other surfaces and in water as solutions or suspensions. Here, it will receive light energy in the form of sunlight. Therefore, it is important to clarify the photodecomposition process of Sumithion for understanding its fate in the environment.

This paper deals with the decomposition of Sumithion by sunlight and ultraviolet (UV) light when it is deposited on silica gel chromatoplates and bean foliage, and dissolved in organic solvents and water. Also, the effect of several pesticide chemicals on the photodecomposition of Sumithion was examined.

MATERIALS AND METHODS

Chemicals. ¹⁴C-Sumithion, O,O-dimethyl-O-(3-methyl-4-nitrophenyl)-phosphorothioate, labeled at 3-methyl group and 3-methyl-4-nitrophenol labeled at 3-methyl group were prepared in this laboratory.¹⁰⁾

The specific activity of ¹⁴C-Sumithion and 3-methyl-4-nitrophenol was 3.16 mCi/mmole and 2.94 mCi/mmole, respectively. The radiochemical purity of each labeled preparation was greater than 99% based on thin-layer chromatography(tlc). The following chemicals were synthesized in this laboratory; Sumithion, sumioxon [O,O-dimethyl-O-(3-methyl-4-nitrophenyl)phosphate], Meobal® (3,4-xylyl N-methylcarbamate), Tsumacide® (*m*-tolyl N-methylcarbamate), Salithion® (2-methoxy-4H-1,3,2-benzodioxaphosphorin-2-sulfide), *d-trans* phenothrin (3-phenoxybenzyl *d-trans* chrysanthemumate) and *d-trans* tetramethrin (3,4,5,6-tetrahydropthalimido-methyl *d-trans* chrysanthemumate). Desmethylsumithion [O-methyl-O-hydrogen-O-(3-methyl-4-nitrophenyl)phosphorothioate], desmethylsumioxon [O-methyl-O-hydrogen-O-(3-methyl-4-nitrophenyl)phosphate] and sumithion S-isomer[O,S-dimethyl-O-(3-methyl-4-nitrophenyl)phosphorothiolate] were prepared by the methods reported previously.⁷⁾ 3-Carboxy-4-nitrophenol, 3-methoxycarbonyl-4-nitrophenol and methyl ester of carboxysumithion [O,O-dimethyl-O-(3-methoxycarbonyl-4-nitrophenyl)phosphorothioate] were prepared according to S. Hosokawa *et al.*⁴⁾ Piperonyl butoxide were supplied by Takasago Perfumery Co. (Tokyo, Japan). DDT (dichlorodiphenyltrichloroethane) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan).

Chromatography. Tlc was accomplished using silica gel 60F-254 (with fluorescent indicator) or silica gel 60 (without fluorescent indicator) precoated chromatoplates (20×20 cm) with 0.25 mm gel thickness (E. Merck, Darmstadt, Germany). Tlc solvent systems and *R_f* values for the photoproducts are given in

TABLE I. TLC SOLVENT SYSTEMS AND *R_f* VALUES FOR SUMITHION AND ITS PHOTOPRODUCTS

Compound	<i>R_f</i> values in indicated solvent systems					
	A	B	C	D	E	F
I Sumithion		0.92	0.75			
II Carboxysumithion		0.60	0.22		0.71	0.80
III Methylparathion		0.92	0.75			
IV Sumioxon	0.18	0.67	0.40	0.24		
V Carboxysumioxon		0.15	0.08			
VI 3-Methyl-4-nitrophenol	0.26	0.80	0.35		0.84	
VII 3-Carboxy-4-nitrophenol		0.37	0.05		0.64	0.75
VIII Sumithion S-isomer	0.24	0.75	0.47	0.50	0.81	

Solvent system A=*n*-hexane-acetone (4:1), B=toluene-ethyl acetate-acetic acid (5: 7: 1), C=toluene-acetic acid (7: 1), D=benzene-ethyl acetate (4:1), E=*n*-butanol-acetic acid-water (4: 1: 2), F=*n*-butanol-acetone-water (4: 5: 1).

Table I. The following methods were used for detection of resolved products; quenching of gel fluorescence when viewed under short and longwave length UV light; spraying with 20% (w/v) potassium hydroxide in methanol followed by heating at 110°C for 10 min and then overspraying with 1.0% diazotized sulfanilic acid (w/v, aqueous); spraying with 1.0% palladium chloride in 1N hydrochloric acid followed by heating for 10 min at 110°C; exposing to iodine vapor. Radioactive products were detected by radioautography and by means of a tlc radioscanner (Aloka model TRM-1B). For quantitation, radioactive gel regions were scraped free from the glass support into scintillation vials for liquid scintillation counting (lsc).

Preparative separation of degradation products was accomplished by silicic-acid column chromatography. Silicic acid (200 g, 100 mesh, Mallinckrodt, St. Louis, Mo. U.S.A.) was suspended in a mixture of toluene-ethyl acetate-acetic acid (5: 7: 1, v/v) to prepare a 50-cm column of 3 cm i.d. This column was developed with 500 ml of the same solvent system. Each fraction (10 ml) was examined by tlc and fractions of similar composition were combined.

Gas-liquid chromatography (glc) for analysis of Sumithion, sumioxon and methylparathion utilized glass columns (1.0 m × 5 mm i.d.) containing an equivalent mixture of 20% DC-QF-1 and 10% DC-200 on Chromosorb W(AW-DMCS, 60~80 mesh) for sumioxon, and 10% SE-30 on Chromosorb W(AW-DMCS, 100~120 mesh) for Sumithion and methylparathion, and a Shimadzu GC-3AF equipped with a flame ionization detector. A helium flow rate of 50 ml/min yielded retention times of 4.1 min for sumioxon, 5.4 min for methylparathion and 6.2 min for Sumithion at 197°C.

Spectroscopy. Infrared spectra (IR) were determined as a potassium bromide pellet or as a thin film on a sodium chloride crystal using a Hitachi infrared spectrometer (model EPI-G3). Nuclear magnetic

resonance spectra (NMR) were recorded as 5% solutions in CD₃OD on a Hitachi high resolution NMR spectrometer (R-20B). Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane and coupling constants (*J*) are expressed in cps.

Photodecomposition. ¹⁴C-Sumithion (110 μ Ci, 1 g) in 100 ml of acetone in a water-cooled, double-walled, fused-quartz immersion well was irradiated with a high pressure mercury vapor lamp (45W, Ushio Electric Co., Osaka, Japan) while air or nitrogen was bubble through the solution. Air was passed through saturated sodium hydroxide solution and then dried in a wash bottle of sulfuric acid prior to bubbling. Nitrogen was passed through a trap containing 10% pyrogallol in saturated sodium hydroxide solution followed by passing through a sulfuric acid bottle. ¹⁴C-Carbon dioxide produced was absorbed in a mixture of methyl cellosolve-ethanolamine (2: 1) and ¹⁴C-volatile products were trapped by a dry ice-acetone trap. Aliquots of the reaction mixture were withdrawn at intervals and analyzed by tlc. The reaction mixture remained was concentrated to dryness and the residual oil was fractionated on a silicic acid column. Fractions of similar composition were combined for further purification by repeated tlc in appropriate solvent systems. The radioactivity of the trapped products was determined by lsc. Equivalent experiments were conducted with; (1) 14-ppm Sumithion solution in water, (2) 0.1% Sumithion in 50% aqueous methanol, (3) 1.0% Sumithion in methanol, (4) 1.0% Sumithion in benzene.

¹⁴C-Sumithion solution in distilled water at 14 ppm was irradiated outdoors with natural sunlight in a 1-liter quartz flask for 3 to 28 hr (about 8 hr each day) during October, 1973 in Takarazuka, Hyogo, Japan. The dark-control flask covered with aluminum foil was similarly exposed to sunlight for 28 hr. Aliquots of the irradiated solution (10 ml) were lyophilized. The residue was dissolved in methanol and analyzed by tlc.

^{14}C -Sumithion or each of related compounds was individually spotted on a tlc plate (without fluorescent indicator) and then exposed to sunlight for 1 to 12 days or UV light for 5 to 180 min at a distance of 6 cm below a 172.5 watt high pressure UV lamp (Taika Kogyo, Osaka, Japan). The temperature of the chromatoplates irradiated with the UV lamp was elevated to about 30°C . The chromatoplates were developed with solvent systems B and C. Radioautography and cochromatography were used for product detection and tentative identification. To examine the effect of various pesticides on Sumithion photodecomposition, each of the pesticide chemicals ($51\mu\text{g}/30\mu\text{l}$ of methanol or chloroform) was spotted at the origin of the tlc plate and ^{14}C -Sumithion ($5.1\mu\text{g}/30\mu\text{l}$ of methanol) was overspotted in the same position. The chromatoplates were exposed to sunlight for 2 days and then developed by the solvent system B. The percent of individual product was determined by Isc of radioactive gel regions.

Photodecomposition of Sumithion deposits on bean leaves. Bean seedlings (*Phaseolus vulgaris*) were used when the plants were 12 to 14 days old. ^{14}C -Sumithion ($84.5\mu\text{g}$) in $50\mu\text{l}$ of ethanol was uniformly applied to the upper surface of each primary leaf (12.5cm^2) by a microsyringe. Immediately after treatment, the plants were placed outside in an unshaded, unprotected area for about 8 hr each day. These studies were made in Takarazuka, Hyogo, Japan, during November, 1973. The residual radioactivity after various time intervals was removed by washing with two separate 50-ml portions of methanol. The leaves after washing were frozen with liquid nitrogen and then extracted twice with 10 ml of methanol. Aliquots of the methanol washings and methanol extracts were subjected to Isc for the determination of the radioactivity and to tlc for the analysis of the radioactive products. The extract

residues were combusted using an oxidizer (Tri-carb automatic sample oxidizer, Packard Instrument Co., U.S.A.) prior to radioanalysis.

RESULTS

Photodecomposition products from irradiation of ^{14}C -Sumithion in various solutions with UV light

Irradiation of ^{14}C -Sumithion in various solutions with UV light in air and nitrogen resulted in a considerable variation in the rate of photodecomposition. The half-life of Sumithion under the conditions studied is listed in Table II. The greatest rate of degradation was found in water solution in air as well as in nitrogen. After 5-min irradiation, 93% of Sumithion was disappeared in air and 87% was lost in nitrogen. The half-life of Sumithion in 50% aqueous methanol was 20

TABLE II. RATE OF PHOTODECOMPOSITION OF SUMITHION IN VARIOUS SOLUTIONS IRRADIATED WITH UV LIGHT

The values in parentheses are percentage of Sumithion decomposed at a time indicated.

Solvent	Concentration	Half-life of Sumithion(min)	
		Air	Nitrogen
Water	14 ppm	< 5(93%)	< 5(87%)
50% Aqueous methanol	0.1%(w/v)	20	60
Acetone	1.0%(w/v)	50	100
Methanol	1.0%(w/v)	100	> 240(44%)
Benzene	1.0%(w/v)	> 360(18%)	> 360(12%)

TABLE III. PHOTODECOMPOSITION OF ^{14}C -SUMITHION IN ACETONE SOLUTION IRRADIATED WITH UV LIGHT IN AIR

Photoproduct	% of recovered radiocarbon as indicated products		
	Irradiation time (min)		
	45	90	180
I Sumithion	54.7	28.3	7.2
II Carboxysumithion	14.3	28.8	37.8
III Methylparathion	0	0	< 0.1
IV Sumioxon	< 0.1	0.7	< 0.1
V Carboxysumioxon	0	3.2	5.3
VI 3-Methyl-4-nitrophenol	0	< 0.1	< 0.1
VII 3-Carboxy-4-nitrophenol	0	2.4	3.8
Carbon dioxide	2.6	5.5	12.6
Unknowns (more than 5 spots and Origin)	13.3	16.4	17.3
Total	84.9	85.3	84.0

min in air and 60 min in nitrogen. The degradation rate in both acetone and methanol solutions was considerably rapid and approximately 2 times faster in air than in nitrogen. The least rate of degradation was found in benzene solution in both air and nitrogen. The rate of photodecomposition is greatly dependent on the solvents used and the presence or absence of air.

In each case, the major photodecomposition products were analyzed by tlc and identified by comparison with the authentic compounds using various criteria. When ^{14}C -Sumithion in acetone solution was irradiated with UV light in air, a number of radioactive products were detected by tlc in solvent systems B and C. Among them, six major radioactive and one non-radioactive products were identified. The chemical nature and percentage of the products are listed in Table III. The main product (II) which had a lower tlc R_f than the parent compound (I) in solvent systems B and C was purified by silicic-acid column chromatography and repeated tlc. This product was identified as carboxysumithion[O,O-dimethyl-O-(3-carboxy-4-nitrophenyl)phosphorothioate] based on the following evidence: NMR (CD_3OD) $\delta=3.82$ (two methoxy 6H, d, $J=14$ cps), $\delta=7.15\sim 8.05$ (aromatic 3H, m); IR (direct), 3000~2500 and 1700 (COOH), 1570 and 1370 (NO_2), 1215 (P-O-aryl), 1030 cm^{-1} (P-O-alkyl); positive to palladium chloride test (P=S); methylation (diazomethane in 50% methanol in ether)

produced methyl ester of carboxysumithion (tlc criterion, $R_f=0.6$ in 4:1 ethyl acetate-chloroform). The presence of methylparathion (III) was confirmed by glc examination of the reaction mixture in comparison with the authentic sample. However, its amount was negligible. Product IV was found to be sumioxon based on glc and tlc cochromatography with the authentic compound in solvent systems B, C and D. Product V was isolated by column chromatography and repeated tlc. This product was assigned the structure O,O-dimethyl-O-(3-carboxy-4-nitrophenyl) phosphate (carboxysumioxon) based on the following evidence. The NMR spectrum was similar to that of carboxysumithion except the different coupling constant of methoxy groups; NMR (CD_3OD), $\delta=3.88$ (two methoxy 6H, d, $J=11$ cps), $\delta=7.23\sim 8.05$ (aromatic 3H, m). This product(V) was obtained by the oxidation of carboxysumithion (product II) with *m*-chloroperbenzoic acid in dichloromethane. Methylation of this product (V) with diazomethane in 50% methanol in ether produced 3-methoxycarbonyl-4-nitrophenol which was identified by cochromatography with the authentic compound ($R_f=0.5$ in 2:1 benzene-ethyl acetate). A minor product (VI) was found to be 3-methyl-4-nitrophenol. Product VII was identified as 3-carboxy-4-nitrophenol on the basis of identical tlc behavior and IR spectrum which showed hydroxy absorption at 3600, carbonyl at 3200~2500 and 1700, and nitro

TABLE IV. PHOTODECOMPOSITION OF ^{14}C -SUMITHION IN WATER SOLUTION EXPOSED TO SUNLIGHT

Photoproduct	% of recovered radiocarbon as indicated products			
	3	Exposure time (hr)		dark (28 hr)
		11	28	
I Sumithion	82.9	54.3	19.7	97.9
II Carboxysumithion	1.6	7.3	17.0	0.5
IV Sumioxon	0.7	1.8	3.3	0.4
VI 3-Methyl-4-nitrophenol	0.9	2.4	3.9	0.3
VII 3-Carboxy-4-nitrophenol	1.0	1.8	3.1	0
VIII Sumithion S-isomer	1.3	3.0	3.9	0.4
Unknowns	7.4	17.9	25.1	0.1
Origin (humic acids)	3.8	11.7	25.7	0.6
Total	99.6	99.7	99.3	100.0

at 1580 and 1350 cm^{-1} . The product remained at the origin in tlc solvent systems B and C was isolated by column chromatography. This product has the following characteristics: mp, more than 300°C (dec.); IR, 3500, 1700, 1200 and 800 cm^{-1} (broad); soluble in 1 N sodium hydroxide and in methanol but insoluble in water and nonpolar organic solvents. These properties were very similar to those of polymeric humic acids produced from 2,4-dichlorophenoxyacetic acid.¹¹⁾ Thus, the product at the origin seems to be a sort of polymeric humic acids. ^{14}C -Carbon dioxide was found as a photodecomposition product, amounting to 2.6% at 45-min irradiation and 12.6% at 3-hr irradiation. Also, the same products in almost same proportions were present in water, 50% aqueous methanol, methanol and benzene solutions on irradiation with UV light in air, although the rate of photodecomposition

varied with the solvents. Therefore, similar photochemical reactions seem to occur in various solutions of Sumithion on irradiation with UV light in air.

Under nitrogen, characteristic photoproducts which were obtained in the presence of air were not produced in various solutions of Sumithion on irradiation with UV light. In each case, major products were polymeric humic acids remaining at the origin in tlc solvent systems B and C. In addition to these products, only trace amounts of sumithion S-isomer and 3-methyl-4-nitrophenol were detected in 50% aqueous methanol in nitrogen. Sumithion S-isomer was identified by cochromatography with the authentic compound in solvent systems A, B and C.

Photodecomposition of ^{14}C -Sumithion in water solution exposed to sunlight

TABLE V. PHOTODECOMPOSITION OF ^{14}C -SUMITHION ON SILICA GEL CHROMATOPLATES IRRADIATED WITH UV LIGHT

Photoproduct	% of recovered radiocarbon as indicated products			
	5	Irradiation time (min)		180
		15	60	
I Sumithion	65.4	46.4	28.5	9.0
II Carboxysumithion	3.7	4.3	2.7	1.4
IV Sumioxon	5.5	4.6	3.4	2.7
V Carboxysumioxon	0.9	1.0	0.8	0.2
VI 3-Methyl-4-nitrophenol	2.8	1.8	1.2	0.4
Unknowns	1.4	0.1	0.9	0.1
Origin (humic acids)	10.0	13.0	9.2	6.2
Total	89.7	71.1	46.7	19.8

TABLE VI. PHOTODECOMPOSITION OF ^{14}C -SUMITHION ON SILICA GEL CHROMATOPLATES EXPOSED TO SUNLIGHT

Photoproduct	% of recovered radiocarbon as indicated products			
	1	Days after application		12
		3	6	
I Sumithion	85.3	73.3	58.9	35.0
II Carboxysumithion	0.9	2.0	3.0	4.6
IV Sumioxon	1.8	3.1	5.5	7.4
V Carboxysumioxon	0.4	1.1	2.0	2.8
VI 3-Methyl-4-nitrophenol	1.5	1.9	2.0	2.0
VII 3-Carboxy-4-nitrophenol	0	1.2	2.8	4.2
Unknowns	1.9	1.7	1.6	1.9
Origin (humic acids)	4.2	6.1	6.8	10.9
Total	96.2	90.4	82.7	61.3

On exposure of ^{14}C -Sumithion to sunlight in water solution at 14 ppm, the parent compound disappeared rapidly, degrading into more than five products. Table IV shows the percentage of the initial radioactivity which was recovered as individual degradation products at various intervals after exposure to sunlight. In this case, five of major degradation products were identified, by cochromatography with the authentic compounds, as carboxysumithion (main), sumioxon, sumithion S-isomer, 3-methyl-4-nitrophenol and 3-carboxy-4-nitrophenol. These products except sumithion S-isomer were obtained in the solutions irradiated with UV light in air. Carboxysumioxon was not formed under the condition tested. Sumithion S-isomer was found as a minor product in aqueous methanol on irradiation with UV light in nitrogen, but not found in air. Therefore, on exposure of Sumithion to sunlight in water, it underwent several photochemical reactions which occurred in the solutions irradiated with UV light in both air and nitrogen. When held in the dark, Sumithion suffered very little degradation in water solution. Thus, it is apparent that sunlight actually has a significant effect on the degradation of Sumithion in water.

Photodecomposition of ^{14}C -Sumithion deposits on silica gel chromatoplates exposed to UV light or sunlight

Sumithion suffered very rapid decomposition on silica gel chromatoplates exposed to sunlight or UV light. The half-life of Sumithion was approximately 15 min with UV light and around 6 days with sunlight as shown in Tables V and VI. After 15, 60 and 180-min irradiation with UV light, the percentage recoveries were 71.1, 46.7, and 19.8%, respectively, for the total radiocarbon of which 46.4, 28.5 and 9.0%, respectively, was accounted for as Sumithion (Table V). When exposed to sunlight, Sumithion was readily lost from the treated chromatoplates. After 3, 6 and 12 days, 90.4, 82.7 and 61.3% of the applied radiocarbon, respectively, were recovered and 73.3, 58.9 and 35.0%, respectively, were re-

covered as Sumithion (Table VI). The irradiation of ^{14}C -Sumithion with UV light produced at least four products, including ones cochromatographing with carboxysumithion, sumioxon, carboxysumioxon and 3-methyl-4-nitrophenol. These products and 3-carboxy-4-nitrophenol were also formed during the exposure of ^{14}C -Sumithion to sunlight. Sumioxon and carboxysumithion were, in each case, found as major products. Accordingly, the photoproduct pattern on silica gel chromatoplates was similar using sunlight or UV light irradiation except for 3-carboxy-4-nitrophenol produced by sunlight irradiation.

Photodecomposition of carboxysumithion, sumioxon and 3-methyl-4-nitrophenol

Two major photoproducts, carboxysumithion and sumioxon, were preparatively isolated by tlc after irradiation of ^{14}C -Sumithion with UV light on silica gel chromatoplates. These two products as well as ^{14}C -3-methyl-4-nitrophenol were individually spotted on chromatoplates and then irradiated with UV light or sunlight. The half-life of sumioxon, carboxysumithion and 3-methyl-4-nitrophenol was 4.3, 1.8 and 3.9 days, respectively, with sunlight and 3.9, 0.9 and 3.7 hr, respectively, with UV light. Thus, they were less persistent than Sumithion on exposure to sunlight.

Carboxysumithion was degraded into unknowns and polymeric humic acids on chromatoplates by irradiation with both UV light and sunlight. Sumioxon produced 3-methyl-4-nitrophenol and 3-carboxy-4-nitrophenol in addition to unknowns and polymeric humic acids on exposure to sunlight. On irradiation with UV light, sumioxon yielded carboxysumioxon in a very small amount except unknowns and polymeric humic acids. 3-Methyl-4-nitrophenol was mostly degraded into unknowns and polymeric humic acids by both UV light and sunlight irradiation.

When carboxysumithion in acetone solution was irradiated with UV light, it gave carboxysumioxon, 3-carboxy-4-nitrophenol and methyl parathion. Sumioxon yielded carboxysumioxon, 3-methyl-4-nitrophenol and 3-carboxy-

4-nitrophenol under the same condition. Thus, it is evident that sumioxon, carboxysumithion and 3-methyl-4-nitrophenol were further degraded into more polar products and finally into polymeric humic acids by irradiation with both UV light and sunlight.

Exposure of ^{14}C -Sumithion deposits on bean leaves to sunlight

As shown in Table VII, when ^{14}C -Sumithion was applied to bean leaves, the radiocarbon applied was rapidly lost from leaf surfaces. After 1, 3, 6 and 12 days, the recovery of the radiocarbon applied was 74.1, 35.9, 26.4 and 19.5%, respectively, and 45.0, 11.1, 6.2 and 1.8%, respectively, were taken up into the surface wash fractions which included at least four products. Major four products were identified, by cochromatography with the authentic compounds, as carboxysumithion, sumioxon, 3-methyl-4-nitrophenol and 3-carboxy-4-nitrophenol. The relative amount of these products was shown in Table VIII. The

same products were formed during exposure of ^{14}C -Sumithion deposits to sunlight and UV light on silica gel chromatoplates. Although the radiocarbon applied was more rapidly lost on leaf surfaces than on chromatoplates, the product pattern on both silica gel chromatoplates and bean leaves was quite similar.

In the methanol extracts, after 1, 3 and 6 days, 27.8, 23.7 and 19.1% of the radiocarbon applied, respectively, were recovered and Sumithion was accounted for 20.9, 11.3 and 2.7% of the applied radiocarbon, respectively. In addition to this, sumioxon and 3-methyl-4-nitrophenol were found in very small amounts in the methanol extracts.

Effect of various pesticides on Sumithion photodecomposition

The photodecomposition of Sumithion on silica gel chromatoplates was slightly altered by some pesticide chemicals and the product ratio was also changed as shown in Table IX. The carbamate insecticides, Meobal and Tsumacide, slightly reduced the recovery of undecomposed Sumithion from 69.4% to 45.1 and 50.3%, respectively. They increased the formation of sumioxon, unknowns and polymeric humic acids in comparison with Sumithion alone. Also, pyrethroids such as tetramethrin and phenothrin slightly accelerated Sumithion photodecomposition to yield 3-methyl-4-nitrophenol and unknowns in relatively high amounts. On the other hand, the photodecomposition rate was not altered nor was

TABLE VII. DISTRIBUTION OF RADIOCARBON AT VARIOUS DAYS AFTER APPLICATION OF ^{14}C -SUMITHION TO BEAN LEAVES

Fraction	Recovery of applied radiocarbon, %			
	Days after application			
	1	3	6	12
Surface wash	45.0	11.1	6.2	1.8
Methanol extract	27.8	23.7	19.1	16.8
Residues	1.3	1.1	1.1	0.9
Total	74.1	35.9	26.4	19.5

TABLE VIII. PHOTODECOMPOSITION PRODUCTS FORMED ON BEAN LEAVES TREATED WITH ^{14}C -SUMITHION ON EXPOSURE TO SUNLIGHT

		% of recovered radiocarbon as indicated products			
Photoproduct		Days after application			
		1	3	6	12
I	Sumithion	39.7	5.0	0.5	0.3
II	Carboxysumithion	0.4	0.4	0.4	0.1
IV	Sumioxon	1.2	0.7	0.4	0.1
VI	3-Methyl-4-nitrophenol	0.5	0.3	0.2	0
VII	3-Carboxy-4-nitrophenol	0	0	0.2	0.1
	Unknowns	1.6	1.9	1.3	0.2
	Origin (humic acids)	1.6	2.3	3.1	1.2
	Total	45.0	11.1	6.2	1.8

TABLE IX. EFFECT OF VARIOUS PESTICIDES ON THE PHOTODECOMPOSITION OF ^{14}C -SUMITHION EXPOSED TO SUNLIGHT ON SILICA GEL CHROMATOPLATES

Pesticide chemical	% of recovered radiocarbon as indicated products							Total
	I	II	IV	V	VI	Unknowns	Origin	
Sumithion alone	69.4	2.0	2.5	1.4	2.5	4.6	7.4	89.8
+ DDT	63.1	1.8	3.1	1.7	2.7	6.4	8.1	86.9
+ Meobal	45.1	3.4	9.5	2.7	3.0	10.0	14.1	87.8
+ Tsumacide	50.3	3.3	5.1	2.0	2.4	9.3	14.3	86.8
+ Salithion	62.1	1.7	1.9	0.9	2.7	8.8	13.6	91.7
+ Sulfoxide	58.5	3.0	2.8	0.9	2.5	11.7	10.3	89.7
+ Piperonyl butoxide	56.8	3.2	2.5	1.1	3.7	14.7	7.5	89.5
+ Tetramethrin	46.6	3.8	4.8	1.8	6.1	13.8	9.5	86.2
+ Phenothrin	44.4	3.9	4.0	1.9	6.4	13.2	9.8	83.6

I=Sumithion, II=Carboxysumithion, IV=Sumioxon, V=Carboxysumioxon, VI=3-Methyl-4-nitrophenol, Origin=polymeric humic acids.

FIG. 1. Photodecomposition Pathways of Sumithion.

the production ratio changed by DDT and Salithion. Sulfoxide and piperonyl butoxide did not exhibit a significant effect on Sumithion degradation.

DISCUSSION

Extensive studies on the photodecomposition of organophosphorus insecticides are quite limited. However, it is known that parathion is converted into paraoxon and S-ethyl isomer of parathion on irradiation with UV light and sunlight.¹²⁾ In addition, J. R. Grunwell and R. H. Erickson¹³⁾ reported that the photodecomposition of parathion in aqueous solutions gave O,O,S-triethylthiophosphate as the major product, lesser amounts of O,O,O-triethylthiophosphate, triethylphosphate and paraoxon. J. R. Pardue *et al.*¹⁴⁾ indicated that diazinon yielded O,O-diethyl-O-[2-(2'-

hydroxy-2'-propyl)-4-methyl-6-pyrimidinyl] phosphorothioate (hydroxydiazinon) on irradiation with UV light. This product as well as the oxygen analog of diazinon and 2-isopropyl-4-methylpyrimidin-6-ol were also found in the diazinon field-sprayed kale.

When solutions or residual deposits of Sumithion were irradiated with UV light or sunlight in the presence of air, it underwent several photochemical reactions. The initial reactions are of three types; (1) oxidation of the P=S group to P=O group, (2) oxidation of *m*-methyl group to carboxyl group, (3) cleavage of P-O-aryl linkage to give corresponding phenols. In addition, isomerization of Sumithion to sumithion S-isomer occurred in aqueous methanol solution irradiated with UV light and water solution exposed to sunlight. The photodecomposition pathways of Sumithion deduced from the identified photoproducts are shown

in Fig. 1. The main photochemical reaction which initially took place in various solutions of Sumithion was the formation of carboxy-sumithion, which was further degraded into carboxysumioxon, 3-carboxy-4-nitrophenol and methylparathion, and finally into polymeric humic acids. When residual deposits of Sumithion were irradiated with UV light or sunlight, sumioxon and carboxysumithion were obtained as major products. Sumioxon was subsequently degraded into carboxysumioxon, 3-carboxy-4-nitrophenol and 3-methyl-4-nitrophenol, but, unlike solutions, carboxysumithion yielded unknowns and polymeric humic acids. At least a significant part of Sumithion photoproducts was finally converted to polymeric humic acids. Also, Sumithion deposits on leaf surfaces underwent oxidation of $P=S$ to $P=O$, oxidation of *m*-methyl to carboxyl and $P-O$ -aryl cleavage like deposits on silica gel chromatoplates. Thus, Sumithion residues in the environment appear to suffer, at least in part, these photochemical reactions observed in this study.

It is revealed that Sumithion is rapidly metabolized in mammals to give desmethylsumithion, desmethylsumioxon, 3-methyl-4-nitrophenol and its conjugates as major metabolites.¹⁻⁴⁾ In and on plants,^{1,6,7)} Sumithion underwent oxidation of $P=S$ to $P=O$, $P-O$ -aryl cleavage, $P-O$ -alkyl cleavage and isomerization to sumithion *S*-isomer. Although carboxysumithion was found on the leaf surface of the bean plants treated with Sumithion, it was not found in previous studies.^{1,6,7)} Cleavage of $P-O$ -alkyl linkage did not occur in the present study. The differences in these studies may be due in part to the experimental conditions. Sumithion was reduced to amino sumithion [*O*, *O*-dimethyl-*O*-(3-methyl-4-aminophenyl) phosphorothioate] in microorganisms.^{8,9)} However, in this study, reduction of nitro group to amino group was not observed as a photochemical reaction of Sumithion.

Contact between various pesticide chemicals occurs in the environment due directly to application of mixture of compounds or indirectly to contamination within the environment.

Therefore, there is a possibility of a photosensitizing pesticide chemical altering the persistence of Sumithion residues on treated crops and in the environment. G. W. Ivie and J. E. Casida¹⁵⁾ reported that rotenone acts as a photosensitizer to accelerate the photodecomposition of various types of insecticide chemicals, including Sumithion. Furthermore, they indicated that Sumithion is highly susceptible to photosensitization and several of pesticides tested have photosensitizing activity against Sumithion.¹⁶⁾ In this study, the carbamate and pyrethroid insecticides slightly accelerated the photodecomposition of Sumithion. It seems that certain of these interactions occur on plant foliage exposed to sunlight.

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