was observed when the suggested experimental procedures were followed.

Analytical Results. Values obtained from the individual analyses of 350 leaf disks, grouped in seven replicates of 50, ranged from 4.12 to 4.93 $\mu g/cm^2$; the overall average was 4.62 $\mu g/cm^2$. In contrast, three values obtained with the official AOAC method, where 50 disks constituted a single sample, were 4.05, 4.42, and 4.95, and the overall average was 4.47 $\mu g/cm^2$. These results validate the reliability of this rapid method. The significance of individual leaf analyses is well demonstrated in previous papers (Chiba, 1973; Chiba et al., 1973).

In this paper, the amount of carbaryl has been expressed as either $\mu g/cm^2$ of leaf surface or $\mu g/20$ mL of alkaline solution for convenience. If ppm values are necessary, conversion is simple; 1 $\mu g/cm^2$ is approximately equivalent to 100 $\mu g/g$ of leaf (Chiba and Northover, 1977).

CONCLUSION

The speed and simplicity of this method of analysis for carbaryl make it useful for studying spray distribution, fate of spray deposits, and wash effect of rainfall (Williams, 1961) on orchard trees. With it, an analyst can readily analyze 250 leaf disks in a day. Where a colorimeter or spectrophotometer is not available, semiquantitative determination is possible by color matching which is an added advantage. A portable comparator is also a useful tool in the field. Deposits on one side of leaf only can also be measured by wiping off the other side of the leaf before removing the disk (Herne and Chiba, 1975; Chiba et al., 1978). At present this method is only suitable for measuring carbaryl deposits on leaves and is not applicable for other materials such as foodstuffs.

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Fate of *O*-[4-[(4-Chlorophenyl)thio]phenyl] *O*-Ethyl *S*-Propyl Phosphorothioate (RH-0994) in Cotton

Don L. Bull* and G. Wayne Ivie

After a single topical application to individual cotton leaves of field-grown cotton, residues of [^{14}C]RH-0994 [*O*-[4-[(4-chlorophenyl)thio]phenyl] *O*-ethyl *S*-propyl phosphorothioate] and its intact ester derivatives, either on the leaf surface or within the leaf, were essentially depleted at 14-days posttreatment. Studies of the distribution of radioactive residues in cotton plants after 10 spray applications of [^{14}C]RH-0994 [1.12 kg ha^{-1} (application)$^{-1}$] at 5-day intervals indicated that appreciable levels of radioactive material, including the parent compound and its intact ester derivatives, accumulated on foliage that was present during sprays. Mature cottonseed and lint from bolls that opened after treatments had been stopped also contained ~2 ppm of [^{14}C]RH-0994 equivalents; however, results of solvent extraction studies suggested that these residues did not include RH-0994 or its intact ester derivatives. Radioactive products of [^{14}C]RH-0994 identified in plants included the sulfoxide and sulfone derivatives of the intact ester, produced by oxidation of the thioether sulfur, and three substituted phenols, which were produced by hydrolysis of the respective esters and were present in both free and conjugated forms.

The experimental organophosphorus (OP) insecticide *O*-[4-[(4-chlorophenyl)thio]phenyl] *O*-ethyl *S*-propyl phosphorothioate (RH-0994, I) is being developed for possible use in controlling *Heliothis* spp. pests of cotton. Technical-grade RH-0994 is a dark amber-colored oil that is essentially insoluble in water but is soluble in most organic solvents. The acute oral toxicity (LD_{50}) to rats is 320 mg/kg and the acute dermal toxicity (LD_{50}) to rabbits is 1180 mg/kg (Hurt, 1980). This report describes studies of the fate of RH-0994 after application to cotton plants.

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EXPERIMENTAL SECTION

Chemicals. [^{14}C]RH-0994 (I), formulated as an emulsifiable concentrate (4 EC, specific activity 3.23 mCi/g of active ingredient (AI); radiochemical purity of AI was 91%), was supplied by the Rohm and Haas Co., Spring House, PA. The molecule was uniformly radiolabeled in the *P*-*O*-phenyl moiety. Also provided were unlabeled, pure samples of technical-grade RH-0994 as well as samples of the potential metabolites: II, *O*-[4-[(4-chlorophenyl)sulfinyl]phenyl] *O*-ethyl *S*-propyl phosphorothioate; III, *O*-[4-[(4-chlorophenyl)sulfonyl]phenyl] *O*-ethyl *S*-propyl phosphorothioate; IV, 4-[(4-chlorophenyl)thio]-phenol; V, 4-[(4-chlorophenyl)sulfinyl]phenol; VI, 4-[(4-chlorophenyl)sulfonyl]phenol. Structures of these chem-

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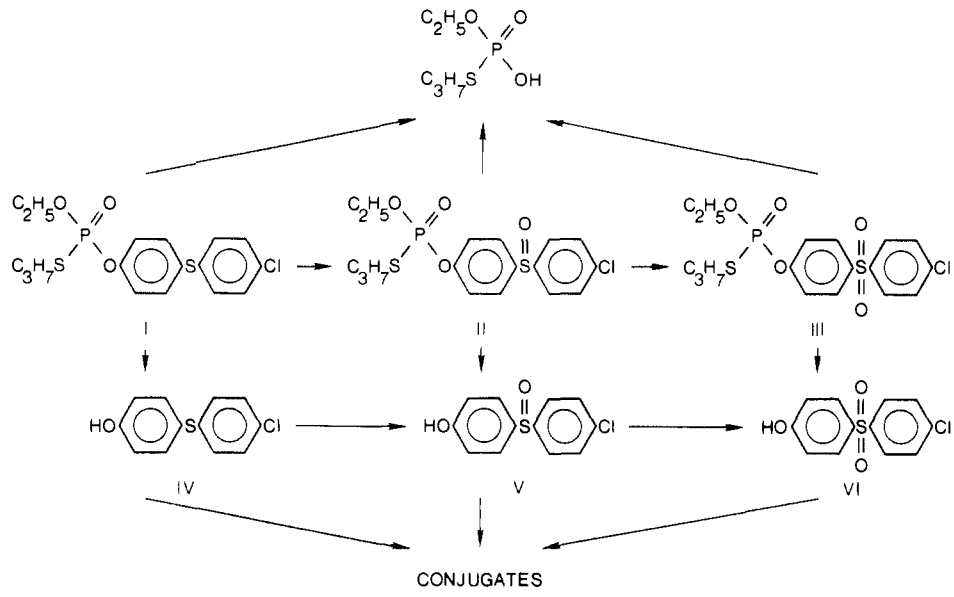

Figure 1. Proposed pathway for the formation of metabolites of RH-0994 (numbered compounds) detected in cotton plants.

icals are shown in Figure 1.

The methyl ethers of the three phenolic compounds (IV, V, and VI) were synthesized for use as analytical standards by allowing an acetone solution of each phenol to react with an excess of diazomethane. This reaction went to completion, and after removal of excess diazomethane, further purification was not necessary. Structures of these methyl ethers were confirmed by mass spectral analyses (vide infra); they are designated VII, VIII, and IX, respectively.

Plant Studies. Cotton plants of the Stoneville 213 variety were grown at College Station, TX, in an irrigated field with the customary procedures, except that no insecticides were applied for pest control.

Individual cotton leaves were used for short-term studies of the absorption and metabolism of [^{14}C]RH-0994. Fully expanded leaves were each treated in situ with 100 μg of AI in 100 μL of an aqueous emulsion of the radioactive EC formulation. The solutions were applied with a micropipet and spread as uniformly as possible over the upper surface of the leaf.

Triplicate samples of treated leaves were analyzed at the specified times posttreatment to determine the distribution and nature of radioactive materials. Unabsorbed radioactivity was recovered by rinsing leaves thoroughly with methanol (external rinse). Rinsed leaves were then homogenized with a mixture (9:1 v/v) of acetone and water (50 mL/leaf). Tissue solids were removed via centrifugation and reextracted twice by homogenization with 50-mL portions of acetone (internal extract). Then the extracted tissues were air-dried and analyzed via oxygen combustion (Bull and Ivie, 1976) to measure bound radiocarbon (unextractable). External rinses were radioassayed, reduced under vacuum to a convenient volume, and then analyzed (vide infra) by thin-layer chromatography (TLC). Combined fractions from internal extracts were radioassayed, and then the acetone was removed under vacuum. The remaining aqueous portion was partitioned twice against methylene chloride (1:5 v/v), and the aqueous and organic fractions were separated and radioassayed. The latter fractions were dried over anhydrous sodium sulfate, concentrated, and then analyzed with TLC. Aqueous fractions were lyophilized and were then dissolved in a solution of 1 N HCl, sealed in glass ampules, and heated at 100 °C for 4 h. After this hydrolysis, samples were adjusted to ca. pH 1 and partitioned twice against methylene chloride (1:5 v/v). The fractions were separated and radioassayed, and the organic portion was analyzed with TLC as described.

A separate study was conducted to determine the nature and distribution of residues on cotton plants after a season-long schedule of spray applications that was designed to approximate the anticipated maximum use of RH-0994 in insect control. An isolated plot (1.7 m^2) of cotton was sprayed 10 times at ~5-day intervals with an aqueous emulsion of the EC formulation of [^{14}C]RH-0994 at a rate equivalent to 1.12 kg of AI in 93.5 L of water/ha (187 mg of AI/application). Treatments were initiated July 24 at the onset of fruiting and terminated Sept 5, 1979, just before the first bolls began to open. (The treated cotton was enclosed in a screened cage to prevent infestation by insects).

Seed cotton was collected from open bolls first on Sept 25 and then again on Nov 2 after all bolls had opened. All foliage and immature fruit were manually removed from the treated cotton on Oct 1. At the same time, all of the leaves, fruit, etc. shed by the treated plants were collected, as were samples of native grass growing in the cage. On Nov 2, regrowth foliage was removed from the plants, and then all of the stalks and roots were collected.

The different samples were held and processed separately. Except for the seed cotton, all plant materials were dried in an oven for 24 h at 50 °C and then ground in a Wiley mill to pass a 20-mesh screen. Lint and seed were separated with a laboratory roller gin. Subsamples of seed were delinted with concentrated sulfuric acid, washed thoroughly, dried, and then ground either whole or after separation of hull and kernel. All these samples were analyzed by oxygen combustion (Bull and Ivie, 1976). In addition, subsamples of all plant materials except lint and seed were soaked for 48 h in a mixture of acetone and water (9:1 v/v) and then extracted and analyzed as described for individual leaves.

In attempts to identify radioactive residues in seeds, ground samples were extracted (8 h) in a Soxhlet apparatus first with hexane and then again with acetonitrile. Subsamples of the dried extracted residues were futher extracted by homogenization with methanol and hydrochloric acid (99:1 v/v) or with a 4% ethanolic solution of sodium hydroxide. Other subsamples of seeds were planted in moist sand, and the seedlings that developed were harvested just before they began to form true leaves. About

Table I. Thin-Layer Chromatographic Behavior of RH-0994 and Certain of Its Derivatives

compd	R_f value in indicated system[a,b]			
	A	B	C	D
I (RH-0994)	0.86	0.83	0.55	0.81
II	0.62	0.65	0.27	0.41
III	0.78	0.78	0.34	0.69
IV	0.52	0.70	0.23	0.77
V	0.23	0.34	0.10	0.29
VI	0.30	0.47	0.12	0.40
VII	0.68	0.91	0.85	0.91
VIII	0.42	0.74	0.46	0.73
IX	0.60	0.84	0.58	0.83

[a] Precoated silica gel plates used with the following solvent mixtures (v/v): (A) benzene and methanol, 9:1; (B) chloroform, hexane, and acetone, 6:3:2; (C) heptane, chloroform, and methanol, 9:4:1; (D) benzene, ethanol, and acetic acid, 93:7:1. [b] Compounds VII–IX are the respective methyl ethers of compounds IV–VI; all others are identified in Figure 1.

half of these seedlings were separated into cotyledons and petiole plus root, dried, and analyzed via oxygen combustion. The remaining seedlings were extracted and analyzed as described for individual mature leaves. Lint was extracted (8 h) in a Soxhlet apparatus with acetone.

Core samples (0–22.5 cm deep) of soil were taken periodically from the treated plot and then divided into 7.5-cm sections, dried, and analyzed for radiocarbon content by combustion at 1000 °C in an oxygen atmosphere as described by Bull et al. (1970).

Analytical Methods. Thin-layer chromatography of different samples was done with glass plates precoated with silica gel (silica gel 60 F-254, 0.25 mm thick; EM Laboratories, Inc., Elmsford, NY). Different combinations of solvent mixtures described in Table I were used for two-dimensional analyses of appropriate samples. Identifications of resolved compounds were based on the coincidence of radioactive areas, located by autoradiography with X-ray film, with authentic standards detected under ultraviolet light. (R_f values in different solvent systems of available analytical standards are listed in Table I.)

Radioactive areas scraped from plates as well as aliquots of different extracts were quantified by liquid scintillation counting; appropriate corrections were made for quenching.

The structures of the aforementioned methyl ethers of the three phenolic derivatives of RH-0994 were confirmed by mass spectral analyses (Bull and Ivie, 1976) conducted with a Varian-Mat-CH-7 spectrometer coupled with a Varian 2700 gas chromatograph and a 620 L Varian computer (Varian Associates, Palo Alto, CA). These methyl ethers were used as secondary standards to support initial identifications of the parent phenols (IV, V, and VI) in certain extracts of treated plants. For this, methylene chloride fractions containing mixtures of different degradation products of RH-0994 were extracted with 0.1 N sodium hydroxide to recover the phenols. The latter fraction was acidified to ca. pH 1 and then reextracted with methylene chloride to recover the free phenols in relatively pure form. The methylene chloride was removed under vacuum, and then a solution of diazomethane in ether was added and allowed to react for several minutes with the residual mixture of phenols. Diazomethane was removed under a stream of nitrogen, and the solution of methylated materials was cochromatographed with each of the analytical standards VII, VIII, and IX.

RESULTS AND DISCUSSION

Plant Studies. Short-term studies of the fate of [^{14}C]RH-0994 after a single foliar application to cotton indicated (Table II) that residues of RH-0994 and its alteration products were not persistent on leaf surfaces; the half-life of the applied ^{14}C was ~1 day, and only ~5% of the dose was unabsorbed at 14-days posttreatment. In addition to the parent compound, the external rinses of leaves contained varying amounts of the two ester derivatives of RH-0994 (II and III), which are formed by addition of one or two oxygen atoms, respectively, at the sulfur ether. Although II was an impurity (~3%) in the [^{14}C]RH-0994 treatment solution, levels of this compound did increase in foliar rinses during the first 3 days. Also detected were two phenolic products (V and VI) and two unidentified products (unknowns A and B). The unidentified materials were also present (~3–4%, Table II) in the [^{14}C]RH-0994 treatment solutions. Relative concentrations of unknown(s) A, which was (were) represented by radioactivity that remained at the base line of TLC plates, increased through 7-days posttreatment, but unknown(s) B was (were) not detected in any extracts after the first 8 h. Thus, it appears almost certain that unknown A was in fact a transformation product of RH-0994 on cotton, whereas unknown B was not.

Table II. Absorption and Metabolism of [^{14}C]RH-0994[a] by Individual Cotton Leaves: Topical Dose of 100 μg/Leaf

nature of radioact[b]	% of dose at indicated days posttreatment[c]					
	0	1/3	1	3	7	14
External Rinse						
I (RH-0994)	89.7	43.1	38.6	16.7	2.8	0.6
II	3.4	5.3	5.3	6.2	3.1	1.6
III	0.0	3.9	4.0	3.1	2.5	1.0
V	0.0	0.0	0.0	0.7	0.3	0.2
VI	0.0	0.0	0.1	0.5	0.4	0.5
unknown(s) A	3.2	8.6	6.9	7.2	4.9	1.3
unknown(s) B	3.7	0.5	0.0	0.0	0.0	0.0
subtotal	100.0	61.4	54.9	34.4	14.0	5.2
Internal Extract						
I (RH-0994)		14.6	18.1	15.8	9.9	2.8
II		1.6	2.0	3.0	3.6	1.7
III		0.4	0.5	0.7	1.4	0.7
IV		0.2	0.3	0.3	0.6	0.6
V		1.3	2.9	7.6	11.7	12.2
VI		0.3	0.9	2.2	3.5	5.1
unknown(s) A		0.6	0.8	1.7	4.5	3.6
water soluble		0.4	1.1	3.3	4.7	5.5
unextractable		4.7	5.3	10.5	15.5	10.9
subtotal	0.0	24.1	31.9	45.1	55.4	43.1
total recovered	100.0	85.5	86.8	79.5	69.4	48.3

[a] EC formulation in aqueous suspension. [b] See Figure 1 for identity of compounds I–VI; unknown(s) A = baseline radioactivity (TLC) and B = two products less polar than RH-0994; water-soluble radioactivity represents the balance remaining after hydrolysis of initial aqueous fractions and extraction with methylene chloride. [c] Data represent averages of three replicates with three leaves per replicate per time of collection.

RH-0994 and/or its transformation products were readily absorbed by leaves; ~55% of the applied dose was recovered in the leaf extract after 7 days. The compound appeared to be metabolized rapidly in leaves; both of the oxidation products (II and III) and small amounts of the three free phenols (IV, V, and VI) were detected in the methylene chloride fraction of solvent-partitioned samples. Levels of RH-0994 and its ester derivatives were maximum at 1-day posttreatment (~21%) and then declined to ~5% of the dose after 14 days. When the aqueous fractions of the initial solvent-partitioning samples were hydrolyzed, ~75–80% of the radioactive material was converted to an organosoluble form that consisted entirely of

Table III. Radioactive Residues in Cotton Plants Treated in the Field with [^{14}C]RH-0994[a]

plant sample[b]	date collected	ppm of ^{14}C equiv RH-0994 ± SE	wet wt, g	dry wt, g
whole seed	9/25	1.8 ± <0.1	–	494.3
hull		1.3 ± <0.1		
kernel		1.9 ± <0.1		
seedlings[b]	(9/25)			
cotyledons		1.8 ± <0.1	–	2.2
petiole plus root		1.3 ± <0.1		1.6
seed hull		1.1 ± <0.1		2.0
whole seed	11/2	2.1 ± <0.1		201.5
hull		1.6 ± <0.1		
kernel		2.2 ± <0.1		
seedlings	(11/2)			
cotyledons		1.9 ± <0.1		2.0
petiole plus root		1.5 ± <0.1		1.2
seed hull		1.2 ± <0.1		2.0
lint	9/25	2.3 ± 0.4		305.7
lint	11/2	1.8 ± 0.3		328.5
TL-alive	10/1	420.8 ± 3.5	1700	425.0
TL-dead	10/1	728.6 ± 4.1		205.0
regrowth leaves	11/2	2.7 ± 0.1	320	80.0
bracts	11/2	42.6 ± 0.8	422	326.5
stalks	11/2	52.2 ± 0.3	1048	607.0
roots	11/2	4.3 ± 0.2	219	88.0
grass	10/1	16.2 ± 0.6	–	100.0

[a] Treatments [1.12 kg of AI ha^{-1} (application)$^{-1}$] applied on July 24 and 30, Aug 3, 8, 13, 17, 22, 27, and 31, and Sept 5, 1979. Measurable rainfall on July 26, 27, and 31 and Aug 7, 11, 16, and 22. At least four combustion analyses were made of each plant sample. [b] Seedlings were grown from subsamples of the same seed collections used for residue analyses. TL designates leaves, either dead and fallen from plants or alive and still on plants, that were present during treatments.

the free phenolic compounds IV, V, and VI. Thus, these phenolic derivatives, which were formed by the initial hydrolytic cleavage of RH-0994 or its toxic derivatives, were apparently rapidly incorporated into (presumably) glycosidic conjugates. (The amounts of the three phenolic compounds shown in Table II include the portions liberated by hydrolysis; water-soluble radioactivity represents that remaining after methylene chloride extraction of hydrolyzed samples.) The total recovery of applied radioactivity declined steadily. This is a common phenomenon (Bull, 1972; Bull et al., 1976) that can probably be attributed to volatilization of materials from leaf surfaces as well as to translocation of water-soluble transformation products. A tentative schematic pathway for the formation of metabolites of RH-0994 identified in cotton leaves is shown in Figure 1.

Results of studies of the distribution and nature of radioactive residues in cotton plants after multiple, season-long applications of [^{14}C]RH-0994 are shown in Tables III and IV. Both lint and mature cottonseed from each of the collection dates contained ~2 ppm of [^{14}C]RH-0994 equivalents. Since bolls were not open while sprays were applied, the radiocarbon in lint and seeds could not have resulted from contact contamination. Solvent extraction of the lint failed to recover any of the radioactive material. Attempts to extract and identify the radioactive material in seeds were also unsuccessful. Soxhlet extraction with hexane removed the oil and <5% of the radiocarbon. Further Soxhlet extraction of the seed residue with acetonitrile recovered no radioactivity: neither did homogenization and extraction with acidified methanol. Final homogenization of the extracted residue with an alcoholic solution of sodium hydroxide resulted in the recovery of ~15–20% of the radioactive material, but we were unable to clean up sufficient amounts for further analyses. Combustion analyses indicated that seedlings grown from the radioactive seeds contained approximately the same levels of radiocarbon as seed (Table III). However, solvent extraction of subsamples of these seedlings led to the recovery of only insignificant (<5%) amounts of the radioactive material present. While not conclusive, these results suggest that neither RH-0994 nor its intact ester derivatives were present in lint or seed.

Rather large levels of radioactive residues were detected in foliage that was present while treatments were applied (Table III; TL-alive, ~420 ppm, TL-dead, ~730 ppm). Solvent extraction recovered ~70% of the radioactivity associated with these foliage samples, and TLC analyses of the extracts revealed the presence of RH-0994 (Table IV), its two intact ester oxidation products (II and III), and the three phenolic hydrolysis products (IV, V, and VI). Regrowth foliage contained only 2.7 ppm of radiocarbon, and TLC analyses indicated that this radioactive material consisted of II, V, and VI, as well as unidentified products (Table IV). Because the woody parts (stalks and roots) of the treated plants contained a similar array of radioactive products (Table IV), their appearance in the new growth might be expected. The parent compound was found in stems (~6%) but was not detected in new growth. This may be attributable to a lack of translocation due to the insolubility of RH-0994 in water.

Native grass growing in the treated plot contained ~16 ppm of radiocarbon; this included the ester derivative II (14.8%) as well as two of the phenolic products, V (20.7%) and VI (14.0%). The radioactive material in grass may have resulted from contamination by sprays and also by

Table IV. Nature of Radiocarbon in Dried Plant Materials from a Plot of Cotton Treated with [^{14}C]RH-0994

		% of total radioactive material as[a]									
plant material	ppm	A	C	I[e]	II	III	IV	V	VI	H_2O soluble[b]	residue[c]
cotton											
stem	52.2	1.8	2.3	5.7	11.3	0.0	0.6	32.4	6.5	14.7	24.7
root	4.3	7.9	0.0	0.0	16.0	0.0	0.0	19.9	11.2	8.1	37.0
new growth	2.7	3.0	0.0	0.0	11.0	0.0	0.0	36.0	9.8	10.0	30.2
bracts	42.6	0.6	0.8	6.5	11.9	2.1	0.0	39.4	17.3	7.4	14.0
TL-dead	728.6	4.2	0.3	9.6	15.5	2.4	1.4	22.8	9.6	2.3	31.9
TL-alive	420.8	5.1	0.5	6.6	6.2	0.8	1.3	30.1	13.4	3.5	32.5
grass											
leaves	16.2	3.9	0.0	0.0	14.8	0.0	0.0	20.7	14.0	4.5	42.1
combined[d]	204.3	4.3	0.5	7.1	11.0	1.7	0.2	23.1	11.2	4.0	36.9

[a] See Figure 1 for identity of compounds I-VI; unknowns A and C represent radioactivity at and just above the base line, respectively. [b] Radiocarbon that could not be extracted after acid hydrolysis of the water-soluble fraction of the initial extract. [c] Radiocarbon that was not extracted from the dry plant material. [d] All of the ground plant materials were combined, mixed thoroughly, and subsampled for analysis. [e] RH-0994.

uptake from soil contaminated by runoff. Periodic analyses of the soil of the treated plot indicated that essentially all (>95%) of the radioactive material detected was located near the surface (0–7.5 cm deep). Residues in that layer on Aug 3, Sept 7, Nov 2, and Dec 4, 1979, were 0.3 ± <0.1 (SE), 1.1 ± <0.1, 0.7 ± <0.1, and 0.3 ± <0.1 ppm, respectively. Although the nature of these radioactive residues was not determined, their levels clearly declined progressively with time after treatments were terminated.

Although our studies have shown that single applications of RH-0994 are not unusually persistent either on foliar surfaces or in the plant system following absorption, they do indicate that season-long multiple applications may result in the appearance of residues in seeds and other parts of treated plants. Based on the extractability of the radiocarbon in seeds, it seems almost certain that the residues are not in the form of RH-0994 or its intact ester derivatives.

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Photodecomposition of Pentachlorophenol in Water

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Exposure of aqueous pentachlorophenol (PCP) solutions to either sunlight or laboratory ultraviolet light resulted in rapid degradation at pH 7.3 and slower degradation at pH 3.3. Displacement of chloride by hydroxide produced tetrachlorocatechol, tetrachlororesorcinol, and tetrachlorohydroquinone which subsequently were air-oxidized to chloranil, hydroxyquinones, and eventually 2,3-dichloromaleic acid (DCM). This acid photodecomposed more slowly to carbon dioxide, chloride, and unidentified organic fragments. Photoreduction of PCP to tetra- (TCP) and trichlorophenols also occurred, as did formation of a cyclic diketone, $C_5H_2Cl_2O_2$. Examination of local field waters revealed PCP and TCP but no DCM.

Pentachlorophenol (PCP) is a major industrial chemical and pesticide used worldwide for the protection of wood and wood products against insects and microorganisms. It also has received extensive use in rice and sugar production and in water treatment. Most of its uses offer the potential for water pollution, and, indeed, PCP has been found in natural waters in such widely separated places as Hawaii (Bevenue et al., 1972), Delaware (Fountaine et al., 1976), The Netherlands (Wegman and Hofstee, 1979), and West Germany (Weber and Ernst, 1978).

Aqueous solutions of PCP absorb strongly within the sunlight region of the spectrum (λ_{max} 320 nm); Hiatt et al. (1960) and Mitchell (1961) first mentioned the photodecomposition, and Kuwahara et al. (1966a,b, 1969) isolated tetrachlororesorcinol, chloranilic acid, and complex chlorinated ethers following the irradiation of relatively concentrated (2%) aqueous PCP solutions. Crosby and Hamadmad (1971) also observed PCP photoreduction to tri- and tetrachlorophenols in organic solvents.

The purpose of the present work was to investigate the rate of PCP photodecomposition in dilute aqueous solutions more nearly characteristic of current use, to identify photodecomposition products, and to suggest degradative pathways by which the products may be explained.

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MATERIALS AND METHODS

Materials. Most reagents and intermediates were purchased from chemical supply houses and were used as received; solvents were redistilled shortly before use. Pentachlorophenol (Puriss, Aldrich Chemical Co.) was recrystallized 3 times from benzene, mp 188.5 °C, and was homogeneous on gas chromatography (GLC). Diazomethane was generated from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (de Boer and Backer, 1963).

Pentachlorophenyl chloroacetate was prepared from PCP and chloroacetyl chloride (Kupryszewski and Wojnowski, 1962), mp 120–130 °C.

Tetrachlororesorcinol was prepared by dissolving 1 g of 3-chloro-5-methoxyphenol (Aldrich) in 125 mL of redistilled carbon tetrachloride and introducing chlorine gas slowly for 30 min. The solvent was removed by vacuum evaporation, the solid residue was fused with pyridine hydrochloride (5 g) for 1 h at 210 °C, the resulting cake was dissolved in 200 mL of 5% aqueous HCl and extracted into ethyl ether, and the combined ether extracts were evaporated. Recrystallization of the crude product twice from water gave an 80% yield of white crystals, mp 140.5 °C (140–141 °C; Heilbron, 1965), *m/e* 246 with an isotope

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