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Photodegradation of Leptophos

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Leptophos (O- (4-bromo-2,5-dichlorophenyl) O-methyl phenylphosphonothioate) is an insecticide whose residual nature and persistance have been studied by a number of workers. LEUCK et al. (1969, 1970) reported that this compound degrades rather slowly in coastal Bermuda grass and in forage corn. Corn plants still retained 50% of leptophos residues 21 days after treatment. JOHNSON et al. (1971) showed that leptophos disappears from sprayed plants less rapidly than do many organophosphorus insecticides. Residues of both the parent compound and its oxon remained on straws 63 days after wheat treatment (STRUBLE & McDONALD 1973). AHARONSON & BEN-AZIZ (1974) found that there was only a 20% reduction in leptophos residues in tomato leaves 3 weeks after application. Only in tobacco plants did leptophos decline rapidly; residues were low or nonexistent in tobacco when grown in soil treated with the insecticide or when the plants were treated foliarly (HARRIS 1973, DOROUGH & WHITTACRE 1977).

Leptophos was widely used for control of cotton insects in Egypt until the summer of 1977. Indications that leptophos is a neurotoxic chemical has been reported by ABOU-DONIA et al. (1974) and ABOU-DONIA & PREISSIG (1976). This compound was accused of poisoning and killing about 1,300 water buffalo -es in the Nile Delta in Summer 1971, and symptoms of neurotoxicity were observed long after the spraying season was over (SHEA 1974). Stability of leptophos in the local environment was therefore pertinent. Here, we report our findings on leptophos photodecomposition and its degradation products using ultraviolet (U.V.) light and direct sunlight.

MATERIAL AND METHODS

Exposure Procedure: Analytical grade samples of leptophos, its oxon (O-analogue), and 4-bromo-2,5-dichlorophenol were supplied by Velsicol Chemical Corp. (Chicago, Ill.). Acetone solution of leptophos was prepared and appropriate aliquots were transferred to a glass dish (2.5-cm i.d.). After

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evaporation of acetone with a gentle stream of air, a thin dry film of chemical was formed (100 ug/cm^2); the dishes were then exposed to either U.V. (254 nm) or direct sunlight. At a given interval (Tables 1 & 3) residues in two dishes were quantitatively transferred to a test tube using chloroform. Chloroform rinsings were concentrated for analysis. Also a 100 mL solution of leptophos in methanol (0.5 %) was exposed to direct sunlight in a closed 250-mL Erlenmeyer flask. At each time interval (Table 3), two 5-mL aliquots were pipeted in a test tube, and concentrated for analysis.

Chemical analysis: From each tube, a proper aliquot was spotted on thin layer (TLC) plates (Silica gel G, 250 nm), and standard chemicals were spotted on a separate plate. Plates were developed with hexane-ether (85: 15, v/v), and DCQ reagent (2,6-dibromo-p-benzoquinone-4-chloroimine, 0.5% in cyclohexane) was used to locate leptophos and its degradation products (Table 2). The corresponding areas of silica gel for the samples were scrapped and residues were eluted with chloroform-acetone mixture (1:1, v/v) into a stoppered test tube. Solvent extracts were evaporated to dryness and residues were subjected to the colorimetric determination procedure. This consists of hydrolysis of leptophos and its oxon by adding 1 mL sodium methylate solution (2%) to each tube, the tubes were tightly closed and heated on a boiling water bath for 5 min after which 1.0 mL of 50% ethanol was added and heating continued for additional 5 min. The hydrolysis product (phenol) was determined colorimetrically using the 4-amino antipyrine reagent according to the method of BRACHA & BONARD (1966) as modified by RISKALLAH et al. (1978). In case of phenol determination the addition of sodium methylate and ethanol were omitted. Standard curves for leptophos, its oxon, and phenol were carried out using this combined procedure of TLC and colorimetric analysis. The recovery of these chemicals under these conditions were leptophos 100, oxon 95, and phenol 75%. These percentages were used in the computation of data reported in Tables 1 & 3.

For qualitative analysis, several chromogenic reagents were used to locate the various photodegradation products of leptophos (Table 2). These reagents were previously described by MARCH et al. (1954) and ZWEIG (1967).

RESULTS AND DISCUSSION

Our results indicate that leptophos is a rather stable organophosphorus insecticide. After exposure to U.V. for 24 h and sunlight for 65 days relatively large quantities of the original chemical remained unchanged (Tables 1 & 3). In each case, oxon (C, Table 2) was the first product detected on TLC plates followed by the formation of phenol derivative (D, Table 2). These two products account for the major photodegradation products formed. Four unknown products (A,B,E, and F, Table 2) were also formed as minor degradation products. FUKUTO et al. (1973) reported that the photolytic sequence for leptophos was

TABLE 1

Leptophos degradation by U.V.[a]

Time Intervals (hours)	Percent as of initial of leptophos and its photodegradation products detected at indicated intervals			
	Leptophos	Leptophos phenol	Leptophos oxon	(E + F)[b]
0	100	ND[c]	ND	ND
0.5	95	0.4	2.6	1.3
2.0	90	2.7	3.4	2.8
6.0	72	6.5	5.2	4.0
24	47	25	9.2	5.3

a Average of two experiments, each carried out in duplicates.
b The unknown E and F were detected colorimetrically as leptophos phenol after hydrolysis with sodium methylate and expressed as percent of initials, see Table 2.
c ND = not detectable.

TABLE 2

Color response and R_f values of Leptophos and its photodegradation products.

TLC Spots	R_f (x 100)[a] 1	2	DCQ	Perchloric-Molybdate	Silver nitrate	Cochromatographed with
A	0	-	Red	Blue	NR[b]	-
B	7	-	Brown	Blue	NR	-
C	21	2	Blue	Blue	Light grey	Oxon
D	38	20	Violet	NR	Dark grey	Phenol
E	44	-	Red	Blue	Grey	-
F	50	-	Red	Blue	Light grey	-
G	70	76	Red	Blue	Grey	Leptophos

a Solvent system 1 = hexane-ether (8.5 : 1.5, v/v); 2 = hexane-benzene, (9:1, v/v).
b NR = No response.

TABLE 3

Leptophos degradation as thin dry film or as methanol solution by sunlight[a]

Time Intervals (days)	Percent, as of initial, of leptophos and its photodegradation products detected at indicated intervals			
	Leptophos	Leptophos phenol	Leptophos oxon	(E)[b]
		Thin Dry Film		
0	100	ND[c]	ND	ND
1	93	ND	1.0	ND
3	85	ND	-	ND
6	65	2.4	2.7	ND
9	62	-	4.4	ND
12	58	3.2	4.8	ND
15	50	5.5	7.7	ND
28	45	7.8	9.5	0.9
35	42	8.3	11	2.3
65	37	12	12	3.6
		Methanol Solution		
0	100	ND[c]	ND	ND
1	98	ND	ND	ND
3	95	ND	ND	ND
6	93	ND	3.9	ND
9	91	1.6	4.7	ND
12	77	1.6	6.2	ND
15	75	2.5	6.2	ND
21	69	3.3	7.6	ND
28	59	5.0	8.2	3.0
35	54	6.6	9.5	4.2
65	45	10	13	5.6

a Results are average of two duplicates.
b and c . see footnotes in Table 1.

shown to include leptophos-oxon, phenylphosphonic acid, O-methyl phenylphosphonothioic acid and leptophos-phenol. It was also reported that desbromo leptophos (O- (2,5-dichlorophenyl) O-methyl phenylphosphonothionate) was detected in substantial amounts after photolysis of leptophos (Velsicol Chemical Corp. 1971). In contrast this compound did not appear in the present work, although standard chemical was spotted along with the samples on the same TLC plate.

Each of the degradation products formed by U.V. light contained the phenol moiety of leptophos except A and B products (Table 2). These phenol-containing products accounted for more than 85% of the original amount of leptophos after 24 h exposure to U.V. light (Table 1). Each of the phenol and oxon derivatives were identified by TLC using two solvent systems and by cochromatography with the respective standards using several color reagants (Table 2). Two unknown degradation products, A and B with low R_f values (Table 2), i.e. highly polar chemicals, were not detected since they gave negative reaction with both silver nitrate and the colorimetric procedure used. In respect of the E and F degradation products, they were detected usually at low quantities Leptophos half life ($t_{\frac{1}{2}}$) was computed from data in Table 1 to be about 21 h. After one day exposure to U.V. light, phenol was the major degradation product (ca. 25%) while oxon (ca. 9%) was relatively less. U.V. exposure of leptophos was monitored by TLC analysis at several time intervals. Oxon derivative was the first product to be detected on TLC plates up to 2 h exposure while phenol was formed at larger quantities during the remaining intervals. These results might indicate that oxidation of leptophos to its oxon derivative is the initial photolytic reaction which is followed by hydrolysis to its phenol derivative.

The same degradation products were formed by sunlight irradiation. The only qualitative differences were that the unknown product F was not detected after sunlight irradiation and a minor amount (5%) of the unknown product E appeared only after exposure up to one month (Table 3). TLC analysis indicated that the formation of different degradation products was faster as a thin dry film than in methanol solution. In the latter case,the four degradation products A, B, oxon and phenol did not appear before 6 to 9 days, while the same compounds were detected after only 1 to 3 days in case of the dry film of leptophos. As in case of U.V. irradiation, oxon and phenol were quantitatively the major photodegradation products. At the end of sunlight exposure period (65 days) the detected amounts of both phenol and oxon were approximately equal and ranging from 20 to 25% of the initial deposit of leptophos (Table 3). A considerable amount of leptophos (ca. 40%) remained unchanged after 65 days of exposure to sunlight either in methanol solution or as a thin dry film.

Photodegradation of leptophos was relatively slower when exposed in methanol solution ($t_{\frac{1}{2}}$ = 50 days) than when exposed as a thin dry film ($t_{\frac{1}{2}}$ = 20 days). Methanol can be considered as a protecting solvent due to its tendency to shift the U.V. absorption maximum to shorter wavelength, thus reducing the molar absorptivity at 254 nm (EBERLE & GUNTHER 1965). The U.V. component of sunlight is usually responsible, in most instances, for all chemical changes which occur to many insecticide

chemicals (CROSBY 1969, MATSUMURA 1973).

In the present study leptophos is degraded by U V. light and sunlight to yield two major photodegradation products, oxon and phenol. These two products are reported to be inhibitory to the mitochondrial electron transport system but not the leptophos itself (WINSTON & PARDINI 1976). Therefore, toxicological studies should be conducted not only using the parent insecticide but also its environmental degradation products such as those formed by sunlight and U.V. light.

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