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Fate of 3,3-Dimethyl-1-(methylthio)-2-butanone *O*-(Methylcarbamoyl)oxime (Diamond Shamrock DS-15647) in Cotton Plants and Soil

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In field-grown cotton plants, the carbamate pesticide Diamond Shamrock DS-15647 (3,3-dimethyl-1-(methylthio)-2-butanone *O*-(methylcarbamoyl)oxime) was rapidly oxidized to its toxic sulfoxide derivative, which was further oxidized, but more slowly, to the more toxic sulfone form. Degradation of the toxic forms occurred primarily by conversion to unidentified water-soluble products. In soil, the chemical changes of DS-15647 were similar to those found in plants, but they proceeded at slower rates. Cotton seeds that had been surface treated with DS-15647 and planted in the greenhouse absorbed 20% of the dose after 1 day. The sulfoxide and sulfone derivatives were the primary products recovered from plants grown from the treated seeds. In tests with several species of insects, DS-15647 applied topically was more effective than the sulfoxide or sulfone derivatives. The sulfone form was the most potent anticholinesterase agent.

Diamond Shamrock DS-15647 (3,3-dimethyl-1-(methylthio)-2-butanone *O*-(methylcarbamoyl)oxime), a new carbamate pesticide being developed by Diamond Shamrock Corp., Cleveland, Ohio, has shown potential systemic and contact insecticidal properties against certain phytophagous pests. For example, granular formulations of DS-15647 applied in the seed furrow at the time cotton is planted have demonstrated good control of thrips (*Frankliniella* spp.), the cotton aphid (*Aphis gossypii* Glover), the cotton fleahopper (*Pseudatomescelis seriatus* (Reuter)), the serpentine leafminer (*Liriomyza brassicae* (Riley)), and spider mites (*Tetranychus* spp.) (Davis and Cowan, 1974).

The fate of DS-15647 in biological systems has not been determined. However, the metabolism of a structurally similar carbamate, aldicarb [Temik; 2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbomyl)oxime], has been extensively studied in cotton plants (Bartley *et al.*, 1970; Bull, 1968; Coppedge *et al.*, 1967; Metcalf *et al.*, 1966), in insects (Bull *et al.*, 1967a; Metcalf *et al.*, 1966), in potatoes (Andrawes *et al.*, 1971b), and in soil (Andrawes *et al.*, 1971a; Bull, 1968; Bull *et al.*, 1970; Coppedge *et al.*, 1967). These investigations revealed that aldicarb is oxidized to toxic sulfinyl and sulfonyl derivatives that are degraded by hydrolysis to oximes or by conversion to other nontoxic metabolites. The present paper reports the results of similar studies designed to provide a general understanding of the fate of DS-15647 in cotton plants and soil.

EXPERIMENTAL SECTION

Chemicals. Quantities of ^{35}S-labeled DS-15647 and its sulfonyl derivative DS-20238 (3,3-dimethyl-1-(methylsulfonyl)-2-butanone *O*-(methylcarbamoyl)oxime) (initial specific activities of 18 and 2.2 mCi/mmol, respectively) were supplied by Diamond Shamrock Corp., Cleveland, Ohio. The labeled compounds were greater than 99% pure, as shown by thin-layer chromatography (tlc) and autoradiography. Nonradioactive chemicals used included DS-15647, DS-17839 (3,3-dimethyl-1-(methylsulfinyl)-2-butanone *O*-(methylcarbamoyl)oxime), DS-20238, DS-15619 (3,3-dimethyl-1-(methylthio)-2-butanone oxime), DS-20243 (3,3-dimethyl-1-(methylsulfinyl)-2-butanone oxime), and DS-20242 (3,3-dimethyl-1-(methylsulfonyl)-2-butanone oxime).

DS-15647 and its metabolites were resolved by tlc on glass plates coated (0.25-mm thick) with silica gel G by using solvent mixtures of: chloroform, ethyl acetate, and ethyl ether (6:2.5:2, v/v); chloroform, ethyl acetate, and butyl ether (6:2:2, v/v); or chloroform, ethyl acetate, butyl ether, and dioxane (4:2:2:2, v/v). Identification of metabolites was based on cochromatography of radioactive compounds with the authentic standards that were located colorimetrically by exposure to iodine vapors.

Radioassays of extracts or radioactive areas from chromatograms were made by liquid scintillation at ambient temperature. Data were corrected for radioactive decay and quenching.

TEST PROCEDURES AND RESULTS

Toxicity Studies. The relative toxicities of the three biologically active compounds (DS-15647 and its sulfoxide and sulfone) were investigated both *in vivo* and *in vitro*. The *in vivo* toxicity of the compounds to certain insect species associated with cotton was compared by determining the LD_{50} values of topical applications (serial dilutions in acetone solutions) to adult boll weevils (*Anthonomus grandis* Boheman), adult convergent lady beetles (*Hippodamia convergens* Guerin-Meneville), 2nd stage larvae of the common green lacewing (*Chrysopa carnea* Stephens), and 3rd stage larvae of the tobacco budworm

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Table I. Toxicity of DS-15647 and Its Sulfoxide and Sulfone Derivatives

Compound	LD_{50}, μg/insect				AntiChE activity, I_{50} *M*
	Boll weevil adult	Lady beetle adult	*Chrysopa* larvae	Tobacco budworm larvae	
DS-15647	0.16	0.15	0.01	20.0	5.25×10^{-6}
Sulfoxide	3.90	1.70			2.68×10^{-6}
Sulfone	3.50	0.36			7.57×10^{-7}

Table II. Chromatographic Behavior of DS-15647 and Its Metabolites

Compound	R_f values in indicated tlc system[a]		
	A	B	C
DS-15647	0.73	0.56	0.77
DS-15647 sulfoxide	0.10	0.02	0.16
DS-15647 sulfone	0.29	0.15	0.53
Oxime	0.84	0.72	0.79
Oxime sulfoxide	0.23	0.10	0.40
Oxime sulfone	0.56	0.42	0.72
Unknown A	0.90		
Unknown B	0.52		
Unknown C	0.40		
Unknown(s) D	0.00		

[a] A = chloroform–ethyl acetate–ethyl ether, 6:2.5:2. B = chloroform–ethyl acetate–butyl ether, 6:2:2. C = chloroform–ethyl acetate–butyl ether–dioxane, 4:2:2:2.

(*Heliothis virescens* (F.)). All test insects were reared in the laboratory, the boll weevils and tobacco budworms on a modified wheat germ diet (Vanderzant, 1967) and the lady beetles and green lacewings as described by Bull *et al.* (1973). *In vitro* toxicities were compared by assessing the anticholinesterase (antiChE) activity of each compound against bovine erythrocyte acetylcholinesterase (Sigma Chemical Co., St. Louis, Mo.) by a modified Hestrin colorimetric procedure (Simpson *et al.*, 1964).

The results of topical toxicity tests indicated that DS-15647 was more active than either of its oxidized derivatives against the insect species tested (Table I). Also, all three compounds exhibited good antiChE activity, but DS-15647 sulfone proved to be the most potent.

DS-15647 Metabolism by Plants in the Field. Fully expanded leaves of cotton plants (10- to 12-leaf stage, Deltapine Smoothleaf variety) grown in the field in normal conditions were treated individually with 10 μl of an aqueous solution containing 100 μg of ^{35}S-labeled DS-15647 by using the petiole injection method described by Bull *et al.* (1967b). At specified times, triplicate samples of treated leaves (petioles included) were collected, chopped coarsely, and homogenized individually in an acetone–water (9:1, v/v) solution (10 ml/g of fresh weight). Solids in the homogenates were removed by centrifugation and then extracted two more times with acetone. The extracts were combined for quantitative radioassays and then reduced under vacuum to volumes convenient for chromatography; duplicate samples of each extract were analyzed. The R_f values determined for DS-15647 and its metabolites are listed in Table II. Radioactivity that could not be extracted from the plant material was assayed after digestion of the dried residue in 20 ml of HNO_3.

In the cotton leaves, DS-15647 was rapidly oxidized to its sulfinyl derivative as shown by the distribution of radioactivity in the "0-hr" samples processed within 30 min after treatment (Table III). (Preliminary experiments in which cotton leaves were fortified with ^{35}S-DS-15647 indicated that less than 10% of the compound was oxidized to DS-15647 sulfoxide during extraction.) Metabolism of the parent compound, primarily through oxidation to the sulfoxide, was essentially complete after 4 days. The more stable sulfoxide was the major metabolite recovered in extracts of all samples and represented 10% of the injected dose after 56 days. DS-15647 sulfone reached a peak concentration of 7.5% at 16 days.

The radioactivity designated unknown(s) D remained at the origin during chromatography. Investigations into the nature of the unknown(s) revealed that the area consisted of polar products that were unextractable from aqueous solutions. Resolution of the water-soluble radioactivity by paper chromatography (pc) on Whatman 3 mm paper in a 40:9:1 (v/v) mixture of acetonitrile, water, and ammonium hydroxide revealed the presence of at least six metabolites. Although no further identification of the unknown compounds was attempted, samples of the aqueous fraction were tested for antiChE activity by using the method previously described. Aliquots containing as much as 3-μg equivalents of DS-15647 exhibited no detectable inhibitory activity.

DS-15647 Metabolism by Excised Leaves. Since almost 50% of the injected dose in the field study could not be accounted for after 32 days, an attempt was made to determine whether the loss of radioactivity from individual leaves occurred because of translocation or volatilization. For tests of possible loss *via* translocation, excised leaves treated by petiole injection in the field were removed immediately from the plant and transferred to

Table III. Relative Concentrations of ^{35}S-Labeled DS-15647 and Its Metabolites in Leaves of Field-Grown Cotton (Petiole Injection of 100 μg/Leaf)

Compound	% of applied dose at indicated days after treatment[a]							
	0	1	2	4	8	16	32	56
Oxime	1.1	0.1	T	0	0	0	0	0
DS-15647	28.2	8.0	2.0	0.2	0	0	0	0
Unknown B	0	0	0	0	0.2	0.2	0.2	0.2
Unknown C	0	0	0	0	0	0	0	0.1
Sulfone	4.3	2.6	3.8	5.2	5.0	7.5	6.5	4.0
Oxime sulfoxide	0	0.8	1.0	0.8	0.5	0.6	0.6	0.5
Sulfoxide	61.1	73.6	71.0	60.9	41.5	35.7	17.7	10.1
Unknown(s) D	2.2	2.3	2.3	4.3	6.2	11.4	18.0	19.8
Unextractable	3.1	7.2	7.2	7.4	8.4	7.8	7.4	8.4
Lost	0	5.4	12.7	21.2	38.2	36.8	49.6	56.9

[a] Average of duplicate chromatograms of triplicate samples from each of two experiments.

Table IV. Relative Concentrations of ^{35}S-Labeled DS-15647 and Its Metabolites in Excised Cotton Leaves (Petiole Injection of 100 μg/Leaf)

Compound	% of applied dose at indicated days after treatment[a]					
	0	1	2	4	8	16
Oxime	0.8	0.1	0.1	0	0	0
DS-15647	17.6	3.1	0.8	0.1	0	0
Unknown B	0	0	0	0.2	0.2	0.1
Unknown C	0	0	0	0	0.3	0.2
Sulfone	3.7	2.3	3.3	4.3	4.9	6.1
Oxime sulfoxide	0	0.5	0.6	0.6	1.0	0.9
Sulfoxide	73.5	78.6	72.6	67.9	63.1	47.8
Unknown(s) D	1.9	3.4	3.1	3.8	5.1	8.5
Unextractable	2.5	4.9	4.8	6.7	7.6	9.0
Lost	0	7.1	14.7	16.4	17.8	27.4

[a] Average of duplicate chromatograms of triplicate samples.

flasks containing distilled water. The leaves were then held in the laboratory in continuous light at room temperature (27 ± 3°) and analyzed at intervals (through 16 days) with procedures identical to those described. As in the field tests, DS-15647 sulfoxide was the major metabolite recovered at all times (Table IV) and the increased concentrations of the compound which were recovered indicated that it had been metabolized slower than in the field. Concentrations of the other metabolites were slightly less than those found in the analysis of leaves from plants grown in the field. Also, the water in which the excised leaves were held was sampled periodically for radioactivity, but only insignificant amounts were found. Although it was not known whether the transport system of the excised leaves was still functional, the absence of radioactivity in the water suggested that the lost portion of the dose may have been volatilized rather than translocated. Therefore, three adjacent leaves on individual cotton plants growing in the greenhouse were treated by petiole injection. Then at 7 and 28 days after treatment, all plant material was harvested and separated into three portions: (1) treated leaves with the petioles and stem; (2) all material including the stem below the treated leaves; and (3) all material above the treated leaves. Each portion was then assayed separately with the HNO_3 digestion technique. Less than 0.1% of the recovered radioactivity was found below the treatment zone, and only minor amounts (2 to 4%) were present in plant material above the treatment zone. Although these results provided further indirect evidence that the loss was probably the result of volatilization, attempts to trap volatile radioactivity from excised leaves by the method of Coppedge *et al.* (1967) were not successful.

DS-15647 Sulfone Metabolism. The individual fate of any secondary toxicant must be assessed as well as that of the parent material. However, the initial oxidation of DS-15647 was so rapid in cotton plants that studies with the parent material were primarily studies of the sulfinyl derivative. Then since the potential mammalian toxicity of the sulfone was so important, separate studies were made of its fate on cotton. Leaves were treated by petiole injection of 100 μg of ^{35}S-labeled DS-15647 sulfone and processed as described for the study of the metabolism of DS-15647. The results (Table V) revealed that the sulfone was more stable than either DS-15647 or the sulfoxide; it was the major product recovered in all extracts, exceeded only by concentrations of unknown(s) D after 32 days. The nature of the radioactivity in unknown(s) D was investigated as in the study of the metabolism of DS-15647 and was found to be water soluble. Subsequent analysis of the water-soluble radioactivity by pc revealed the presence of at least four metabolites, each with R_f values identical to those of four of the metabolites found in the aqueous fraction from extracts of leaves treated with DS-15647. Areas of radioactivity on tlc autoradiograms of the plant extracts exhibited chromatographic properties similar to those of DS-15647 sulfoxide and its oxime. The occurrence of such a biological reduction of aldicarb–sulfone in cotton plants was suggested by Metcalf *et al.* (1966) and Coppedge *et al.* (1967) but refuted by Bull (1968). However, since the concentrations of these two metabolites produced from the sulfone would be expected to be very small during the metabolism of the parent compound (Table III), positive identification was not attempted in this study.

Seed Treatment Studies. Since seed treatment at planting may be the preferred method of using DS-15647, preliminary investigations were made of the fate of the compound in seedlings grown from treated seed. Acid-delinted cotton seeds (Deltapine Smoothleaf variety) were treated at the rate of 0.5 lb of toxicant/100 lb of seed (450 μg/seed) by applying 50 μl of an acetone solution containing radiolabeled DS-15647 to individual seeds. After the solvent evaporated, the seeds were planted in a mixture of Lufkin fine sandy loam and sand in 1-gal cans and allowed to germinate and grow in the greenhouse. (Plants were watered from the bottom to minimize leaching of the radioactivity.) At the specified intervals, triplicate samples of one seed or seedling were taken for analysis. Prior to emergence of the cotyledons, the seeds were processed by extracting the seed coat (external) and seed meat (internal) separately. After emergence, separate extracts were made of whole seedlings, cotyledons, or true leaves. The results indicated that the metabolism of DS-15647 in the seeds and seedlings was essentially the same as that in mature plants (Table VI). However, trace amounts of a metabolite (unknown A) not found in the plant extracts from the other tests were recovered in 1- and 2-day seed meat extracts. The recovery of radioactivity from internal extracts was a good indication that a portion of the applied dose (20.8% at 1 day after treatment) was absorbed by the seed meat. Also, a comparison of the distribution

Table V. Relative Concentrations of ^{35}S-Labeled DS-15647 Sulfone and Its Metabolites in Leaves of Field-Grown Cotton (Petiole Injection of 100 μg/Leaf)

Compound	% of applied dose at indicated days after treatment[a]						
	0	1	2	4	8	16	32
Unknown B	1.3	0.4	0.2	0.6	0.3	0.1	0.2
Unknown C	0	0.9	0.8	0.5	0.5	0.2	0.1
Sulfone	94.7	88.2	83.8	75.2	58.1	33.2	21.1
Oxime sulfoxide (?)	1.0	1.5	1.1	1.4	0.8	1.0	0.4
Sulfoxide (?)	1.5	3.9	3.9	3.3	2.1	4.0	1.1
Unknown(s) D	0.7	3.0	4.7	8.0	10.4	26.1	32.5
Unextractable	0.8	1.3	2.0	3.1	4.2	6.4	7.7
Lost	0	0.8	3.5	7.9	23.6	29.0	36.9

[a] Average of duplicate chromatograms of triplicate samples.

Table VI. Relative Concentrations of ^{35}S-Labeled DS-15647 and Its Metabolites in Cotton Seeds and Seedling Plants after Seed Treatment (450 μg/Seed)

	% of recovered radioactivity at indicated days after treatment[a]							
	1 (seeds)		2 (seeds)		3 (seeds)		4 (seeds)	
Compound	Ext	Int	Ext	Int	Ext	Int	Ext	Int
Unknown A	0	0.1	0	T	0	0	0	0
Oxime	0.9	0.2	0.8	0.2	4.1	0.1	2.9	0
DS-15647	87.6	89.5	65.3	68.4	39.9	0.2	28.1	0
Unknown B	0	0	0	0	0	0	0	T
Unknown C	0	0	0	0	0	0	0	0.3
Sulfone	0.7	0.6	2.0	1.0	8.0	8.0	6.0	9.7
Oxime sulfoxide	0	0.5	0	0.3	0	0.8	0	0.7
Sulfoxide	10.4	8.4	31.1	28.5	45.1	82.2	58.2	82.3
Unknown(s) D	0.4	0.7	0.8	1.6	2.9	8.7	4.8	7.0
% of total dose recovered	13.8	20.8	5.1	12.9	4.9	4.5	3.9	10.3

	7 (seedlings), whole	14 (seedlings)		21 (seedlings)	
		Cotyl	Leaves	Cotyl	Leaves
Oxime	0	0	0	0	0
DS-15647	0	0	0	0	0
Unknown B	0.1	0.1	0	0.4	1.6
Unknown C	0.2	0.2	0	0.4	0.9
Sulfone	14.7	21.4	22.3	26.7	26.6
Oxime sulfoxide	0.9	1.0	0	1.0	1.6
Sulfoxide	77.9	69.5	71.6	60.3	59.6
Unknown(s) D	6.2	7.8	6.1	11.3	9.7
% of total dose recovered	12.7	26.9	0.2	19.3	1.7

[a] Average of duplicate chromatograms of triplicate samples.

of metabolites in the external and internal extracts indicated that DS-15647 was oxidized slowly by the internal tissues prior to emergence of the primary root from the seed. (Emergence of the primary root occurred between the 2nd and 3rd day after planting.) Thereafter, oxidation was rapid, and no DS-15647 was recovered from internal extracts after 3 days. DS-15647 sulfoxide and DS-15647 sulfone were the principal metabolites found in seedlings and comprised 85 to 92% of the recovered activity. However, the relative concentrations of the sulfonyl form in seedlings were greater (2×) than those found in mature plants and reached 26% after 21 days. In addition, the results demonstrated continued seedling uptake of radioactivity that had diffused from the treated seed into the surrounding soil since the greater amounts of the radiolabel were recovered from seedlings at 14 and 21 days (27.1 and 22% of the applied dose) than at 7 days (12.7%).

Fate of DS-15647 in Soil in the Field. The chemical changes and movement of DS-15647 in soil were investigated in the field during the growing season. Procedures used were similar to those described by Bull *et al.* (1970), which included the burial of stainless steel screen packets containing 40 g of sieved soil (Lufkin fine sandy loam) that had been mixed with 500 μg of ^{35}S-labeled DS-15647. At specified intervals, triplicate packets were retrieved for analysis (Bull *et al.*, 1970). In addition, samples of the soil 5 cm above and below each packet were taken for assays of radioactivity and moisture content. (The area where this test was conducted was not irrigated, but rainfall of 18 cm was recorded during the period of the test.)

The characterization of the radioactivity (Table VII) extracted from the treated soil indicated that the chemical changes in DS-15647 were similar to those found in plants, but in soil they proceeded at a slower rate. DS-15647 was the predominant product recovered through 7 days; thereafter, the sulfinyl derivative had the highest concentration. However, 68.6% of the applied dose was lost from the treated soil in the packets after 7 days. (None of the

Table VII. Relative Concentrations of ^{35}S-Labeled DS-15647 and Its Metabolites Recovered from Treated Soil in Buried Packets Exposed to Seasonal Conditions (500 μg/Treatment)

	% of applied dose at indicated days after treatment[a]					
Compound	0	3	7	14	28	56
Oxime	0.8	0.5	0.3	T	0	0
DS-15647	92.9	49.2	14.5	0.6	0.1	0
Unknown B	0	0	0	0.1	0.1	0
Unknown C	0	0	0	0.1	0.2	0
Sulfone	0.7	1.1	1.5	1.5	1.6	0
Oxime sulfoxide	0	0	0	0.5	0.5	0
Sulfoxide	4.6	9.3	12.5	12.0	8.8	0.4
Unknown(s) D	0.4	0.8	0.5	0.4	0.2	0
Unextractable	0.6	1.5	2.1	1.2	0.6	0
Lost	0	37.6	68.6	83.6	87.9	99.6

[a] Average of duplicate chromatograms of triplicate samples.

Table VIII. Movement of ^{35}S-Labeled DS-15647 in Soil under Field Conditions. Unclassified Radioactivity and Soil Moisture above or below (5 cm) Buried Packets of Treated Soil

	Days after treatment				
	3	7	14	28	56
μg equivalents recovered from packets	312	157	82	60	2
Ppm above	0.149	0.370	0.646	0.700	0.080
Ppm below	0.372	0.587	0.648	0.900	0.160
Soil moisture above, %	7.5	7.6	7.1	2.9	9.5
Soil moisture below, %	7.8	9.1	6.0	3.2	10.5

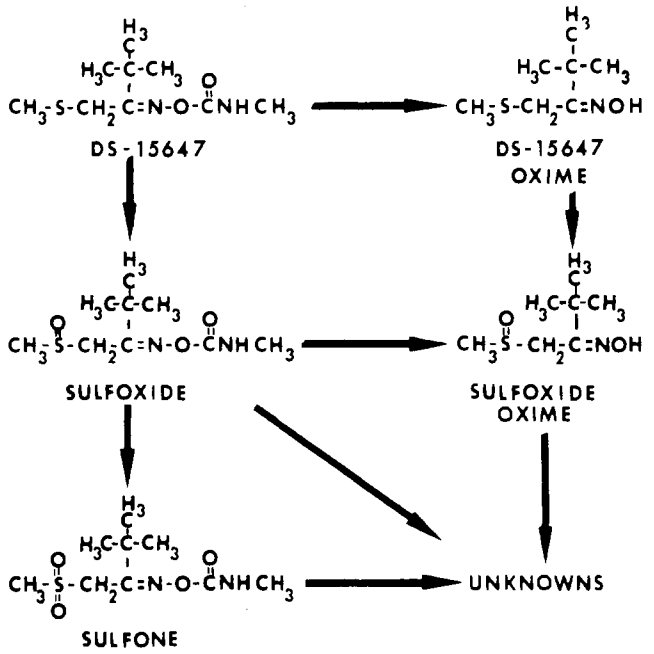

Figure 1. Proposed metabolic pathway of DS-15647 in cotton plants.

treated soil was lost.) The movement of radioactivity from the packets was primarily downward, though some upward movement was demonstrated (Table VIII). The distribution of metabolites in the samples taken from the soil surrounding the packets resembled that for the treated soil.

DISCUSSION

The results of these studies make it possible to construct a tentative pathway for the metabolism of DS-15647 (Figure 1). The major route of metabolism appeared to be the oxidation of DS-15647 to its sulfoxide and the subsequent oxidation of the latter to the sulfone. The rate of the initial reaction was decisively more rapid than that of the second, particularly in plants. Degradation of the toxic forms occurred primarily by conversion to water-soluble products (unknown D). The oximes of DS-15647 and its sulfoxide were also detected and may have been intermediates in the formation of water-soluble metabolites because the concentrations did not accumulate. Unknown A was recovered only in extracts of seed meats from treated seeds. Unknowns B and C were found in all tests, and their increased concentrations shown in the metabolism of DS-15647 sulfone suggest that they may have been derived from the sulfonyl form. The close similarity in the chromatographic properties of unknown B and oxime sulfone suggests that the materials may have been identical.

The concentrations of DS-15647, its sulfoxide and sulfone derivatives, and water-soluble metabolites in leaves of cotton plants growing in the field were comparable to those reported in a similar study of aldicarb and its equivalent metabolites (Bull, 1968). Investigations to determine the nature and toxicity of the water-soluble products formed from aldicarb in cotton plants have revealed the presence of as many as ten compounds (Bartley *et al.*, 1970); six of the metabolites were subsequently identified and found to be of low oral toxicity to rats. Based on the similarities in structure and in the metabolism of DS-15647 and aldicarb in cotton plants, it is reasonable to tentatively assume that the water-soluble metabolites of DS-15647 might also have a low order of toxicity. Indeed the results of the anticholinesterase assays in our study tend to support this conclusion.

However, from the limited study of the toxicity of DS-15647, the relative toxicities of the toxic forms of DS-15647 and aldicarb are dissimilar. The parent compounds of both carbamates are of high mammalian toxicity and have acute oral LD_{50}'s to rats of 1.0 and 8.5 mg/kg for aldicarb (Weiden *et al.*, 1965) and DS-15647 (Diamond Shamrock Corp., 1973), respectively. The sulfoxide was the most potent antiChE agent among the aldicarb compounds (Bull, 1968; Knaak *et al.*, 1966; Metcalf *et al.*, 1966; Payne *et al.*, 1966), but the greatest antiChE activity among the DS-15647 forms was exhibited by the sulfone. In tests in which the toxicants were applied topically to insects, aldicarb and its sulfoxide were generally similar in effectiveness, and both were much more effective than the sulfone (Bull, 1968; Metcalf *et al.*, 1966; Payne *et al.*, 1966). Topical LD_{50}'s of aldicarb and its sulfoxide and sulfone to boll weevil adults were 0.22, 0.42, and >25.0 μg/insect, respectively (Bull, 1968). A comparison of these data with the results from our study indicated that the difference in toxicity between comparable toxic forms of DS-15647 and aldicarb was most significant between the sulfonyl derivatives. Additional evidence of the effectiveness of DS-15647 sulfone was shown in the tests with lady beetle adults. Since the sulfoxide and sulfone forms are the major toxicants expected to be present in cotton plants, this toxicity relationship could be of some importance in the effectiveness of treatment with DS-15647.

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