Marshall, T. C.; Dorough, H. W. Bioavailability in rats of bound and conjugated plant carbamate insecticide residues. *J. Agric. Food Chem.* **1977**, *25*, 1003–1009.
McLafferty, F. W. *Interpretation of mass spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980.
Nobel, R. M.; Hamilton, D. J.; Osborne, W. J. Stability of pyrethroids on wheat in storage. *Pestic. Sci.* **1982**, *13*, 246–252.
Paulson, G. D.; Jackobsen, A. M.; Still, G. G. Animal metabolism of prophan (isopropyl carbamilate), the fate of residues in alfalfa when consumed by the rat and sheep. *Pestic. Biochem. Physiol.* **1975**, *5*, 523–528.
Soderlund, D. M.; Casida, J. E. *Substrate specificity of mouse-liver microsomal enzymes in pyrethroids metabolism in Synthetic Pyrethroids*; ACS Symposium Series 42; American Chemical Society: Washington, DC, 1977; pp 162–172.
Sutherland, M. L. Nature of propanil bound residues in rice plants as measured by plant fractionation and animal bioavailability experiment, in Bound and Conjugated Pesticide Residues. *ACS Symp. Ser.* **1976**, *No. 29*, 153–165.
Unai, T.; Casida, J. E. Synthesis of isomeric 3-(2,2-dichlorovinyl)-2-hydroxymethyl-2-methylcyclopropanecarboxylic acids and other permethrin metabolites. *J. Agric. Food Chem.* **1977**, *25*, 979–987.

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[3+2] Cycloaddition of 1,3,4-Oxadiazol-2-ylhydrazones to Aryl Isothiocyanates and Fungitoxicity of the Resulting Thiadiazolidines

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[3+2] cycloaddition of 1,3,4-oxadiazol-2-ylhydrazones IVa–f to aryl isothiocyanates yielded a novel class of compounds, 2-(arylimino)-3-(5-aryl-1,3,4-oxadiazol-2-yl)-5,5-dimethyl-1,3,4-thiadiazolidines, and the corresponding 5-methyl-5-phenyl derivatives Va–l. Condensation of 5-aryl-2-hydrazino-1,3,4-oxadiazoles IIIa–c with the appropriate ketone in equimolar quantity furnished the requisite hydrazones IVa–f. The required 5-aryl-2-hydrazino-1,3,4-oxadiazoles IIIa–c were prepared by diazotization of 2-amino-1,3,4-oxadiazoles Ia–c, followed by treatment with Zn and glacial acetic acid. Compounds Va–l have been compared with a standard commercial fungicide Dithane M-45 (manganous ethylene bis(dithiocarbamate) with zinc ions), for their fungitoxic action against *Aspergillus niger* and *Fusarium oxysporium*, and results have been correlated with the structural features of the tested compounds.

Many 1,3,4-oxadiazoles are known to display a broad spectrum of useful pesticidal activity (Meek, 1972; Stachler and Sachse, 1977; Rhone-Poulenc, 1968). Similarly, a number of 1,3,4-thiadiazoline and -thiadiazolidine derivatives, especially those bearing 2-substituted imino groups, are known to display important pesticidal activity (Paul et al., 1981; Dahle, 1977; Nuesslein and Arndt, 1977; Russo and Santagati, 1976). In view of these factors and with the hope of achieving antifungal compounds of high potency, the biolabile 1,3,4-oxadiazole and 1,3,4-thiadiazolidine nuclei have been combined to probe how this combination could enhance antifungal action. The investigation appeared quite interesting as the 2-(arylimino)-3-(5-aryl-1,3,4-oxadiazol-2-yl)-5,5-dimethyl-1,3,4-thiadiazolidines and the corresponding 5-methyl-5-phenyl derivatives Va–l reported herein have been synthesized for the first time.

The reaction sequence leading to the formation of Va–l is given in Scheme I. In the synthesis of Va–l, a novel class of heterocycles, aryl isothiocyanates act as dienophiles and the hydrazones IVa–f as dienes (aza dienes). This is an interesting example of hetero-Diels–Alder synthesis. The [3+2] cycloaddition of hydrazones IVa–f to aryl isothiocyanates was carried out at 50–60 °C in acetone to yield Va–l in 67–81% yields (Table I). The required 2-amino-5-aryl-1,3,4-oxadiazoles Ia–c were prepared by oxidative cyclization of aldehyde semicarbazones with bromine (Gibson, 1962). Diazotization of compound I followed by treatment with Zn and glacial acetic acid resulted in the formation of the precursor hydrazines IIIa–c, which, when treated with ketones, afforded the requisite hydrazones IVa–f.

Scheme I

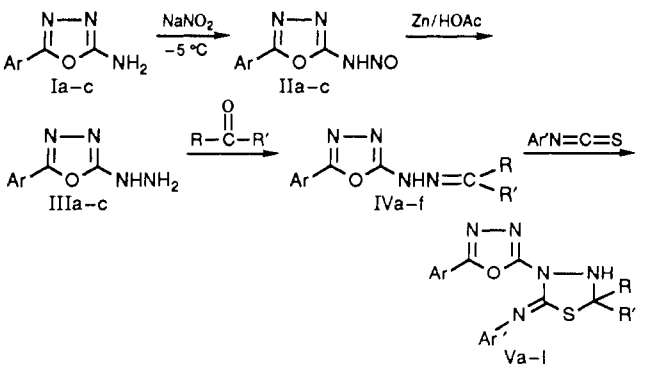

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Table I. Yields, Melting Points, Molecular Formulas, and Elemental Analyses of Compounds Va–l

compd V	Ar	Ar′	yield, %	mp, °C	mol formula	found (calcd), % N	found (calcd), % S
			R = R′ = Me				
a	C_6H_5	C_6H_5	73	165	$C_{18}H_{17}N_5OS$	20.02 (19.97)	9.22 (9.11)
b	4-ClC_6H_4	C_6H_5	71	154	$C_{18}H_{16}ClN_5OS$	18.05 (18.15)	8.45 (8.30)
c	4-$CH_3OC_6H_4$	C_6H_5	77	173–174	$C_{19}H_{19}N_5O_2S$	18.24 (18.37)	8.40 (8.39)
d	C_6H_5	4-ClC_6H_4	79	170–172	$C_{18}H_{16}ClN_5OS$	18.34 (18.15)	8.12 (8.30)
e	4-ClC_6H_4	4-ClC_6H_4	73	162–163	$C_{18}H_{15}Cl_2N_5OS$	16.80 (16.66)	7.77 (7.61)
f	4-$CH_3OC_6H_4$	4-ClC_6H_4	74	180–182	$C_{19}H_{18}ClN_5O_2S$	16.62 (16.84)	7.82 (7.70)
			R, R′ = Me, C_6H_5				
g	C_6H_5	C_6H_5	75	154–155	$C_{23}H_{19}N_5OS$	16.76 (16.94)	7.84 (7.74)
h	4-ClC_6H_4	C_6H_5	78	180–181	$C_{23}H_{18}ClN_5OS$	15.72 (15.64)	7.35 (7.15)
i	4-$CH_3OC_6H_4$	C_6H_5	81	185–187	$C_{24}H_{21}N_5O_2S$	15.85 (15.80)	7.15 (7.22)
j	C_6H_5	4-ClC_6H_4	69	190–191	$C_{23}H_{18}ClN_5OS$	15.65 (15.64)	7.04 (7.15)
k	4-ClC_6H_4	4-ClC_6H_4	67	174–176	$C_{23}H_{17}Cl_2N_5OS$	14.75 (14.52)	6.65 (6.63)
l	4-$CH_3OC_6H_4$	4-ClC_6H_4	68	188–189	$C_{24}H_{20}ClN_5O_2S$	14.55 (14.65)	6.76 (6.70)

Table II. Spectral Data of Compounds Va–l

compd V	IR (KBr), cm^{-1} N—H	IR (KBr), cm^{-1} C=N (exocyclic)	IR (KBr), cm^{-1} C=N (cyclic)	^1H NMR ($CDCl_3$–DMSO-d_6)	MS/M^+, m/z
a	3250	1655	1625	1.42 (6 H, s, C_5-Me_2), 7.24–8.00 (10 H, m, aromatic H), 5.42 (1 H, br s, NH)	351
b	3255	1650	1620	1.44 (6 H, s, C_5-Me_2), 7.44–8.20 (9 H, m, aromatic H), 5.44 (1 H, br s, NH)	385, 387
c	3250	1680	1620	1.42 (6 H, s, C_5-Me_2), 7.20–8.20 (9 H, m, aromatic H), 5.38 (1 H, br s, NH), 3.74 (3 H, s, OCH_3)	381
d	3260	1660	1630	1.46 (6 H, s, C_5-Me_2), 7.54–8.20 (9 H, m, aromatic H), 5.42 (1 H, br s, NH)	385, 387
e	3255	1655	1630	1.44 (6 H, s, C_5-Me_2), 7.10–8.00 (8 H, m, aromatic H), 5.40 (1 H, br s, NH)	420, 424
f	3250	1655	1625	1.42 (6 H, s, C_5-Me_2), 7.20–8.20 (8 H, m, aromatic H), 5.44 (1 H, br s, NH), 3.76 (3 H, s, OCH_3)	415, 417
g	3255	1650	1620	2.40 (3 H, s, C_5-Me), 7.20–8.00 (15 H, m, aromatic H), 5.38 (1 H, br s, NH)	413
h	3260	1655	1625	2.42 (3 H, s, C_5-Me), 7.20–8.20 (14 H, m, aromatic H), 5.44 (1 H, br s, NH)	447, 449
i	3250	1660	1625	2.46 (3 H, s, C_5-Me), 7.00–8.20 (14 H, m, aromatic H), 5.38 (1 H, br s, NH), 3.74 (3 H, s, OCH_3)	443
j	3255	1660	1620	2.40 (3 H, s, C_5-Me), 7.22–8.22 (14 H, m, aromatic H), 5.42 (1 H, br s, NH)	447, 449
k	3260	1655	1620	2.44 (3 H, s, C_5-Me), 6.98–8.20 (13 H, m, aromatic H), 5.40 (1 H, br s, NH)	482, 486
l	3255	1650	1630	2.42 (3 H, s, C_5-Me), 7.00–8.00 (13 H, m, aromatic H), 5.42 (1 H, br s, NH), 3.76 (3 H, s, OCH_3)	477, 479

The structural assignments of the synthesized compounds were based on their elemental analysis, IR, ^1H NMR, and mass spectral data (Tables I and II).

The antifungal activities of compounds Va–l were evaluated in vitro against *Aspergillus niger* and *Fusarium oxysporium* at three concentrations with Dithane M-45, a commercial fungicide, as standard (Table III). Of the 12 compounds tested (Va–l), Ve, Vh, and Vk displayed antifungal activities on the order of Dithane M-45 against both test fungi at 1000 ppm.

EXPERIMENTAL SECTION

Melting points were determined in open glass capillaries and are uncorrected. IR spectra in KBr were recorded on a Perkin-Elmer 157 spectrophotometer. ^1H NMR spectra were recorded on a EM-360L (60-MHz) NMR spectrometer in $CDCl_3$–DMSO-d_6 with TMS as internal reference; chemical shifts are expressed in δ. Mass spectra were recorded on a JEOL JMS-D-300 instrument.

2-Amino-5-aryl-1,3,4-oxadiazoles Ia–c. These were prepared by oxidative cyclization of apropriate aldehyde semicarbazones with bromine in glacial acetic acid in the presence of anhydrous sodium acetate (Gibson, 1962). Data for compounds Ia–c agreed well with analytical data already reported in the literature (Gehlen and Moechel, 1962; Gibson, 1962; Hoggarth, 1949).

5-Aryl-2-nitrosamino-1,3,4-oxadiazoles IIa–c. These were prepared by diazotization of 2-amino-5-aryl-1,3,4-oxadiazoles Ia–c with sodium nitrite and dilute HCl (50:50, v/v) at −5 °C. Data for compounds IIa–c agreed well with analytical data already reported in the literature (Stoue and Fehrenbach, 1929; Bhattacharya, 1979).

5-Aryl-2-hydrazino-1,3,4-oxadiazoles IIIa–c. 5-Aryl-2-

Table III. Fungicidal Screening Results of Compounds IVa–d and Va–l

	av % inhibn against					
	A. niger			*F. oxysporium*		
compd	1000 ppm	100 ppm	10 ppm	1000 ppm	100 ppm	10 ppm
IVa	40.4	30.4	12.8	41.3	32.1	13.1
b	42.2	29.6	12.2	32.2	30.6	11.2
c	38.8	28.8	15.7	40.7	29.3	13.8
d	43.5	32.6	18.3	42.5	30.4	15.0
Va	75.8	53.8	39.8	75.4	49.6	47.4
b	96.4	58.6	38.6	97.6	49.8	43.6
c	72.4	49.6	39.4	72.6	47.4	42.4
d	80.6	54.4	44.4	80.4	54.6	43.4
e	98.0	44.6	44.8	99.4	48.4	47.8
f	73.4	46.4	42.4	72.4	49.4	42.8
g	77.4	48.4	46.6	76.6	50.8	48.8
h	98.5	53.6	47.8	99.8	53.5	46.8
i	75.5	42.5	39.8	74.1	41.4	47.6
j	80.8	59.4	48.4	88.8	58.6	47.8
k	99.4	44.6	43.8	99.8	43.4	46.4
l	75.8	50.6	43.8	74.4	47.6	39.6
Dithane M-45	100	80.8	66.5	100	85.3	62.2

nitrosamino-1,3,4-oxadiazoles IIa–c (0.1 M) were refluxed with Zn granules (16 g) in glacial acetic acid (60 mL) for 2 h. The mixture was filtered, and the filtrate was made alkaline with sodium carbonate solution to yield 5-aryl-2-hydrazino-1,3,4-oxadiazoles IIIa–c, which were filtered and washed with water. The hydrazino compounds, being unstable, were used immediately in the next step.

Acetone/Acetophenone 5-Aryl-1,3,4-oxadiazol-2-ylhydrazones IVa–f. A mixture of 5-phenyl-2-hydrazino-1,3,4-oxadiazole (IIIa; 17.6 g, 0.1 mol) and acetone (5.8 g, 0.1 mol) in absolute ethanol was refluxed for 1–2 h. Desired ketone IVa (1,3,4-oxadiazol-2-ylhydrazone) crystallized on cooling the reaction mixture. It was filtered and recrystallized from EtOH–H_2O (80:20, v/v), yield 28.4 g (78%); mp 148–150 °C; IR 1660 (exocyclic C=N), 1625 cm^{-1} (cyclic C=N). Anal. Found for $C_{11}H_{12}N_4O$: C, 60.92; H, 5.61; N, 25.82. Calcd: C, 61.11; H, 5.55; N, 25.92.

The following compounds were similarly prepared and recrystallized from ethanol.

IVb: yield 82%; mp 154–155 °C; IR 1665 (exocyclic C=N), 1620 cm^{-1} (cyclic C=N); Anal. Found for $C_{11}H_{11}ClN_4O$: C, 52.62; H, 4.50; N, 22.32. Calcd: C, 52.69; H, 4.39; N, 22.35.

IVc: yield 84%; mp 165–167 °C; IR 1660 (exocyclic C=N), 1625 cm^{-1} (cyclic C=N). Anal. Found for $C_{12}H_{14}N_4O_2$: C, 58.41; H, 5.55; N, 22.70. Calcd: C, 58.53; H, 5.69; N, 22.76.

IVd: yield 81%; mp 185–187 °C; IR 1670 (exocyclic C=N), 1615 cm^{-1} (cyclic C=N); Anal. Found for $C_{16}H_{14}N_4O$: C, 68.92; H, 5.00; N, 20.00. Calcd: C, 69.06; H, 5.03; N, 20.14.

IVe: yield 80%; mp 174–175 °C, IR 1670 (exocyclic C=N), 1620 cm^{-1} (cyclic C=N). Anal. Found for $C_{14}H_{13}ClN_4O$: C, 61.22; H, 4.22; N, 17.82. Calcd: C, 61.44; H, 4.16; N, 17.92.

IVf: yield 81%; mp 188–189 °C; IR 1665 (exocyclic C=N), 1615 cm^{-1} (cyclic C=N). Anal. Found for $C_{17}H_{16}N_4O_2$: C, 65.96; H, 5.00; N, 18.02. Calcd: C, 66.23; H, 5.15; N, 18.18.

2-(Arylimino)-3-(5-aryl-1,3,4-oxadiazol-2-yl)-5,5-dimethyl-1,3,4-thiadiazolidines and the Corresponding 5-Methyl-5-phenyl Derivatives Va–l. To a solution of EtONa (0.01 mol) in EtOH (25 mL) was added the ketone 1,3,4-oxadiazol-2-ylhydrazone (0.01 mol, portionwise with stirring at room temperature). The reaction mixture was further stirred for $^1/_2$ h, and then aryl isothiocyanate (0.01 mol) was added portionwise at room temperature. The reaction mixture was stirred for a further 1 h at room temperature followed by stirring at 50–60 °C for $^1/_2$ h. The reaction mixture was cooled and quenched with water, and the product thus obtained was recrystallized from ethanol. Yields, melting points, molecular formulas, and elemental analyses of the compounds (Va–l) thus synthesized are recorded in Table I. The spectral data are given in Table II.

Fungicidal Screening. The pure cultures of test fungi (*A. niger*, *F. oxysporium*), the pathogenicity of which was already verified, were obtained from the Division of Mycology and Plant Pathology, Indian Agricultural Research Institute, Delhi. Agar (bacteriological grade) supplied by Sarabhai M. Chemicals was used as such. Compounds Va–l were screened by the agar plate technique (Horsfall, 1945) using Czapek's agar medium at 1000, 100, and 10 ppm concentrations as described earlier (Yadav et al., 1988). Dithane M-45 was also tested under similar conditions for comparison. The antifungal activities displayed by test compounds Va–l are summarized in Table III.

RESULTS AND DISCUSSION

It is evident from the screening data (Table III) that all the tested compounds (Va–l) inhibited more than 72% growth of both test fungi at 1000 ppm concentration. Of these, the most active compounds (Vb, Ve, Vh, Vk) exhibited fungicidal action almost equivalent to that of Dithane M-45 at 1000 ppm concentration and inhibited 38–48% growth of both the fungal species even at 10 ppm concentration.

Although some of the screened compounds (Vb, Ve, Vh, and Vk) were highly toxic to *A. niger* and *F. oxysporium* at 1000 ppm, their toxicity decreased abruptly at 100, and 10 ppm. Compounds Va–l exhibited fungicidal activity higher than their parent compounds IVa–f, presumably due to introduction of the >NCS–moiety, which is well-known to induce toxicity in many pesticides (Donald, 1955; Singh and Yadav, 1976). Compounds Va–f incorporating 5,5-dimethyl groups are less active than their analogues bearing 5-methyl-5-phenyl (Vg–l) at 1000 ppm against both test fungi. In general, compounds having chlorophenyl group were more potent than those without chloro group. As such, compounds with two chlorophenyl groups were more active than those with only one chlorophenyl group.

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LITERATURE CITED

Bhattacharya, B. K. Search for New Heterocyclic Pesticides. Ph.D. Thesis, Gorakhpur University, 1979.

Dahle, N. A. U.S. Patent 4020078, 1977; *Chem. Abstr.* **1978**, *89*, 6327.

Donald, E. H. *Chemistry of Pesticides*; Van Nostrand: New York, 1955; p 295.

Gehlen, H.; Moechel, K. Oxidation of Aldehyde Semicarbazones to 2-Amino-1,3,4-oxadiazoles and their conversion into 1-Acylsemicarbazides. *Ann.* **1962**, *651*, 133–136; *Chem. Abstr.* **1962**, *57*, 3424.

Gibson, M. S. Hydrazones. III. Intramolecular 1,3-Dipolar Addition Involving Nitro and carbonyl groups. *Tetrahedron* **1962**, *18*, 1377–1380.

Hoggarth, E. Compounds Related to Thiosemicarbazide. Part III. 1-Benzoyl-S-Methylisothiosemicarbazides. *J. Chem. Soc.* **1949**, 1918–1923.

Horsfall, J. G. Quantitative Bioassay of Fungicides in the Laboratory. *Bot. Rev.* **1945**, *11*, 357–397.

Meek, W. H. U.S. Patent 3641045, 1972; *Chem. Abstr.* **1972**, *76*, 126991.

Nuesslein, L.; Arndt, F. Ger. Offen. 2621647, 1977; *Chem. Abstr.* **1978**, *88*, 105349.

Paul, H.; Sitte, A.; Wessel, R. Ger. Patent 314 (4), 1981, 359–364; *Chem. Abstr.* **1982**, 12462.

Rhone-Poulenc S. A. Brit. Pat. 110500, 1968; *Chem. Abstr.* **1968**, *69*, 52143.

Russo, F.; Santagati, M. *Farmaco. Ed. Sci.* **1976**, *31* (1), 41; *Chem. Abstr.* **1976**, *84*, 90090.

Singh, H.; Yadav, L. D. S. Synthesis of some 5-Aryl-2 Heteroaryl/heteroarylamino-1,3,4-oxadiazoles as Potential Fungicides. *Agric. Biol. Chem.* **1976**, *40* (4), 759–764.
Stachler, G.; Sachse, B. German Offen. 541388, 1977; *Chem. Abstr.* **1977**, *87*, 23292.
Stoue, R.; Fehrenbach, K. Amino derivatives of 1-Thio- and furo-3,4-diazoles. *J. Prakt. Chem.* **1929**, *122*, 289–318; *Chem. Abstr.* **1930**, *24*, 114.
Yadav, L. D. S.; Misra, A. R.; Singh, H. Ring Transformation of Michael Adducts of 4-Benzylidene-5-oxazolones and 3-Mercapto-*s*-Triazoles to 2,3-Dihydro-4*H*-*s*-triazolo[3,4-*b*]-[1,3]thiazine-4-ones with Some Antifungal Activity. *J. Agric. Food Chem.* **1988**, *36*, 633–636.

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Metabolism of [^{14}C]Quizalofop-ethyl in Soybean and Cotton Plants

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The metabolism of [*phenyl*-U-^{14}C]quizalofop-ethyl or [*quinoxaline*-^{14}C]quizalofop-ethyl was investigated in soybean and cotton plants. [^{14}C]Quizalofop-ethyl was applied to soybean or cotton plants at 4 oz of AI/acre as a postemergence spray, and plant samples were harvested initially (day 0) and at 3, 6, and 13.5 (maturity) weeks after treatment. No detectable ^{14}C residues (<0.01 ppm) were found in mature beans or pods, whereas the mature fiber and seeds from the cotton contained 0.08 and 0.09 ppm total ^{14}C residues, respectively. The proposed metabolic pathway of quizalofop-ethyl was similar in both soybean and cotton plants. In the foliage, quizalofop-ethyl was rapidly metabolized to 2-[4-[(6-chloroquinoxalin-2-yl)oxy]phenoxy]propanoic acid (quizalofop) that metabolized to the phenol metabolites 6-chloroquinoxalin-2-ol and 2-(4-hydroxyphenoxy)propanoic acid. Glucose conjugates of quizalofop possibly were formed since addition of β-glucosidase to aqueous extracts (containing polar ^{14}C residues) of soybean foliage slowly released [^{14}C]quizalofop.

Quizalofop-ethyl (ethyl 2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoate, the active ingredient in ASSURE herbicide, a registered product of Du Pont in the United States) is used to control both annual and perennial grass weeds in broadleaf crops. Tolerant crops include alfalfa, bean, cabbage, canola, carrot, lettuce, potato, soybean, sugar beet, tobacco, tomato, and turnip.

The metabolic pathways of phenoxyphenoxy herbicides similar to quizalofop-ethyl have been reported. Shimabukuro et al. (1979), Jacobson and Shimabukuro (1984), and Gorbach et al. (1977) studied the metabolism of diclofop in oat and wheat plants. The metabolic pathway of quizalofop in tolerant plants has not been reported previously. This study establishes the metabolic pathways of quizalofop-ethyl in two tolerant crops, soybean and cotton. The accumulation potential of quizalofop-ethyl residues in mature soybeans and cotton fibers and seeds was also determined. When either the phenyl or the phenylquinoxaline portion of the quizalofop-ethyl molecule was radiolabeled with ^{14}C, it was possible to follow the metabolic fate of both ring structures of the quizalofop-ethyl molecule.

MATERIALS

Quizalofop-ethyl (ethyl 2-[4-[(6-chloro-2-quinoxalinyl)oxy]phenoxy]propanoate) was uniformly labeled on the phenyl ring or the phenyl portion of the quinoxaline ring. In the cotton study, the specific activities of [*phenyl*-U-^{14}C]quizalofop ethyl and [*quinoxaline*-^{14}C]quizalofop-ethyl were 10.9 and 9.7 μCi/mg, respectively. In the soybean study, [*phenyl*-U-^{14}C]quizalofop-ethyl and [*quinoxaline*-^{14}C]quizalofop-ethyl each had a specific activity of 12.4 μCi/mg. The radiochemical purities were greater than 99%. Nonradiolabeled standards of quizalofop-ethyl and potential metabolites were synthesized at the Agricultural Products Department, E. I. du Pont de Nemours and Co., Inc. (Wilmington, DE).

All solvents used in the extraction and analytical procedures of both studies were high-performance liquid chromatography (HPLC) grade (Fisher Scientific, Fair Lawn, NJ), except methyl ethyl ketone, which was reagent grade. β-Glucosidase (Type II), cellulase (Type I), and protease were purchased from Sigma Chemical Co. (St. Louis, MO). All other common chemicals were reagent grade or better.

EXPERIMENTAL METHODS

Plant Growth and Treatment. Soybean plants (Williams variety) were field grown near Newark, DE. The soybean plants, at the second trifoliate leaf stage, were divided into two plots, and a postemergence spray of [*phenyl*-U-^{14}C]quizalofop-ethyl (40.0 mg; 495 μCi), dissolved in 500 μL of 4% Atlox 3408F (ICI America) in xylene and diluted with 130 mL of water, was applied to the foliage in the first plot at 4.1 oz of AI/acre. [*quinoxaline*-^{14}C]Quizalofop-ethyl (37.8 mg; 467 μCi), dissolved in 500 μL of 4% Atlox 3408F in xylene and diluted with 130 mL of water, was sprayed on the foliage in the second plot at 3.9 oz of AI/acre.

Cotton plants (Coker 310, 15 in. tall) were field grown near Fayetteville, NC, and divided into two plots. A postemergence spray of [*phenyl*-U-^{14}C]quizalofop-ethyl (47.7 mg; 520 μCi), dissolved in 25 mL of acetone and diluted with 150 mL of water, was sprayed on the foliage of the cotton plants in one plot, and [*quinoxaline*-^{14}C]quizalofop-ethyl (48.0 mg; 466 μCi), dis-

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