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Received for review August 24, 1978. Accepted January 8, 1979.

Structure-Activity Relationships for Antidotes to Thiocarbamate Herbicides in Corn

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Seventeen different amides and one carbamate were synthesized as possible antidotes for six different thiocarbamate herbicides in corn. Only six of the 18 compounds failed to show significant antidote activity for at least one thiocarbamate herbicide. In quartz sand nutrient culture, dichloroacetamides were significantly more active than monochloro or trichloro analogues as antidotes for molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbothioate) or cycloate (*S*-ethyl *N*-ethylthiocyclohexanecarbamate). In quartz sand nutrient culture, various dichloroacetamides varying in N substituents were highly effective as antidotes for particular thiocarbamate herbicides with essentially identical N substituents. However, when applied to soil, R25788 (*N,N*-diallyl-2,2-dichloroacetamide) was the most effective antidote for at least five different thiocarbamates, apparently due to greater availability for uptake from the soil. We conclude that amides that are closely similar in structure to various thiocarbamate herbicides are often effective antidotes to these herbicides in corn.

N,N-Diallyl-2,2-dichloroacetamide (R-25788) was developed as a selective antidote to either EPTC (*S*-ethyl *N,N*-dipropylthiocarbamate) or butylate (*S*-ethyl *N,N*-diisobutylthiocarbamate) in corn (*Zea mays* L.) by Pallos et al. (1977) in 1972. Although extensive research of a practical and mechanistic nature has been conducted [see reviews by Blair et al. (1976) and Pallos and Casida (1978)], there is not yet full agreement on the actual mechanisms involved for the action of either the thiocarbamate herbicides or the dichloroacetamide antidotes for these herbicides in corn. Lay and Casida (1978) have proposed that the sulfur atom of EPTC or other thiocarbamates is highly important for phytotoxicity because of the production of the EPTC-sulfoxide, a highly toxic oxidizing metabolite within corn. They propose that glutathione-SH complexes with and detoxifies these sulfoxides and that glutathione-SH production is enhanced by the dichloroacetamide antidotes. Wilkinson (1978a) has shown that EPTC effects on fatty acid synthesis in several plants can be reversed by R-25788. In a more recent report, Wilkinson (1978b) has shown that EPTC influences the synthesis of kaurene, an intermediate in the production of gibberellic acid. Thus it is possible that the antidote may be acting at the hormone level as well.

In an earlier study (Stephenson et al., 1978), it was established that amides closely similar in structure to EPTC were even more effective than R-25788 as antidotes for EPTC in corn grown in a "soil free" system. The purpose of the study reported herein was to determine whether similar structure-activity relationships could be observed among series of analogues "closely similar" to other thiocarbamate herbicides.

MATERIALS AND METHODS

Synthesis of Amide Analogues. The amide antidote analogues were synthesized from the appropriate acid

chlorides and amines as previously described (Stephenson et al., 1978). Overall yields were typically 50-60% (see Supplementary Material Available paragraph).

Quartz Sand Nutrient Culture Bioassay. Corn (*Zea mays* L. United Hybrid 106, Stewart 2501, Golden Beaver) was germinated in petri dishes at 24 °C and then transferred to quartz sand nutrient culture in styrofoam cups as previously described (Stephenson et al., 1978). The plants were maintained in a growth room with a 16-h photoperiod with 46 klux light intensity at 24 °C and an 8-h dark period at 20 °C. Appropriate combinations of herbicide and antidote solutions were added simultaneously in 20-mL volumes of nutrient solution to the quartz sand. Treatments were applied twice at 2 and 4 days after transplanting. The plants were maintained with half-strength Hoagland's nutrient solution until harvested 10-11 days after transplanting.

Bioassays in Soil. Some bioassays were repeated in soil. Most conditions were the same except that the pregerminated seeds were transferred to soil in 10-cm peat pots. The appropriate treatments were applied in 50-mL volumes of H₂O when the corn seedlings began to emerge. After treatment a thin layer of soil was added to the surface of each pot to prevent losses by volatilization. Ten days later, this treatment procedure was repeated. Fertility was maintained by weekly watering with soluble 20-20-20 fertilizer until the plants were harvested 20 days after transplanting. The soil was 10% clay, 56% sand, 30% silt, and 4% organic matter and had a pH of 7.4.


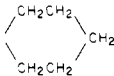


Statistical Procedures. All individual experiments were conducted twice with at least four replicates per treatment. Corn shoot weights were obtained after oven drying. Data were subjected to analysis of variance and Duncan's Multiple Range Tests to facilitate comparisons of antidote activity.

RESULTS AND DISCUSSION

Antidotes for Molinate. Six different dichloroacetamides varying in N substituents were synthesized as possible antidotes for molinate (*S*-ethyl hexahydro-1*H*-

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Table I. Comparative Activity of Various Dichloroacetamides as Antidotes to Molinate in Corn Grown in Quartz Sand Nutrient Culture

antidotes added to molinate ^a			
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CHCl}_2\text{CN} \\ \diagup \quad \diagdown \\ \text{R}_1 \quad \text{R}_2 \end{array}$			
code	amide chains		corn injury (% reduc. in shoot dry wt)
	R ₁	R ₂	
aa ^b	-CH ₂ CH=CH ₂	-CH ₂ CH=CH ₂	32 c
pp	-CH ₂ CH ₂ CH ₃	-CH ₂ CH ₂ CH ₃	45 b
I			27 c
II			45 b
hm			27 c
III			18 d
	control, molinate alone ^a		55 a
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{SCN} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CH}_2\text{CH}_2 \\ \text{CH}_2\text{CH}_2\text{CH}_2 \end{array}$		

^a Molinate and potential antidotes were applied simultaneously at concentrations of 10⁻⁴ M in quartz sand nutrient culture to 4-day germinated corn seedlings. Plants were harvested 10-11 days after treatment. Means (of four replicates) followed by unlike letters significantly differ (0.05 level, ANOV and Duncan's). ^b Also known by the no. R-25788.

azepine-1-carbothioate) in corn. Included in the series was *N,N*-diallyl-2,2-dichloroacetamide (code aa) or R-25788. In this study, molinate at 10⁻⁴ M alone in quartz sand nutrient culture reduced corn shoot growth to less than 50% of the control (Table I). Very little protection from molinate was afforded by simultaneous treatment with either the *N,N*-dipropyl dichloroacetamide (pp) or the cyclic *N*-piperidinyldichloroacetamide (II) having five methylene carbons. Cyclic amides with four or six methylene carbons had good activity as antidotes; however, the most effective antidote to molinate in corn was found to be morpholinyl-2,2-dichloroacetamide which has an oxygen in the ring. At equal concentrations of 10⁻⁴ M, this latter antidote reduced molinate injury from 55% to less than 20% (Table I).

A series of morpholinyl analogues was then synthesized and assayed for activity as molinate antidotes to examine the importance of chlorination of the acetyl group [as was done earlier for EPTC, Stephenson et al. (1978)]. Inclusion of two chlorines on the methyl carbon provided the most effective morpholinyl derivative (III) with respect to antidote activity for molinate (Table II). It is apparent from this study that dichloroacetamides with cyclic structures similar to that of molinate can be highly active antidotes to molinate applied to corn growing in a soil-free system.

Comparative Activity of Five Dichloroacetamides as Antidotes for Five Different Thiocarbamate Herbicides. To further test the theory that structurally similar compounds can be active as antidotes for thiocarbamate herbicides in corn, four different dichloroacetamides were synthesized as possible antidotes for five different thiocarbamate herbicides, varying primarily in the N substituents. Since dichloroacetamides had proven to be so consistently effective for reducing EPTC (Ste-

Table II. Influence of Varying Acid Chain Chlorination on the Activity of *N*-Morpholinylacetamides as Antidotes for Molinate in Corn Grown in Quartz Sand Nutrient Culture

morpholinyl antidotes added to molinate ^a		
code	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R} \text{---} \text{N} \text{---} \text{C} \text{---} \text{O} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{O} \end{array}$	corn injury (% reduc. in shoot dry wt)
IV	CH ₃	50 a
V	CH ₂ Cl	35 b
III	CHCl ₂	18 c
VI	CCl ₃	55 a
control, molinate alone ^a		

^a Molinate and potential antidotes were applied simultaneously at concentrations of 10⁻⁴ M in quartz sand nutrient culture to 4-day germinated corn seedlings. Plants were harvested 10-11 days after treatment. Means (of four replicates) followed by unlike letters significantly differ (0.05 level, ANOV and Duncan's).

phenson et al., 1978) or molinate injury (Table II), all of the analogues synthesized for this study were dichloroacetamides. The N substituents in the potential antidotes were the same as those of the five thiocarbamate herbicides; R-25788 (aa) was also included in each experiment (Table III). The concentrations of the five thiocarbamate herbicides were varied so that corn shoot growth would be no more than 60% of the control in the absence of antidotes (Table III). The various antidotes were applied at 10⁻⁴ M and 3.5 kg/ha in nutrient culture and soil, respectively. In quartz sand nutrient culture, the various herbicides alone reduced corn shoot growth to 58% of the control or less (Figure 1). With the exception of *N,N*-

Table III. Structure and Application Rate for Five Thiocarbamate Herbicides and Five Corresponding Dichloroacetamides Evaluated for Antagonistic Interactions within Corn Grown in Either Quartz Sand Nutrient Culture or Soil

code	name	herbicides structure	application rate		antidotes ^a	
			nutrient culture ($\times 10^{-4}$ M)	soil (kg/ha)	code	structure
(E)	EPTC		1.0	7	(aa) ^b	
(V)	vernolate		1.3	9	(pp)	
(P)	pebulate		1.3	18	(eb)	
(M)	molinate		2.2	22	(hm)	
(B)	butylate		10.3	27	(ib)	

^a Antidote application rates were 10^{-4} M and 3.5 kg/ha in nutrient culture and soil, respectively. ^b Also known by no. R25788.

dipropyl-1,1-dichloroacetamide (pp) as an antidote to EPTC (E), total prevention of herbicide injury was not observed with any of the antidotes. This allowed us to discern any apparent structure-activity relationships. In every instance the compound most similar in structure to a particular herbicide was highly active as an antidote to that herbicide in corn. Of particular interest is the fact that the *N,N*-diisobutyl (ib) and the *N*-hexamethylenyl (hm) analogues were very poor antidotes for all but butylate (B) and molinate (M), respectively, the two thiocarbamates which were "most similar" to them in structure. Furthermore, except for vernolate (V) and pebulate, the widely used R-25788 (aa) was significantly less active (0.05 level) as an antidote for the various herbicides than the compounds with structures "more similar" to those herbicides.

In the soil bioassay some important similarities and some important differences in structure-activity relationships were apparent. In agreement with the nutrient culture results, each of the four *N*-substituted amide analogues had good antidote activity in soil for the particular thiocarbamate herbicide with identical *N* substituents (Figure 1). However, in most instances, the "most similar" antidotes were not as effective when applied to soil as was R-25788 (aa).

Antidotes for Cycloate in Corn and Oats. Cycloate (*S*-ethyl *N*-ethylthiocyclohexanecarbamate) is another thiocarbamate herbicide which is widely used for the selective control of nutsedges (*Cyperus* sp.), annual grasses, and other annual weeds in sugar beets, red beets, and spinach (Hilton et al., 1974). It lacks sufficient selectivity for use in grass crops and has received little attention in studies with antidotes to see if its selectivity can be improved. In one report, Pallos et al. (1978) showed that R-25788 had some activity as an antidote for cycloate in corn but R-25788 was much less effective for cycloate than for butylate or vernolate. In the present study, eight

different cyclic amides were synthesized to examine the antidote activity of compounds closely similar in structure to cycloate. The quartz sand nutrient culture bioassay was again employed. The *N*-phenylamides with chlorines on the rings (VII and VIII) had essentially no antidote activity for cycloate in corn (Table IV). [It should be noted that compound VII in Table IV is the herbicide propanil (3',4'-dichloropropionanilide).] Surprisingly, among the *N*-ethyl-dichloroacetamides, very high antidote activity for cycloate in corn was observed when either a cyclohexyl ring (X) or a phenyl ring (XII) was the second *N* substituent. Among various *N*-phenylamides (XI-XIV), a familiar structure-activity relationship was again apparent, with greater antidote activity being observed for the dichloroacetamide (XII) than for equivalent monochloro (XI) or trichloro (XIII) analogues. This study again establishes that amide compounds similar in structure to particular thiocarbamates can be highly active as antidotes for these herbicides in corn.

In contrast to earlier studies with EPTC, an antidote even more similar to cycloate than the above dichloroacetamides, namely, ethyl *N*-phenyl-*N*-ethylcarbamate (XIV), had no activity as an antidote for cycloate under the conditions of this test, whereas *N,N*-dipropyl-*N*-ethylcarbamate had good activity as an antidote for EPTC. In both of these cases, the major difference between the antidote and the herbicide is the inclusion of an oxygen instead of the sulfur in the antidote. It is also apparent that effective antidotes for cycloate in corn are selective since at equivalent physiological rates no antidote activity was observed for cycloate in oats. Thus, our empirical observation that effective antidotes for thiocarbamate herbicides in corn have structures similar to those of the herbicide may not be applicable for other crops or for other families of herbicides. In this connection it should be noted that we have not yet found structurally related compounds to be active as antidotes for the thiocarbamate

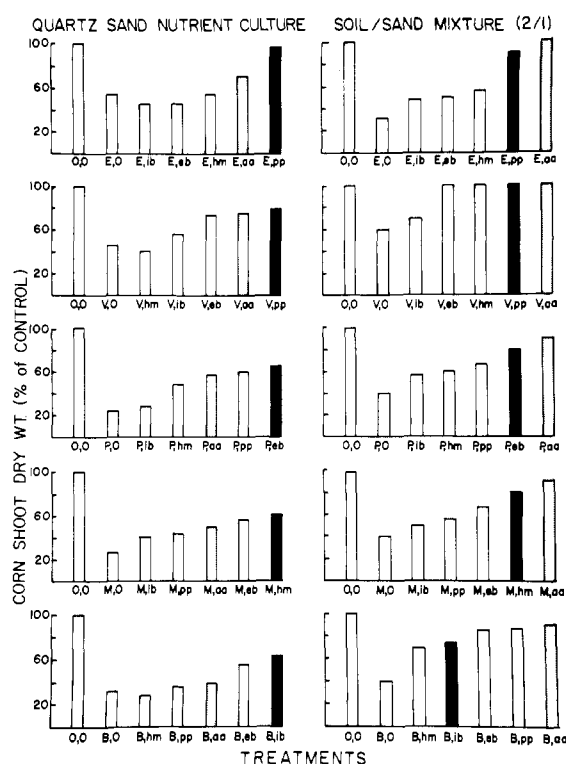
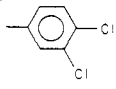
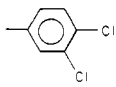
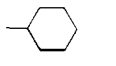
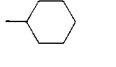
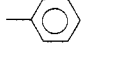
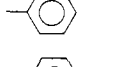
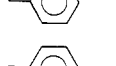
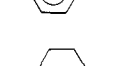
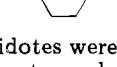


Figure 1. Comparative activity of *N,N*-diallyl- (aa), *N*-ethyl-*N*-butyl- (eb), *N,N*-diisobutyl- (ib), *N*-hexamethylenyl- (hm), and *N,N*-dipropyl- (pp) dichloroacetamides as antidotes to EPTC (E), vernolate (V), pebulate (P), molinate (M), or butylate (B) in corn grown in either quartz sand nutrient culture or soil. Within each herbicide experiment, means (of four replicates) varying by more than 9% significantly differ (0.05 level, ANOV and Duncan's). Refer to Table III for structures and application rates. In each graph the antidote "most similar" to the respective herbicide is illustrated by the solid black bar.

herbicide triallate [*S*-(2,3,3-trichloroallyl) diisopropylthiocarbamate] in corn, oats, or wheat. Also, one particular antidote compound that provides a slight exception to this theory in nutrient culture bioassays is *N*-morpholinyl-2,2-dichloroacetamide (III) (with an oxygen and four methylene groups in the ring). In the present study (Tables I and II) and in the earlier study (Stephenson et al., 1978), it had greater antidote activity to either molinate or EPTC than antidotes more closely similar to either of these herbicides.

In the earlier study (Stephenson et al., 1978), the structure-activity relationships for antidotes to EPTC were developed with the same soil-free bioassay as employed herein. For good antidote activity to EPTC, electro-negative groups in the acid side of the molecule were required. Dichloroacetyl groups or ethoxycarbonyl groups provided the highest antidote activity. Highest antidote activity was observed with dichloroacetamides or ethyl carbamates which possessed two *N* substituents closely similar to the two *N*-propyl groups of EPTC such as two propyl, allyl, or ethyl groups. Within this study, highly active antidotes to EPTC were also highly active as antidotes to vernolate, a very similar thiocarbamate herbicide. In fact, nearly identical structure-activity relationships were apparent for five antidotes to these two herbicides in corn grown in either nutrient culture or soil. Conversely, *N*-ethyl-*N*-butyl- (eb), *N,N*-diisobutyl- (ib), and *N*-hexamethylenyl- (hm) dichloroacetamides were not useful antidotes for EPTC or vernolate which carry *N,N*-dipropyl groups but were highly active as antidotes for pebulate, butylate, and molinate which have *N*-ethyl-*N*-butyl, *N*-

Table IV. Comparative Activity of Various Anilides as Antidotes to Cycloate in Corn and Oats Grown in Quartz Sand Nutrient Culture

code	various amides evaluated as antidotes for cycloate in corn and oats			injury ^a	
	R ₁	R ₂	R ₃	corn, %	oats, %
VII	CH ₃ CH ₂	H		55 a	
VIII	CH ₃ CH ₂	CH ₃		55 a	
IX	CH ₃ CH ₂	CH ₂ CH ₃		40 b	65 b
X	CHCl ₂	CH ₂ CH ₃		12 c	55 a
XI	CH ₂ Cl	CH ₂ CH ₃		55 a	55 a
XII	CHCl ₂	CH ₂ CH ₃		10 c	50 a
XIII	CCl ₃	CH ₂ CH ₃		45 b	52 a
XIV	CH ₃ CH ₂ O	CH ₂ CH ₃		52 a	53 a
	control, cycloate alone CH ₃ CH ₂ S	CH ₂ CH ₃		55 a	50 a

^a Cycloate and potential antidotes were evaluated at equimolar concentrations in quartz sand nutrient culture. The concentrations were 10⁻⁴ M and 5 × 10⁻⁵ M for corn and oats, respectively. The data are the means of four replicates and were subjected to ANOV and Duncan's. Within each column means followed by unlike letters significantly differ (0.05 level).

N-diisobutyl, and *N*-hexamethylenyl substituents, respectively. Molinate and cycloate are different from EPTC in structure in that they have cyclic *N* substituents instead of two propyl groups. In spite of this, the same relationship between activity and chlorination of the acetyl group was observed. For EPTC (Stephenson et al., 1978), molinate (Tables I and II), and cycloate (Table IV), the dichloroacetamides are consistently more active than analogues with three, one, or no chlorines. While ethoxycarbonyl analogues were effective antidotes for EPTC (Stephenson et al., 1978), the same was not true for antidotes to cycloate (Table IV).

These structure-activity relationships, which demonstrate the high activity of antidotes with structures similar to the herbicides, were more apparent in quartz sand nutrient culture than in soil. It is likely that if bioassays in soil had not been employed in the original evaluation of antidotes to thiocarbamates (Pallos et al., 1977), R-25788 may not have been selected from hundreds of different analogues for wide use as an antidote to both EPTC and butylate. However, with highly effective soil applied pesticides of any kind, high activity at the site of action within the organism must be balanced with availability to the organism for uptake and movement to the site of action from the soil environment. It is apparent from its consistently good activity in nutrient culture that R-25788 has

a good affinity for the site(s) of thiocarbamate action in corn. Its even more consistent activity in soil, in relation to other antidotes, is an indication that it is not readily adsorbed and made unavailable to the plant. Further indication of this is the fact that in soil-free systems, equal concentrations of R-25788 and herbicide (Tables I and III) are often required for total prevention of herbicide injury, whereas in soil, antidote to herbicide ratios of 1:2 (Table III), 1:10, or less (Pallos et al., 1978) can be totally effective.

Possibly the most interesting aspect of the thiocarbamate dichloroacetamide antagonism in corn is its unique occurrence in corn but not other plant species. Lay and Casida (1978) do not propose that EPTC toxicity via EPTC-sulfoxide production is specific to corn. They explain the selectivity of this antagonism by suggesting that the antidote action of R-25788 via elevation of glutathione levels is unique to corn. It is tempting for the present authors to suggest that competitive inhibition between similar antidotes and thiocarbamates in corn is a possible mechanism; however, in the absence of structure-activity studies with isolated systems, such a suggestion is premature. If competitive inhibition were operative, the sites of action involved in corn must be uniquely accessible to both herbicide and antidote to explain the selectivity of the antagonistic relationship. Also the high activity of different antidotes for each different thiocarbamate herbicide implies that the different thiocarbamate herbicides have slightly different sites of action in corn. Thus while the structure-activity theory for antidotes to EPTC has simplified the search for effective antidotes to vernolate, pebulate, molinate, butylate, cycloate, and possibly other thiocarbamates, it has not clarified our understanding of thiocarbamate action in corn or other plants.

ACKNOWLEDGMENT

We thank E. Pelly for technical assistance and Abbott Laboratories for giving a sample of *N*-ethylcyclohexylamine. G. G. Halliday of Chipman Chemicals Ltd. is also thanked for assistance in preparing various antidote formulations.

Supplementary Material Available: Spectral data used to characterize the antidotes (2 pages). Ordering information is given on any current masthead page.

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Received for review July 13, 1978. Accepted December 7, 1978. This work was supported by the National Research Council of Canada.

Synthesis and Synergistic Activity of Dillapiole Based Pyrethrum Synergists

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Twelve compounds were synthesized by chemical transformation of dillapiole (2,3-dimethoxy-4,5-methylenedioxyallylbenzene), one of the chief constituents of *Anethum sowa* Roxb. (Indian dill) seed oil. All of these compounds exhibit synergism better than piperonyl butoxide toward pyrethrum against flour beetles (*Tribolium castaneum* Herbst.). Isolation of dillapiole, its conversion to the above compounds, and their infrared and nuclear magnetic resonance spectra, R_M values, and factors of synergism are reported in this paper.

Synergists are chemicals capable of enhancing the toxicity of an insecticide. Most of the commercial synergists known for pyrethrum, such as piperonyl butoxide (I; Wachs, 1947, 1951) (see Scheme I); sulfoxide (II; Synerholm et al., 1947); and *n*-propyl isome (III; Synerholm and Hartzell, 1945) are manufactured from safrole (IV), which is available in limited supply. Dillapiole (V), the chief undesirable constituent (up to 35%) of oil of *Anethum Sowa* Roxb. (Indian dill), has already been

reported earlier as a synergist for pyrethrum (Gulati and Parmar, 1969a). It has now been tried as an alternative raw material for more potent pyrethrum synergists.

Several new derivatives of V, obtained mostly by modification of the allyl side chain, have shown good synergism for pyrethrum against flour beetles (*Tribolium castaneum* Herbst.).

MATERIALS AND METHODS

All boiling points are uncorrected. All compounds were finally purified by column chromatography over activated silica gel. Thin-layer chromatography was carried out on silica gel plates impregnated with silver nitrate, and the spots were visualized after warming with H_2SO_4 (20%). Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. NMR spectra were recorded nor-

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