RESULTS AND DISCUSSION

The recovery of ronnel from eggs fortified with the pure compound at levels of 1–40 ppb averaged 74.5% with this method. The detection limit for ronnel in eggs was 0.5 ppb.

The recovery of the oxygen analog of ronnel from eggs fortified with pure analog at levels of 4–80 ppb averaged 72.1% with this method. The detection limit for the oxygen analog by this method was 2.0 ppb. One of the reasons for a detection limit this high is the inability of the cleanup column to completely remove all residue from the oxygen analog extract. This residue causes a masking effect and excessive background when subjected to analysis by gas chromatography.

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Antidotes Protect Corn from Thiocarbamate Herbicide Injury

N,N-Diallyldichloroacetamide and related compounds added in small amounts to EPTC (*S*-ethyl dipropylthiocarbamate) or other thiocarbamate herbicides prevent the onset of herbicide injury to corn plants and greatly increase crop yields. Antidotes of this type provide a novel method to obtain greater selectivity and new crop uses for the nonpersistent thiocarbamate herbicides.

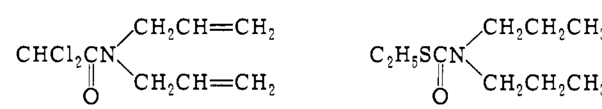
A new concept in weed control involves the use of antidotes to protect crops from herbicide injury (Hoffman, 1962, 1969). We have recently found a new class of herbicide antidotes (Stauffer Chemical Co., 1972) which are superior to previously described compounds for protecting corn from injury by EPTC (*S*-ethyl dipropylthiocarbamate) and other thiocarbamate herbicides.

EPTC, an established herbicide, has many desirable characteristics including low toxicity to mammals and wildlife. It also undergoes rapid degradation in the environment so it is appropriate for use in a crop rotation sequence. Yet, at the levels applied for weed control, it is frequently phytotoxic to corn plants limiting its usefulness on this major crop.

Antidote screening tests were carried out in the greenhouse by incorporating EPTC into loamy sand soil at an excessive rate of 6.7 kg/ha, so that corn planted in the soil was severely injured. The soil was placed in 21 × 31 × 9 cm metal flats to a depth of 7 cm. Hundreds of compounds were synthesized and tested for antidotal activity by coating the corn seeds with up to 0.5% of the compound by weight of the seeds and planting ten seeds per flat 2 cm deep in the soil containing EPTC. The coating was done by placing 50 mg of the compound in a glass vial with 10 g of corn seeds, sealing, and shaking the vial. After growing in the greenhouse for 2 weeks, corn plants were evaluated for injury. The crop injury was rated as follows: the number of plants which showed leaf-rolling and stem-twisting injury symptoms in the treatment were multiplied by 100 and divided by the number of plants in the treatment. Table I gives the results of these tests with 16 compounds chosen from several hundred known active structures.

The most active EPTC antidotes are the N,N-disubstituted dichloroacetamides. The monochloroacetamides are generally less active than the dichloroacetamides. A variety of substituents on the nitrogen atom including alkyl, haloalkyl, alkenyl, and heterocyclic groups impart various degrees of protective activity. Usually compounds having two substituents on the nitrogen atom are more active than those with only one substituent.

Further tests at lower rates showed that *N,N*-diallyl-2,2-dichloroacetamide (R-25788) is the most active in the group and well suited for practical application. When applied at a rate of only 0.1% by weight of the corn seed, it provided complete protection from EPTC at 6.7 kg/ha. Of even greater interest was the discovery that a mixture of EPTC and R-25788 applied to the soil before the seeds were planted still gave complete protection of corn without affecting the control of weeds.



R-25788
antidote

EPTC
herbicide

1 part R-25788
+
12 parts EPTC

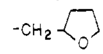
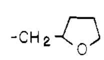
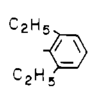
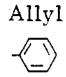
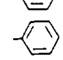
Eradicane
new corn herbicide

In a loamy sand soil, 0.035 kg/ha of R-25788 was sufficient to protect corn from 3.4 kg/ha of EPTC, while two- and fourfold larger doses of R-25788 were needed for complete protection when the herbicide level was increased two- and fourfold, respectively. Thus, a linear relationship exists between the amount of herbicide applied and the amount of antidote required. Only about 1 part of antidote is needed per 100 parts of EPTC to protect corn plants in the greenhouse. When applied alone, R-25788 has no effect on corn even at 5.6 kg/ha.

While the antidote protects corn from the action of EPTC, it affords no such protection to 24 different species of weeds even at the ratio of 1.1 kg/ha of antidote to 2.2 kg/ha of EPTC. These weeds include johnson grass (*Sorghum halepense*), nutsedge (*Cyprus spp.*), and wild cane (*Sorghum bicolor*), which are of great economic importance worldwide.

The results of tests carried out to determine if R-25788 protects corn from other thiocarbamate herbicides are reported in Table II. The results show that two other commercial thiocarbamates behave like EPTC but antidote protection to the corn plant is incomplete with one herbicide of the same chemical class.

Table I. Effect of Mono- and Dichloroacetamides as Seed Treatments at about 0.5% by Weight in Protecting Corn from Injury by EPTC Incorporated in the Soil at 6.7 kg/ha

Substituents on nitrogen		
R	R[1]	Corn injury, %
Monochloroacetamides: $CH_2ClC(O)NRR^1$		
H	CH_2CH_2Br	10
H	$-C(C_2H_5)_2-CN$	10
H		10
H	Methallyl	0
H	*tert*-Butyl	0
Allyl	Allyl	30
Dichloroacetamides: $CHCl_2C(O)NRR^1$		
H	Allyl	10
H	$-C(C_2H_5)_2-CN$	10
H	Methallyl	0
H		0
H		0
C_2H_5	C_2H_5	0
n-C_3H_7	n-C_3H_7	0
Allyl	Allyl	0[a]
Allyl		0
i-C_3H_7		0
Check (no antidote, EPTC alone)		90

[a] R-25788.

The antidote *N,N*-diallyldichloroacetamide was introduced commercially in 1973 in the herbicide and antidote mixture Eradicane. This product contains 1 part of antidote for 12 parts of EPTC, clearly much more antidote than is needed in the greenhouse. This high margin of safety is employed to counter the unpredictable effects of the variable field environment. Data from Rains and Fletchall (1973) show the remarkable effectiveness and crop safety of this antidote–EPTC mixture in Table III. (For further information see also Rains and Fletchall, 1971; Chang et al., 1972, 1973a,b, 1974; Smith et al., 1973; Heikes and Swink, 1973; Schmer et al., 1973; Spotanski and Burnside, 1973.)

R-25788 is relatively nontoxic to laboratory animals by acute oral or dermal application. The acute oral LD_{50} for rats is 2000 mg/kg and the acute dermal LD_{50} for rabbits is greater than 4640 mg/kg. It is not an eye irritant for rabbits. R-25788 undergoes rapid metabolism in soil, plants, and animals.

At the rates used, R-25788 is not phytotoxic; yet, when it is added in small amounts to a class of known herbicides and the mixture is applied in the field, this antidote alleviates the undesired phytotoxic effects of these herbicides. The antidote–EPTC mixture is very effective in weed control and safe on corn, the largest crop in the United States and second largest in the world.

Table II. Effect of the Antidote R-25788 on Corn Injury Caused by Different Thiocarbamate Herbicides

Herbicide, kg/ha	Antidote, kg/ha	Corn injury, %
Vernolate,[a] 6.7	0	90
Vernolate, 6.7	0.14	0
Butylate,[b] 8.9	0	20
Butylate, 8.9	0.14	0
Cycloate,[c] 6.7	0	90
Cycloate, 6.7	0.14	50

[a] *S*-Propyl dipropylthiocarbamate. [b] *S*-Ethyl diisobutylthiocarbamate. [c] *S*-Ethyl cyclohexylethylthiocarbamate.

Table III. Effect of the Antidote on Corn Yields in Field Trials[a]

Treatment	Yield, kg/ha
Check (with weeds)	19.0
EPTC, 6.7 kg/ha	43.6
EPTC, 6.7 kg/ha, + R-25788, 0.56 kg/ha	98.6
Handweeded control	96.5

[a] Rains and Fletchall, 1973.

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