Chemistry and Action of Herbicide Antidotes

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Preface

Chemical herbicides play a major role in promoting high crop yields by reducing competition from undesired weed species for available nutrients, water, light, and other essential environmental factors. They also replace more expensive labor and mechanical methods for weed control. For maximum utility in crop production, herbicides must have a high degree of selective toxicity, i.e., injury to undesirable plant species but not to crops.

Selectivity may be governed by one or more factors including herbicide penetration, uptake, translocation, and metabolism. For example, corn plants have an inherent ability to detoxify chloro-s-triazine herbicides at a rate that far exceeds the detoxication potential of certain weed species associated with corn culture. There are other groups of chemical herbicides that have desirable attributes in weed control but do not possess in all instances a sufficient margin of selectivity. An added degree of selectivity can often be achieved by critical timing of application, suitable placement of the herbicide, or now by a third approach with chemical safening agents, the subject of this book.

The term "herbicide antidotes" may or may not be the best description of these chemical agents. "Herbicide antagonists," "crop protectants," and "herbicide safeners" may be just as appropriate and are indeed used interchangeably in this developing field. The first practical breakthrough with chemical safeners was achieved by Otto Hoffmann of Gulf Oil Chemicals Company, the "father of herbicide antidotes." He found that 1,8-naphthalic anhydride is active as a seed treatment antidote for thiocarbamate herbicide injury in corn. This development is useful only under restricted conditions involving prior treatment of crop seeds with the safener. The next historical highlight in the development of herbicide safeners was the discovery of the action of dichloroacetamides by Stauffer Chemical Company researchers. These compounds provide a high measure of protection to corn plants from injury associated with the use of thiocarbamate herbicides. Furthermore, most of these compounds do not require treatment of crop seeds but can be jointly formulated or applied as a tank mix.

Several investigators have developed evidence to pinpoint significant facets of the mode of action of herbicide safeners. Studies of this type lay the fundamental background for improvements in antidote design and use.

If this emerging field of herbicide antidotes leads to better applications of modern herbicides and to improvements in crop production and yields, it is well worth the effort of the many researchers active in this area. The editors hope and anticipate that this book will contribute to an understanding of the chemical and biochemical basis for the further development of herbicide antidotes. The contributions contained herein were presented at a symposium under the same title at the 173rd National Meeting of the American Chemical Society held in New Orleans, Louisiana, on March 24, 1977. The editors express special thanks to Julius J. Menn for suggestions and encouragement in organizing this symposium.

We share the convictions expressed in the following quote from André and Jean Mayer [*Daedalus* **103**, 83 (1974)]:

> Few scientists think of agriculture as the chief, or the model, science. Many, indeed, do not consider it a science at all. Yet it was the first science—the mother of sciences; it remains the science that makes human life possible; and it may well be that, before the century is over, the success or failure of science as a whole will be judged by the success or failure of agriculture.

Part I

Introduction

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Part VI Summary

HERBICIDE ANTIDOTES: FROM CONCEPT TO PRACTICE

Otto L. Hoffmann
Gulf Oil Chemicals Company

Herbicide antidotes in the past few years have gone from experimental curiosities to practical realities. Initial observations that led to the commercial products were 2,4,6-trichlorophenoxyacetic acid (2,4,6-T) antagonism of 2,4-D on tomato and the total inactivation of barban by 2,4-D. The development of a fast, cheap and accurate detection method for herbicide antidotes led to the development of 1,8-naphthalic anhydride as an antidote for thiocarbamate, chloroacetanilide and dithiocarbamate herbicides on corn. In addition to these families of chemicals 1,8-naphthalic anhydride also has utility for antidoting alachlor on sorghum and rice, molinate on rice and barban on tame oats. Besides naphthalic anhydride some halogenated alkanoic acid amide-type chemicals have shown antidoting properties against several herbicides.

I. INTRODUCTION

The picture in Figure 1, shown at the 1969 meeting of the Weed Science Society of America, illustrates total antidoting of a lethal rate of EPTC (S-ethyl dipropylthiocarbamate) on corn with 1,8-naphthalic anhydride (1). Only one ounce per acre (70 g/ha) of this antidote was needed to counteract the effect of nearly 100 times greater quantity of EPTC. For the first time, it was possible to chemically control unwanted plant growth while permitting the growth of an economic crop of the same genus, species and variety. This finding served as an impetus for several organizations to initiate research on antidote-type chemicals. Once this information was available, it appeared so simple, but getting to this result entailed many trials over the time span of 21 years.

Fig. 1. Corn antidoted against 6 lb/A EPTC by dusting seed before planting with 0.5% by weight 1,8-naphthalic anhydride. Untreated corn seed planted on right row.

II. PHENOXYACETIC ACIDS AND OTHER GROWTH REGULATORS AS ANTIDOTES

My first interest in herbicide antidotes was aroused in 1947 in a greenhouse filled with tomato plants that were sprayed with 2,4-D (2,4-dichlorophenoxyacetic acid) analogs. The vents had not been opened until well into the afternoon of a hot summer day. At first glance, all of the plants, including the untreated controls, appeared to be dying from 2,4-D fumes. However, closer inspection showed plants that had been treated with 2,4,6-T (2,4,6-trichlorophenoxyacetic acid) were apparently normal. This antagonistic relationship between 2,4,6-T and 2,4-D is illustrated in Figure 2 (2,3).

2,4,6-T was found to antagonize all types of rapid growth, such as cell elongation and multiplication on tomatoes, and seemed to fit into what was then a popular explanation of biological chemical interactions - the lock and key mechanism. It did not antagonize a lethal rate of 2,4-D. So do tomato plants "grow to death?" The use of antidotes

Fig. 2. 2,4-D antidoted with 2,4,6-T on tomatoes. Left to right: check; 2,4-D 10 ppm; 2,4-D 10 ppm, 2,4,6-T 100 ppm; 2,4,6-T 1000 ppm (3).

as a research tool had been found to be productive in vitamin research (4) since the vitamin, p-aminobenzoic acid, was discovered through its antagonism of the bactericide, sulfanilamide.

The lock and key explanation of antidote action did not apply to the total antidoting of oats of another herbicide, barban (4-chloro-2-butynyl-m-chlorocarbanilate) by 2,4-D (5). Structures of 2,4-D and barban are quite dissimilar and they do have different growth actions which could possibly explain their antagonism. 2,4-D accelerates plant growth whereas barban slows down growth. Both would fit into the growth regulatory category in Overbeek's division of herbicides (6).

An effort was made to find a practical use for the effect between barban and 2,4-D. For this purpose, seed treatments would be necessary because foliar spray of barban and an antidote would antagonize both the wild oat pest and the wheat crop. However, 2,4-D, 2,4,6-T and MCPA (2-methyl-4-chlorophenoxyacetic acid), all of which antidoted barban as foliar sprays, were too toxic to be useful as seed treatments. From screening trials, chemicals had been found which caused deformed foliage on tomatoes,as did 2,4-D, 2,4,6-T and MCPA, but which were safe as dressings on grass crop seed. Many of the growth regulators when tested by applying to wheat seed proved to be barban antidotes and prevented injury from high rates on wheat. This finding is illustrated in Figure 3 by reduction of wheat injury, when the seed was treated before planting with 1 oz/bu (1 g/kg) of 4'-chloro-2-hydroxyimino acetanilide (7-9).

Fig. 3. Barban antidoted with 4'-chloro-2-hydroxyimino acetanilide on wheat. Left to right: 2 lb/A barban, 1 oz/bu antidote; 2 lb/A barban, no antidote; 1 lb/A barban, 1 oz/bu antidote; 1 lb/A barban, no antidote. In each pot wheat is on the left side and oats on the right.

III. NEED FOR ANTIDOTES

In considering a systematic approach to antidote research several factors that could contribute to a successful outcome were investigated. Let us look first at the need for antidotes.

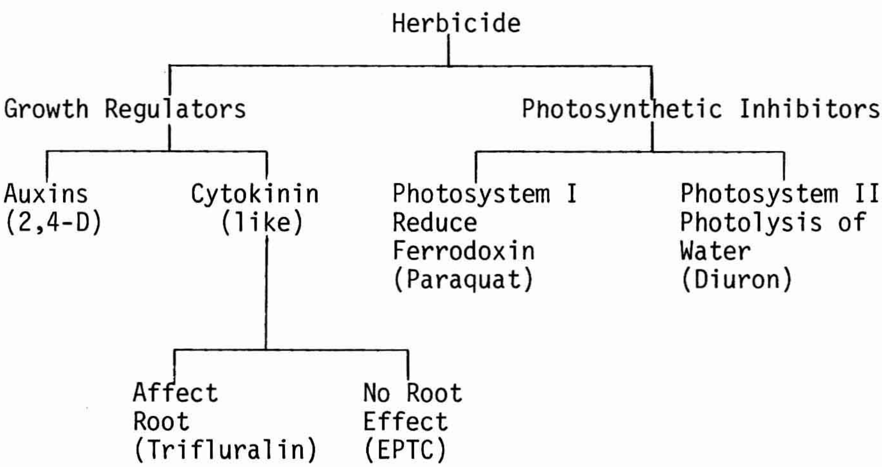
If we accept the desirability of chemical weed control in place of cultural weed control, then it is apparent that if even one weed species escapes the applied herbicide, at least some mechanical control will be necessary. It is doubtful if we will ever find a chemical that by itself will selectively control the following problems: weedy corn in a seed corn field, shattercane in a grain sorghum field, red rice in a rice field, wild oats in a tame oat field, weedy millets in a millet field, or wild beets in a sugar beet field. Even now, after some 40 years or more of chemical weed control, there are no totally satisfactory broadleafed herbicides for broadleaf crops; no totally satisfactory grass herbicides for grass crops.

IV. CONSIDERATIONS IN SCREENING METHODS FOR ANTIDOTE DETECTION

For progress in antidote research an economical detection method was desirable. For screening procedures we need to consider the crops, the herbicides and operation mechanics.

To test an antidote on 100 herbicides and 50 annual crops gives a potential of 5000 observations needed to completely evaluate each candidate at one rate. But an antidote rate may fail because it is either so high it causes crop injury or so low that it is ineffective. With only two antidote rates to measure activity, a complete evaluation of a candidate antidote on 100 herbicides would require 10,000 items of data. Therefore, to be practical both the herbicides and the crops for screening would have to be selected.

Overbeek's (6) classification of herbicides was useful for selecting candidate compounds as he divided herbicides into growth regulators and photosynthetic inhibitors. These two groups can be divided on the basis of antidote response as shown in the following scheme.



In the growth regulator group are auxins, represented by 2,4-D, as determined by the tomato response and cytokininlike (10) herbicides, which are recognized by the oat response. The cytokinins can be further divided: those that affect root growth as does trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) and those that don't affect root growth as represented by EPTC. The group of photosynthetic inhibitors can be divided into those that affect photosystem I,as represented by paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride), and those that affect photosystem II as represented by diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea]. A representative herbicide from each group would have to serve in an initial screen. As representatives of the different groups, five herbicides were chosen: 2,4-D, EPTC, trifluralin, paraquat and diuron. Four of these groups can be antidoted to some extent on some crop. The antidoting of 2,4-D has already been mentioned. Trifluralin can be antidoted on corn in petri plate tests. However, soil tests did not lead to acceptable results. Paraquat can be antidoted with oxidation-reduction compounds, when both paraquat and the antidote are applied as sprays. Paraquat at 0.25 oz/A (18 g/ha) can be antidoted with ferrous sulfate at 2 lb/A (2240 g/ha) (Figure 4). Seed treatment of wheat with ferrous sulfate gave only a minimal antidoting response.

Fig. 4. Paraquat antidoted with ferrous sulfate on wheat and oats. Left to right: check; paraquat 0.25 oz/A; paraquat 0.25 oz/A, ferrous sulfate 2 lb/A.

No success was achieved in antidoting diuron or other herbicides affecting photosystem II. Over 6,000 chemicals were tested against this type of herbicide with no detectable antidoting. Figure 5 illustrates one test of over 2,000 candidate antidotes with an experimental urea herbicide.

Fig. 5. No antidoting of Hill reaction inhibitors was achieved on over 6,000 tests. In this picture of over 2,000 antidote candidates, corn check plants stand out boldly.

V. CORN-EPTC SCREEN FOR ANTIDOTES

EPTC was selected as a candidate herbicide for the group of cytokinins not affecting root growth. From previous work (7) it was known that EPTC could be antidoted on corn.

The procedure for screening antidotes on EPTC was as follows: to 5 g corn seed in a 3-dram vial (Wheaton is best) were added 150 mg (3%) or 25 mg (0.25%) chemical and 0.050 ml (1%) methanol. The seed was shaken in a Spex mixer grinder for 20 seconds. The methanol acted as a grinding aid and sticker for the chemical. The seed acted as grinding pellets. With over 99% of the chemicals tested, size reduction and adherence at 3% was excellent. Only a few viscous tars gave poor coverage with this treatment method.

Five seeds of each of the treatments were planted in loam soil in flats 1.5 in (3.8 cm) from five untreated seeds