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FATE OF DIFLUBENZURON AFTER APPLICATION TO COTTON AND THE BOLL WEEVIL[1],[2]

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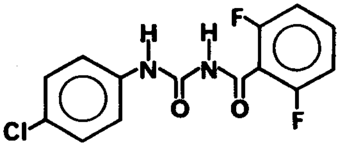
ABSTRACT

Very little diflubenzuron is absorbed by the leaves of cotton plants treated by foliar application. This compound adheres well to foliage and is highly resistant to photodegradation on foliar surfaces and to metabolism within leaves. However, this unusual persistance of diflubenzuron on cotton does not result in the accumulation of significant residues in seeds. The chemical is somewhat stable in soil as long as it is associated with plant litter, and it does not leach appreciably.

Diflubenzuron is active against female boll weevils exposed by either ingestion or contact. It inhibits the hatch of eggs of exposed females if sufficient concentrations are secreted into the eggs. As time after exposure is extended, treated females recover fertility, and retreatment is required to maintain a significant suppression of egg hatch.

INTRODUCTION

Diflubenzuron (*N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide; Dimilin®, TH-6040) is an insect growth regulator (IGR) introduced by Phillips-Duphar B. V., Amsterdam, Holland and developed in the U.S.A. by Thompson-Hayward Chemical Co., Kansas City, KS. This product is registered by the Environmental Protection Agency for use in controlling the gypsy moth, Lymantria dispar (L.), and the boll weevil, *Anthonomus grandis* Boheman. Diflubenzuron interferes with the synthesis of chitin (Mulder and Gijswijt 1973), an essential component of the cuticle of certain invertebrates. This unique effect, which disrupts normal moulting and development, drastically narrows the range of the faunal specificity of the IGR. Furthermore, as described by Ables et al. (1980), the apparent interspecific selectivity among certain insect biocenoses, by which the effect of the IGR favors natural enemies, enhances the potential of diflubenzuron as a tool in integrated control of some important pest species.



We review here the fate of diflubenzuron after application to cotton plants or to boll weevils.

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[1] In cooperation with the Texas Agricultural Experiment Station, Texas A&M University, College Station, TX 77843.

[2] This paper reports the results of research only. Mention of a pesticide in this paper does not constitute a recommendation for use by the USDA nor does it imply registration under FIFRA as amended.

DISCUSSION

Formulation Chemistry. Technical diflubenzuron is a crystalline material that is virtually insoluble (ca. 0.2 mg/L at 20°C) in water (Martin and Worthing 1977). Thus, the chemical is formulated as a water-dispersible powder (W-25, 25% AI) for use in commercial applications. Since particle size of the active ingredient is a key factor influencing the activity of diflubenzuron (Verloop and Ferrell 1979), the compound is milled prior to formulation to produce particles ranging in size from 2 to 5 μ.

In field applications against the boll weevil, an aqueous suspension of diflubenzuron is combined with an emulsifiable paraffinic crop oil. This practice is based on results of studies of Lloyd et al. (1977) who found that sprays of diflubenzuron-water suspensions were somewhat less effective against the boll weevil than mixtures of diflubenzuron and water with oil.

Fate In Cotton. Available evidence (Bull and Ivie 1978, Mansager et al. 1979) indicates that whatever the method of foliar application, there is very little absorption of diflubenzuron by cotton. For example, when individual leaves of field-grown cotton were treated manually with a single application of an aqueous suspension of ^{14}C-labeled diflubenzuron (W-25, 100 μg AI/leaf), ca. 90% of the dose was recovered from leaf surfaces at 14 days posttreatment; only ca. 5% was recovered in internal extracts of methanol-rinsed leaves, and $<$ 1% was detected in extracted leaf tissues (Bull and Ivie 1978). Similarly in greenhouse studies, Mansager et al. (1979) found there was no significant absorption through 48 days posttreatment of potted cotton plants with sprays of an aqueous formulation of ^{14}C-labeled diflubenzuron. In both aforementioned studies, analyses of unabsorbed and absorbed radioactive material revealed that unchanged diflubenzuron accounted for $>$ 98% of the total radiocarbon present. These results indicate that the chemical is highly resistant to decomposition, either by photodegradation on foliar surfaces or by metabolism within the leaves of cotton. Similar results documenting the persistence of foliar residues and the stability of diflubenzuron have been reported in studies with soybeans, cabbage, corn, and apples (Verloop and Ferrell 1977).

Also, in season-long studies with small plots (1.7 m^2) of cotton treated at 5-day intervals with multiple spray applications of ^{14}C-labeled diflubenzuron (70 g AI in 9.35 L crop oil and 93.5 L water/ha), Bull and Ivie (1978) demonstrated that there was little accumulation of radiocarbon in the mature seed. Less than 0.01 ppm of ^{14}C-labeled diflubenzuron equivalents were found in seed from cotton plants treated 6 times, and only ca. 0.02 ppm in those from plants treated 10 times. However, radioactive residues were rather high in other parts of the plants, particularly in foliage (ca. 40 to 125 ppm) present during treatments. Mansager et al. (1979) found that cotton seeds from greenhouse-grown plants treated with 3 foliar applications of diflubenzuron (600 μg/plant/treatment) contained ca. 0.05-0.09 ppm of ^{14}C-labeled diflubenzuron equivalents. They could not chemically characterize the radioactivity in seeds, but did prove that it was not diflubenzuron.

The available evidence thus indicates that diflubenzuron is quite persistent after application to cotton. In the field, this IGR probably would be lost from treated foliage primarily through physical effects such as wind abrasion or rain-washing or because of the fall of senescent leaves. The recommended treatment schedule, a maximum of 6 applications of diflubenzuron with no more than 421 g AI/ha during a season, should establish good coverage of plant foliage without resulting in the development of hazardous residues in seed.

Fate In Soil. Soil can be contaminated with diflubenzuron directly by runoff of sprays or indirectly when brought into contact with treated plant materials. As a part of the aforementioned study of the fate of multiple applications of ^{14}C-labeled diflubenzuron on cotton, Bull and Ivie (1978) shredded the treated cotton plants at harvest and cultivated them into the soil of the same plots upon which the treated cotton was grown. Subsequent analyses of soil cores (0-22.5 cm deep) demonstrated that diflubenzuron was somewhat stable under the test conditions: when the tests were initiated in early fall, initial levels of ^{14}C-labeled diflubenzuron equivalents (ca. 0.3 ppm in the 0-7.5 cm soil layer) did not begin to decline appreciably until the middle of the following summer (ca. 9 months). During this period, much of the radioactivity (ca. 80%) in soil could be recovered by extraction with appropriate solvents, and the content was predominately (> 95%) diflubenzuron. Studies in the laboratory (Bull and Shaver 1980) and in the field (Bull and Ivie 1978) indicated that diflubenzuron does not leach appreciably in different types of soil. Also, a year-long field study indicated that residues of diflubenzuron were concentrated near the surface (0-7.5 cm) and did not tend to move down or laterally. The eventual decline of residues of diflubenzuron in the treated plots probably was caused by increased accessibility of the molecule to different mechanisms of degradation in soil as a result of the progressive decay of the plant material with which it was associated. There is evidence (Don Nye, Thompson-Hayward Co.; private communication) that diflubenzuron is highly stable on leaf litter. On the other hand, the chemical apparently is degraded rapidly when applied directly to soil (Verloop and Ferrell 1977, Mansager et al. 1979).

In another related study, Bull and Ivie (1978) demonstrated that a variety of rotational crops (wheat, beans, collards, radish, native grass, and weeds) grown in the aforementioned multiple-treatment plots all developed low levels of radioactive residues. These residues were generally higher in plants grown in the plot receiving the most treatments, but the amounts that accumulated in the edible portions were insufficient to cause concern.

Fate In The Boll Weevil. Appropriate treatment of the boll weevil with diflubenzuron results in failure of the eggs to hatch (Moore and Taft 1975). In this insect as in others such as *Spodoptera littoralis* (Boisduval) (Ascher and Nemny 1974); the house fly, *Musca domestica* L., (Grosscurt 1976); and stable flies, *Stomoxys calcitrans* (L.), and horn flies, *Haematobia irritans* (L.), (Wright and Spates 1976, Wright and Harris 1976); the embryonic development in an egg from a treated female appears normal until the expected time for eclosion. Grosscurt (1976) concluded that, in the house fly, the affected embryo developed into a larva that was unable to leave the egg. He attributed this failure to the effects of diflubenzuron in disrupting the formation of chitin in the larval cuticle, followed by an incapacity to use the muscles. Moore et al. (1978) reached a similar conclusion in their study of the boll weevil.

There is ample evidence that the IGR action of diflubenzuron against the boll weevil is manifested in the adult females, and that the chemical is effective when ingested or when it is administered as a contact treatment. Moreover, it appears likely that the females must be treated directly with the chemical for maximum effect. Moore et al. (1978) found that treated males probably could not transfer sufficient diflubenzuron during copulation to cause a subsequent inhibition of egg hatch. Although topically-treated males did transfer enough diflubenzuron through physical contact with females to cause some inhibition, the insects used for their tests were confined continuously (10 of each sex) in small (63x63x125 mm) cages. Thus, it appears questionable that such an indirect exposure of females to diflubenzuron would be of importance in the field.

In studies of the fate of ^{14}C-labeled diflubenzuron after topical application to adult virgin female boll weevils, Bull and Ivie (1980) demonstrated that the chemical was absorbed very slowly and did not accumulate in large amounts internally (Fig. 1). At 8 days posttreatment, ca. 64% of the applied diflubenzuron was unabsorbed and internal radioactive material never exceeded 4%. Only ca. 3% of the applied diflubenzuron was metabolized by hydrolysis and conjugation reactions. Still and Leopold (1978) found no

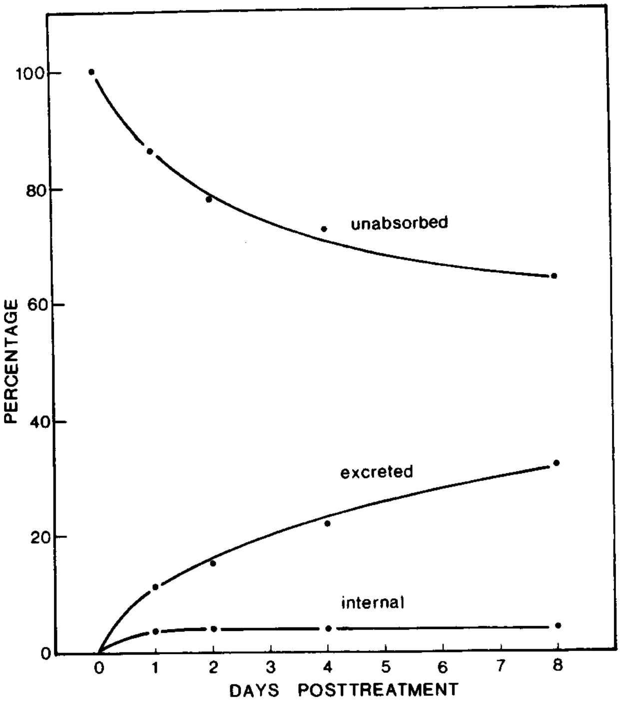

FIG. 1. Absorption of ^{14}C-labeled diflubenzuron after topical treatment of adult virgin female boll weevils. Dose of 1 μg/insect. (Adapted from Bull and Ivie 1980.)

evidence that diflubenzuron was metabolized in boll weevils treated by immersion or injection or by feeding on treated cotton squares. On the other hand, Chang and Stokes (1979) reported that boll weevils metabolized and excreted as much as 19% of an injected dose of diflubenzuron in the form of water-soluble conjugates.

Bull and Ivie (1980) studied the secretion and fate of ^{14}C-labeled diflubenzuron in eggs after a single topical application to adult female boll weevils (Fig. 2). At 4 days posttreatment, eggs of treated females contained ca. 2.24 ppm of ^{14}C-labeled diflubenzuron equivalents. Radiocarbon in subsequent daily samples of eggs declined progressively to ca. 0.4 ppm at 26 days posttreatment. Periodic analyses of eggs during the experimental period revealed that all the radiocarbon in eggs was unchanged diflubenzuron.

In the same study, Bull and Ivie (1980) made daily observations of the hatch of subsamples of eggs from treated insects (Fig. 2). Hatch was inhibited by ca. 80% through 10 days posttreatment and then recovered fairly rapidly to a hatch level of 80-90% at 22 days posttreatment. At the 50% hatch level, which occurred at ca. 16 days posttreatment, the diflubenzuron content of eggs was ca. 0.6 ppm. These results support previous observations in the laboratory by others (McLaughlin 1976, Moore et al. 1978) that the effects of oral or topical doses of diflubenzuron on boll weevils are transitory; the insect regains fertility fairly rapidly, and retreatment is needed for continued suppression of egg hatch.

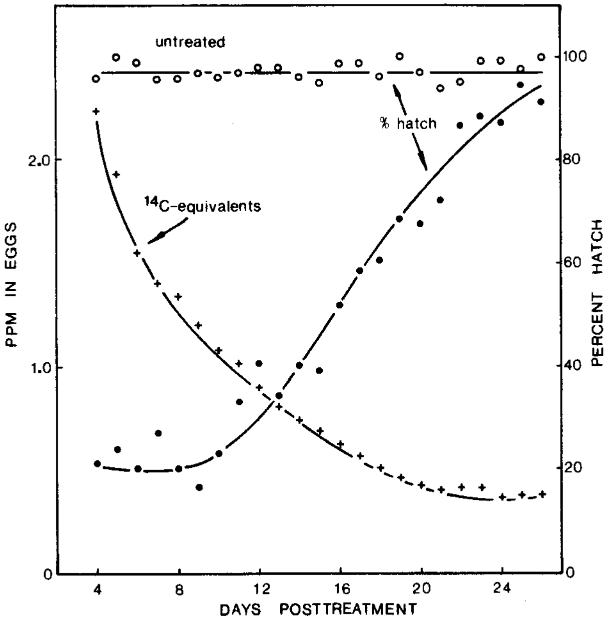

FIG. 2. Secretion of ^{14}C-labeled diflubenzuron into eggs and hatch of eggs after treatment of adult female boll weevils. Virgin females treated and then paired with untreated males. Dose of 1 µg/insect. (Adapted from Bull and Ivie 1980.)

CONCLUSIONS

The fact that diflubenzuron adheres well to foliage and is quite stable and persistent on the surfaces of treated plant suggests that the recommended 6 applications in the field should provide thorough coverage of plants during the course of the treatment schedule and perhaps allow some period of continued protection after sprays are terminated. However, as subsequent articles of this publication will note, we know that boll weevil infestations in the field can reestablish quickly upon cessation of diflubenzuron treatments. Laboratory tests discussed herein indicate that the level of diflubenzuron secreted into eggs is a critical factor influencing their hatchability. These laboratory tests also demonstrated that treated female boll weevils recover fertility rapidly after single doses of diflubenzuron and this recovery seems to be related to the total clearance of diflubenzuron residues from the insect's system with an attendant reduction in the secretion of diflubenzuron into eggs to below critical activity levels.

It would appear that the full potential of diflubenzuron as a suppressant of boll weevil populations may be only realized if active field populations are treated regularly, perhaps weekly, during the entire period of crop vulnerability. The magnitude of such control programs would, of course, depend on the relative abundance and seasonal distribution of the boll weevil. Obviously, a very thorough scouting program to detect and estimate weevil populations and strict control of the timing and coverage of diflubenzuron applications would be required to achieve maximum effectiveness.

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