

A RAPID METHOD OF SPRAY DEPOSIT MEASUREMENT
AND ITS USE IN NEW APPLE ORCHARDS

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Summary Large numbers of leaf deposit measurements are required to determine the levels and variations of spray deposition in plantation crops. Use of fluorescent additive in the spray liquid enables large numbers of deposits to be recorded quickly in an automated fluorimeter. This technique has been used for the assessment of spraying machine performance in both conventional and intensively planted apple orchards. The results give reliable mean deposit values and frequency distribution curves for the occurrence of each level of deposit; these curves provide a clear indication of the efficiency of the spraying machine. Such data provide a basis for achieving adequate biological control with the maximum economy of spray chemical. Further economies may be achieved with improved distribution of chemical throughout the tree.

Sommaire En cas d'une pulvérisation en vergers la mesure d'une quantité importante de dépôts sur les feuilles est nécessaire pour déterminer la densité et la variation du dépôt. L'emploi d'un additif fluorescent dans la bouillie facilite l'enregistrement rapide des dépôts au moyen d'un fluorimètre automatique. On s'est servi de cette technique pour juger l'efficacité des pulvérisateurs dans des pommeraies traditionnelles et à culture intensive. On a obtenu des valeurs moyennes de dépôt satisfaisantes et des courbes de distribution des fréquences pour chaque densité de dépôt. Ces courbes offrent en plus une bonne indication de l'efficacité du pulvérisateur. De telles données fournissent des possibilités d'allier un contrôle biologique suffisant à une épargne maximum de matière active. On pourrait peut-être réaliser d'autres économies par suite d'une amélioration de la répartition de la matière active sur tout l'arbre.

INTRODUCTION

The control of pests and diseases of plants depends not only on the amount of active chemical deposited on the plant but also on the evenness of the distribution of this material over the plant surfaces. A spraying machine has to be designed to give an even distribution of spray of the required drop size over these surfaces. The assessment of a spraying machine required a method of measuring the amount and distribution of spray on leaves and use of a fluorescent additive to the spray liquid for this purpose is the most suitable method.

Byass (1969) has shown that a good agreement can be achieved between direct measurements of fluorochrome on leaves and the measurement of active chemical sprayed by the same machine on the same crops. Fluorescence measurements are faster by a factor of at least 10 compared with the chemical measurements of simple active

materials and the latter gives information relating only to groups of leaves because of the relative insensitivity of these techniques. He also showed that measurements from several thousand leaf samples were required to compare the uniformity of deposition of materials in different treatments of an apple tree, or similar targets, with reasonable sensitivity.

A rapid method of making such measurements has been developed and its use to determine the levels and variations of spray deposits being obtained in both conventional and new, intensively planted, apple orchards is described.

METHODS

The trees were sprayed with a 0.4% (w:v) suspension of MT grade Saturn Yellow fluorescent pigment in water. This pigment is a powder which requires to be mixed with a wetting agent before dispersal in water; with a density of 1.4, this material also requires agitation to maintain the suspension but only of the same nature as is normally used when suspension formulations of pesticides are used. When the spray deposit was dry about a 60 m length of tree row was sampled for each test using up to nine sampling regions in each tree. Whole leaf trusses were picked to give a total of about 60 trusses from each region; ninety upper leaf and under leaf samples were taken from these trusses. Not more than two upper and two under leaf samples were punched from one truss and at least one was normally taken from each truss picked.

Each sample leaf disc was punched in the field into a circular polypropylene holder using a pneumatic leaf punch, which accumulated the filled holders in a tubular magazine; the leaf disc was held in position by means of an annulus of adhesive previously applied to the holder. When the tubular magazine was full it was sealed and brought back to the laboratory: an attachment held the magazine in place and allowed the samples to drop into the fluorimeter in turn. All the readings were made using a Fluorometer Model 110 manufactured by G.K. Turner Associates; this is a null-point instrument where the balance is normally achieved by the manual rotation of a shutter which progressively changes the amount of light in a beam with which the sample emission is compared. This instrument was automated by providing an electrical drive to the dial and sensing the null-point electronically; at the instant of balance a voltage which indicated the fluorimeter dial reading was recorded by data-logging equipment. A new sample was automatically fed into the fluorimeter on the completion of each rotation of the dial. The sample was presented in the fluorimeter such that the incident illumination beam and the fluorescent emission light beam were equally inclined on opposite sides of the normal to the surface being read, and the distances from lamp and photomultiplier were 3 cm. Under these conditions a 1 cm diameter disc of leaf presents a suitable sample area for the fluorimeter. A 0.4% strength of fluorochrome was chosen to enable spray deposits of the order of $0.015 \mu\text{l cm}^{-2}$ and greater to be measured. Unsprayed leaves picked before the experiment were used to offset the fluorimeter scale so that these leaves were read as zero. Variations from leaf to leaf in this "blank" reading limit the sensitivity of the method but at this concentration variations in natural fluorescence become negligible. The fluorimeter dial was calibrated with known amounts of Saturn Yellow to enable the results to be interpreted as volume of spray per unit area of leaf.

SCOPE OF METHOD

Three operators can test one spraying machine in about four hours of field work. This involves sampling unsprayed leaves, setting up the sprayer and adding the fluorochrome, spraying a plot of trees, picking the sample trusses and punching discs from these using two leaf punches. The samples can then be stored at reduced temperatures (about 3°C) for several days until they are measured. The fluorimeter will read about 150 samples per hour. Allowance for warming-up, setting-up, periodic checking of the instrument, and stoppages for the insertion of samples means that an overall average of 100 samples per hour throughout the working day can be achieved.

RESULTS

Measurements have already been made comparing the application from two different sprayers in a conventional bush apple tree orchard in full leaf and at fortnightly intervals through the growing period in an intensive plantation. Results of a comparison between two machines in an intensive orchard are given in Table 1 and the corresponding deposit frequency distribution curves are shown in Fig. 1. Mean deposit values for "full-leaf" condition in bush apples and at various stages throughout the season in spindlebush apples are given in Table 2.

CONCLUSIONS

It has been shown that the number of deposits measured (90 for upper and 90 for under-leaf surface in each region of the tree) is of the right order to demonstrate significant differences in spray uniformity and deposits achieved with different spraying machines. The "full-leaf" deposits in the bush and small-tree orchards indicate that the mean dose will be fairly similar when the same amount per acre is applied. Economies in spray chemical in the intensive orchards must therefore come from improved distribution of chemical throughout the trees. This technique for assessing under-dosed areas means that the way is now clear to economise in the treatment of the new intensive orchards by improved distribution of material in foliage which is close to the sprayer outlet; also by improved matching of dose to target area in treatment early in the season.

With the large numbers of readings available from these tests it is possible to construct reliable frequency distribution curves for the occurrence of each level of deposit, rather than merely measure mean deposits. The shape of the curve, especially the measure of under-dosed area, gives a much better indication of the machine's efficiency. Accurate spray deposit figures are essential for the provision of adequate biological control with the maximum economy. This method of assessment provides the means for making such economies on a rational basis.

TABLE 1

Mean spray deposits ($\mu\text{l.cm}^{-2}$) achieved by two different
spraying machines in spindlebush apple trees

Machine	Leaf surface	Region 1	Region 2	Region 3	Region 4	Region 5	Region 6
1	Upper	0.38	0.23	0.26	0.22	0.28	0.16
	Under	0.66	0.42	0.44	0.49	0.50	0.35
2	Upper	0.31	0.25	0.21	0.23	0.29	0.15
	Under	0.58	0.48	0.42	0.44	0.35	0.22

S.E.M. = 0.024

L.S.D. between machines (5%) = 0.066

Region 1 Foliage at lowest positions in centre of tree
 Region 2 Outer foliage at mid-height
 Region 3 Foliage in centre of tree at mid-height
 Region 4 Outer foliage at mid-height on opposite side of tree to Region 2
 Region 5 Foliage in the lower region where adjacent trees meet
 Region 6 Uppermost foliage above Region 5

TABLE 2

Mean spray deposits ($\mu\text{l.cm}^{-2}$) in bush and spindlebush apples

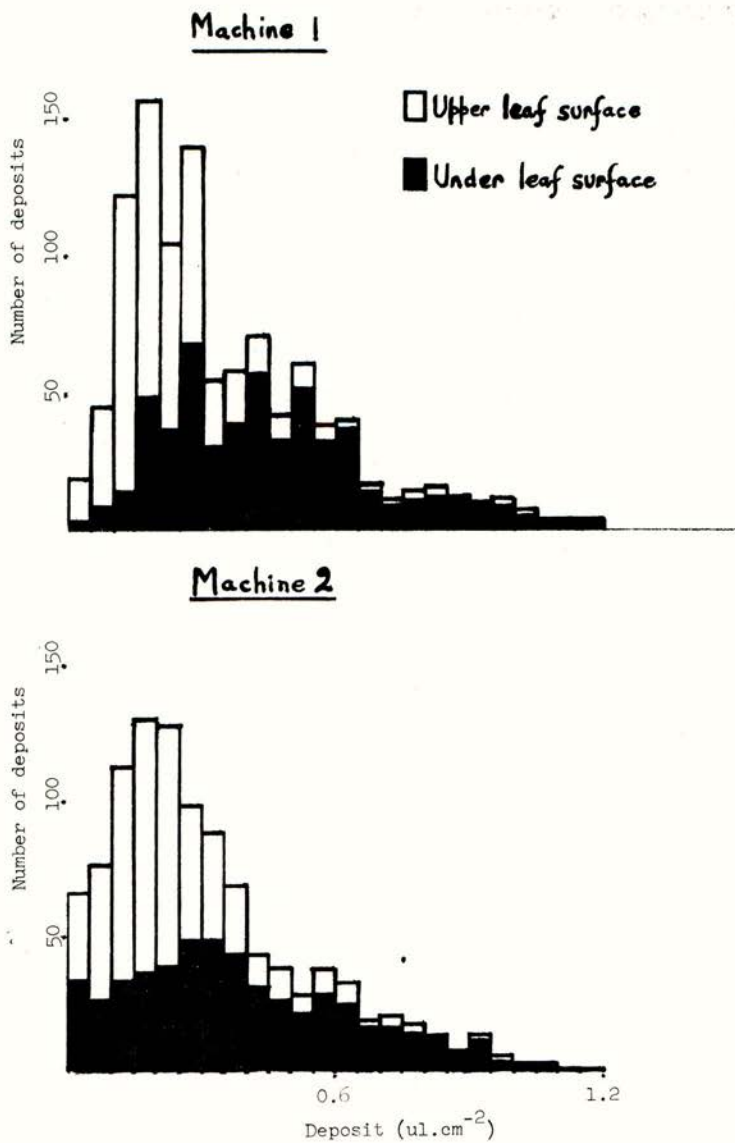
Tree type	Growth stage	Spraying details	Upper leaf	Under leaf	Total
Spindlebush	Pre-blossom	20 gal/ac; 4 mile/h	0.31	0.82	0.57
	Post-blossom	20 gal/ac; 4 mile/h	0.13	0.40	0.27
	Full leaf	40 gal/ac; 4 mile/h	0.25	0.58	0.42
Bush	Full leaf	50 gal/ac; 4 mile/h	0.24	0.71	0.48

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Figure 1

Distribution of occurrence of each level of deposit.



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DEVELOPMENT OF AN IMPROVED FORMULATION OF DAZOMET

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Summary The suitability of four formulations of dazomet for use at low soil temperatures on three soil types was investigated in laboratory tests. Activity was compared using a bioassay test on Poa annua and Stellaria media seeds. The activity of dazomet increased as the prill particle size decreased. Overall, the prill formulation UK 4 with the lowest particle size spectrum gave results similar to the powder formulation of dazomet. Both the powder and UK 4 prill showed similar activity at 7°C and 18°C, although sterilisation was more rapid at the higher temperature. At 2°C activity appeared enhanced for both formulations. Also at 2°C, with rates of dazomet between 38 and 76 g a.i./m², sterilisation 6 - 12cm below the depth of dazomet treatment was obtained, particularly on the loam and coarse sandy loam soils. Activity of dazomet was diminished on a very fine sandy loam soil, compared with the coarse sandy loam and loam soils.

Résumé Des essais de laboratoire ont été conduits sur trois types de sol pour examiner la valeur de 4 formulations de dazomet pour une utilisation dans un sol dont la température est basse. Leur action a été comparée en utilisant un test biologique sur des graines de Poa annua et de Stellaria media. L'efficacité du dazomet a augmenté quand la taille des particules diminuait. Dans l'ensemble, la formulation UK 4 avec le spectre de particules de plus petite taille a donné des résultats semblables à ceux de la formulation poudre de dazomet. La poudre, comme UK 4, ont montre une action identique à une température de 7 et 18 degrés. Bien que la sterilisation ait été plus rapide à la température la plus élevée. A 2 degrés C, l'action des deux formulations paraissait être augmentée. Egalement à 2 degrés C on a obtenu une sterilisation sur 6 à 12 cm sous la couche traitée avec dazomet, particulièrement dans les sols limoneux et sablo-limoneux grossier avec des doses de dazomet comprises entre 38 et 76 g m.a./m². L'action de dazomet a été réduite dans un sol sablo-limoneux très fin par rapport au sol sablo-limoneux grossier et au sol limoneux.

INTRODUCTION

The soil sterilant properties of dazomet, which breaks down to the active gas methylisothiocyanate on contact with moist soil, have been known for a number of years. Originally dazomet was formulated as a powder, but the need for a product which could be distributed mechanically resulted in the development of a prilled or granule formulation (Lush et al 1967).

At present, dazomet is not recommended for use when soil temperatures are below 7°C. However, experiments with dazomet for the control of Heterodera rostochiensis (Rothamsted Experimental Station 1970) and Ditylenchus dipsaci (Whitehead and Tite, 1972) have indicated that dazomet can be effective when applied in the late autumn.

The suitability of various formulations of dazomet for use at a range of soil temperatures on various soils was investigated in the laboratory.

METHOD AND MATERIALS

The basis of the experimental method consisted of columns of soil 36 cm high and 15 cm in diameter, in polythene bags. The bags were filled with 15 cm of untreated soil containing plant seeds and topped with 20 cm of dazomet treated soil also containing plant seeds. At given time intervals soil samples were removed from the polythene bag at 15 cm, 25 cm and 30 cm depths and germination tests carried out on the plant species. Plant seeds were used as convenient test organisms in bioassays of dazomet activity.

The day prior to treatment the soils were seeded with Stellaria media and Poa annua seeds in sufficient quantity to give an average density of 50 seeds of each species in a 6 cm x 2.5 cm cylindrical sampling probe. After treatment the bags were stored at temperatures of 2°C ($\pm 0.5^\circ\text{C}$), 7°C ($\pm 1.0^\circ\text{C}$) and at 18°C ($\pm 0.25^\circ\text{C}$). At given time intervals soil samples were removed from the bags at depths of 15 cm, 25 cm, and 30 cm. Sampling was with a 2.5 cm diameter borer inserted to a depth of 6 cm into the soil. After removal of the soil, a 5 x 2.5 cm sealed specimen tube was inserted to prevent soil subsidence, and the bag resealed. The soil samples were placed on a 25 mesh/inch sieve and were washed for approximately one minute. This process removed any dazomet particles, but retained the plant seeds. The seeds and remaining soil were placed on moist filter paper and stored at 18°C. As treatments were found to retard seed germination, samples were stored for a minimum of 24 days before germination was assessed.

The following soil types were used (soil texture according to the ADAS assessment method):

1. Coarse sandy loam: pH 7.7, 2.5% O.M. and 9% moisture content.
2. Loam soil: pH 6.9, 4.6% O.M. and 15% moisture content.
3. Very fine sandy loam: pH 6.7, 5.3% O.M. and 22% moisture content.

Although moisture levels varied greatly between the three soil types, the soils were judged to be ideal for seed germination. This criterion is in accordance with the recommendations for determining optimal soil moisture levels prior to dazomet application.

The formulations of dazomet used were:-

Dazomet powder - 85% a.i.

Dazomet prills -

UK 2

UK 3

UK 4

Particle sizes

500 - 1000 μ	max. 5%	85%	-
400 - 500 μ	} 20%	13%	-
300 - 400 μ		2%	10%
200 - 300 μ	53%	-	10%
100 - 200 μ	20%	-	70%
< 100 μ	2%	-	10%

Dazomet prills are all 98-99% a.i.

RESULTS

Table 1

Seed Mortality at 2°C

Formulation Rate-g/m ² a.i.	UK 2			UK 3			UK 4			POWDER			
	76.0	38.0	19.0	76.0	38.0	19.0	76.0	38.0	19.0	76.0	38.0	19.0	
Days after treatment	Depth in cm.												
1	15	-	-	-	-	-	-	-	-	-	-	-	-
	25	-	-	-	-	-	-	-	-	-	-	-	-
	30	-	-	-	-	-	-	-	-	-	-	-	-
3	15	- S -	-	-	-	-	-	- S X	- S -	-	-	-	-
	25	-	-	-	-	-	-	-	-	-	-	-	-
	30	-	-	-	-	-	-	-	-	-	-	-	-
7	15	Ⓓ S X	- S -	-	-	-	- S -	L S X	L S X	- S -	L S X	L S X	- S -
	25	-	-	-	-	-	-	Ⓓ S -	- S -	-	L S -	-	-
	30	-	-	-	-	-	-	-	-	-	-	-	-
14	15	L S X	Ⓓ S (X)	- S -	Ⓓ S -	-	-	L S X	L S X	L S X	L S X	L S (X)	L S (X)
	25	- S -	-	-	-	-	-	L S X	- S -	-	L S (X)	L -	-
	30	-	-	-	-	-	-	L S -	-	-	Ⓓ -	-	-
28	15	L S X	L S X	L S -	L S -	L -	-	L S X	L S X	L S X	L S X	L S (X)	L S X
	25	L S -	-	-	-	-	-	L S X	L S -	-	L S (X)	L S -	-
	30	-	-	-	-	-	-	L S -	-	-	L -	L -	-
56	15	L S X	L S X	L S -	L S -	L -	-	L S X	L S X	L S X	L S X	L S X	L S X
	25	L S -	Ⓓ -	-	-	-	-	L S X	L S -	L -	L S X	L S -	L -
	30	-	-	-	-	-	-	L S -	Ⓓ -	-	L -	L -	-

see Key under Table 3

Table 2

Seed Mortality at 7°C

Formulation	Rate-g/m ² a.i.	UK 2			UK 3			UK 4			POWDER		
		76.0	38.0	19.0	76.0	38.0	19.0	76.0	38.0	19.0	76.0	38.0	19.0
Days after treatment	Depth in cm.												
1	15	-	-	-	-	-	-	-	-	-	-	S	-
	25	-	-	-	-	-	-	-	-	-	-	-	-
	30	-	-	-	-	-	-	-	-	-	-	-	-
3	15	- S X	-	-	-	-	-	- S X	- S -	- (S) -	L S (X)	- S (X)	-
	25	-	-	-	-	-	-	-	-	-	-	-	-
	30	-	-	-	-	-	-	-	-	-	-	-	-
7	15	L S (X)	- S -	-	- S -	-	-	L S X	(L) S (X)	- S -	L S (X)	L S (X)	- S -
	25	-	-	-	-	-	-	- S -	- (S) -	-	L S -	-	-
	30	-	-	-	-	-	-	-	-	-	-	-	-
14	15	L S X	L S -	-	L S -	-	-	L S X	L S X	L S -	L S X	L S X	L S -
	25	-	-	-	-	-	-	- S -	- (S) -	-	L S -	-	-
	30	-	-	-	-	-	-	-	-	-	-	-	-
28	15	L S X	L S -	-	L S -	(L) -	-	L S X	L S X	L (S) -	L S X	L S (X)	L S -
	25	L -	-	-	-	-	-	L S -	- S -	-	L S -	-	-
	30	-	-	-	-	-	-	-	-	-	L -	-	-
56	15	L S X	L S -	L -	L S -	L -	-	L S X	L S X	L S -	L S X	L S X	L S -
	25	L -	-	-	-	-	-	L S -	- S -	-	L S -	L -	-
	30	-	-	-	-	-	-	-	-	-	L -	-	-

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see Key under Table 3

Table 3

Seed Mortality at 18°C

Formulation	Rate-g/m ² a.i.	UK 3			UK 4			POWDER		
		76.0	38.0	19.0	76.0	38.0	19.0	76.0	38.0	19.0
Days after treatment	Depth in cm.									
1	15	---	---	---	L S X	- S -	---	Ⓛ S X	Ⓛ S -	---
	25	---	---	---	---	---	---	---	---	---
	30	---	---	---	---	---	---	---	---	---
3	15	- S -	---	---	L S X	L S X	- S -	L S X	L S X	L S -
	25	---	---	---	---	---	---	Ⓛ S ⊗	---	---
	30	---	---	---	---	---	---	---	---	---
7	15	L S -	Ⓛ - -	---	L S X	L S X	- S -	L S X	L S X	L S -
	25	---	---	---	- S -	---	---	L S ⊗	Ⓛ - -	---
	30	---	---	---	---	---	---	---	---	---
14	15	L S -	L - -	---	L S X	L S X	L S -	L S X	Ⓛ S X	L S -
	25	Ⓛ - -	---	---	L ⊗ -	---	---	L S ⊗	L - -	---
	30	---	---	---	L - -	---	---	---	---	---
28	15	L S -	L - -	---	L S X	L S X	L S -	L S X	L S X	L S -
	25	---	---	---	L S -	---	---	L S ⊗	L - -	---
	30	---	---	---	L - -	---	---	Ⓛ - -	---	---
56	15	L S -	L - -	---	L S X	L S X	L S -	L S X	L S X	L S -
	25	---	---	---	L S -	---	---	L S ⊗	L - -	---
	30	---	---	---	L - -	---	---	Ⓛ - -	---	---

Key: L = total sterilisation of both plant species in the loam soil
 S = " " " " " " " " " coarse sandy loam soil
 X = " " " " " " " " " very fine sandy loam soil
 Ⓛ ⊗ or ⊗ encircled = 95-99% sterilisation in the respective soil
 - = seeds still viable

UK 2 formulation not tested at 18°C

UK 3 formulation in very fine sandy loam did not achieve sterilisation with any rate or temperature.

DISCUSSION

With the four formulations of dazomet tested, activity increased as prill particle size decreased. The UK 3 prill, the coarsest formulation tested, gave consistently poor results on all three soils. UK 2, with a finer prill size range, gave some improvement in activity, but was still markedly inferior compared to the powder or UK 4 prill. The UK 4 formulation of dazomet gave results comparable with the powder, although slight differences did occur. Whilst the powder appeared slightly more active on a loam soil, the UK 4 prill gave marginally better results on the coarse sandy loam and very fine sandy loam soils.

Dazomet was shown to be active over the wide range of temperatures tested, from 2°C to 18°C. Both the powder and UK 4 prill showed similar activity at 7°C and 18°C although the rate of sterilisation was faster at the higher temperature. At 2°C, activity of both the powder and UK 4 prill was greater than at higher temperatures. Neither formulation gave control of the weed seeds on the very fine sandy loam soil at equivalent rates of 19 g a.i./m² at 7°C or 18°C; nevertheless control was obtained at 2°C in the 15 cm layer. The rate of control appeared to be no slower at 2°C compared to 7°C.

Also, it appeared that methylisothiocyanate gas was moving from the treated area downwards into the untreated zone. This was most marked at 2°C and at the higher rates of dazomet used. On the very fine sandy loam soil, control of weed seeds reached 5 cm below the treated zone, but only at 2°C combined with the high rate of 76 g a.i./m² of the UK 4 prill or powder. The ease of translocation was affected by soil type, the greatest activity being demonstrated in the loam soil at low temperatures.

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AG CHLORDANE AS SOIL INSECTICIDE.

RESIDUES IN SUGAR BEET, MAIZE, POTATO, CARROT, AND SOIL

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Summary AG chlordane, alone and with parathion, was evaluated as soil insecticide, mainly against Agriotes spp. in sugar beet, maize and potato. AG chlordane remains effective over the long term from seeding to harvest; but, for quick knockdown of mature Agriotes larvae, chlordane was supplemented by parathion. Residues of alpha- and gamma-chlordane in sugar beet roots and potato tubers are small. No residue was detectable in grain or stalk of maize; none was found within the tissue of clean maize foliage, but residues on unwashed surfaces of leaves from the field are ascribed to airborne particles of treated soil. In view of dairy cattle feeding studies, elsewhere in press, residues in beet, maize, potato should be acceptable. Analytical evidence suggests that alpha- and gamma-chlordane are chemically stable in soil, not readily dissipated either by evaporation or leaching from the upper 15 cm profile.

Resumé Chlordane AG s'est confirmé comme un bon insecticide du sol, principalement contre Agriotes spp. pour les cultures de betteraves à sucre, maïs, et pomme de terre. Son efficacité couvre une période très longue, mais il faut lui ajouter du parathion pour obtenir un effet de "knockdown" sur les taupins mûrs. Les résidus dans les betteraves et pommes de terre sont très bas et pour le maïs n'ont pas été détectés dans les grains et tiges. Quelques résidus se trouvent sur les feuilles, mais ils disparaissent après un lavage détergent: sans doute, sont-ils dus au sol pulvérulent traité, entraîné par le vent. De récentes études sur l'alimentation des vaches laitières laissent prévoir que nos résultats sont bien acceptables. Les analyses montrent la grande stabilité chimique des deux isomères du chlordane dans le sol et leur résistance à l'évaporation et à la percolation dans les premiers 15 cm.

INTRODUCTION

In Italy, as at 29 August 1973, granular formulations containing up to 4% of certain persistent organochlorine insecticides are allowed once every four years as soil treatments for crops of sugar beet, maize, potato, tobacco and ornamentals. Seed dressings with up to 10% organochlorines may be applied without restriction to seeds of any kind. Formulations of certain organophosphorus insecticides also are used commercially; but, as they are less persistent and more hazardous in use, none can yet ideally substitute the organochlorines as soil insecticides.

Studies in which the alpha-and/or gamma-isomers of chlordane were fed to mammals (Dorough and Hemken 1973, Korte 1967, Polen *et al* 1971, Poonawalla and Korte 1971, Schwemmer *et al* 1970) yielded data which have collectively shown that the vast majority of any ingested chlordane is metabolised to water-soluble compounds that are soon excreted, whereas very little is to be found in milk of dairy cattle.

Field trials reported by Dorough and Pass 1972, Dorough et al 1972, Furness 1971, Kovacs and Maini 1972, Tafuri et al 1973, have shown what quantities of the alpha- and gamma-isomers of chlordane may pass from the soil into alfalfa, sugar beet, maize, potato, lettuce, and carrot. Except in the instance of carrot, residues on or in the edible parts of these crops are small at harvest time.

From these standpoints, AG chlordane (code HCS-3260), which consists 70% of the alpha- and 25% of the gamma-isomers of chlordane, seemed promising for commercial development. We had two main objectives: first, to evaluate its properties as a soil insecticide; secondly, to provide specimens of soils and edible parts of crops for analytical and other investigations, so leading to observations concerning stability of the alpha- and gamma-isomers in the soil, their movement in the soil profile and in airborne particles of soil, and to considerations affecting rotation of crops.

METHOD AND MATERIALS

The need in Italy for soil insecticides is principally for use against Agriotes spp. (wireworms); although, since restrictions were lately imposed against organochlorines, certain coleoptera eg Bothynoderes punctiventris and Chaetocnema tibialis also have begun to cause serious damage.

It is notoriously difficult to find fields and to lay down well-replicated plots where infestation by Agriotes spp. is uniform throughout. For trials purposes we customarily locate badly infested crops of alfalfa or winter wheat whose fields in the following spring are to be reserved for sugar beet, maize or potato. Then, at harvest time, by collating the numbers of holes in root crops or the numbers of surviving maize plants or the yields from test plots against the corresponding data from controls, important differences in insecticidal efficacy can be discerned. However, this procedure is not ideal because holes in root crops and destruction of maize plants are, for the most part, the work of Agriotes spp. not less than 2 years old; whereas, the organochlorine insecticides are more effective against the younger larvae which seldom cause such serious damage. It is mainly by the continuous action of organochlorines upon the young larvae in the field that the population of adults is best brought under control. This must be recognised when our results for insecticidal efficacy have to be interpreted.

AG chlordane contains 95% of octachloro-4,7-methanotetrahydroindane as two stereoisomers, viz 70% of the cis- or alpha- with 25% of the trans- or gamma-isomer, which together constitute the active ingredients (Furness, 1971). Granular or e.c. formulations were used as indicated in the Tables, where dosages are expressed in terms of total octachloro-4,7-methanotetrahydroindane, ie alpha + gamma isomers.

For 1971-1972 experiments concerned with chemical stability of the alpha- and gamma-isomers in soil, with the movement of these isomers down the soil profile, and with residues in crops, a field at Carpi in Modena Province was reserved. The soil, containing 3.54% organic matter, was of loamy silt-clay of pH 7.48 and bulk density 1.25 g/cm³. This field was marked out for experiments with sugar beet on 500 m², maize on 1000 m², and potato on 500 m². The respective areas were divided and subdivided into plots for soil treatments of various kinds and random four-fold replications of each variant. Granular formulations of AG chlordane, with or without parathion, were spread manually, and e.c. formulations were applied by knapsack sprayer. These were incorporated very lightly for sugar beet and maize. For potato the insecticides were applied only at the bottom or on the sides of the furrow; and there the local concentrations must have been much greater than our tabulated data indicate. After harvesting sugar beet in August 1971, the soils in that area were planted to carrot in March 1972.

Samples of the root crops were brushed to remove the soil, but were not washed, before chopping into sub-samples to be preserved at -12°C for analysis. The Velsicol gas-chromatographic method AM-0494 was followed without any major amendment of principle; except that, for the more efficient recovery of chlordane, soil samples were extracted with n-hexane/iso-propanol with the addition of water, according to Saha (1971). By these procedures recoveries of alpha- and gamma-chlordane were between 74% and 91% for the range 0.02-1.00 ppm in soils, and between 60% and 105% for the range 0.02-0.50 ppm in the various crops, except that there was difficulty in getting such satisfactory recoveries from leaves of maize in which chlordane residues were 0.05 ppm or less. Other details of the analytical procedure have been recorded by Kovács and Maini (1972).

RESULTS

Insecticidal efficacy

Partly because the population of Agriotes spp. was not uniformly distributed over our chosen test area, and partly because the roots are damaged more seriously by mature larvae than by the younger larvae of Agriotes which are the more susceptible to organochlorines, the data of Tables 1 and 2 are not wholly satisfying; but they are typical of our experience. According to Duncan's multiple range test we have denoted by unlike postscripts those data which differ significantly at the % level.

Table 1 Granular parathion alone provided such immediate protection for maize that 91.0% of the plants were enabled to survive at site no.1. But short term protection of the majority of young plants does not suffice to guarantee high yield of grain; yield is dependent also upon continuous protection of the root up to harvest. At site no.2, for example, the higher yields coincided with treatments by the more persistent AG chlordane. The granular formulation of AG chlordane/parathion provides both for early knockdown and long term control of Agriotes spp.

Table 1

Performance of some granular soil insecticides against Agriotes spp. in maize

Formulation	Rate kg a.i./ha	Site No. 1		Site No. 2	
		Number of surviving plants in three rows at harvest		Yield per plot of 38m ² kg	
AG chlordane 10G	3.0	66.6	h	14.02	a
AG chlordane 10G	5.0	80.0	defg	13.25	ab
Parathion 10G	4.0	91.0	abcde	12.05	bcde
AG chlordane 4G	1.6	87.6	abcdef	12.80	abcd
Parathion 4G	1.6				
Heptachlor 4G	1.6	83.8	abc		
Untreated témoin	-	30.7	i	10.42	e
Best competitive treatment		100.0	a	14.02	a

Table 2 For minimising the numbers of holes caused by Agriotes spp. (columns i, v, vii) granules of parathion at 2.5 kg a.i./ha can hardly be surpassed except by AG chlordane at 5.0 kg a.i./ha in column (vii). However, when it is a question of compromise between getting the best yield of ware potato tubers and minimising toxicological hazards both to farmer and consumer, there are advantages in granular formulations providing both AG chlordane and parathion each 1.0 kg a.i./ha.

Sugar beet Experiments with AG chlordane, at rates up to 1.44 kg a.i./ha, against Bothynoderes punctiventris or Chaetocnema tibialis have not been promising. We are, however, studying its control over Agriotes spp. in sugar beet.

Table 2

Performance of some granular soil insecticides against *Agriotes* spp. in potato

(Granules placed only within the furrow)

Formulation	Rate kg a.i./ha	Site No. 3				Site No. 4				
		1970				1971		1972		
		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)
AG chlordane 10G	2.0					9.2	62.8			
AG chlordane 10G	2.5	24ab	154ab	137.5	36.5					
AG chlordane 10G	3.0					3.5	85.9			
AG chlordane 33G	5.0							13.5ab	63.8	49.9
Parathion 10G	2.5	15a	126a	155.5	40.0	1.2	95.2	21.7bc	41.7	46.2
AG chlordane 4G	1.0	17a	207ab	144.0	41.5	3.7	85.1			
Parathion 4G	1.0									
Heptachlor 4G	1.0	26ab	156ab	160.5	37.5					
Untreated (témoin)	-	45bc	231ab	135.0	50.5	24.7	0.0	37.2c	0.0	47.4
				ns						ns

1970 (i) number of holes, due to *Agriotes* spp. in all tubers of a 50m² plot1970 (ii) number of holes, due to *Noctuidae*, in all tubers of a 50m² plot1970 (iii) kg of ware potatoes from 50m²1970 (iv) kg of unsaleable potatoes from 50m²1971 (v) number of holes, due to *Agriotes* spp., in all tubers of a 50m² plot

1972 (vii)]

1971 (vi)] % control of *Agriotes* spp. calculated relative to untreated (témoin)

1972 (viii)]

1972 (ix) kg of ware potatoes from two rows

Residues in soils and crops

Residue data, quoted in Tables 3-8, are the means of at least two analyses on each sample and are compensated for incomplete recovery by the analytical procedure. However, the chlordane contents of crops from untreated controls have not been deducted from those of treated plots. By some previous history the soil at Carpi contained traces of certain persistent organochlorines, and our tabulated data have been compensated for its apparent chlordane content which pre-dated our treatments.

Table 3 During the period March 1971-March 1972 this soil remained undisturbed except for the sowing (11 Mar 1971) and harvesting (19 Aug 1971) of sugar beet. Analyses of samples from soil surface and soil profile show how the chlordane has moved downward from the surface layer mainly into the section 0.5-5cm deep but only slightly into the deeper profile. These data cannot be integrated over the 15 cm profile because the boundary between the surface layer, in which chlordane was at first mainly concentrated, and the next lower layer could not be sharply defined.

Table 4 Our procedure here for sampling and analysing whole soil cores automatically integrates the chlordane contents down the 0-15 cm section of the profile, so that data opposite (a) and (b) within each square bracket may properly be compared. Comparison of the aggregate data from (a) with the aggregate from (b) shows that alpha- and gamma-chlordane neither evaporate quickly nor leach very much below the 15 cm depth during 344 days. We comment on this again in the Discussion.

Table 5 Residues translocated to sugar beet leaves are very low, except apparently in one instance of treatment with Gran. 9.0 kg a.i./ha upon which, also, we shall comment in the Discussion. Residues in sugar beet roots are low, and of the order reported by Van Steyvoort *et al* (1971). However, residues in carrots grown in the same soil one year later are by no means negligible.

Table 3

Residues in three separate layers of soil profiles down to depths of 15 cm

- (a) 30 March 1971, 20 days after soil treatment, and after sowing sugar beet
 (b) 29 March 1972, 385 days after treatment, before rotovating and sowing carrot
parts per million

AG chlordane kg a.i./ha date	alpha-isomer			gamma-isomer			alpha plus gamma			
	depth cm			depth cm			depth cm			
	surface	0.5-5	5-15	surface	0.5-5	5-15	surface	0.5-5	5-15	
Untreated	a	0.04	0.00	0.00	0.03	0.00	0.00	0.07	0.00	0.00
	b	0.04	0.07	0.06	0.02	0.04	0.03	0.06	0.11	0.08
Granular 4.5	a	10.07	5.09	0.56	3.57	1.70	0.20	13.67	6.80	0.76
	b	4.60	5.19	2.35	1.93	2.11	0.87	6.53	7.30	3.23
Granular 9.0	a	14.92	2.81	0.17	5.54	0.99	0.04	20.46	3.80	0.21
	b	9.40	15.73	3.23	3.91	5.44	1.08	13.31	21.17	4.32
e.c. 4.5	a	9.75	0.96	0.12	3.26	0.25	0.02	13.01	1.21	0.14
	b	3.85	4.26	0.43	1.46	1.44	0.17	5.32	5.70	0.60
e.c. 9.0	a	18.87	2.44	0.20	6.72	0.90	0.05	25.63	3.34	0.25
	b	7.29	8.70	0.89	2.84	3.14	0.34	10.13	11.84	1.23

Table 4

Residues in whole soil cores to depth 15 cm

- (a) 19 August 1971, 162 days after soil treatment, at sugar beet harvest
 (b) 28 July 1972, 506 days after soil treatment at carrot harvest
parts per million

AG chlordane kg a.i./ha	alpha-isomer		gamma-isomer		alpha + gamma	
	(a)	(b)	(a)	(b)	(a)	(b)
Untreated	0.04	0.04	0.03	0.03	0.07	0.07
Granular 4.5	1.99	1.10	0.88	0.44	2.87	1.54
Granular 9.0	4.80	3.53	1.91	1.38	6.71	4.91
e.c. 4.5	2.36	2.92	0.92	1.06	3.28	3.98
e.c. 9.0	3.58	4.17	1.25	1.54	4.83	5.71

Table 5

Residues in/on sugar beet (leaves and roots) cropped and harvested 1971
 and in/on carrot cropped and harvested at same site 1972

Residues in untreated témoin samples not deducted from treated samples

parts per million

AG chlordane kg a.i./ha	Sugar beet leaves			Sugar beet roots			Carrot		
	alpha	gamma	total	alpha	gamma	total	alpha	gamma	total
Untreated	<0.005	<0.005	<0.010	0.009	0.007	0.016	0.012	0.005	0.017
Gran., 4.5	<0.005	<0.005	<0.010	0.021	0.011	0.032	0.185	0.074	0.259
Gran., 9.0	0.142	0.049	0.191	0.066	0.019	0.085	0.417	0.172	0.589
e.c., 4.5	0.021	0.009	0.030	0.037	0.011	0.048	0.161	0.053	0.214
e.c., 9.0	0.025	0.009	0.034	0.035	0.011	0.046	0.198	0.067	0.265

Table 6

Residues in soils planted with maize

(a) 5 May 1971, 21 days after treatment, three separate layers of profile to 15 cm
 (b) 20 September 1971, 159 days after treatment, whole soil cores to depth 15 cm

parts per million

AG chlordane kg a.i./ha	date	alpha-isomer			gamma-isomer			alpha + gamma		
		surface	0.5-5	5-15	surface	0.5-5	5-15	surface	0.5-5	5-15
Untreated	[a	-	-	0.06	-	-	0.03	-	-	0.09
	b		0.014			0.014			0.028	
Granular 4.5	[a	3.99	6.25	0.79	1.26	2.40	0.28	5.25	8.65	1.07
	b		1.224			0.495			1.719	
Granular 9.0	[a	6.01	13.25	2.79	2.54	4.50	0.98	8.55	17.75	3.77
	b		2.417			0.917			3.334	
e.c. 4.5	[a	4.75	2.64	0.78	1.57	0.95	0.27	6.32	3.59	1.05
	b		1.842			0.743			2.585	
e.c. 9.0	[a	10.46	7.43	1.66	3.57	2.57	0.53	14.03	10.00	2.19
	b		3.070			1.132			4.202	

Table 7

Residues on leaves, in/on stalks and grain of maize harvested 1971

parts per million

AG chlordane Formulation	kg a.i./ha	Leaves			Stalks	Grain
		alpha	gamma	total	alpha + gamma	alpha + gamma
Untreated	-	0.058	0.028	0.086	<0.005	<0.005
Granular	4.5	0.118	0.051	0.169	<0.005	<0.005
Granular	9.0	0.085	0.039	0.124	<0.005	<0.005
e.c.	4.5	0.111	0.042	0.153	<0.005	<0.005
e.c.	9.0	0.225	0.081	0.306	<0.005	<0.005

Table 8

Residues in/on potato tubers harvested 22 July 1971

Granules spread and e.c. sprayed only in the furrow on 15 March
 prior to planting 16 March 1971

Formulation	Rate kg a.i./ha	alpha-isomer ppm	gamma-isomer ppm	alpha+gamma ppm
Untreated	-	0.001	0.003	0.004
AG chlordane	[2.25	0.020	0.027	0.047
10% granules	4.50	0.094	0.066	0.160
AG chlordane	[2.25	0.135	0.058	0.193
e.c. 480g a.i./l	4.50	0.275	0.101	0.376

Table 6 These data show chlordane contents (a) for each of three successively deeper layers of soil 21 days after treatment, and (b) for whole soil cores 159 days after treatment with AG chlordane. These again support the opinion, more fully expressed in the Discussion, that chlordane isomers are rather stable in the soil.

Table 7 No appreciable chlordane residue was found in stalks or grain of maize; but, when the maize is grown as in ordinary agricultural practice, it is always possible to detect residues on the leaves. This will be explained in the Discussion.

Table 8 Residues in/on potato tubers are always greater following the spraying of e.c. formulations than after spreading of granules in the furrow. For this observation, however, we can offer no completely satisfactory explanation.

DISCUSSION

Properties of AG chlordane for control of Agriotes spp. cannot be adequately evaluated in one or two seasons for reasons given at the beginning of the preceding section. Accordingly, through longer experience of its influence on the younger Agriotes larvae, it still remains to be ascertained whether its persistence in the soil eventually would enable AG chlordane to control a population of mature larvae; and this could be determined best during continuous use in large scale agriculture. Meanwhile it seems necessary to specify the use of AG chlordane in association with some other insecticide which, during its own short term, contributes rapid knockdown of mature Agriotes larvae. Combinations of AG chlordane and parathion, conforming to present regulations in Italy, provide protection both for maize and potato in the short and long term.

Residues in/on roots of sugar beet, grain and stalks of maize, tubers of potato are small. It was formerly difficult to correlate quantitatively residues in/on leaves of maize or sugar beet with dosage of AG chlordane applied to the soil; and, because no appreciable residues had been detected in stalk of maize (Bundesanstalt für Pflanzenschutz reported by Furness 1971, Dorough and Pass 1972, Petrosini 1973, Tafuri et al 1973), it had seemed improbable that chlordane translocates through the plant from soil to foliage. This opinion has now been confirmed in different ways. First, it has been shown that the fatty tissue of Ostrinia nubilalis larvae, which have bored through the stalk of maize, is free from chlordane and oxchlordane. Secondly, leaves of maize washed with water and detergent contain <0.005 ppm of chlordane; whereas, on unwashed leaves from the same plant, 0.132 ppm was found. Thirdly, when maize is grown in the laboratory in soil containing 38 ppm AG chlordane which was irrigated but covered so as to preclude possibility of upward drift of soil particles, stalk and unwashed leaves at maturity each contain <0.005 ppm. We believe that, whenever detected, the presence of alpha- and gamma-chlordane on maize leaves is due to drift of airborne particles from the surfaces of treated soils; and it is possible that the foliage of other plants, eg sugar beet, becomes contaminated in the same fortuitous manner (see Table 5 Gran., 9.0 kg a.i./ha). Even so, fodder prepared from whole unwashed maize plants (Tafuri et al 1973) or from sugar beet tops contains only very small residues of chlordane.

Recently Dorough and Hemken (1973) concluded trials in which AG chlordane was fed at several concentrations, from about 0.013 to 100 ppm, in the diets of dairy cattle. Some of their chosen concentrations are, of course, much greater than could occur in feedingstuffs as a consequence of uses of AG chlordane foreseen in our own present report. However, their numerical data show that the quantities of alpha- and gamma-chlordane and of oxchlordane which occur in milk or which accumulate in body fat are very small fractions only of the total ingested chlordane. Thus, coupling the research of Dorough and Hemken (1973) with our own crop residue data in advance of European feeding trials, we would anticipate no serious residues of alpha- or gamma-chlordane or of oxchlordane in dairy products if AG chlordane should be employed as soil insecticide at dosages corresponding with the foregoing Tables.

If any stable and non-volatile substance be spread uniformly over soil of bulk density 1.25 g/cm^3 , as at Modena, at 4.5 kg/ha and incorporated 15 cm deep, its mean concentration in this profile would be 2.4 ppm ; similarly 9.0 kg/ha would correspond with 4.8 ppm . Table 4 and Table 6 (opposite the date b) show the concentrations of alpha- and gamma-chlordane remaining in soils some hundreds of days after soil treatments of various kinds. These data, considered in aggregate so as to even sampling and other practical errors, show that residues which remain for so long conform to the summation of applied dosages to within one part in twenty-five. Thus, it is concluded, both alpha- and gamma-isomers stay mainly where they were placed or as they were incorporated in the soil, subject neither to appreciable chemical change nor to much physical movement either by evaporation or by leaching during several hundreds of days. The consequences for subsequent rotation of crops are under study.

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CHLORODIMEFORM: MAIN CHARACTERISTICS IN RELATION
TO PRACTICAL APPLICATION

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Summary Recent developments relating to the insecticidal action of chlorodimeform are discussed, and aspects concerning the ovicidal action and the residual effect of the compound are outlined. The role played by the vapour phase of chlorodimeform is described and the results of field trials that demonstrate its mobility and off-target action are presented.

Résumé De récents développements relatifs à l'action insecticide du chlorodimeforme font actuellement l'objet d'une discussion dans laquelle les aspects concernant l'action ovicide et l'effet résiduel du composé sont mis en évidence. On y décrit en outre le rôle que joue la phase gazeuse du chlorodimeforme; les résultats d'essais de plein champ démontrant sa mobilité ainsi que son action sur l'environnement de l'objectif (off-target action) y sont également présentés.

INTRODUCTION

Chlorodimeform, also known as C-8514 or chlorphenamidine*, was first introduced in 1966 as an acaricide with ovicidal and adulticidal action against both OP-resistant and OP-susceptible strains of a number of Tetranychidae. Insecticidal activity was demonstrated against Lepidoptera such as codling moth (*Laspeyresia pomonella*) and Egyptian cotton leafworm (*Spodoptera littoralis*). Eggs of the latter could be controlled by both contact sprays and exposure to chlorodimeform vapour (4 mg/m³) (Dittrich 1967a).

Chemically, chlorodimeform is a formamidine (N'-(4-chloro-2-methylphenyl)-N,N dimethylformamidine) and therefore is not related to any of the common classes of chemicals used for pest control.

It was demonstrated that spidermite adults and eggs showed that physical reactions to treatment with chlorodimeform were entirely different from those caused by standard acaricides, and in vitro tests confirmed that chlorodimeform is not an inhibitor of houseflyhead cholinesterase. It is apparent that this chemical has a mode of action which is different from that of cholinesterase inhibition. In fact, two modes of action have been demonstrated. Which of the two is the main one remains uncertain; also, further effects of chlorodimeform may possibly come to light. Aziz and Knowles (1972) and Beeman (unpublished data) demonstrated that chlorodimeform inhibits monoamine oxidase (MAO) in vitro. Abo-Khatwa and Hollingworth (1972), working with German cockroaches (*Blattella germanica*), showed that chlorodimeform prevents oxidative phosphorylation and stimulates mitochondrial ATP-ase activity, and suggest-

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ed that these actions contribute to its toxicity. If MAO inhibition or the former plus action on oxidative metabolism are the decisive effects in insects and mites, then the significance of these findings is that chlorodimeform has a different mode of action to that of existing pesticides, and that cross-resistance to existing pesticides is not likely to occur. This view is corroborated by evidence which shows that chlorodimeform is at least as toxic to OP-resistant as it is to OP-sensitive strains of spidermites. There exist other indications that OP-resistance may be negatively correlated to chlorodimeform's toxicity (Dittrich 1969). Chlorodimeform may be absorbed by the roots and is translocated xylematically to the foliage in both annuals and woody perennials. The compound is also absorbed by the foliage from spray deposits as well as from a vapour-saturated atmosphere, and is again released in the vapour phase at concentrations toxic to eggs of mites and insects.

Insecticidal activity is virtually limited to Lepidoptera and certain Homoptera. The resulting selective action and almost complete inactivity against most members of the orders Coleoptera, Diptera and Heteroptera, presents an interesting aspect, which is being exploited in integrated control programmes in cotton.

OVICIDAL EFFECT

In both mites and insects, the ovicidal effect is more pronounced than the larvicidal and adulticidal effects. In those insects that are affected by chlorodimeform, economical rates of application are generally ineffective against adult and later instar larvae, whilst the eggs are often effectively controlled. This ovicidal effect, against a wide range of lepidopterous insect pests, is now recognized as a major asset of the compound. It offers an entirely new approach to pest control, whereby ovicidal treatments may be timed to coincide with periods of heavy egg deposition, or, in instances where this is not practical because of overlapping populations, applications may be made at fixed intervals. Selectively timed sprays to hit heavy egg deposits are now practiced for control of cotton leafworms (Spodoptera spp.) and cotton bollworms (Heliothis spp.). Research and field workers seeking to establish the ovicidal effect of chlorodimeform against insect eggs are, however, warned that failure to prevent hatching must not immediately be interpreted as a lack of effect, as it is our experience that the larvae tend to succumb shortly after emergence from the eggs. This is particularly the case if eggs are left to hatch on treated foliage.

An example of the practical value of the ovicidal effect under field conditions is given in the following table which shows the results of a series of aerial applications at 500 g a.i./ha against heavy egg lays of American cotton bollworm in Australia. Compared to a fairly high rate of a mixture of DDT and Endrin, control is excellent, showing a superior residual action. The good results may safely be attributed to contact and residual kill of eggs and emerging larvae.

Table 1

Effect of chlorodimeform against *H. armigera* under controlled field conditions

Chemical & Rate	Assessment	Counts of eggs and larvae per 10 X 1 m row (days)											
		-2	0	+1	+3	0	+1	+3	0	+1	0	+3	
chlorodimeform 500 g a.i./ha	Eggs	92		116	218		292	275		262		109	
	1-3 larvae	6	E	1	2	E	0	12	D	7	E	5	
	4-6 larvae	1		1	1		3	0		1		6	
Total larvae		7	Y	2	3	Y	3	12	Y	8	Y	11	
Endrin + DDT 16 + 64 fl. oz.	Eggs	90		174	273		273	288		202		90	
	1-3 larvae	1	S	0	11	S	11	30	P	8	P	6	
	4-6 larvae	3	S	2	2	S	2	0	S	1	S	17	
Total larvae		4		2	13		13	30		9		23	

Application: Aircraft at 2 U.S. gal per acre, 20 acre plots

Interval between application: 5 days

Previous treatments: All plots sprayed with chlorodimeform 500 g a.i./ha for 3 previous spray applications

An additional aspect of the ovicidal effect requires specific mention. It was noted that both mite and Lepidoptera eggs were more susceptible to chlorodimeform shortly before eclosion time. For this reason, dipping tests using freshly laid eggs often show disappointing results. If fresh eggs are used, they should be treated on the foliage and remain there until the test has been terminated, so that chlorodimeform vapour from external and internal deposits of the leaf may continue to have its effect on the maturing egg.

EFFECT AGAINST ADULT LEPIDOPTERA

Observations made shortly after application of chlorodimeform against rice stemborers in the field repeatedly showed that adults of both *Tryporyza* and *Chilo* spp. became hyperactive and uncoordinated in flight. Many also landed in the water, unable to fly again. Similar observations were recorded by Etheridge (1972) when checking the effect of chlorodimeform against bollworm moth (*Heliothis zea*). He noticed hyperactivity to such a violent degree that, after two days, wings were so badly damaged that flight was impossible. The same author also showed that moths of both bollworms and tobacco budworms (*Heliothis virescens*), after being treated with two dosage levels, laid fewer eggs, while significantly fewer of the eggs laid by treated moths hatched.

Table 2

The effect of chlorodimeform, fed to *Heliothis* moths, on oviposition and larval eclosion (modified from ETHERIDGE, 1972)

	Chlorodimeform concentration (ppm)							
	0		2 X 10 ³				4 X 10 ³	
	No. of eggs 4 days	% (2) Eclosion	No. of eggs 4 days	% (2) Eclosion	No. of eggs 4 days	% (2) Eclosion	No. of eggs 4 days	% (2) Eclosion
<i>H. zea</i>	185.2 b	64.9 b	3.6 b	0.00 b	3.2 a	0.00 a		
<i>H. virescens</i>	439.4 b	82.8 b	191.4 a	62.10 b	134.2 a	42.55 a		

- (1) Numbers within each species not followed by the same letter are significantly different at the 0.05 level. (Duncan's multiple range test)
- (2) Percentages within each species not followed by the same letter are significantly different at the 0.05 level.

This effect was more evident in bollworms than in tobacco budworm. Field trials invariably show that the latter require higher rates of application.

RESIDUAL ACTION

The relatively high vapour pressure of chlorodimeform suggests a short residual efficacy after foliar applications. Both laboratory and field trials, however, indicate that residual action is considerably longer than the high vapour pressure would suggest. Residual effect against eggs of carmine spidermite (Tetranychus telarius) in laboratory trials is at least 7 days.

Under practical field conditions, it has been shown repeatedly that eggs of Egyptian cotton leafworm, deposited as long as 9 days after aerial application of 750 g a.i./ha, are effectively controlled. The effect on egg masses is clearly correlated to the time interval between application and oviposition. Egg masses laid within 3 days after treatment may usually be expected not to hatch, whilst larvae from egg masses laid later than that are observed to die within 6-24 hours after emergence. The time required depends on the interval between treatment and oviposition. The method used to make these observations was as follows:

Application was made by tractor-drawn mistblowers or aircraft. Before and several times after application, freshly laid egg masses were marked by plastic streamers attached to the leaves on which the egg masses had been laid. Marked egg masses were inspected at regular intervals throughout the duration of the trial. In one such trial carried out during 1972, 500 g a.i. provided control of 34 out of 36 egg masses marked on the 8th day after application.

Table 3

The residual effect of chlorodimeform applied from
the air against egg masses of S. littoralis

Treatment	Stage assessed	MD*	CD*	MD	CD	MD	CD	MD	CD
		7.	13.	13.	16.	16.	20.	20.	23.
1 l./ha	Hatchings up to 6 mm	12	6/12	-	-	-	-	-	-
	Layings	11	10/12	16	15/16	36	34/36	6	4/6
1.25 l./ha	Hatchings up to 6 mm	10	8/10	-	-	-	-	-	-
	Layings	14	13/14	10	10/10	13	13/13	6	5/6
1.5 l./ha	Hatchings up to 6 mm	16	14/16	-	-	-	-	-	-
	Layings	17	16/17	13	12/13	8	8/8	6	6/6

* MD = marking date (August 1972)

CD = counting date (August 1972)

= number of dead hatchings or layings/number of marked ones

Date of application: 12.8.72

Results from similar trials against spiny bollworm (Earias insulana) were also satisfactory, but the residual effect was considerably shorter. 82 % of eggs marked 4 days after application were killed, whilst only 25 % of those marked on the 6th day were killed.

Field work against bollworms (Heliothis spp.) in Central America and Mexico has shown that residual action against these insects does not reach that obtained against Egyptian cotton leafworm. Our field experiences since 1968 have, however, taught us that intervals between chlorodimeform-containing sprays may be lengthened considerably compared to standards.

Spray programmes containing chlorodimeform in straight sprays or tank mixtures with standards are now common practice, resulting in a reduced number of applica-

tions. Where up to 25 applications were once required, 15-20 treatments suffice when chlorodimeform is used in the programme. In such cases, a regular field scouting programme is necessary to establish the optimum timing for application. Where field scouting is not practical and a fixed-time programme has to be followed, as is often the case in the USA, relatively short intervals against bollworm species are recommended at low rates of application. The USA registered label recommends chlorodimeform applications at 5 day intervals at 140 g and 280 g a.i. per hectare against cotton bollworm and tobacco budworm respectively.

In the case of rice stemborers, the residual action is also of considerable length after both foliar and paddy water application. Under laboratory conditions, hatching larvae are controlled, even if treatment was carried out up to 14 days before infestation with egg masses. In spite of the generally poor effect against Lepidoptera larvae, the degree of control obtained against rice stemborers is remarkable. It is at least in part attributed to an anti-feeding effect, which was readily demonstrated against third instar stemborer larvae in laboratory tests, using leaf sheaths dipped in chlorodimeform solutions. Feeding was reduced by 85 % at a concentration of 5 ppm (Ikeyama and Maekawa 1973).

Under field conditions, it is now general practice to control rice borers by making 3 to 4 applications at intervals of from 2 to 3 weeks, depending on whether foliar sprays or granular applications are made. In the case of paddy water applications, the optimum rate lies at 750 g a.i., while for foliar sprays, 500 g a.i. suffices for control of rice stemborers (*Chilo* and *Tryporyza* spp.).

The fairly long residual effect obtained under both laboratory and field conditions with various crops points to foliar absorption and subsequent release of chlorodimeform at ovicidal concentrations. There exists no doubt that under tropical and subtropical weather conditions, surface residues on foliage will not remain effective for more than a few days. This is further substantiated by the observation that a heavy overhead irrigation or rain, following 24 hours after application to cotton, does not reduce the residual action in the field.

OFF-TARGET VAPOUR PHASE ACTIVITY

The activity of chlorodimeform vapour needs further mention since it can reach far beyond the treated target area. This was first observed in small plot trials against the highly susceptible rice stemborers. It was noticed that infestation levels in control plots situated downwind from chlorodimeform-treated plots were far below the average. Attempts are being made to make practical use of this characteristic. Critical field trials indicate that in paddy rice a spot application method, whereby the entire dose for a 20-40 m² area is applied to one spot in the centre, suffices for effective borer control over the whole area.

Table 4

The effect of spot applications of chlorodimeform at 500 g a.i./ha versus broadcast application against stemborers in paddy rice

	% Dead heart		Yield in kg/ha
	40 DAT*	60 DAT	
1. 2 g a.i./10 m ² spot application	0.3	0.35	3313
2. 4 g a.i./20 m ² spot application	0.9	0.95	3209
3. 8 g a.i./40 m ² spot application	1.4	1.1	3096
4. broadcast	1.1	0.7	3243
5. control	12.4	20.5	2660

*DAT = days after transplanting

Timing of applications: 24, 44, 64 DAT

as 50%⁶⁶¹ mf

Whether this effect is mainly achieved by diffusion through the water or by vapour above the water surface remains unclear. However, experience with other paddy rice insecticides, such as diazinon and phosphamidon, which have a much lower vapour pressure and a limited lateral effect, suggests that vapour activity is mainly responsible. The fact that vapour may affect susceptible species over considerable distances, is further demonstrated by the Japanese restrictions on the use of chlorodimeform, which prohibit spray applications within 300 metres of mulberry trees used for silk production. This is important for research workers carrying out field experiments, because small plot trials in which chlorodimeform is included can give misleading results, both in the chlorodimeform and in bordering plots.

In order to establish the practical value of this effect in row crops, a number of trials in vegetables were carried out in Switzerland, results of which are summarized below. Granular formulations containing 7.5 % of chlorodimeform were in each instance applied to the soil surface between the rows in bands of 5 to 10 cm width. Treated plots were separated from the untreated control plots by untreated buffer strips, wide enough to prevent interference. Assessments were carried out in the centre of each plot, as a dilution effect towards the edges is usually noticeable.

Table 5

The effect of one inter-row application of two chlorodimeform formulations at 5 kg a.i./ha to leekmoth (*Aerolepsa assectella*, Plutellidae)

Treatment	Number of larvae per 50 plants				% infestation
	Rep I	Rep II	Rep III	Rep IV	
Formulation A	9	7	9	5	15.0
Formulation B	11	8	6	10	17.5
Control	27	31	24	27	54.5

Date of planting 24.5.73 / Date of treatment 31.7.73 / Date of assessment 11.9.73

The infestation assessed on the 11th of September was caused by the 2nd generation of the insect, which had developed during the last week in August. This implies that a residual action of at least 1 month was being achieved.

Table 6

Control of whiteflies (*Trialeurodes vaporariorum*) in brussels sprouts with a single post-planting application of chlorodimeform at 5 kg a.i./ha

Treatments	Number of whitefly adults per plant*										Total	
	Rep I	Rep II	Rep III	Rep IV	Rep V	Rep VI	Rep VII	Rep VIII	Rep IX	Rep X		
chlorodimeform	39	17	26	22	11	19	23	23	19	18	217	
7.5 % granular	28	27	33	20	25	29	16	38	16	16	248	
Control	Rep I	177	211	225	138	161	123	133	142	85	103	1488
	Rep II	103	103	117	131	160	178	130	92	124	81	1219

Date of planting 28.6.73 / Date of application 16.7.73 / Date of assessment 21.8.73

* on 10 leaves per plant

In a third experiment, a developing infestation of cabbage moth (*Mamestra brassicae*) in brussels sprouts was still being suppressed 8 weeks after an inter-row application of chlorodimeform.

Table 7

The control of cabbage moth in brussels sprouts 8 weeks after application of two chlorodimeform formulations at 5 kg a.i./ha

Treatment	Number of larvae per 10 plants				Mean
	Rep I	Rep II	Rep III	Rep IV	
Formulation A	2	1	0	2	1.25
Formulation B	1	1	0	0	0.5
Control	5	7	11	14	9.25

In two similar trials carried out in the USA during 1972 in cabbage, 5 kg a.i. applied between the rows shortly after transplanting, provided commercially satisfactory control of cabbage looper (Trichoplusia ni) and imported cabbageworm (Pieris rapae) over a full season.

Although the above results undoubtedly demonstrate the off-target action of the vapour, it should be emphasized that these results must be considered as preliminary. Further work is required, to establish at what minimum rates, under which conditions, and on what crops, satisfactory results can be achieved.

Whether the effect in these trials is due to an actual kill of eggs and young larvae or is the result of a repellent effect remains to be clarified.

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NOTES

FIELD EVALUATION OF CARBENDAZIM* (BAS 346F)
AS A FUNGICIDE ON APPLES

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Summary Carbendazim is a benzimidazole fungicide active against a range of apple diseases. In a series of trials carried out in 1972 it was shown to control Podosphaera leucotricha and Venturia inaequalis satisfactorily, both on its own and used in combination with dinocap in an alternating fungicidal spray programme. Heavier fruit set and greater fruit numbers at harvest than equivalent standard programmes were recorded. The combined programme also gave good fruit finish and may have assisted red spider mite suppression. As frequent spraying against Podosphaera leucotricha still appears necessary under U.K. conditions, the most economic way for fruit growers to use carbendazim and other materials of its type, may be in an alternating spray programme with cheaper mildewicides such as dinocap.

INTRODUCTION

Recent years have produced a considerable amount of evidence to show the effectiveness of the benzimidazole group of fungicides against a range of diseases affecting apples. Some work in 1971 with a recently introduced member of this group carbendazim (methyl-2-benzimidazole carbamate, previously known as BAS 346F) had shown control of such diseases as Podosphaera leucotricha (apple mildew) and Venturia inaequalis (apple scab) similar to benomyl. In these trials applications of carbendazim were given to apples at 10 - 14 day intervals throughout a full spraying season.

For the 1972 season, the results of which form the basis of this paper, it was decided to use carbendazim in a fungicidal programme alternating with dinocap from pink bud stage onwards. From reports it seemed that 10 day spraying against apple mildew was still advantageous (Burchill and Williamson 1970) even when using benomyl, although longer intervals of up to 22 days between sprays gave good control of apple scab (Byrde et al 1970). Furthermore, an alternating programme of benomyl and dinocap was shown to give good control of both apple scab and apple mildew (Burchill et al 1971) and there are obvious economic advantages to the grower from using a combination of two such materials.

In addition to evaluating disease control, benomyl has been shown on several occasions to increase the amount of fruit russet at harvest (Byrde et al 1969, 1970 and 1971, Burchill et al 1971). It was therefore necessary to assess whether carbendazim produced similar effects, both on its own and used alternately with dinocap. Fruit numbers have sometimes, though not invariably, been increased by the use of benomyl (Williams et al 1970, Burchill et al 1971 and Byrde et al 1971) and this was also examined in the trials.

* proposed common name

METHOD AND MATERIALS

Carbendazim was applied to all sites as a foliar spray, using a 50% wettable powder formulation (BAS 3460F, now marketed as Bavistin), used at 0.025% a.i. both as a sole fungicide and alternating with dinocap 0.025 or 0.05% a.i. in replicated trials in which other standard materials were included. Plot size ranged from 1 - 3 trees per plot. Unreplicated grower applications compared a programme of carbendazim at 0.5 lb a.i. in 50 - 100 gal/ac alternating with dinocap against standard spray programmes. In both cases a 10-day spray schedule was used from late bud burst (mid April) to end of extension growth (mid-end July). The first dinocap spray was given at pink bud. Where captan was compared for scab control in the replicated trials it was applied at a constant 0.1%.

Secondary infections of apple mildew were scored by two methods: in Series A (Table 1) and grower trials 1 - 10 (Table 3) by assessing percentage of infection on the 3rd, 5th and 7th leaves on young shoots. In Series B (Table 2) and grower trials 11 - 16 by scoring presence or absence on the first 5 fully developed leaves on young shoots.

Apple leaf scab was scored similarly to apple mildew; apple fruit scab, on the one site on which it occurred, both on severity and on presence or absence.

Fruit finish was expressed as a percentage of 100 fruits taken at random on an average of ten trees per treatment and put in 4 categories varying from no russet to cracking and severe russet. Data given in Table 4 was obtained by marking branches on 10 trees selected at random throughout the treated blocks of the grower trials (most in excess of two acres each) and expressing the set as a percentage of blossom trusses.

RESULTS

Apple Mildew

Although 1972 generally was not regarded as a year of severe apple mildew infection, Tables 1 and 2 show the presence of quite high levels in some of the untreated controls. In the replicated plots (Series A) the carbendazim/dinocap schedule appears to have given slightly better results than either the carbendazim or benomyl programmes but these were quite satisfactory. Series B trials show a reverse of this trend with benomyl and dinocap performing as well as any treatment. At Site 1 no treatment gave particularly good control, though all were better than untreated, but this site was note-worthy for the presnece of a very high level of primary mildew before treatments started.

Table 1

Secondary mildew and scab control
(replicated trials, series A)

Treatments	Sites	Secondary mildew % leaf area infection on extension growth				Apple scab % infection	
		1	2	3	4	Fruit	Leaf
carbendazim alternating with dinocap (10 day/10 day)		11.3	6.4	5.5	8.3	0.2	0
carbendazim (10 - 14 day)		15.1	-	6.6	8.0	0.2	0
benomyl (10 - 14 day)		12.3	9.1	7.4	8.6	0	0
untreated		37.3	17.8	37.0	16.2	19.7	3.6

Table 2

Secondary mildew and scab control
(replicated trials, series B)

Treatments	Sites	Secondary mildew % leaf area infection on extension growth				Apple scab % leaves infected	
		1	2	3	4	1	2
carbendazim alternating with dinocap (10 day/10 day)		49.4	8.0	30.6	6.0	2.6	2.4
carbendazim (10 - 14 day)		27.8	5.0	24.8	7.6	0.8	2.4
benomyl (10 - 14 day)		43.4	5.4	18.8	7.8	0.4	0.8
dinocap plus captan (10 - 14 day)		44.4	-	14.8	7.5	5.4	1.0
untreated		83.0	24.8	82.4	46.3	34.4	38.0

On the grower trials sites, where comparisons included dinocap, benomyl, binapacryl, thiophanate-methyl and lime sulphur, Table 3 shows that carbendazim/dinocap performed invariably as well as comparisons and sometimes very much better. The alternating schedule proved easy to follow and no practical difficulties were reported.

Table 3

Secondary mildew control (grower trials)
% leaves infected

Site No.	carbendazim alternating with dinocap (10 day/10 day)	standard comparison (10 day)	mildewicide used in standard programme	cultivar
1.	39.4	44.6	dinocap	Cox's Orange Pippin
2.	31.5	31.1	dinocap	"-
3.	11.1	11.6	benomyl, binapacryl	"-
4.	19.5	27.6	dinocap	"-
5.	29.2	54.7	dinocap	"-
6.	9.0	12.0	binapacryl	"-
7.	14.1	25.6	dinocap	"-
8.	13.1	12.3	dinocap	"-
9.	9.1	18.2	binapacryl	Bramley Seedling
10.	16.0	64.8	lime sulphur	Cox's Orange Pippin
11.	7.0	14.2	benomyl	"-
12.	3.7	2.1	dinocap	"-
13.	4.4	3.3	thiophanate-methyl	"-
14.	10.2	14.1	dinocap	"-
15.	7.9	11.8	dinocap	"-
16.	2.1	3.0	dinocap	"-

Apple Scab

This only occurred in some replicated sites with none at all in the grower trials. Tables 1 and 2 show that 1 leaf scab and 1 fruit scab outbreak were recorded in Series A and 2 sites showed leaf scab in Series B. It is important to note that carbendazim at 20-day intervals was sufficient to contain a nearly 20% fruit infection at Site 1, Series A. High levels of leaf scab at Sites 1 and 2, Series B, were controlled satisfactorily by all treatments but with benomyl being marginally the best.

Fruit set

Because of considerable variability in blossoming which occurs in any orchard, and was especially noticeable in 1972, fruit set was not assessed in the replicated plot trials. Table 4 shows records taken from grower sites using standard materials as comparison.

Results show that on all sites carbendazim/dinocap gave better initial fruit set than captan + dinocap treatments. On one site initial set with benomyl was better but on another with thiophanate-methyl it was not as good. Fruit counts at harvest largely followed those obtained earlier but the treatment differences were

often less pronounced. This increase in fruit numbers was accompanied by a tendency, which was not very marked, for slightly smaller fruits at sites where the yield was heaviest. As total yields were very variable they were not recorded.

Table 4

Fruit numbers as % set of blossom trusses (grower trials)

Site	cultivar	carbendazim/dinocap		standard comparison		fungicides used in standard programmes
		fruitlet (June)	harvest (October)	fruitlet (June)	harvest (October)	
1	Cox's Orange Pippin	36	19	77	14	benomyl
2a	Cox's Orange Pippin	41	21	20	10	dinocap + captan
2b	Bramley	27	-*	8	-*	dinocap + captan
3	Kidd's Orange Red	96	66	66	55	thiophanate-methyl
4	Cox's Orange Pippin	266	124	49	35	dinocap + captan
5	Cox's Orange Pippin	114	-*	87	-*	dinocap + captan
6	Cox's Orange Pippin	225	189	152	103	dinocap + captan
7	Cox's Orange Pippin	127	99	58	47	dinocap + captan

* Yield figures not obtainable

Red Spider Mite

Red spider populations were low throughout all trial sites and few meaningful records were obtained. Where measurable populations occurred it appeared that carbendazim/dinocap gave better suppression than carbendazim or benomyl alone but less than dinocap used exclusively.

Fruit Finish

Results from the three recorded replicated trials were variable. The only marked difference between treatments was at site 3 when captan + dinocap gave better results than either carbendazim or benomyl and especially the carbendazim/dinocap treatments. There was, however, considerable variation in size between trees on this site, and the smaller trees tended to show more russeting, irrespective of treatment. These results differ from the rather more extensive grower trials (Table 6) where carbendazim/dinocap gave results fully comparable to dinocap + captan, and better where it was compared, than benomyl. An interesting result is from site 4 where with the cultivar Kidd's Orange Red, known to be sensitive to some fungicides and always a heavily russeted variety, carbendazim/dinocap gave the better result.

Table 5

Fruit finish (replicated trials)
% of apples classed as 1st or 2nd grade

Treatments	Site	1	2	3
	carbendazim alternating with dinocap		24.5	79.2
carbendazim		25.5	-	72.2
benomyl		19.5	61.7	73.7
dinocap + captan		-	-	87.7
untreated		14.2	47.5	63.2

Table 6

Fruit finish (grower trials series B)
% apples in all grades at harvest

Site	carbendazim/ dinocap				dinocap/captan				benomyl				thiophanate- methyl				cultivar
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	
1	38	40	70	5	26	41	23	10	23	39	31	7					Cox's Orange Pippin
2a	20	52	16	12	17	41	32	10									Cox's Orange Pippin
2b	48	31	18	3	53	35	11	1									Bramley
3	37	35	22	6	35	31	14	20	21	26	36	17	32	44	13	11	Cox's Orange Pippin
4	7	24	40	29	0	17	33	50									Kidd's Orange Red
5	22	54	23	1	22	56	21	1									Cox's Orange Pippin
6a	27	48	19	6	22	38	30	10									Cox's Orange Pippin
6b	58	34	4	4	33	53	8	6									Worcester Pearmain
7	31	51	13	5	22	62	16	1	12	57	20	11					Cox's Orange Pippin

Grade categories

Category 1	No russet - good finish
Category 2	Light russet - class 1 or 2 fruit
Category 3	Moderate russet - poor quality fruit
Category 4	Cracking and severe russet - unmarketable

DISCUSSION

In these trials carbendazim gave generally satisfactory control of apple scab, equivalent to other materials. It was shown to have a beneficial effect on fruit set and certainly from the grower trials results, when used alternatively with dinocap, to give fruit finish at harvest equal to captan + dinocap and better than benomyl.

Used at 20-day intervals carbendazim gave satisfactory control of apple scab and there seems no need to apply it more frequently. At 10-day intervals it also gave good control of apple mildew used on its own but this generally was not any better than an alternating carbendazim/dinocap programme. For economic reasons and the fact that the dinocap used frequently has been shown to be as efficient as any fungicide at controlling the disease (Burchill *et al* 1971), this combined programme can be recommended. It is possible that it will also help control other diseases such as *Gloeosporium* spp. and other storage rots, apple canker and blossom wilt. This is under further investigation.

Although heavier fruit set and greater fruit numbers tend to have been accompanied by smaller fruits, the effects are not outstanding. In any case, they could probably be mitigated by changes in managerial practice such as heavier pruning, fruit thinning, heavier feeding or irrigation.

As with other benzimidazoles, carbendazim appears to give little or no control of red spider mite but used alternating with dinocap should give some suppression which would be supplemented by normal acaracides.

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NOTES

FIELD EVALUATION OF 5-NITRO-ISOPHTHALIC DIISOPROPYL ESTER (BAS 3000F) FOR THE CONTROL OF APPLE MILDEW, PODOSPHAERA LEUCOTRICHA, IN THE EUROPEAN COMMUNITY

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Summary BAS 3000F was applied at 0.025% and 0.05% at intervals of ten and fourteen days. Combined treatments of BAS 3000F and carbendazim, proposed common name for methyl-2-benzimidazole carbamate, were also applied, both as a ten-day alternating programme and a fourteen-day tank mix. Trials were carried out on a range of varieties in three European countries. BAS 3000F applied alone or in combination with carbendazim invariably gave better mildew control than comparison materials. The best mildew control was obtained with BAS 3000F at ten-day intervals. No phytotoxicity has been observed with BAS 3000F, which has given leaf and fruit finish comparable to standard materials.

Résumé BAS 3000F à 0.025% et à 0.05% a été appliqué à des intervalles de 10 et 14 jours. Des traitements combinés de BAS 3000F et de carbendazim, nom commun propose pour le methyl-2-benzimidazole carbamate, ont aussi été appliqués en mélange de cuve selon un programme d'alternance de 10 et 14 jours. Les essais ont été conduits sur une série de variétés dans trois pays européens. BAS 3000F appliqué seul ou en mélange avec le carbendazim a toujours donné un meilleur contrôle contre l'oidium que les produits de référence. Le meilleur contrôle de l'oidium a été obtenu avec BAS 3000F employé tous les 10 jours. Aucune phytotoxicité n'a été observée avec BAS 3000F, qui a donné un bon aspect du feuillage et du fruit comparable à celui des produits de référence.

INTRODUCTION

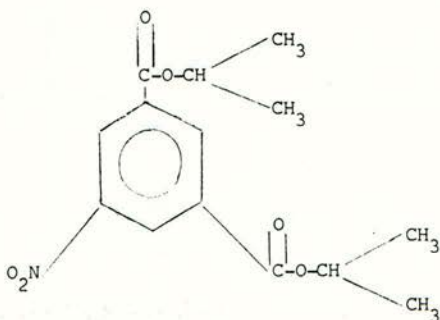
BAS 3000F is a non-systemic fungicide with specific activity against powdery mildews. It was developed at the research laboratories of BASF AG, Ludwigshafen, Germany. Initial development work was carried out in Germany and Belgium in 1969 and 1970, where the material was shown to give good mildew control with some eradicant action. Further confirmation of the curative properties of BAS 3000F was reported from East Malling Research Station (Frick 1972).

During the last few years it has been shown that the control of mildew with systemic fungicides of the methyl-2-benzimidazole type is not always successful; this is especially true in fruit growing.

In the search for new substances for the use in crop protection, we came across the specific efficacy of dialkyl-substituted 5-nitro-isophthalic esters* against

* Synthesized by Dr. R. Polster, BASF Aktiengesellschaft, Ludwigshafen.

mildew. Of the active ingredients tested, the following ester was both safe and highly effective:



5-nitro-isophthalic diisopropyl ester

Melting point: 65°C. Practically insoluble in water; good solubility in most organic solvents.

Low mammalian toxicity: acute LD 50: 6400 mg/kg p.o. rat for the formulated product (50% a.i.).

A number of replicated trials were carried out in Belgium, England and Germany to evaluate BAS 3000F in comparison with a range of existing mildew fungicides.

METHOD AND MATERIALS

BAS 3000F is a 50% w.p. formulation of 5-nitro-isophthalic diisopropyl ester. All applications were made in high volume (approx 2000 - 3000 l/ha), all trees being sprayed to run-off. Plot size varied from 2-3 trees and treatments were replicated 2-4 times. Mildew was assessed either by the Townsend-Heuburger (Wenzl 1948) formula, or by the BBA Method (1966). The effectiveness of the materials is also expressed using Abbott's formula (Abbott 1925). 100-400 leaves per treatment were examined. Fruit finish was assessed by recording the percentage fruit free from russet.

In all cases, mildew sprays were applied from pink bud to the end of extension growth, however in the trials carried out in Germany wettable sulphur was applied in place of all treatments pre-blossom.

RESULTS

In 1969 and 1970 in Belgium, trials were carried out on the varieties Golden Delicious and Cox's Orange Pippin. Comparisons were made with dinocap, benomyl, quinomethionate and wettable sulphur.

Table 1

The effect of BAS 3000F on apple mildew 1969 (Belgium)

Treatments	Trial	Trial 1		Trial 2		Trial 3	
	Cultivar rate of use	Golden Delicious A	Golden Delicious B	Golden Delicious A	Golden Delicious B	Cox O.P. A	Cox O.P. B
	a.i. %						
BAS 3000F	0.05	1.0	97.3	1.85	95.0	4.35	89.1
dinocap	0.025	4.0	89.4	3.5	90.6	9.5	76.2
benomyl	0.02	4.85	87.2	5.35	85.6	-	-
sulphur	0.05	-	-	3.15	91.5	-	-
quinomethionate	0.035	-	-	2.15	94.2	6.65	83.4
control		38.0	-	37.15	-	40.0	-

A = mean % infection - Townsend-Heuburger method
 B = % effectiveness - Abbott's formula

Table 2

The effect of BAS 3000F on apple mildew 1970 (Belgium)

Treatments	Trial	Trial 1		Trial 2		Trial 3		Trial 4	
	Cultivar rate of use	Golden Delicious A	Golden Delicious B	Golden Delicious A	Golden Delicious B	Cox O.P. A	Cox O.P. B	Golden Delicious A	Golden Delicious B
	a.i. %								
BAS 3000F	0.05	0.5	97.6	0.0	100.0	3.6	88.5	2.8	92.6
dinocap	0.025	1.5	92.8	1.0	92.0	7.5	76.0	8.8	76.8
benomyl	0.05	1.7	91.9	1.0	92.0	5.6	82.4	12.0	68.4
quinomethionate	0.035	-	-	-	-	6.2	80.3	-	-
sulphur	0.025	-	-	-	-	-	-	85.5	85.5
control		21.0	-	12.5	-	32.0	-	27.7	-

A = mean % infection - Townsend-Heuburger method

Spraying interval 10-14 days

B = % effectiveness - Abbott's formula

Tables 1 and 2 show 3000F to be the most effective treatment throughout.

In 1972 10 trials on a range of varieties compared 3000F with standard materials at 10-14 day intervals.

Table 3

The effect of BAS 3000F on apple mildew 1972 (Belgium)

Treatments	Trial	Trial I*		Trial II		Trial III		Trial IV		Trial V		Trial VI	
	Cultivar	Golden Delicious		Jonathan		Cox's O.P.		Golden Delicious		Boskoop		Golden Delicious	
	rate of use	A	B	A	B	A	B	A	B	A	B	A	B
	a.i. %												
dinocap	0.025	5.3	84.4	21.0	62.2	27.2	63.2	15.2	79.5	21.5	66.4	9.8	84.1
thiophanate-methyl	0.0525	5.0	85.2	-	-	12.6	82.9	22.1	70.4	19.0	70.3	-	-
benomyl	0.02	3.0	91.1	15.0	73.0	17.5	76.3	-	-	-	-	10.2	83.5
BAS 3000F	0.05	0.5	98.5	2.5	95.5	5.7	92.3	1.6	97.8	8.2	87.2	0.8	98.7
control		34.0	-	55.7	-	74.0	-	74.7	-	64.0	-	62.0	-

*benomyl 0.05%

A = mean % infection - Townsend-Heuburger method
B = % effectiveness - Abbot's formulaSpraying Interval 10-14 days

Table 4

The effect of BAS 3000F on apple mildew 1972 (England)

Treatment	Interval in days	Rate of use conc ⁿ a.i.	% secondary mildew	
			Site A	Site B
Untreated		per cent	65.0	91.7
BAS 3000F	10	0.025	15.9	22.1
BAS 3000F	10	0.05	17.3	18.4
BAS 3000F (alternating) carbendazim	10	0.025 0.025	20.4	25.9
dinocap	10	0.05	25.6	30.6

cultivar Cox's Orange Pippin

Table 5

The effect of BAS 3000F on apple mildew 1972 (England)

Primary mildew control 1972-3 (% blossom infection)

Treatment	Rate of use conc ⁿ a.i.	Site A		Site B	
		pre- treatment	post- treatment	pre- treatment	post- treatment
Untreated	per cent	15.6	27.75	2.5	12.5
BAS 3000F	0.025	17.8	5.125	2.1	1.1
BAS 3000F	0.05	16.4	6.0	3.0	0.8
BAS 3000F (alt.) carbendazim	0.025 0.025	18.1	7.75	2.7	1.0
dinocap	0.05	17.6	9.125	2.9	2.3

The level of infection increased in untreated plots despite severe winter pruning.

Table 6

The effect of BAS 3000F on apple mildew 1972 (Germany)

Spraying interval 14 days. Cultivar Idared

Treatments	Rate of use a.i. %	% secondary mildew	% number of leaves infected
1. Untreated		36.5	83.0
2. binapacryl	0.05%	3.2	18.9
3. BAS 3000F	0.05%	0.9	5.9
4. sulphur	0.3%	1.9	12.9
5. benomyl	0.025%	8.2	31.1
6. dinocap	0.05%	10.9	37.2
7. thiophanate-methyl	0.05%	7.8	21.8
8. thiophanate-methyl	0.05%*	1.6	9.9

* spraying interval 5-6 days

In all trials BAS 3000F gave excellent mildew control and the improvement over standard materials was in many cases exceptional.

In 1973 three trials in the U.K. compared applications of BAS 3000F at 10-day intervals and 14-day intervals. Combined treatments with carbendazim were also included.

Table 7

The effect of BAS 3000F alone and combined treatments with carbendazim on apple mildew 1973 (England)

Treatment	Interval in days	Rate of use a.i. %	% secondary mildew		
			Site A	Site B	Site C
Untreated		per cent	22.9	67.4	50.2
BAS 3000F	10	0.025	2.3	3.7	2.1
BAS 3000F	14	0.025	2.8	7.7	5.1
BAS 3000F (alternating) carbendazim	10	0.025 0.025	2.0	4.4	4.4
BAS 3000F + carbendazim	14	0.025 0.015	3.1	5.9	1.9
carbendazim	10	0.025	6.0	15.5	14.5
dinocap (alternating)		0.025			
binapacryl	10	0.0375	6.0	15.1	9.0
thiophanate-methyl		0.05	7.8	15.4	26.3
	Cultivar		Scarlet Pimpernel	Cox's Orange Pippin	Cox's Orange Pippin

BAS 3000F at 10-day intervals gave on average marginally the better mildew control, however the combined treatments with carbendazim were only fractionally less effective. The three standard programmes carbendazim/dinocap, binapacryl, and thiophanate-methyl gave markedly inferior mildew control.

Leaf finish

Where detailed assessments were made the application of thiophanate-methyl at 5-6 day intervals gave the better leaf finish, whereas the poorer finish was observed with binapacryl. In general, however, leaf finish was satisfactory with all treatments, including BAS 3000F.

Fruit finish

Table 8

The effect of BAS 3000F on fruit finish (Belgium)

% fruit free from russet

Treatments	1969		1970			
	Cox's O.P.	Golden Delicious	Golden Delicious	Cox's O.P.	Golden Delicious	Golden Delicious
Untreated	81.0	27.0	68.0	93.7	76.2	45.5
BAS 3000F + polyram 0.18%	98.0	47.0	76.5	97.2	82.2	52.0
dinocap + polyram 0.18%	91.0	53.5	-	-	-	-
dinocap + Calyram*	-	-	76.5	96.0	82.2	54.5
benomyl 0.025%	-	-	72.0	92.5	79.2	43.0

* Calyram = formulation containing polyram + captan

Table 9

The effect of BAS 3000F on fruit finish 1972 (England)

% fruit free from russet

Treatments	Site C*	Site A
Untreated	34.0	7.5
BAS 3000F 0.025% + captan 0.1%	45.75	16.75
BAS 3000F 0.05% + captan 0.1%	47.5	13.0
dinocap 0.05% + captan 0.1%	56.25	12.75
BAS 3000F 0.025%/carbendazim 0.025%	44.0	12.25

* variable site Cultivar Cox's O.P. Cox's O.P.

BAS 3000F in general gave fruit finish comparable to that of dinocap and superior to both benomyl and the untreated control.

Red spider mite

It appears that BAS 3000F has no effect on the population of red spider mite.

DISCUSSION

The series of trials reported show conclusively the exceptional activity of BAS 3000F in controlling apple mildew. Its effectiveness at intervals up to 14 days has consistently been superior to dinocap, binapacryl, sulphur, benomyl and thiophanate-methyl. Combined treatments of BAS 3000F and carbendazim have also given excellent mildew control as well as promising control of apple scab.

BAS 3000F has given good leaf finish throughout and the fruit finish was comparable with that of dinocap and superior to that of benomyl and the untreated control. Mixtures of BAS 3000F with commonly used insecticides have been applied without any apparent compatibility problems.

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TOXICITY OF PIRIMICARB AND OTHER PESTICIDES

TO COCCINELLIDS AND SYRPHIDS

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Summary During laboratory testing of pesticide toxicity to adults of Coccinella septempunctata, pirimicarb and tricyclohexyltin hydroxide, both separately and mixed, have been found harmless, phosphamidon partially harmful. Demephion, thiometon, tetrachlorvinphos, ethoate-methyl, pirimiphos-methyl, and especially mevinphos and fenitrothion have been harmful. The larvae of syrphids have been relatively tolerant to vamidothion. Puparia of the syrphids have not been seriously damaged by any of the pesticides examined.

INTRODUCTION

Within the scope of the integrated protection against aphids we studied toxicity of insecticides to natural aphid enemies. In this report we show the results of studying the effects of pirimicarb and other insecticides on Coccinella septempunctata and immature stages of syrphids. Pirimicarb has been also tested in a mixture with the miticide tricyclohexyltin hydroxide for the purpose of combined integrated protection against aphids and spider mites.

METHOD AND MATERIALS

The used pesticides were as follows: pirimicarb (Pirimor, w.p., 50%), tricyclohexyltin hydroxide (Plictran, w.p., 25%), pirimiphos-methyl (Actellic, e.c., 50%), vamidothion (Kilval, e.c., 40%), phosphamidon (Dimecron, e.c., 50%), demephion (Tinox, e.c., 50%), thiometon (Intration, e.c., 50%), tetrachlorvinphos (Gardona, e.c., 24%), ethoate-methyl (Fitics, e.c., 40%), mevinphos (Phosdrin, e.c., 24%), fenitrothion (Motation, e.c., 50%), malathion (Fosfotion, e.c., 50%). The pesticides were used at concentrations recommended for aphid control, eventually also/or at concentrations 5 times higher or 5 times or 25 times lower.

The adults of C. septempunctata were collected in the second half of July on various field crops attacked by aphids. A light colour indicated newly emerged adults. A mixture of both sexes with a prevalence of females was used (the male : female ratio was 1:1, 2-1, 7). The specimens were put to petri dishes of 11 cm inner diameter, ten in each dish, the dishes having the top open and covered with a 10 mesh nylon screen tissue. In each test 40 or 50 specimens were used (4 or 5 dishes). The dishes with the coccinellids were treated with a hand spraying apparatus at 1 ml/100 cm² (i.e. 1000 l/ha). After 10 minutes the coccinellids were transferred to other dishes lined with filter paper, provided with a cabbage leaf infested by cabbage aphids and maintained under laboratory conditions. The trials were evaluated at the period of the stabilised number of died and/or moribund specimens

generally 48 hours after spraying.

The syrphids were bred from eggs laid by gravid females caught in the open. The following species were used: Metasyrphus luniger, M. corollae and Episyrphus balteatus. In the trial with larvae, 13 larvae were used for each test and comprised: M. corollae - 3 larvae of the second instar and 5 larvae of the third instar; E. balteatus - 3 larvae of the second and 2 larvae of the third instar. The larvae were immersed in the insecticide solution for 30 seconds, left wet for 6 minutes and then transferred to petri dishes as provided for the coccinellids. The larvae which succeeded in pupating and developing into adults were evaluated as intact. The puparia of the syrphids were treated with spraying apparatus similarly as the coccinellids. Fifteen puparia were used for every insecticide - 5 of M. luniger, 5 of M. corollae and 5 of E. balteatus. The numbers of emerged adults were counted.

RESULTS

Table 1 shows the results of 4 trials with C. septempunctata. In Table 2 the results are arranged according to concentrations - 5 times higher, normal, 5 times and 25 times lower. The tables show that, for adults of C. septempunctata, the aphicide pirimicarb and miticide tricyclohexyltin hydroxide, including the combination of both the pesticides, are harmless, vamidothion is also relatively harmless and phosphamidon is somewhat toxic. Others especially mevinphos and fenitrothion, proved toxic.

Four insecticides were tried on the larvae of the syrphids, each at 3 concentrations (n , $n/2$ and $n/4$). Total mortalities in all 3 concentrations were following: 33% - vamidothion, 70% - thiometon, 83% - fenitrothion and 93% - pirimicarb. In the trials with the puparia of syrphids most survived after spraying with any of the insecticides tested at normal concentrations: pirimicarb, thiometon, mevinphos, vamidothion (more than 90% survived); phosphamidon, malathion, pirimiphos-methyl, tetrachlorvinphos, fenitrothion (more than 55% survived).

DISCUSSION

Our results confirmed reports of the considerable toxicity of mevinphos (Bonnemaison 1962, Shorey 1963, Gratwick 1965) and of fenitrothion to coccinellids (Kowalska, Szcepańska 1971), the lower toxicity of phosphamidon (Shorey 1963, Lingren, Ridgway 1967), the considerable harmlessness of vamidothion (Bonnemaison, 1962) and of non-toxicity of pirimicarb (Baranyovits, Ghosh 1969, Baranyovits 1970, Láska 1972). The toxicity of thiometon was found to be higher than recent reports (Zelený 1965, Wiackowski, Dronka 1968). Sol and Sanders (1959) tested a number of insecticides on the larvae of syrphids, but only malathion was used both in their and our trials. This insecticide reported by Sol and Sanders to be highly toxic, caused only partial damage to the puparia in our trials.

Acknowledgements

We express our thanks to Ing. J. Mentberger, Ing. J. Klumpar CSc. and Ing. P. Singer for valuable information on the insecticides used.

Table 1

The effect (%) of pesticides on the adults of *Coccinella septempunctata*

Trial No.	Pesticide	Concentration	Effect
1 ⁺	pirimicarb	0.05%	0
	pirimicarb	0.25%	14
	pirimicarb	0.5%	50
	mevinphos	0.005%	94
	mevinphos	0.024%	100
	thiometon	0.04%	100
	thiometon	0.2%	100
2	pirimicarb	0.05%	2
	vamidothion	0.05%	2
	demephion	0.005%	16
	vamidothion	0.25%	87
	demephion	0.025%	100
	ethoate-methyl	0.02	100
	ethoate-methyl	0.1%	100
3	ethoate-methyl	0.004%	22
	thiometon	0.004%	74
	mevinphos	0.001%	97
	thiometon	0.02%	100
	fenitrothion	0.004%	100
4	pirimicarb + tricyclo- hexyltin hydroxide	0.03%	0
	tricyclohexyltin hydroxide	0.0075%	2
	tricyclohexyltin hydroxide	0.0875%	2
	phosphamidon	0.01%	8
	tetrachlorvinphos	0.0024%	8
	pirimicarb + tricyclo- hexyltin hydroxide	0.15%	10
	thiometon	0.004%	29
	tetrachlorvinphos	0.012%	43
	phosphamidon	0.05%	80
	pirimiphos-methyl	0.02%	100

+ according to the data already given by Láška (1972)

Table 2

The results (effect in %) arranged according to the rate of
overdosing or underdosing

Pesticide	5-fold the normal concn.	normal concn.	1/5 normal concn.	1/25 normal concn.
tricyclohexyltin hydroxide	2	2	-	-
pirimicarb	15	0 - 2	-	-
tricyclohexyltin hydroxide + pirimicarb	10	0	-	-
vamidothion	87	2	-	-
phosphamidon	-	80	8	-
demephion	-	100	16	-
thiometon	100	100	29 - 74	-
tetrachlorvinphos	-	-	43	8
ethoate-methyl	-	100	100	22
pirimiphos-methyl	-	100	-	-
mevinphos	-	100	94	97
fenitrothion	-	-	-	100

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O,O-DIETHYL PHTHALIMIDOPHOSPHONOTHIOATE, A NEW FUNGICIDE

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Summary O,O-diethyl phthalimidophosphonothioate* has shown excellent control of powdery mildew (Sphaerotheca, Podosphaera, Erysiphe) in ornamentals, cucurbits, apple, peach, cereals and turf at dosages of 0.02-0.05% a.i. Higher rates (0.04-0.08% a.i.) are required for the control of apple scab (Venturia inaequalis), frog-eye leaf spot (Physalospora malorum), cherry leaf spot (Coccomyces hiemalis), rose black spot (Diplocarpon rosae) and peach brown rot (Monilinia fructicola).

The dosage required depends on spray intervals, crop growth, fungal attack and climatic conditions. To ensure satisfactory control, good coverage is necessary. The chemical is both preventive and curative in action. It has a low level of toxicity.

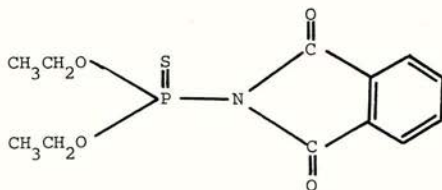
INTRODUCTION

PLONDREL 50 W fungicide was previously known by the code name Millie and the formulation number M 2452. The active ingredient O,O-diethyl phthalimidophosphonothioate is also known as DOWCO* 199, and is referred to as such in this report.

PHYSICAL AND CHEMICAL PROPERTIES

Chemical name: O,O-diethyl phthalimidophosphonothioate

Structure:



Molecular weight: 299.29
Appearance : white flat crystals
Melting point : 83 - 84° C
Odour : slight thiophosphate
Vapour pressure : 1.45 x 10⁻⁶ mm Hg at 25° C

*Marketed by the Dow Chemical Company under the registered trademark "PLONDREL"

Solubility in g/100 g solvent at 23.5° C: n-hexane 1.3; cyclohexane 2.6; ethanol 7.1; carbon tetrachloride 48.8; o-xylene 71.0; ethyl acetate 79.3; benzene 130.0

FORMULATION

To date field tests have been conducted with a wettable powder formulation containing 50% DOWCO 199. An emulsifiable concentrate, containing 20% DOWCO 199, is also under development.

TOXICOLOGY

DOWCO 199 has a very low acute oral toxicity.

Table 1

Route	Animal	LD 50 mg/kg
Acute oral	Rat (M)	5660
	Rat (F)	4930
	Rabbit	1000
	Guinea Pig	5600
	Chick	4500
Acute dermal	Rabbit	>2000
Acute intraperitoneal	Rat	975

Eye contact irritation tests in rabbits with DOWCO 199 produced only mild conjunctivitis, subsiding within 24 hours, whether the eyes were washed or not after application.

Harlequin fish have an LD 50 (96 hours) of 19.4 ppm for DOWCO 199.

For bees the LD 50 at 48 hours is in excess of 100 µg/bee by topical and oral administration. This dose is far greater than could be achieved by normal field use and thus classifies DOWCO 199 as non-toxic to bees.

A wildlife survey conducted in apple orchards in England, following a normal season's treatment with DOWCO 199, showed no adverse effect on any species of wildlife.

DOWCO 199 is non-toxic to earthworms (*Lumbricus terrestris*). After 14 days exposure at rates up to 8.4 kg active/hectare no qualitative or quantitative changes were observed between worms in treated and untreated soil.

No adverse effects were observed in either male or female rats fed DOWCO 199 in their diets at a level of 0.1% for 102 days. This is equivalent to an average daily chemical consumption for males and females of 51 and 66 mg/kg/day respectively. At 196 mg/kg/day of DOWCO 199 the only effect was a slight depression of plasma cholinesterase.

The compound showed no delayed neurotoxic effect in hens when tested by a standard procedure.

Teratogenic studies in rats, at 500 mg/kg/day and rabbits at 200 mg/kg/day, showed no adverse effects. A three-generation reproduction study in rats is being conducted.

Skin sensitization treatment of guinea pigs with DOWCO 199 50% w.p. resulted in delayed type skin sensitization in one out of ten test animals. During extensive field tests and commercial use in many countries, some cases of allergic reaction or skin sensitization have been reported.

METABOLISM

The main plant metabolite has been identified as N-(diethoxyphosphenyl) phthalamic acid. It has an acute oral LD 50 in rats of 7950 mg/kg, and when fed to rats for 92 days, showed no effect at 1000 mg/kg/day.

RESIDUES

Residues in apples following commercial spray programmes with DOWCO 199 were less than 0.5 ppm of DOWCO 199 three weeks after the last application.

In glasshouse cucumbers and in field melons and gherkins, residues of less than 0.1 ppm DOWCO 199 were obtained three days after the last application.

BIOLOGICAL ACTIVITY

DOWCO 199 has been tested in a large number of field trials. It has shown excellent control of powdery mildew (Sphaerotheca, Podosphaera and Erysiphe), in ornamentals, cucurbits, apple, peach, cereals and turf at dosages of 0.02-0.05 % a.i.

Higher rates (0.04-0.09% a.i.) are required for the control of apple scab (Venturia inaequalis), frog-eye leaf spot (Physalospora malorum), cherry leaf spot (Coccomyces hiemalis), rose black spot (Diplocarpon rosae) and peach brown rot (Monilinia fructicola).

DOWCO 199 is both preventive and curative in action. In a glasshouse trial in roses, at equivalent dosages it was more effective than the standards benomyl and dodemorph.

Table 2

Preventive and curative action against powdery mildew in roses of
DOWCO 199 (A), benomyl (B) and dodemorph (C)

Conc. in ppm	% Attack Preventive			% Action Curative		
	A	B	C	A	B	C
1600					90	100
400	10	60	80	100	50	20
100	30	60	90	100	0	0
25	50	70	80	70		
0	90					

1. Ornamentals (Outdoor and under glass)

DOWCO 199 at 0.025-0.050% a.i. gave excellent control of powdery mildew on ornamentals such as roses, chrysanthemum, begonia, cineraria, kalanchoe, saintpaulia, antirrhinum, cyclamen, gerbera, streptocarpus and cissus without signs of phytotoxicity, even at elevated temperatures.

DOWCO 199 acts rapidly and effects can be seen within a few days after application.

Table 3

Roses % mildew infection (Glasshouse)

	% a.i.	spray 3	May		June		July
			10	17	spray 13	26	4
Control		3.5	11.8	0.6	4.9	10.4	8.0
dodemorph	0.1	5.7	5.0	0.2	4.0	2.5	1.0
DOWCO 199	0.05	5.7	1.6	0.1	4.0	0.9	0.7

The dosage of DOWCO 199 required depends on spray interval, crop growth and mildew attack. To ensure satisfactory control, good coverage of leaves both top, underneath and stems is necessary. In glasshouses under practical conditions (sprayed through the crop with high pressure 30-50 atmos. and tee-jet nozzles), growers have observed a residual action of 6-8 weeks with DOWCO 199 at 0.05% a.i.

2. Vegetables (Outdoor and under glass)

DOWCO 199 on outdoor crops applied at 7-14 days interval at the same dosages as for ornamentals, or at 300-400 g a.i./ha, provides outstanding control of powdery mildew on cucurbits (cucumbers, squash, melons).

Satisfactory control is also obtained under glass at dosages of 0.025-0.050% a.i. In Holland, DOWCO 199 0.05% a.i. was slightly better than 0.0375% a.i.

Table 4

Cucumber powdery mildew attack rating 0 - 5 (0 = no attack)

% a.i.	Trial 1		Trial 2	
	spray Oct. 20	Nov. 20	spray July 6	July 13
Control	1.4	2.8	3.1	3.4
chloraniformethane	0.006	1.0	2.8	1.2
DOWCO 199	0.0375	1.2	3.0	0.75
DOWCO 199	0.05	1.1	2.9	0.7

3. Orchards

- a) Powdery mildew: DOWCO 199 gave better results than the standard dinocap when compared at equivalent dosages and a similar spraying schedule.

In trials in France (Table 5) with a 15-day spray interval, best results were obtained with DOWCO 199 0.1% a.i. followed by DOWCO 199 0.06 and 0.03% a.i. DOWCO 199 at 0.03% a.i. has still a better activity against mildew than dinocap at the registered rate of 0.025% a.i.

Table 5

Orchards, France - powdery mildew and scab control

Object	Dosage a.i.	Mildew infection on 100 shoots August 24	Scab spots on 100 leaves June 30
captan + DOWCO 199	0.15 0.03	15.1	4.1
captan + DOWCO 199	0.15 0.06	4.8	4.5
DOWCO 199	0.1	1.7	4.2
captan + DOWCO 199	0.075 0.03	8.6	13.7
captan + dinocap (standard)	0.15 0.025	32.9	10.1
Control		100.0	100.0

On Cox's Orange in Germany, sprayed from April 17 until June 26 seven times, DOWCO 199 0.04% a.i. gave better results than the standards benomyl 0.025% a.i. and dinocap 0.025% a.i. (Table 6)

Table 6

Orchards, Germany - powdery mildew control

	% a.i.	Mildew attack
DOWCO 199	0.04	1.56
benomyl	0.025	2.21
dinocap	0.025	2.49
Control		3.17

1 = no attack
4 = very heavy

- b) Powdery mildew/scab complex: The rates for mildew control do not give adequate protection against scab when compared to standard scab fungicides. For scab control a dosage of 0.06-0.09% a.i. may be needed (Table 7 - Trial from Italy).

Table 7

Orchards, Italy - scab control

	% a.i.	% infected leaves
DOWCO 199	0.03	47
DOWCO 199	0.06	12
DOWCO 199	0.09	7
dodine	0.04	19
thiophanate-methyl	0.07	13

(15 sprays from March 16 - August 14)

In England, scab control with DOWCO 199 at 0.75 kg a.i./ha is equal to the standard captan at 2.5 kg a.i./ha. As DOWCO 199 at this rate also has good control against mildew, the possibility exists to protect the crop against scab and mildew at this dosage.

DOWCO 199 at 0.03-0.05% a.i. applied in combination with standard scab fungicides makes it possible to reduce the normal recommended rate of these scab fungicides; with half of the dosage (Table 5), the result against scab was just below the standard, but with two thirds of the normal scab fungicide rate an excellent control of the mildew/scab complex is given. This year an extensive trial programme with fungicide mixtures is planned to find the optimum combination.

Under certain climatic conditions russetting of Golden Delicious apples may occur. In those countries (France, Switzerland, Holland) where this problem has been observed, improved formulations are being evaluated.

4. Cereals

During 1973 trials were carried out in the U.K. by Farm Protection Ltd. for the control of powdery mildew (Erysiphe graminis) on winter wheat, winter barley and spring wheat.

DOWCO 199 20% e.c. was applied at rates ranging from 250 - 550 g a.i./ha and compared with standard tridemorph at 526 c.c. a.i./ha. Water volume was 333 l/ha.

On winter wheat and winter barley, tridemorph and all rates of DOWCO 199 reduced mildew levels, but no yield response could be detected.

On spring barley 450 and 550 g a.i./ha of DOWCO 199 gave persistent control of mildew equivalent to tridemorph for more than four weeks post-application, though the initial visual control at 450 g a.i./ha was not

as good as tridemorph.

Significant yield increases were noted on one trial only, but an overall mean of the three trials showed that DOWCO 199 at 550 g a.i./ha gave a 10% yield increase equivalent to tridemorph and DOWCO 199 at 450 g a.i./ha gave 7.5% yield increase.

No phytotoxicity was observed on any of the cereal varieties used when DOWCO 199 was applied at 1000 g a.i./ha.

Extensive trials are in progress in Europe to evaluate the efficacy of DOWCO 199, both alone and in mixtures with other fungicides (maneb and benomyl) for the control of other cereal diseases such as Septoria spp. and Fusarium spp.

Acknowledgements

We acknowledge the work on cereals in the U.K. by Farm Protection Limited and also the work of many of our colleagues in the European Products Group of the Dow Chemical Company, whose results have contributed to this paper. We also wish to acknowledge the earlier work on this product of Dr. H. Tolkmith and Dr. D. Mussell of Dow Chemical U.S.A.

AC 92,100 - A NEW SOIL INSECTICIDE

E. Brad Fagan

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Summary AC 92,100, S-(tert-butylthio)methyl O,O-diethyl phosphorodithioate, is an experimental insecticide that possesses excellent initial and extended residual activity against the major soil-inhabiting insect pests. Some foliar insect control from application of granules to the soil has been noted. Effective rates range from 1.0 to 3.0 kg a.i./ha depending on the crop, soil type and insect pest. AC 92,100 appears to be relatively non-phytotoxic and can be placed in the furrow with the seed on most crops.

INTRODUCTION

AC 92,100 is an experimental organophosphate insecticide discovered by American Cyanamid Company at its Agricultural Research Center in Princeton, New Jersey. This insecticide is the tertiary butyl homologue of phorate and has demonstrated superior initial and residual activity against the postembryonic stages of Coleoptera and Diptera in the soil. AC 92,100 is currently under development worldwide.

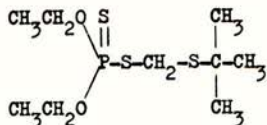
MATERIAL

Chemical and Physical Properties

Chemical name: S-(tert-butylthio)methyl O,O-diethyl phosphorodithioate

Other designations: ENT-27,920

Structural formula:



Empirical formula: $\text{C}_9\text{H}_{21}\text{O}_2\text{PS}_3$

Molecular weight: 288.43

Color and state: Clear, colorless to pale pink liquid

Purity: 85.0% - 88.0%

Boiling point: 69°C at 0.1 mm Hg.

Melting point: -29.2°C

Flash point: >87°C Tag Open Cup

Vapor pressure: 0.8 mm Hg at 250°C
3.7 mm Hg at 60°C

Density: 1.105 g/ml at 24°C

Formulations: 5% and 10% granules

Toxicology

All standard studies have been completed or are under way by American Cyanamid Company or by independent toxicological laboratories to determine the toxicological characteristics of AC 92,100. On the basis of acute toxicity data given below AC 92,100 is considered to be highly toxic by all normal routes of exposure; therefore, extreme care should be taken in handling and using the insecticide.

	Acute Oral	Acute Dermal
	LD ₅₀ - Male rat	LD ₅₀ - Male rabbit
Commercial grade technical	1.6 mg/kg	1.0 mg/kg
10% granular (attaclay)	12.3 mg/kg	25.0 mg/kg
5% granular (attaclay)	23.0 mg/kg	71.0 mg/kg

RESULTS

AC 92,100 has been found highly effective against soil insects and has demonstrated some activity against foliar insects following application to the soil. The major crops and related insect pests on which AC 92,100 has shown outstanding effectiveness are outlined below along with some supporting performance data.

Sugar Beet

Data from extensive field trials conducted since 1971 in the United States and Canada show that AC 92,100 is an excellent insecticide for control of the sugar beet root maggot, Tetanops myopaeformis. Granules were applied at the rate of 1.1 kg a.i./ha in a 17.8 cm band at planting time or banded over the plants prior to the root maggot oviposition period.

In 1972 field trials conducted in Italy, AC 92,100 10-G was broadcast and lightly incorporated (2-3 cm) prior to seeding. Control of flea beetles, Chaetocnema tibialis, and weevils, Cleonus mendicus was good at 2 kg a.i./ha of AC 92,100 and at 3 kg a.i./ha provided excellent protection against weevil damage to sugar beet roots, even at 12 weeks after application (table 1). Examination of the roots at harvest time (194 days after application) showed that protection was not complete against late infestation. There was no phytotoxicity.

Table 1

Activity of AC 92,100 against Flea Beetles, Chaetocnema tibialis, and Weevils, Cleonus mendicus, on Sugar Beet in Italy, 1972*

	Kg a.i./ha	Flea beetle control <u>47 days after application</u>		Weevil control <u>85 days after application</u>		Control (%)
		Average number foliar erosions/ 50 plants/plot	Control (%)	Average number/50 beets/plot Infested roots	Number of erosions	
AC 92,100 10-G	3.0	62	96.9	1.7	1.7	99.3
AC 92,100 10-G	2.0	164	91.7	18.7	30.0	78.4
Phorate 10-G	2.5	171	91.4	18.7	138.7	75.9
Check		1977		63.7	33.7	

* Data from S.I.A.P.A., Bologna, Italy

Dunning and Winder (1973) compared several granular insecticides applied into the seed furrow on sugar beets for control of pygmy mangold beetle, Atomaria linearis. AC 92,100 10-G at 0.7 kg a.i./ha was one of the most effective treatments, giving 78% establishment of seedlings following a very severe attack of pygmy mangold beetle.

Trials were conducted in France in 1972 to control mangold flies, Pegomya betae; millipedes, Blaniulus guttulatus; and aphids, Aphis fabae, on sugar beets. AC 92,100 10-G applied in the seed furrow at 300 g a.i./ha resulted in control equal to that obtained with aldicarb at the rate of 750 g a.i./ha, with no phytotoxicity. Slight transient phytotoxicity was noted when AC 92,100 was applied in furrow at 600 g a.i./ha.

Potatoes

In the United Kingdom two trials were conducted in 1972 on potatoes for control of aphids, one on mineral soil and one on an organic soil. A 10% granular formulation of AC 92,100 was compared with phorate 10-G, both being applied in the furrow at planting. On the mineral soil, 1.1 kg a.i./ha of AC 92,100 gave similar control of aphids for 13 weeks, as 1.7 kg a.i./ha of phorate. On the organic soil 1.7 kg a.i./ha of AC 92,100 was as effective as 2.2 kg a.i./ha of phorate, giving 12 weeks of control.

Trials were carried out in Italy in 1972 comparing planting-time furrow applications of granular formulations of AC 92,100, fonofos, and parathion for control of wireworms, Agriotes spp., and Colorado potato beetle, Leptinotarsa decemlineata. AC 92,100 at 2.0 kg a.i./ha reduced the percentage of wireworm damaged potatoes by 91 to 96% compared with 91% for fonofos at 2 kg a.i./ha and 42 to 64% for 2.5 kg a.i./ha of parathion (Table 2). In another trial, control of Colorado potato beetle was significantly better with 1.5 kg a.i./ha of AC 92,100 than with 2 kg a.i./ha of phorate and the residual activity extended beyond nine weeks.

Table 2

Activity of AC 92,100 applied in the furrow at planting for control of wireworms, Agriotes spp., in field trials on potatoes in Italy, 1972*

Insecticide formulation	Dosage (kg a.i./ha)	Control (%)	
		Trial 1	Trial 2
AC 92,100 10-G	3.0	-	96
	2.0	91	96
Fonofos 10-G	2.0	91	-
Parathion 10-G	2.5	64	42

* Data from S.I.A.P.A., Galliera (Bologna), Italy

Similar control of wireworms, Conoderus spp. and Melanotus spp. has been recorded in trials on potatoes in the United States. In a typical trial application of AC 92,100 15-G at 3.3 kg a.i./ha in the furrow with the seed piece only 3.8% of the potatoes showed wireworm injury compared to 33% for the check (Table 3).

Table 3

Activity of AC 92,100 applied in the furrow with the seed pieces for control of wireworms, *Conoderus* spp. and *Melanotus* spp. on potatoes in the United States, 1971*

<u>Insecticide formulation</u>	<u>Dosage (kg a.i./ha)</u>	<u>Wireworm injury (%)</u>
AC 92,100 15-G	3.3 1.6	3.75 7.50
Fonofos 10-G	4.4	8.25
Carbofuran 10-G	3.3	8.00
Phorate 10-G	3.3 1.6	4.50 8.75
Check	-	33.25

* Data from Dr. R.M. Baranowski, University of Florida, Gainesville

Maize

AC 92,100 is presently being developed in the United States as a soil insecticide to control chlorinated hydrocarbon-resistant corn rootworm larvae, *Diabrotica* spp. Rates of 0.76 to 1.1 kg a.i./ha, applied either in the furrow or in a 17.8 cm band at planting time, have given consistently good control in extensive field trials since 1971.

In 1972, four trials were conducted in France where AC 92,100 5-G was applied in the furrow at 600 g a.i./ha. Very good control of symphyliids, *Scutigerella immaculata*, and wireworms, *Agriotes* spp., was obtained (Table 4).

Table 4

Effect of symphyliid, *Scutigerella immaculata*, and wireworm, *Agriotes* spp., control with AC 92,100 on the yield of corn in France, 1972*

	Dosage (g a.i./ha in furrow)	Effects of symphyliid control on yield (kg/ha)		Effects of wireworm control on yield (kg/ha)	
		<u>Trial 1</u>	<u>Trial 2</u>	<u>Trial 1</u>	<u>Trial 2</u>
AC 92,100 5-G	600	13,116	15,032	10,555	9,619
Fonofos 5-G	350	14,030	14,418	10,643	9,407
Fonofos 5-G	4000	14,185	14,311	11,062	10,256
Parathion 5-G	1000	13,116			10,057
Heptachlor 5-G	3000				9,870
Check	-	5,970	13,350	7,350	6,430

* Data from PROCIDA, Paris, France

Brassicae Crops

Wheatley (1973a) compared several granular insecticides for control of cabbage root fly, Erioischia brassicae, in transplanted cauliflower. AC 92,100 10-G was as effective as the standard chlorfenvinphos. Sub surface band application was more effective than surface band application.

In 1972, two trials were conducted in Italy to evaluate the effectiveness of AC 92,100 against the cabbage root fly. Granular formulations were broadcast and lightly incorporated before transplanting cabbage and cauliflower. In both trials there was little difference in control between rates of 2 and 3 kg a.i./ha of AC 92,100 and 3 kg a.i./ha of chlorfenvinphos on cabbage or fonofos on cauliflower.

Similar results have been obtained in the United States against the cabbage maggot, Erioischia brassicae. The results of a 1972 trial in New York (Table 5) indicate that AC 92,100 15-G at 1.1 kg a.i./ha provided better protection against cabbage maggot injury than four other standard materials at the same rate.

Table 5

Activity of AC 92,100 applied at planting time to evaluate control of cabbage maggot, Erioischia brassicae, on cabbage in the U.S. 1972*

<u>Insecticide formulation</u>	<u>Dosage (Kg a.i./ha)</u>	<u>Seedlings/4,6 m</u>	<u>No. maggot tunnels/20 roots</u>
AC 92,100 15-G	1.1	123	8
Diazinon 14-G	1.1	98	20
Carbofuran 10-G	1.1	142	9
Fonofos 4-E	1.1	123	16
Fensulfothion 6-E	1.1	77	17
Check	-	145	26

* Data from Dr. C.J. Eckenrode, New York State Agricultural Experiment Station, Geneva

Carrots

Two trials were carried out on carrots for control of carrot rust fly, Psila rosae, in the U.K. by Wheatley (1973b) in 1972, one on a mineral soil and one on an organic soil. On both soils AC 92,100 10-G was more effective than the standard phorate granule at equal rates, both products being applied by bow-wave application at drilling.

Maskell and Gair (1973) also evaluated bow-wave applications of AC 92,100 10-G on two soil types in the U.K. On mineral soil 1.7 kg a.i./ha gave significantly better carrot fly control than phorate at the same rate, while on the organic soil 2.2 kg a.i./ha of AC 92,100 was better than 3.4 kg a.i./ha of phorate.

Cotton

Data from preliminary trials in the U.S. and Brazil indicate that AC 92,100 granules applied in the furrow at 1.0 to 2.0 kg a.i./ha provide very good control of aphids, thrips and other early-season insect pests.

Phytotoxicity

Granular AC 92,100 applied to the soil in a band, by bow-wave application, in the furrow or broadcast appears to be significantly less phytotoxic than many of the standard organophosphate insecticides. In field trials conducted in the U.S., 11 kg a.i./ha applied in the furrow or in a 17.8 cm band to maize, 19.8 kg a.i./ha applied in the furrow to potatoes and 6.6 kg a.i./ha applied in the furrow to direct-seeded cabbage did not cause significant phytotoxicity.

Contrary to the observations in Europe the previous year, applications of AC 92,100 into the seed furrow on sugar beets in 1973 caused unacceptable phytotoxicity. However, no phytotoxicity resulted from applications made on the soil surface in front of the seed drill. Additional studies are planned on sugar beets to determine application rates and methods.

DISCUSSION

Data from field tests since 1971 have been consistent in demonstrating the superior insecticidal activity of AC 92,100, primarily against soil insect pests. AC 92,100 should be considered as a potential replacement for chlorinated hydrocarbon insecticides and should continue to be a candidate for evaluation in research programs involving the control of any insects by granular application to the soil.

Acknowledgements

Thanks are due to Professor A. Kovács, S.I.A.P.A., Bologna, Italy; PROCIDA, Paris, France; Dr. R.M. Baranowski, University of Florida, Gainesville; and Dr. C.J. Eckenrode, New York State Agricultural Experiment Station, Geneva, for permission to use their research data.

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AMITRAZ* - A NOVEL ACARICIDE WITH SELECTIVE INSECTICIDAL PROPERTIES

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Summary Amitraz is the proposed common name for 1,5-di-(2,4-dimethyl-phenyl)-5-methyl-1,5,5-triazapenta-1,4-diene, a new acaricide with selective insecticidal properties. Mammalian acute oral LD₅₀ varies according to species between 100-1600 mg/kg and dermal toxicity to rats is over 1600 mg/kg. It is relatively non-toxic to bees and predatory insects.

Laboratory tests demonstrated that amitraz was effective against all stages of the red spider mite, Tetranychus urticae.

During the past three years amitraz has been evaluated for the control of mites in over thirty countries, in trials covering a wide range of acaricidal resistance, crops and climatic conditions. Control of Panonychus spp is obtained with applications of 0.02-0.04% a.i.; on Tetranychus spp slightly higher rates are required for the same level of control.

The compound has also shown good activity against a variety of insect pests such as aphids, pear sucker and scale insects.

Amitraz is safe on nearly all crops and is compatible with a wide range of other pesticides.

Residues arising from the use of amitraz are currently being studied.

Résumé Amitraz est le nom ordinaire proposé pour le 1,5-di-(2,4-diméthyl-phenyl)-5-méthyl-1,5,5-triazapenta-1,4-diène, un nouvel acaricide avec des propriétés sélectives insecticides. La LD₅₀ (dose létale) orale des mammifères varie selon les espèces entre 100-1600 mg/kg et pour les rats, la toxicité cutanée est de plus de 1600 mg/kg. Il est relativement non-toxique pour les abeilles et insectes prédateurs.

Des tests de laboratoire ont montré que l'amitraz est efficace à tous les stades de l'araignée - rouge, Tetranychus urticae.

Au cours de ces trois dernières années, des essais ont été conduits sur l'amitraz pour le contrôle des acariens dans plus de trente pays et pour étudier la résistance des acaricides, les conditions climatiques et les récoltes. Les résultats prouvent qu'il y a moyen de contrôler les espèces Panonychus avec des applications de 0,02 - 0,04% a.i. et que pour les espèces Tetranychus, des taux légèrement plus élevés sont tout aussi efficaces.

* Proposed common name - subject to approval by ISO

Il a été également démontré que le composé est très efficace contre toute une série d'insectes tels que les pucerons, le psylle du poirier et les cochenilles. La plupart des récoltes ne sont pas affectées par l'amitraz qui peut être employé avec un grand nombre d'autres pesticides. Les résidus résultant de l'emploi de l'amitraz sont pour le moment à l'étude.

INTRODUCTION

Phytophagous mites are amongst the most important agricultural pests and are found in nearly all parts of the world. It is not only their ubiquity which presents problems, but also the fact that mites have developed resistance to many of the available chemical toxicants. Because of this there is a constant need for acaricides of novel chemical structure.

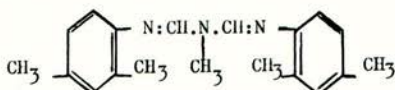
Some years ago, a new group of biologically active compounds, the triazapentadienes, was discovered by The Boots Company Ltd., (Harrison *et al* 1973). The most outstanding member of this group was BTS 27 419, 1-5-di-(2,4-dimethylphenyl)-3-methyl-1,3,5-triazapenta-1,4-diene for which the common name amitraz has been proposed. Amitraz was discovered in 1969 and in laboratory and glasshouse tests showed particular promise for the control of red spider mites and certain species of Hemiptera. Since 1971 the compound has been tested extensively throughout the world in a wide variety of crop and pest situations.

FORMULATION

Amitraz is formulated as a 20% w/v emulsifiable concentrate and this material has been used in all field trials.

CHEMICAL AND PHYSICAL PROPERTIES

Structural formula



Molecular formula $C_{19}H_{23}N_3$

Molecular weight 293

Appearance Off-white crystalline material

Melting point $87-88^{\circ}C$

Solubility Soluble in most organic solvents, 1 g dissolving in 1.5 ml xylene, 2 ml acetone or 42 ml methanol at room temperature; sparingly soluble in water (less than 1 ppm at room temperature).

Vapour pressure 3.8×10^{-7} mm Hg at $20^{\circ}C$

Stability Stable to heating either alone or in dry, inert solvent but undergoes slow hydrolysis in contact with water. Hydrolysis can be prevented by the addition of a stabilising agent such as epichlorhydrin or paraformaldehyde.

TOXICOLOGY

Acute Toxicity

a) Mammals

The acute toxicity of amitraz has been investigated in several mammalian species and the following results obtained:-

<u>Species</u>	<u>Sex</u>	<u>Route</u>	<u>LD₅₀ (mg/kg)</u>
Mouse	Male	Oral	> 1600
Mouse	Male & female	IP	> 200
rat	Male	Oral	Approx 800
rat	Male	IP	Approx 800
rat	Male & female	Inhalation	65 mg/l (6 hr LD ₅₀)
rat	Male	Dermal	> 1600
Guinea pig	Female	Oral	400-800
Rabbit	Female	Oral	> 100
Rabbit	Male & female	Dermal	> 200
Dog	Male & female	Oral	Approx 100*
Baboon	Male & female	Oral	100-250*

* data based on a single experiment with one pair of animals at each dose level.

b) Fish

Rainbow trout	LC ₅₀ (48 hr)	2.7 - 4.0 ppm
Japanese carp	LC ₅₀ (48 hr)	1.17 ppm
Blue Gill	LC ₅₀ (96 hr)	1.34 ppm
Harlequin	LC ₅₀ (96 hr)	3.2 - 4.3 ppm

c) Birds

The toxicity to birds was investigated in accordance with the recommended protocols of the United States EPA and the results were as follows:-

	LC ₅₀ ppm.
Japanese quail	1800
Mallard duck	7000

Chronic Toxicity

Chronic toxicity tests over one year have not produced any marked effects. Rats fed on 200 ppm have shown some slight weight changes compared to controls, but those fed on 15 and 50 ppm have shown no effect. Dogs dosed with 0.1, 0.25 and 1.0 mg/kg daily have not been significantly affected.

BIOLOGICAL ACTIVITY

Amitraz was tested in the laboratory against a range of mite and insect species (Harrison et al 1972). The compound proved to be particularly active on two-spotted mite (Tetranychus urticae), aphids and California red scale (Aonidiella aurantii).

Tests on populations of two-spotted mite and European red mite (Panonychus ulmi) revealed that the compound was effective on mites showing a wide range of acaricidal resistance.

The precise mode of action of amitraz is unknown; it appears to act as a contact poison. The compound is not systemic although it possesses some trans-laminar activity.

FIELD TRIALS

Amitraz has been evaluated for the control of red spider mites and related species in over thirty countries in trials covering a wide range of acaricidal resistance, crops and climatic conditions.

Results indicate that on Panonychus spp control better than or comparable to that of available acaricides has been obtained with applications of 0.02-0.04%. Unlike Tetranychus spp, Panonychus spp are confined mainly to fruit crops. Typical results of field trials on Panonychus are shown in Tables 1 - 3.

Table 1

Comparison of amitraz with other acaricides for the control of European red mite on apples - United Kingdom

Treatment	a.i. ppm	No. of mites per leaf				
		T ₁ *	T ₁ + 14	T ₂ + 7	T ₂ + 36	T ₂ + 72
Amitraz	250	6.8	6.8	14.4	5.5	5.7
	500	4.1	3.8	6.1	2.6	2.0
Chlordimeform	500	3.2	13.3	42.9	19.8	7.7
Dicofol	400	7.6	7.5	22.6	3.7	2.3
Tetradifon	125	3.2	5.5	18.8	14.6	9.2
Phenkapton	200	4.2	3.2	11.4	6.7	4.6
Untreated		5.9	31.6	108.6	-	-

Spray dates 27/5/70, 17/6/70. + over sprayed *Treatment date

Table 2

Control of European red mite on nectarines - France (Shell Chimie)

Treatment	a.i. ppm	No. of mites per 20 leaves			
		T	T + 6	T + 12	T + 26
Amitraz	250	22.5	1.0	0.5	3.5
	500	84.5	5.0	0	0
Tricyclohexyltin hydroxide	300	21.5	0	3.0	3.0
Untreated		11.0	72.5	129.0	73.0

Spray date 15/7/71

Table 3

Control of citrus red mite on oranges - Japan (Nissan Chemical Industries Ltd.)

Treatment	a.i. ppm	No. of mites				
		T	T + 3	T + 11	T + 19	T + 29
Amitraz	150	120	1	1	4	7
	200	164	0	0	3	0
Dicofol		176	0	4	9	29
Untreated		76	32	61	172	164

Spray date 29/5/72

Trials on European red mite have also been carried out on pears, plums and vines and commercially acceptable control has been achieved in all cases.

Against *Tetranychus* spp amitraz has also proved effective although higher rates in the range 0.04-0.05% a.i. are generally required. Unlike *Panonychus* spp, *Tetranychus* spp are found on a wide range of crop plants and typical results are shown in Tables 4-6.

Table 4

Control of two-spotted mite on peaches - Australia

Treatment	a.i. ppm	T ₁	T ₁ +18	T ₁ +36	T ₂ +14	T ₂ +28	T ₂ +50
Amitraz	300	37	17	2	2	2	3
	400	43	19	2	2	1	5
Tricyclohexyltin hydroxide	200	18	3	2	2	1	4
Propargite*	300	19	9	2	5	2	4
Untreated		19	79	45	66	32	51

Spray dates 16/12/71, 25/1/72.

* 2-(p-t-butylphenoxy)cyclohexylpropynyl sulphite.

Table 5

Control of two-spotted mite on apples - Australia

Treatment	a.i. ppm	No. of mites per leaf						
		T ₁	T ₁ +8	T ₁ +35	T ₁ +55	T ₂ +6	T ₂ +22	T ₂ +43
Amitraz	400	1	4	1	5	0	1	1
Tricyclohexyltin hydroxide	200	1	1	1	6	1	1	1
Chlordimeform	940	1	1	1	8	1	4	1
Untreated		1	3	27	27	7	21	16

Spray dates 29/12/71, 22/2/72

Table 6

Control of two-spotted mite on carnations - Italy (Monteshell SpA)

Treatment	a.i. ppm	No. of mites per leaf		
		T + 2	T + 9	T + 15
Amitraz	300	0.13	0.16	0.91
	400	0.06	0.13	0.03
Tricyclohexyltin hydroxide		0.66	0.84	0.66
Untreated		8.06	11.78	11.59

Spray date 22/7/72

Amitraz has also given excellent control of *Tetranychus* spp on pears, plums, cucumbers, tomatoes, beans, peppers, vines and ornamentals.

In addition to the foregoing, amitraz is active against yellow mite of vines (*Eotetranychus carpini*), rust mites (*Eriophyidae*) of apples and citrus, red berry mite of blackberries (*Eriophyes essigi*) and tarsonemid mite of strawberries (*Steneotarsonemus latus*).

An extensive series of grower reliability trials has confirmed the results expressed in the above tables. Results on other mites are more speculative and further work remains to be done.

Although primarily an acaricide, good control of several insect species has been obtained. The compound is active mainly against species of Hemiptera such as aphids, suckers and scale insects. Intensive evaluation on these and other species is in progress.

Some typical results of trials on insect species are shown in Tables 7-9.

Table 7

Control of hop-damson aphid on hops - United Kingdom

Treatment	a.i. ppm	No. of aphids per leaf							
		T ₁	T ₁ +1	T ₁ +7	T ₁ +14	T ₁ +21	T ₂ +28	T ₂ +35	T ₂ +42
Amitraz	400	26.4	9.0	18.7	46.3	70.6	36.1	12.3	8.0
	600	34.9	11.3	15.5	40.6	78.4	17.9	9.2	7.9
Demeton-S-methyl		36.0	8.9	16.2	69.9	150.0	88.5	116.5	135.5
Untreated		44.4	13.8	60.1	108.3	247.7	297.6	409.1	256.7

Spray dates 6/7/72, 28/7/72.

This population is suspected of becoming resistant to organophosphate compounds.

Table 8

Control of black scale on oranges - Italy (Monteshell SpA)

Treatment	a.i. ppm	No. of larvae per leaf	
		T + 5	T + 29
Amitraz	200	13.7	6.4
Phenthoate	500	1.5	0.7
Untreated		120.6	78.6

Spray date 27/7/72

Table 9

Control of pear sucker - USA (American Cyanamid)

Treatment	a.i. ppm	T + 7	T + 18	T + 35	T + 40
Amitraz	500	0	1	4	1
Azinphos-methyl + Endosulfan		40	46	68	-+
Untreated		136	87	91	87

Spray date 18/8/72 + over sprayed

Effects on Non-target Organisms

Vertebrate wildlife surveys have not been intentionally carried out but observations have been made at the trial sites. As would be expected, because of the relatively low toxicity of the compound, no detrimental effects on wild life have been observed.

Amitraz has been shown to be considerably less toxic to bees (*Apis mellifera*) than the reference standard carbaryl. The method used was that described by Reay and Lewis (1966) in which the chemical is applied to the thorax by means of an 'Agla' micrometer syringe. The LD₅₀ of carbaryl is 0.75 µg per bee, whereas that of amitraz is approximately 25 µg per⁵⁰ bee. Amitraz is slower acting, the full effects not being apparent until four days after treatment. Field observations in the U.K. and New Zealand (Clinch 1972) have confirmed its relative safety.

The compound also appears safe to predatory insects such as ladybirds and anthocorid bugs and thrips. Laboratory tests on *Stethorus punctum* and *Adalia bipunctata* demonstrated that the compound was much less toxic than the reference standards azinphos-ethyl and demeton-methyl. Field observations on ladybirds, anthocorid bugs and six-spotted thrips revealed large populations of all species in areas treated with amitraz. Laboratory tests and field observations have shown that amitraz is toxic to phytoseiid mites such as *Phytoseiulus riegl* and *Typhlodromus occidentalis*.

Crop Safety

Amitraz has been applied to over fifty apple varieties and to a wide range of fruits, vegetables and ornamental plants at rates considerably higher than normal, alone and in admixture with other pesticides. With one exception the compound has proved to be safe. The exception is on pears where the compound has been applied

near to harvest under very high temperature conditions; there is some evidence from the Southern hemisphere that discolouration of the area around the lenticels occurs. This is under investigation. No damage to pears grown under temperate conditions has been observed.

Amitraz is compatible with all other pesticides tested so far with the exception of Bordeaux mixture.

Residues

Residues arising from the use of amitraz on a range of crop species are currently being studied and will be reported separately.

Taint studies have been carried out on fruit both from 1971 and 1972 trials. No taint has been found in apples, strawberries, blackcurrants or plums, whether canned, frozen or prepared for jam.

DISCUSSION AND CONCLUSIONS

Much information relating to the performance of amitraz has now been obtained and the following are some of the observations.

The fact that the compound is effective against all stages of mites allows for some flexibility in its use, but nevertheless the timing of control measures is important. It is normal practice in most countries to apply a single spray of acaricide as demanded by the level of mite infestation and this technique has proved highly successful with amitraz. However, if regional climatic conditions are normally conducive to high seasonal mite populations, then two applications ('back to back') have given the best results. The timing of the applications will vary according to local conditions. In the United Kingdom the most successful spray programme for the European red mite has been when the two applications have been applied with an interval of three weeks, the first application being made at approximately 60% egg hatch. Timing of the second application will depend to some extent on the generation time of the mite but the effect of the spray is unlikely to persist for more than four weeks.

There is some evidence for translaminar movement of the compound, but as with most acaricides, good coverage is essential if the mites are to be controlled. Particular care must be taken where low-volume air blast machines are used as it is unlikely that good control will be obtained if the rate of application is less than 500 l/ha.

As regards range of activity, amitraz appears to be particularly effective against Panonychus spp and rates as low as 0.02% a.i. have given good control although these have generally been against citrus red mite or against European red mite at high temperatures. For cooler areas such as Northern Europe, higher rates such as 0.03-0.04% a.i. are recommended and at these rates good control of European red mite has been obtained throughout the trials.

Against Tetranychus spp, in particular, the two-spotted mite, rates of 0.04-0.05% are recommended, the higher rate being necessary where mite pressure is intense, as in areas of low rainfall and consistently high temperature. At these rates, good control of Tetranychus spp has been obtained on a wide range of crops, tea, fruit, soft fruit, citrus, vines, vegetables and ornamentals.

What little work has been done on eriophyid mites suggests that rates similar

Although primarily an acaricide, the compound has given good control of some insect pests especially pear sucker, aphids and scale insects. It is particularly useful against aphids in perennial crops such as hops, where spraying is routine, and against other species, such as woolly aphid, where outbreaks are not sporadic. Lack of a quick 'knock down' precludes its use in annual crops where outbreaks tend to be sporadic and spraying is not carried out routinely. Against pear sucker, excellent results have been obtained in the U.S.A. and Switzerland where this pest has become a severe problem. Rate of use varies but in most cases 0.04-0.05% is required.

Acknowledgements

The authors are grateful for the assistance of their many colleagues in the Research Department of The Boots Company Ltd., both in the United Kingdom and Australia. Particular thanks are also expressed to those collaborators overseas who carried out many of the trials and kindly allowed us to publish their results, and to all growers who allowed trials to be undertaken on their crops.

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DS 15647, 3,3-DIMETHYL-1-METHYLTHIO-2-BUTANONE
O-METHYLCARBAMOYLOXIME, A SYSTEMIC
INSECTICIDE-ACARICIDE

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Summary Three years of field testing demonstrated that DS 15647, 3,3-dimethyl-1-methylthio-2-butanone O-methylcarbamoyloxime, effectively controlled many foliar feeding pests including a number of species from the following orders: Coleoptera, Hemiptera, Homoptera, Diptera, Thysanoptera, and Acarina. Seed treatment and in-furrow applications to cotton at rates of 0.25 to 0.5 lb a.i./ac of DS 15647 provided control of thrips (Frankliniella spp.). In-furrow application of 0.5 to 2.0 lb a.i./ac of DS 15647 to sugar beet in France controlled sugar beet fly (Pegomyia betae) and black aphid (Aphis fabae). Over top application at similar dosages to sugar beet, with 6-8 leaves, controlled both black and green peach aphids (Aphis fabae, Myzus persicae) for up to 6 weeks. On potato, green peach aphid (Myzus persicae), and Colorado potato beetle (Leptinotarsa decemlineata) were controlled by 3.0 lb a.i./ac of DS 15647 applied in-furrow at planting. Additional studies indicated usefulness of DS 15647 on beans, cabbage, grain sorghum, pepper, sunflower, tomato, turnip and wheat.

INTRODUCTION

DS 15647 (ENT 27851), a carbamate pesticide synthesized at the T. R. Evans Research Center, Diamond Shamrock Corporation, was introduced for field testing in 1971. Numerous field trials conducted in the United States, France, Australia, and United Kingdom have demonstrated that DS-15647 is a potent insecticide and acaricide with both contact and systemic action. Limited space allows only a brief study of this new product.

CHEMICAL AND PHYSICAL PROPERTIES

3,3-dimethyl-1-methylthio-2-butanone O-methylcarbamoyloxime has the following chemical structure:

weights was influenced at 100 and 300 ppm, but not at 30 and 70 ppm levels. Gross and microscopic pathological findings were negative. Further studies are underway to further define these preliminary findings.

The acute oral LC_{50} of DS 15647 for Mallard duck and Bobwhite quail was 109 and 43 ppm, respectively. The acute LC_{50} at 96 hours for Bluegill sunfish was 330 ppb and 130 ppb for Rainbow trout.

BIOLOGICAL ACTIVITY

When used as a seed or soil treatment, DS 15647 is absorbed and translocated throughout the foliage where it provides effective protection, for at least 6 weeks, against foliage feeding insects such as aphids, flea beetles, leafhoppers, Colorado potato beetle, and thrips. Soil treatment also provides protection against soil inhabiting pests such as sugar beet maggot. Seed and soil treatments have shown little activity against most Lepidopterous species.

Table 2 summarizes the biological activity against various pests known to be susceptible to DS 15647 under various application schemes.

Table 2

Biological Activity of DS 15647 Insecticide Under Various Application Schemes

Insect	Application Method			
	Seed Treatment	In-Furrow	Side Dress	Over Top
Aphid, Black (<u>Aphis fabae</u>)		+		+
Aphid, Corn Leaf (<u>Rhopalosiphum maidis</u>)		+	+	+
Aphid, Cotton (<u>Aphis gossypii</u>)	+	+		
Aphid, Green Peach (<u>Myzus persicae</u>)		+		+
Aphid, Melon (<u>Aphis hoddypii</u>)		+		
Aphid, Potato (<u>Macrosiphum</u> spp.)		+		
Aster Leafhopper (<u>Macrostelus fascifrons</u>)		+		
Banks Grass Mites (<u>Oligonychus pratensis</u>)		+	+	+
Colorado potato beetle (<u>Leptinotarso decemlineata</u>)		+		
Cotton Leaf Perforator (<u>Bucculatrix thurberiella</u>)		+		
Flea Beetle (<u>Epitrix</u> spp.)		+		
Flea Hopper (<u>Annuraphis maidi-radicis</u>)		+		
Greenbug (<u>Schizaphis graminum</u>)		+	+	+
Leafhoppers (<u>Empoasca</u> spp.)		+		
Mexican Bean Beetle (<u>Epilochna corrupta</u>)		+		
Midge (<u>C. schulzi</u>)		+	+	+
Mites (<u>Tetranychus</u> spp.)		+	+	
Root maggot (<u>Tetanops myopaeformis</u>)	+	+	+	
Sugar Beet Fly (<u>Pegomia betae</u>)		+		
Tarnished Plant Bug (<u>Lygus lineolaris</u>)		+		
Thrips (<u>Frankliniella</u> spp.)	+	+		
White Fly (<u>Trialeurodes vaporarium</u>)		+		

+ indicates commercially acceptable control

TEST RESULTS

Cotton

DS 15647, as seed treatment and in-furrow applications, was evaluated at several locations throughout the cotton growing area of the United States during 1971 and 1972. When compared with the untreated check at 3 locations during 1972, both 0.25 lb and 0.5 lb a.i./cwt of cottonseed provided excellent control of thrips and increased yields (Table 3).

Table 3

DS-15647 Cottonseed Treatment Compared to
Check at 3 Locations in the United States, 1972

Treatment	Dosage lb a.i./cwt	Thrip Control		lb/ac	Yield
		Thrips/ac	% Control		Increase over Check
DS 15647	0.25	33,311	75	1922	96
DS 15647	0.50	22,019	84	2102	276
Check	--	132,684	0	1826	0

In-furrow application of DS 15647 10G at 0.25 and 0.5 lb a.i./ac protected cotton from thrip attack and resulted in increased yields (Table 4).

Table 4

Comparison of DS 15647 10G In-Furrow
Treatment to a Check at 4 Locations in U.S., 1972

Treatment	Dosage lb a.i./ac	Thrip Control		lb/ac	Yield
		Thrips/ac	% Control		Increase over Check
DS 15647	0.25	21,456	88	2191	201
DS 15647	0.50	13,201	92	2323	333
Check	--	171,716	0	1990	0

Both seed treatment and in-furrow application of DS 15647 were effective, however, the in-furrow application provided longer thrip control than did the seed treatment.

Sugar Beet

Sugar beets planted at Villefranche, France, on 11 April, 1973, were treated in-furrow the same day with 0.75 and 1.1 kg a.i./ha of DS 15647 10G. Carbofuran and aldicarb at 0.75 kg a.i./ha were included for comparison. A replicated randomized design was used. Results presented in Table 5 demonstrate control of sugar beet fly (*Pegomyia batae*) and black aphid (*Aphis fabae*) for a period of 55 days. No phytotoxicity was noted.

Table 5

Effect of In-Furrow Application of DS 15647 10G
to Sugar Beets in France, 1973

Treatment	kg a.i./ha	No. of Leaves Attacked by <u>Pegomyia batae</u>	Average No. of Aphids Per Plant
Check	--	84	2.7
DS 15647	0.75	1	0.01
DS 15647	1.1	0	0.0
Carbofuran	0.75	0	0.7
Aldicarb	0.75	0	0.03

Rated 55 days after treatment

Tests at 5 locations in the United Kingdom were established in 1973 where applications were made by dribbling the granules over the top of sugar beet plants in the 4-8 leaf stage. Experimental design was randomized complete blocks replicated 4 times. Treatments included DS 15647 at 0.5, 1.0 and 2.0 lb a.i./ac, disulfoton at 1.0 lb a.i./ac and an untreated check. Varieties used were Sharp's Klein E or Sharp's Klein Megapoly and seeding was done from 4 March, to 6 April, 1973. Ratings at the various sites for control of black aphid (Aphis fabae) were made at 31 to 42 days after treatment. Results presented in Table 6 show that excellent aphid control was obtained with all dosages of DS 15647 for a period of 6 weeks, whereas the efficacy of the standard treatment was markedly lower. Green peach aphids (Myzus persicae) were virtually absent from the plots at the time these ratings were made, but earlier counts clearly demonstrated the effectiveness of DS 15647 on this insect.

Table 6

Effect of Over Top Applications of DS 15647
for Controlling Black Aphid (Aphis fabae) on Sugar Beets
in the U.K., 1973

Treatment	Dosage lb a.i./ac	Percent Control at 5 Locations				
		1	2	3	4	5
Check	--	0	0	0	0	0
DS 15647	0.5	96	98	100	100	99
DS 15647	1.0	96	100	100	100	100
DS 15647	2.0	98	100	100	100	100
Disulfoton	1.0	64	86	90	92	86
Days after treatment		31	37	42	41	33

Potato

Tests were conducted during 1971 and 1972 at 2 locations in Ohio, U.S.A. Planting was done from 12-16 May each year, and the test compounds were applied in-furrow on the same day: DS 15647, disulfoton and aldicarb at 3.0 lb a.i./ac. Plots were replicated 3 times. A summary of the results from these 4 trials (2 locations, 2 years) presented in Table 7, show effective control of Colorado

potato beetle (Leptinotarsa decemlineata) and green peach aphid (Myzus persicae). In comparing yields, the DS 15647 treatment resulted in an average increase of 295 bushels of potato per acre over the untreated check.

Table 7

Average Effectiveness of DS 15647 In-Furrow Applications
in 4 Trials (2 Locations, 2 Years) on Potato in Ohio, U.S.A.,
1971, 1972

Treatment	Dosage lb a.i./ac	Colorado Potato Beetle Larvae/10 ft	Green Peach Aphid/Leaf	Yield bu/ac
Check	--	185.0	45.0	542
DS 15647	3.0	12.1	4.3	837
Disulfoton	3.0	36.2	5.8	701
Aldicarb	3.0	7.2	6.8	760

Average of 3 trials

Other Crops

During 1971 and 1972, field trials on various crops were established throughout the United States. Table 8 lists these crops and also the insect pests controlled with rates of DS 15647 ranging from 0.5 to 3.0 lb a.i./ac.

Table 8

Pests Controlled by DS 15647 on Various Crops
in Field Trials, 1971 and 1972

Crop	Pests
Beans	Aster leafhopper, potato leafhopper, Mexican bean beetle
Cabbage	Green peach aphid, flea beetle
Grain Sorghum	Greenbug, cornleaf aphid, Bank grass mite
Eggplant	Green peach aphid, two-spotted spider mite
Pepper	Green peach aphid
Sunflower	Midge
Tomato	Green peach aphid, whitefly
Turnip	Turnip aphid
Wheat	Greenbug

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NOTES

NRDC 145, A MORE STABLE PYRETHROID

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Summary A recently developed synthetic pyrethroid, NRDC 145 [5-phenoxybenzyl (\pm)-cis,trans-2,2-dimethyl-5-(2,2-dichlorovinyl)-cyclopropane carboxylate] is 10 - 100 times more stable in light than previous pyrethroids, is more active against insects than resmethrin, and has low mammalian toxicity.

Résumé Un pyrétroïde synthétique développé récemment, le NRDC 145, [le (\pm)-cis,trans-2,2-diméthyl-5-(2,2-dichlorovinyle)-cyclopropane carboxylate de 5-phenoxybenzyle] est de 10 à 100 fois plus stable à la lumière que les pyrétroïdes développés précédemment, possède une activité plus grande contre les insectes que la resmethrine, et s'avère peu toxique aux mammifères.

INTRODUCTION

The usefulness of the natural pyrethrins and of most related synthetic compounds is limited by their instability in air and light. There is so far no indication that residues of natural or synthetic pyrethroids harm mammals or wild life in any way, so safe but more stable compounds with otherwise similar chemical and insecticidal properties would be valuable, particularly in horticulture and agriculture. This communication summarises our progress in developing such compounds.

METHODS AND MATERIALS

New compounds:- The preparation of NRDC 159 and NRDC 145 is described elsewhere (Elliott et al 1975 a,b).

Bioassay:- Relative toxicities to houseflies (Musca domestica) and mustard beetles (Phaedon cochleariae) were determined as described (Barlow et al 1971). Drosophila melanogaster and Anopheles stephensi were used to estimate residues on glass (Needham et al 1966) and on plywood, (Barlow and Hadaway 1966) respectively.

Persistence on glass:- A solution of the compound (1 mg) in hexane (1 ml) was evaporated in a Petri dish (diam.40 mm) to leave a film. Dishes were set

aside uncovered near a south-facing window to receive glass-filtered daylight. Others were placed outdoors, covered by a well-fitting quartz plate so that they received full sunlight, with no loss of ultraviolet wavelengths, and attained 50°C on bright days. At intervals residues were extracted by careful rinsing with acetone, which was diluted to 1 ml, then analysed by GLC (flame ionisation).

Persistence on crops:- An aqueous wettable powder formulation from a.i. (0.05%) kaolin (0.2%), wetter (0.02%) and disperser (0.05%) was sprayed on crops of sugar beet and Brussels sprouts at 560 g.a.i./ha. Representative batches of 8 leaves were collected at intervals, their areas measured, then extracted with acetone (200 ml/pair of leaves) at 20° overnight. Acetone was removed by evaporation at reduced pressure and the residue was shaken with hexane (100 ml) to give a solution analysed by GLC (electron capture detector).

Gas liquid chromatography

Flame ionisation detection:- The solution (0.5 - 2_l1.) was injected into a Varian Aerograph 1200 (injector, 270°; oven, 220-230°; detector, 250°; column, 5' x 1/8" 10% SE 30 on Chromasorb W).

Electron capture detection:- The solution (2_l1.) was injected into a Pye 104 (injector 230°; column, 230°; detector 330°; column 4' x 1/8" 5% SE30 on Chromasorb W.) There were no interfering peaks; sensitivity < 1 ng NRDC 143.

RESULTS AND DISCUSSION

The new compounds are derived from the structure of pyrethrin I (Figure 1), the most important constituent of the natural pyrethrins (Elliott and Janes 1973). Pyrethroids very active against insects have a gem-dimethylcyclopropanecarboxylate function held by other groups in a specific conformation with respect to an unsaturated centre, in pyrethrin I, the cis-pentadienyl side chain (Elliott 1971).

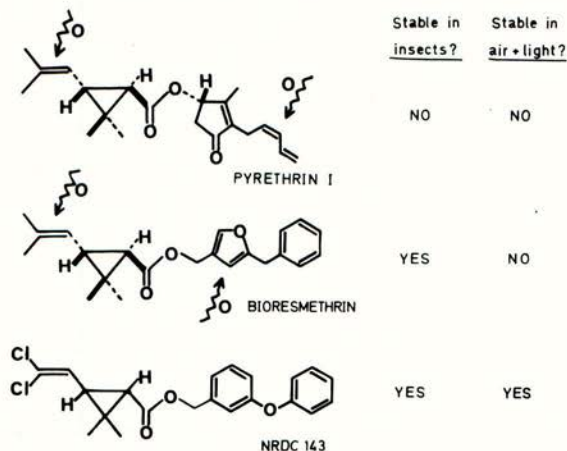


FIGURE 1

Pyrethrin I is unstable because it is readily attacked by oxygen in the air at at least two positions (shown by the arrows) when activating ultraviolet radiation is present (Chen and Casida 1969).

The compound bioresmethrin (Elliott *et al* 1967) (Figure 1) developed from pyrethrin I has the same essential structural features in a molecule that insects, such as normal strains of houseflies, cannot readily detoxify (Farnham 1971). However, it is easily metabolised by mammals and is thus one of the safest and most active insecticides known (Elliott 1971). It still has at least two centres susceptible to attack by oxygen (Figure 1, arrows). The more sensitive of these, the furan ring, can be replaced by a benzene ring to give compounds such as 3-benzylbenzyl and 3-phenoxy-benzyl chrysanthemates, but the insecticidal activity of these esters is lower than that of bioresmethrin. Full insecticidal activity is restored in esters of the dichlorovinyl acid (Elliott *et al* 1973) instead of chrysanthemic acid; this change has the additional advantage of removing the other known photosensitive centre. The resulting compound NRDC 143, tentatively named Permethrin [chemical structure 3-phenoxybenzyl (\pm)-cis,trans-2,2-dimethyl-5-(2,2-dichlorovinyl)-cyclopropane carboxylate; cis,trans ratio, 20:80] is 10-100 times more stable in light than previous pyrethroids and is the main subject of this communication.

The new compound, NRDC 143, has good insecticidal activity in laboratory tests in comparison with other synthetic pyrethroids and established insecticides from other groups (Table 1).

Table 1
Insecticidal Activity

	Approximate relative toxicity to:	
	Houseflies	Mustard beetles
Pyrethrin I	4.8	430
Bioallethrin	24	11
Resmethrin	100 ^a	100 ^b
NRDC 143	140	320
Dieldrin	24	9.7
DDT	9.3	2.6
Parathion	88	19

^aLD50 = 0.012_μg/fly

^bLD50 = 0.011_μg/insect.

The acids in two synthetic pyrethroids are racemic (\pm)-cis,trans forms, so the compounds are directly comparable. As with the cis and trans chrysanthemic acids, one optical form of each of the corresponding dichlorovinyl acids gives esters much more active than does the other (Elliott *et al* 1973a).

Mammalian toxicity values for NRDC 143 (Table 2) measured so far are low; the level of activity with intravenous administration is especially interesting.

Table 2

Mammalian Toxicity - Rats
Approximate lethal dose (mg/kg)^a

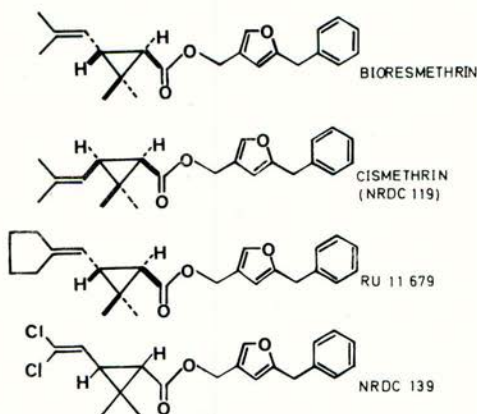
	Oral	Intravenous
Pyrethrin I	260-420	5
Bioallethrin	1000	4
Resmethrin	> 3000	160
NRDC 143	> 1300 ^b 600	> 250 ^b > 140 ^b

- a) Administered in glycerol formal, unless stated otherwise.
b) In corn oil.

Apart from resmethrin (Ueda *et al* 1973) little information is yet available about the mammalian toxicity of photodecomposition products of any pyrethroid, natural or synthetic, but there is no reason to suspect that residues from NRDC 143 should be any more hazardous than those from other pyrethroids; the decomposition products are not toxic to at least one insect species, Drosophila melanogaster (see below).

To compare the stability of the new compound with that of other pyrethroids, films were exposed near a window indoors and analysed at intervals by GLC. The compounds investigated are shown in Figure 2. The first four are esters of

5-BENZYL-3-FURYL METHYL ESTERS



3-PHENOXYBENZYL ESTERS

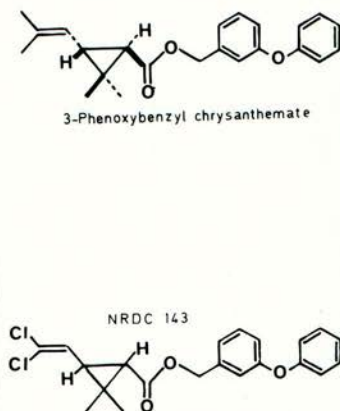


FIGURE 2

5-benzyl-3-furylmethyl alcohol; bioresmethrin (NRDC 107) (Elliott et al 1967) and cismethrin (NRDC 119, RU 12,063) (Lhoste et al 1971) are esters of (+)-trans- and (+)-cis-chrysanthemic acids, respectively, whilst RU 11,679 from (+)-trans-ethanochrysanthemic acid has outstanding insecticidal activity against many insect species. The fourth ester [NRDC 139 (\pm)-cis,trans form] is 2-3 times as active against insects as resmethrin (Elliott et al 1973a). The structures of NRDC 143 and of 3-phenoxybenzyl chrysanthemate are also shown.

Despite the mild indoor conditions, all the esters of 5-benzyl-3-furylmethyl alcohol decomposed within a few hours (Figure 3) - the combination of the dichlorovinyl acid with 5-benzyl-3-furylmethyl alcohol was not, therefore, much improved in this respect. The ethanochrysanthemate also decomposed rapidly (cf Ueda et al 1973). 3-Phenoxybenzyl chrysanthemate was much more stable than the 5-benzyl-3-furylmethyl esters with a half life of about six days, but less stable than NRDC 143, of which 60% remained undecomposed at 20 days. Confirming the results obtained by chemical assay, a very similar range of stabilities was indicated by bioassay (using Drosophila melanogaster) of films on glass indoors (Figure 4).

NRDC 143 also remained effective as a deposit on plywood for more than 12 weeks (Table 3) and under a sunlamp for more than 26 days whereas 3-phenoxybenzyl chrysanthemate lasted less than 4 weeks and 4-8 days, respectively.

Table 3

	Deposits on Plywood	
	Effective period *	
	Northern daylight	Under sunlamps
Natural Pyrethrins	< 4 weeks	< 2 days
Resmethrin	< 4 weeks	< 2 days
3-Phenoxybenzyl chrysanthemate	< 4 weeks	4-8 days
NRDC 143	>12 weeks	>26 days

* Data from F. Barlow

Assayed vs. Anopheles stephensi.

Three compounds (bioresmethrin, 3-phenoxybenzylchrysanthemate and NRDC 143) were compared out of doors under quartz plates, which diminished evaporation by wind and excluded rain, but allowed the ultraviolet range of the sun's spectrum, normally filtered out by glass, to penetrate. On sunny days the temperatures of the films reached 50°C but there was still a significant residue of NRDC 143 undecomposed after ten days. Bioresmethrin decomposed very rapidly and 3-phenoxybenzylchrysanthemate was again more unstable, confirming the additional stability of esters with the dichlorovinyl group (Figure 5).

Finally, NRDC 143 was formulated as a wettable powder and applied to sugar beet and Brussels sprout plants (Figure 6). Analysis of deposits on leaves after various periods by GLC with electron capture detection showed that significant quantities of the compound persisted on both plant surfaces for 10-20 days.

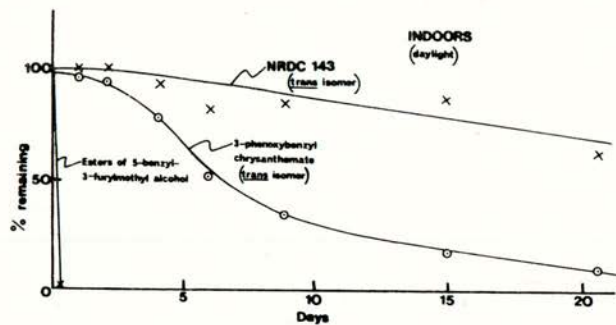


FIGURE 3

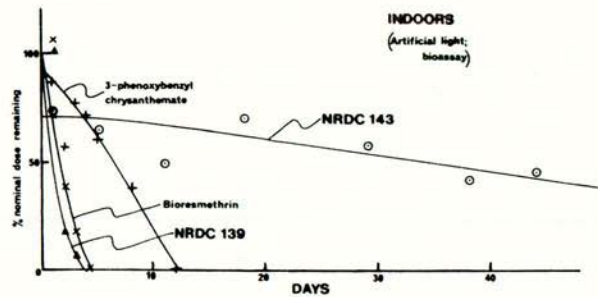


FIGURE 4

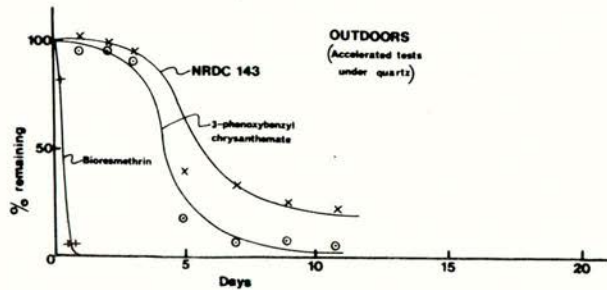


FIGURE 5

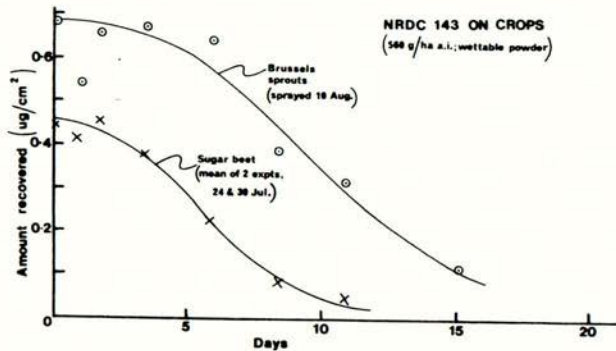


FIGURE 6

In conclusion, therefore, the combination of greater stability with good insecticidal activity and relative safety to mammals shown by NRDC 143 indicates that it may succeed in some insect control applications where less stable, though adequately active, pyrethroids fail.

The new compounds are protected by U.K. Patent Applications Nos. 50838/72 and 59/84/72.

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SMALL SCALE FIELD EXPERIMENTS WITH PH 60-38 AND PH 60-40,
INSECTICIDES INHIBITING CHITIN SYNTHESIS.

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Summary The new insecticidal compounds PH 60-38 and PH 60-40 were tried in the open on larvae of various insect species. The results, both initial and residual, were promising and large scale field experiments are considered justified.

INTRODUCTION

A recent paper (Mulder *et al* 1973) deals with the laboratory evaluation of 1-(4-chlorophenyl)-3-(2,6-dichlorobenzoyl)urea, PH 60-38, and 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea, PH 60-40. Activity on larvae of Coleopterous, Lepidopterous and Dipterous insect species was demonstrated; never were adults affected. The compounds had to be ingested continuously to be effective and appeared to have no plant systemic action.

In the same paper it was stated that death was invariably connected with moulting. Histological preparations revealed severe lesions in the endocuticular tissues of the newly formed integument and it was supposed that as a result the exoskeleton was not rigid enough to resist the muscular traction and the increased turgor during moulting.

In a subsequent communication from our laboratories (Post *et al* 1973) it was demonstrated that the larvicidal properties of these compounds are most probably based on the inhibition of chitin biosynthesis. In the present paper data obtained in small scale field trials are presented. Results of large scale field experiments will soon be published elsewhere.

METHODS AND MATERIALS

As by experience many compounds that look promising in the laboratory fail outdoors, evaluation in small scale field trials was adopted as an intermediate between laboratory experiments and field trials. The experiments were carried out with formulated products. As references commercial formulations of DDT, carbaryl or dimethoate were applied. Of PH 60-38 and PH 60-40 respectively 10% - and 5% - liquid formulations (w/v) and 25%-wetttable powders, containing particles ranging from 5-20 microns or from 2-6 microns, were used.