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A NEW GROUP OF FUNGICIDALLY-ACTIVE METAL CO-ORDINATION COMPOUNDS BASED ON PROCHLORAZ

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Summary Prochloraz, N-propyl-N-(2-(2,4,6-trichlorophenoxy)ethyl)imidazole-1-carboxamide, (coded BTS 40 542) is under development by the Boots Company Limited as a new, broad spectrum fungicide with activity against pathogens of both cereals and broad-leaved crops. However, several of the latter have proved sensitive to foliar applications and related compounds were therefore synthesised with the aim of retaining high activity while increasing the margin of crop safety. This was achieved with a series of metallic complexes, as exemplified by a prochloraz/manganese(II) chloride complex.

Résumé Prochloraz, N-propyl-N-(2-(2,4,6-trichlorophenoxy)ethyl)imidazole-1-carboxamide, (nom de code BTS 40 542) est une molecule actuellement développée par la société the Boots Company Limited c'est un noveau fongicide à large spectre d'activité contre les maladies pathogènes des cultures de cereales et des cultures de végétaux dicotyledones. Parmi ces dernières, de nombreuses se sont montrées sensibles aux applications foliaires. Ceci a conduit à la synthèse de produits analogues dans le but d'accroître la sélectivité tout en conservant une haute activité antipathogène. Le resultat fut obtenu avec une serie de complexes metalliques, comme par exemple le chlorure de manganese(II)/prochloraz.

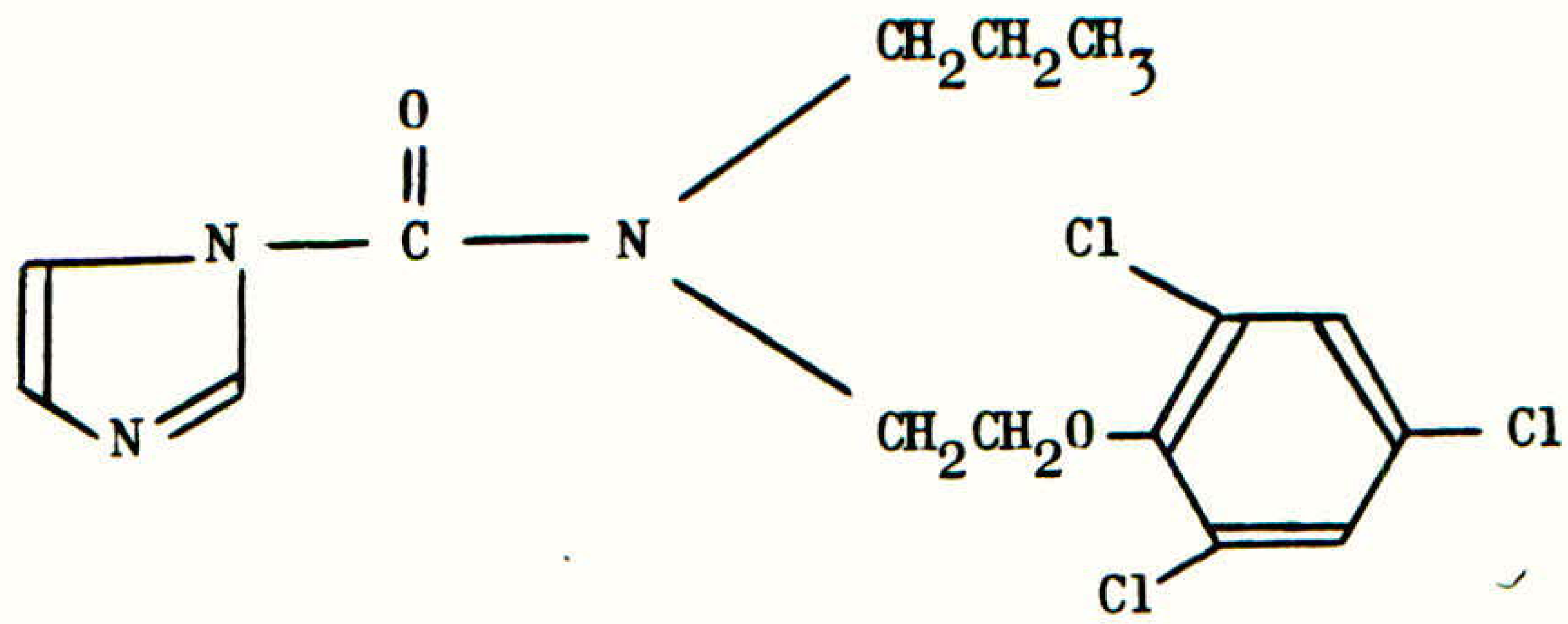
INTRODUCTION

Prochloraz is the common name approved by the BSI and proposed by ISO for N-propyl-N-(2-(2,4,6-trichlorophenoxy)ethyl)imidazole-1-carboxamide (IUPAC). The compound is coded BTS 40 542 and was reported as possessing a broad spectrum of fungicidal activity (Birchmore *et al* 1977) including control of powdery mildew (Weighton *et al* 1977).

It has subsequently been discovered that prochloraz can form stable complexes with a number of inorganic metal salts such as those of manganese(II) and copper(II). In the case of manganese(II) chloride, 2:1 and 4:1 prochloraz/metallic cation complexes have been identified.

Chemistry

Prochloraz is the most active member of a group of 1-carbamoylimidazoles synthesised by the Boots Company over a number of years. Its chemical, physical and biological properties have been described (Birchmore *et al* 1977). Its structure is as follows:



Physical form: white, crystalline solid   Melting point: 38.5-41.0°C

Solubility at 25°C: 5.5 mg/l water; 3500 g/l acetone; 2500 g/l xylene

The high solubility of the compound in solvents such as xylene means that emulsifiable concentrates with active ingredient content of 40-50% can be readily attained. These formulations have given excellent control of foliar diseases in cereals (Weighton et al 1977 and 1979). Its low melting point makes its direct use as a wettable powder difficult and formulations of this type are usually prepared by adsorbing the active ingredient onto an inert carrier such as Celite or a precipitated silica. However, these formulations are difficult to disperse physically.

Prochloraz forms complexes with a variety of metal salts and salts with acids. A number of these have been prepared (Table 1). As can be seen all are solids with relatively high melting points and the salts with acids are significantly more water-soluble than prochloraz or its metal complexes. The metal complexes can be incorporated directly into wettable powder formulations with high active ingredient content.

Table 1

Prochloraz metal complexes and salts with acids

Complexing moiety	Prochloraz/metal (acid) ratio	M.P. °C	Solubility (g/l) Water	Acetone
$CuCl_2$	2:1	136	Insoluble	11
	4:1	133-134	4	50
$MnCl_2$	2:1	140-142	4	11
	4:1	141-142	4	7
$Cu(NO_3)_2$	2:1	124-126	Insoluble	50
$CuBr_2$	2:1	151-153	Insoluble	10
$FeCl_2$	2:1	136-138	10	10
Calcium dodecylbenzene-sulphonate	2:1	145-147	5	5
H_2SO_4	1:1	119	70	10
$(COOH)_2$	1:1	117-118.5	5.5	25

Complexes with salts of nickel, zinc and tin have been obtained but were generally found to be less stable than those with salts of copper(II) and manganese(II). Consequently, biological interest centred on the copper(II) and manganese(II) chloride complexes. Some interest was also retained in the salts with acids but the low pH associated with the hydrogen sulphate outweighed the advantage of water solubility and the oxalate showed no biological or formulation advantages over the two metal complexes.

Investigation of the behaviour of the 2:1 copper(II) and manganese(II) complexes revealed that they were not completely stable in aqueous solution, being converted, in part at least, to the 4:1 complexes. As a result of this finding the 4:1 metal complexes of copper and manganese which are more stable in aqueous solution, were selected for further study. All subsequent development has concentrated on the use of these complexes which, when formulated as wettable powders, produce formulations with excellent dispersion characteristics.

Biology

Prochloraz, formulated as a 25% emulsifiable concentrate, has been shown to control cereal foliar diseases effectively without damage to the crop (Weighton et al 1977, 1979). It has also shown outstanding activity in crops such as turf and rice, and for the control of the storage rot pathogens of fruit and vegetables (Birchmore & Meneley 1979). However, the liquid formulations have shown phytotoxicity to various broad-leaved crops, especially when used in repeated spray programmes (Table 2).

Table 2

Crop safety of prochloraz to peanuts under glasshouse conditions after 1-3 sprays at 7 day intervals

	Spray Number		
Formulation Type*	1	2	3+
25% a.i. e.c.	2.5	4.3	4.3
25% a.i. e.c. + penetrant	3.5	6.2	7.2
25% a.i. d.p.	0	0	0.2

*All sprays applied high volume at 5000 ppm (as a.i.)

+Assessed on scale 0-10 where 0 = no effect and 10 = severe damage

The penetrant added to the formulation clearly considerably increased the extent of damage produced by the emulsifiable concentrate and could not be used in the peanut crop but, even in its absence the liquid formulation produced effects that would be unacceptable in the field. It is a generally accepted rule that in many broad-leaved crops, such as top fruit and cucurbits, powder formulations are preferred to liquids on the basis of phytotoxicity. As mentioned earlier, the formulations of prochloraz adsorbed onto an inert carrier have poor dispersion characteristics. This is not true of the metal complexes.

Trials in Australia (Table 3) showed that formulations of these 4:1 complexes were significantly less damaging to broad-leaved crops, such as tomatoes and cucumbers, than prochloraz emulsifiable concentrates.

Table 3

The comparative crop safety of prochloraz and its 4:1 copper(II) and manganese(II) complexes on cucumbers and tomatoes - Australia

Compound	Formulation type	Rate g a.i./ha	Cucumber crop safety	Tomato crop safety
Prochloraz	25% e.c.	100	0	1.7
		150	1.0	3.7
Prochloraz/Mn 4:1 complex	50% w.p.	100	0	0
		150	0	1.3
Prochloraz/Cu 4:1 complex	50% w.p.	100	0	0
		150	0	0
Dinocap	25% w.p.	250	0	-
Benomyl	50% w.p.	380	0	-
Maneb	80% w.p.	1600	-	0

Crop safety assessed on a 0-5 scale where 0 = no effect and 5 = severe damage

This finding has been confirmed in trials undertaken in Japan, France, U.S.A. and the United Kingdom as well as Australia on a variety of crops including apples and lettuce. Consequently, by formation of the metal co-ordination complexes of prochloraz, the preparation of non-phytotoxic formulations has been possible.

It has also been shown under both laboratory and field conditions that these metal complexes possess a high level of fungicidal activity. Results against barley powdery mildew (*Erysiphe graminis*) in glasshouse trials are shown in Table 4.

Table 4

Comparative activities against barley powdery mildew

Compound	Eradicant 150	Eradicant 100	Eradicant 50	Eradicant 25	Protectant 150
	Rate a.i. (ppm)				Rate a.i. (ppm)
Prochloraz	99	98	97	96	100
Prochloraz/Cu 4:1	83	73	73	77	83
Prochloraz/Mn 4:1	93	92	84	76	95
Tridemorph	88	72	53	35	74

Under field conditions, the complexes have also shown high levels of fungicidal activity, comparing favourably with prochloraz emulsifiable concentrate. Field work has been restricted to the 4:1 manganese complex as this has proved to be the more active of the two most stable complexes (Table 5).

Table 5

Comparative control of cucumber powdery mildew (*Sphaerotheca fuliginea*) and tomato early blight (*Alternaria solani*) by prochloraz and the 4:1 manganese(II) complex - Australian trials

Compound	Formulation	Rate (g a.i./ha)	Cucumber powdery mildew control (%)	Tomato early blight control (%)
Prochloraz	25% e.c.	100	96	89
		150	96	91
Prochloraz/Mn 4:1	50% w.p.	100	100	91
		150	100	91
Dinocap	25% w.p.	250	87	-
Benomyl	50% w.p.	380	87	-
Maneb	80% w.p.	1600	-	91

Whilst prochloraz, as the emulsifiable concentrate, remains the compound of choice for use in cereals, turf and other monocotyledonous crops, it has been shown that wettable powder formulations of the metal complexes (especially the 4:1 manganese(II) complex) retain high fungicidal activity, possess good dispersion characteristics and are non-phytotoxic to broad-leaved crops. In addition, when used in repeat spray programmes, which are common in crops such as cucumbers, tomatoes, apples and peanuts, the complexes are of particular benefit.

CONCLUSION

Prochloraz has been shown to control the fungal pathogens of cereals and a number of pathogens of broad-leaved crops. The emulsifiable concentrates, which are the most active formulation type in cereals can cause damage to certain sensitive broad-leaved crops.

However, manganese(II) complexes of prochloraz have been shown to be both safe and active when applied to broad-leaved crops as wettable powders. Also, the higher melting points of the complexes when compared with that of prochloraz make them much more easily formulated as wettable powders. Further development of prochloraz on specific sensitive crops will be with wettable powders of the 4:1 manganese(II) complex.

Acknowledgements

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TF-138: A NEW FUNGICIDE

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Summary TF-138 is obtained from the cultured broth of *Streptoverticillium rimofaciens* B-98891 and is a new nucleoside antibiotic which has 5-(hydroxymethyl)cytosine as its chromophore. The acute and subacute toxicities to rats and fish are low. It shows weak antimicrobial properties against phytopathogenic fungi, yeasts and bacteria on agar plates. However, it is toxic to 8 genera of powdery mildew fungi at 40-80 mg/l when applied to the foliage of cucumber, rose, apple, grape, barley, tobacco, green peppers, oak and mulberry. No phytotoxicity was observed in any plants treated with 320 or 1280 mg/l. It is also effective against benomyl-resistant strains of *Sphaerotheca fuligenea*.

INTRODUCTION

TF-138, a new fungicide, was discovered at Takeda Chemical Industries Ltd. in 1974. It has been widely tested in the field in many countries in Europe and U.S.A. as well as various Asian countries under this code and the trade mark Mildiomycin and found effective against powdery mildews on many kinds of plants.

CHEMICAL AND PHYSICAL PROPERTIES

Code number	Antibiotic B-98891, TF-138.
Chemical name	(2*R*,4*R*)-2-[(2*R*,5*S*,6*S*)-2-(4-amino-1,2-dihydro-5-hydroxymethyl-2-oxopyrimidin-1-yl)-5,6-dihydro-5-*L*-serylamino-2*H*-pyran-6-yl]-5-guanidino-2,4-dihydroxyvaleric acid.
Structural formula	See figure 1.
Molecular formula and weight	$C_{19}H_{30}N_8O_9 \cdot H_2O$ 532.5
Physical state	Hygroscopic white powder, m.p. >300°C (dec.)
Solubility	Readily soluble in water; sparingly soluble in pyridine, dimethyl sulphoxide, *N*,*N*-dimethylacetamide, dioxane, tetrahydrofuran.
Stability	Stable in neutral, slightly unstable in basic (pH9) and relatively unstable in acids (pH2) aqueous solution.
Formulations	Wettable powder (80 g a.i./kg). Aqueous solution (80 g a.i./kg).

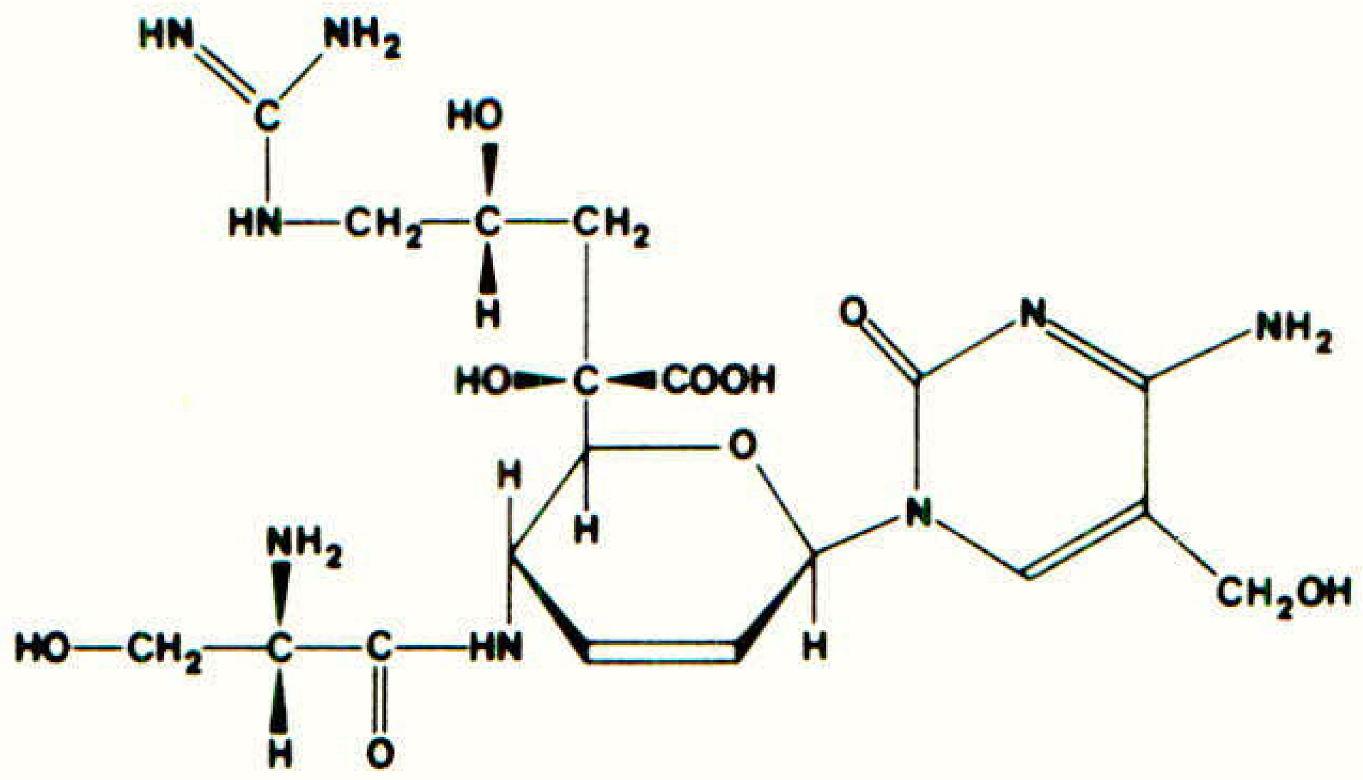

Figure 1 Structure of TF-138

TOXICOLOGY

Acute mammalian toxicity

The acute toxicities to mice and rats are shown in Table 1. No irritation was observed to the skin or eyes of rabbits at a concn. of 1000 mg/l and negative results were obtained from the Ames test for mutagenicity conducted with or without rat liver homogenate.

Table 1

Acute toxicity of TF-138 to rats and mice

Route	LD50 (mg/kg) to rats		LD50 (mg/kg) to mice	
	Male	Female	Male	Female
Oral	4300	4120	5060	5250
Subcutaneous	463	684	1190	1150
Intravenous	885	700	645	599
Intrapenitoneal	679	842	1020	1050
Dermal	>5000	>5000	>5000	>5000

Acute toxicity to fish

The toxicities to fish were: for carp LC50 (72h) >40 mg/l; for killifish LC50 (168h) >40 mg/l; for water fleas (*Daphnia pulex*) LC50 (6h) >20 mg/l.

Chronic toxicity

In 30-day feeding trials no significant adverse effects were observed in mice or rats at 200 mg/kg daily. In a 3-month subacute toxicity study in rats the maximum non-effect level was 50 mg/kg daily. Other long-term chronic studies have so far been favourable.

BIOLOGICAL PROPERTIES

Antimicrobial spectrum

The antimicrobial spectrum was investigated on agar media (Iwasa et al 1978). TF-138 showed relatively strong activity against Mycobacterium phlei, and Rhodotorula rubra, but little activity against Gram-positive & -negative bacteria, yeasts, saprophytic fungi and dermatophytes. Among phytopathogenic fungi tested, Cochliobolus miyabeanus, Sclerotinia sclerotiorum, Botrytis cinerea, Guignardia laricina and Alternaria kikuchiana were relatively susceptible. It was concluded that TF-138 specifically inhibits the growth of Rhodotorula and Mycobacterium species on agar media.

Activity against powdery mildew

The anti-mildew spectrum of TF-138 was examined using powdery mildews on 15 kinds of plant caused by the fungi of 13 species of eight genera (Table 2). The effects of the chemicals were determined by the % area of mildew on the leaves. The % disease control was calculated using the formula:

$$\%\ \text{disease control} = 100 \times \left(1 - \frac{\%\ \text{area of mildew on treated plants}}{\%\ \text{area of mildew on untreated plants}}\right)$$

The % control of TF-138 (80 mg/l) was better than 90% against powdery mildews of cucmber, melon, rose, strawberry, tomato, barley, tobacco, grape, pea, mulberry, and apple. It showed excellent control of the parasitic fungi Sphaerotheca, Erysiphe, Podosphaera, Microsphaera, Uncinula and Cystotheca spp. It was also effective against Leveillula spp., an endoparasitic fungus and Phyllactinia spp.

(See Table 2)

TF-138 was effective against inocula from both untreated and benomyl-treated plots (Table 3), although benomyl and thiophanate-methyl were not fully effective against the inoculum from untreated plots.

Table 3

Effect of TF-138 against benomyl-resistant strain of Sphaerotheca fuliginea on cucumber

Treatment	Concn (mg/l)	Area mildewed (%)* Sources of inoculum: Benomyl plot**	Untreated plot
TF-138	80	0	0
Benomyl	250	89.2	59.2
Thiophanate-methyl	250	95.0	48.3
Dinocap	148	0	0
Untreated	-	96.7	88.3

* Inoculation: May 10; Spray: May 11; Assessed: May 17.
** Inocula from plants sprayed 15 times with benomyl (250 mg/l).

TF-138 was not phytotoxic when sprayed at 160 mg/l on cabbage, small red bean and also the crops shown in Table 2. Besides apple, strawberry and cucumber were not injured by several sprays at 320 and 1280 mg/l respectively. Considerable disease

Table 2

Control of powdery mildew by TF-138

Host plant (cultivar)	Pathogen	Disease control (%) at stated rate (mg a.i./l): TF-138 40	TF-138 80	dinocap 148	quinomethionate 62.5	other fungicides	Date: inoculated	sprayed	assessed
Cucumber (Shinko A)	*Sphaerotheca fuliginea*	95.5	99.1	82.7	100	100[a]	Nov. 14	Nov. 16 and 22	Nov. 29
Melon (Ginsen)	*S. fuliginea*	80.4	92.8	94.8			Feb. 12	Feb. 14	Feb. 29
Rose (Arlene Francis)	*S. pannosa*	96.0	97.8	63.2			---	Mar. 11 and 18	April 1
Strawberry (Hogyoku)	*S. humuli*	96.0	96.3	78.9	50.0	80.9[b]	--	Nov. 21 and 29	Dec. 6
Tobacco (MC)	*Erysisphe cichoracearum*	92.1	93.2	94.0			---	Feb. 8	Feb. 19
Tomato (Fukujyu No.2)	*E. cichoracearum*	87.0	94.8	83.3			June 10	June 12	July 2
Barley (Shigahakkoku 5)	*E. graminis*	90.0	94.5	--	90.0		Mar. 12	Mar. 14	Mar. 26
Garden pea (Usui-mi endo)	*E. pisi*	87.1	88.4	87.4			Jun. 28	July 1	July 10
Red clover	*E. polygoni*	85.1	90.3	46.1			---	June 20	June 27
Oxalis	*Microsphaera ruselli*	97.0	98.7	83.5			June 28	June 29	July 6

Apple (Rall's Janet)	<u>Podosphaera leucotricha</u>	87.9	91.8	92.7			May 22	May 24	May 31
Mulberry (Ichinose)	<u>Phyllactinia moricola</u>	81.6	82.5	88.9			---	Sept. 3 and 10	Oct. 8
Grape (Muscut berry A)	<u>Uncinula necator</u>	100	100	--	--	66.7[c]	---	June 26 July 3, 10 & 17	Aug. 7
Green pepper (Ise)	<u>Leveillula taurica</u>	--	86.5	41.5			Apr. 18	Apr. 19	Apr. 29
Oak	<u>Cystotheca wrightii</u>	50.3	93.4	89.2	55.1		---	Apr. 26	May 3

Formulations used: TF-138 (8% w.p.)
dinocap (37% e.c.)
quinomethionate (25% w.p.)

[a] Wettable sulphur (75% w.p.) at 2.5 g a.i./l - produced severe chlorosis

[b] Polyoxin-B (10% w.p.) at 100 mg a.i./l

[c] Thiophanate-methyl (70% w.p.) at 470 mg a.i./l

control by systemic action of TF-138 was obtained by root-soaking cucumber seedlings in a solution of 10 mg/l. To explore further the systemic effect, possible translaminar action was tested by spraying the upper surfaces of tobacco leaves with TF-138 (80 mg/l) two days after inoculating the lower surfaces (Table 4). Although the upper surfaces were exposed daily to infections by conidia, TF-138 controlled powdery mildew on that surface remarkably, being slightly superior to quinomethionate (83 mg/l). On the lower surfaces, good, if not exceptional, control was obtained by TF-138 and it was superior to quinomethionate which was unsatisfactory. Similar results were also observed on cucumbers.

Table 4

Effect of TF-138 against powdery mildew of tobacco by spraying the upper surfaces of the leaves

Chemicals	concn (mg/l)	Leaf area mildewed (%) for respective surface			
		Dec. 29		Jan. 5	
		Upper	Lower	Upper	Lower
TF-138	80	1.3	2.6	0.7	5.0
Quinomethionate	83	1.5	5.2	2.3	16.3
Untreated	--	23.9	12.4	54.7	19.1

Inoculation: Dec.21 Spraying: Dec. 23 and 29

In glasshouse tests, TF-138 gave no control of various insects, molluscs or nematodes even when applied at many times the normal field concns. However, a mite population was reduced when TF-138 (80 mg/l) was sprayed over cucumber plants to control powdery mildew.

CONCLUSION

TF-138 is a new antifungal antibiotic which has low toxicity to mammals and fish and is specifically effective against many powdery mildews of plants at concns of 40-80 mg/l when applied as a spray to the foliage.

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THE EFFICACY OF NEWLY DEVELOPED DUAL-COMPONENT GRANULAR INSECTICIDES AGAINST CABBAGE ROOT FLY

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Summary Effects of interactions between disulfoton and chlorfenvinphos, mecarbam, fonofos, quinalphos and terbufos on the control of cabbage root fly on field-sown radish were evaluated using log-dose applications of the insecticides formulated in granules either singly or in five dual-component products. When combined with disulfoton, the other insecticides gave better control of the pest than when applied alone at the same rate. A possible interpretation is that the two constituent active ingredients in each formulation acted independently and results are given to support this hypothesis of independent joint action of the insecticides.

INTRODUCTION

Granular formulations of disulfoton, in addition to being effective against cabbage aphid (*Brevicoryne brassicae*) (Linke *et al*, 1961), were reported to give good control of cabbage root fly (*Delia brassicae*) on brassicas when applied mechanically in some early experiments (Makepeace and Smith, 1965). In 1976, disulfoton formulated on fuller's earth was applied to transplanted Brussels sprout plants simultaneously with chlorfenvinphos or carbofuran and was more effective against cabbage aphid than another systemic aphicide, ethiofencarb, used with carbofuran in an experimental dual-component granular formulation (Thompson and Percivall, 1977). The concept of dual-component granular formulations for control of cabbage aphid and cabbage root fly on brassicas has since been developed commercially with the introduction of a product (Double Down: Stauffer Chemical Co. and Pan Britannica Industries) containing disulfoton and fonofos formulated together on a montmorillonite clay of the fuller's earth type (Sinclair and Purnell, 1977). Four experimental dual-component granular formulations containing disulfoton with either chlorfenvinphos, mecarbam, quinalphos or terbufos have also recently become available for testing.

To evaluate possible interactions between the individual insecticides in these dual-component formulations, the protection of radish, which offers an economical testing procedure for the evaluation of insecticides against cabbage root fly larvae (Thompson and Percivall, 1976), was examined in 1979 by applying each insecticide alone and also with disulfoton in a dual-component formulation.

MATERIALS AND METHODS

Site and design of experiment The experiment was done at Wellesbourne on sandy-loam soil which received only a base fertiliser application of 100 kg N/ha, 231 kg P_2O_5/ha and 231 kg K_2O/ha. Radish (cv. French Breakfast Forcing) was sown with Russel close-row seeder units on 8 May at a rate equivalent to 70 g seed/100 m row using a technique developed for log-dose applications of insecticides to this crop (Thompson and Percivall, 1976). Plots comprised 7-m lengths of twin-rows, 15 cm apart and at 70 cm centres. The positions of plots treated with insecticides were randomised within a systematic grid of untreated plots, as described previously for carrot fly evaluation trials (Thompson and Wheatley, 1977). Each insecticide treatment was assigned to one twin-row plot in each of three replicated blocks. Weeds were controlled by a pre-emergence application of propachlor (Ramrod, 65% w.p.) and chlorthal-dimethyl (Dacthal, 75% w.p.) at doses equivalent to 7 kg and 6 kg a.i./ha respectively. The experiment was not irrigated.

Insecticides The insecticides formulated singly on granules were chlorfenvinphos (Birlane; 10% a.i.), disulfoton (Disyston FE-10; 10% a.i.), fonofos (Dyfonate; 10% a.i.), mecarbam (10% a.i.), quinalphos (5% a.i.), and terbuføs (10% a.i.). Three dual-component granular formulations contained 6% disulfoton, together with 4% chlorfenvinphos, or 4% fonofos (Double Down) or 5% terbufos. The other two products contained 5% disulfoton, with either 5% mecarbam or 2.5% quinalphos.

Specially designed, tractor-mounted, multi-V-belt equipment developed at Wellesbourne (Wheatley and Niendorf, 1969) was used to apply, by the bow-wave technique (Makepeace, 1965), continuous logarithmically-changing doses spanning an approximately 16-fold range along the plots (Wheatley, 1971, 1972).

Assessment of cabbage root fly damage On 27 June, each plot was separated into ten 70-cm sub-plots and all radish in each sub-plot were lifted and washed. The numbers of undamaged radish and radish damaged by cabbage root fly larvae were recorded.

Calculations A method proposed by Phelps (1979) for the analysis of data from trials evaluating the performance of continuous, logarithmically-changing doses of insecticides against carrot fly on carrots is also appropriate for similar experiments using radish to evaluate insecticides for control of cabbage root fly (Thompson et al, unpublished); the details will be published elsewhere. By expressing the total numbers of undamaged radish from comparable sub-plots in each of three replicates as proportions of the total numbers harvested in those sub-plots, and by calculating similarly a mean value for untreated sub-plots in the systematic grid, the efficiency of the treatments in decreasing the numbers of cabbage root fly larvae (Wheatley, 1974) was estimated for each dose.

RESULTS

The results (Tables 1 and 2) for all insecticides except disulfoton are shown for the doses 50 and 150 mg a.i./m row, approximately 0.75 and 2.2 times the application rate of chlorfenvinphos and fonofos recommended to control cabbage root fly in brassicas. The wider range of doses presented for disulfoton (Table 1) corresponds to the differing levels of this insecticide in the various dual-component granules (Table 2).

Where each insecticide was applied alone (Table 1), best protection of the radish at 50 and 150 mg a.i./row was obtained by terbufos, 88 and 98% being undamaged, which corresponded to calculated 81 and 98% decreases respectively in the numbers of cabbage root fly larvae. In contrast, disulfoton gave the least protection and even at 300 mg a.i./m row only 77% of the radish were undamaged, corresponding to a 61% decrease in the numbers of larvae. Of the other insecticides, only chlorfenvinphos and quinalphos at 150 mg a.i./m row gave more than 90% undamaged radish and calculated decreases in the numbers of cabbage root fly larvae damaging the plants.

Table 2 shows the per cent undamaged radish and a comparison of the decrease in the numbers of cabbage root fly larvae calculated from a regression of the control achieved by the dual-component granule against the log-dose and from the regressions for the separate components, assuming independent joint action. Whereas all of the insecticides when applied singly at 50 mg a.i./m row resulted in less than 90% of the radish being undamaged and less than 90% decrease in the numbers of cabbage root fly larvae, both quinalphos and chlorfenvinphos in combination with disulfoton exceeded this performance. At 150 mg a.i./m row, all of the chemicals in combination

Table 1

The performance of the single-component granular formulations for protecting radish against cabbage root fly damage

Insecticide	Dose at which response interpolated (mg a.i./m row)	% undamaged radish (95% confidence limits)	% decrease in no. larvae (95% confidence limits)
Chlorfenvinphos	50	84 (80-87)	73 (66-78)
	150	98 (97-99)	97 (96-98)
Fonofos	50	82 (78-86)	71 (62-77)
	150	92 (89-94)	86 (82-90)
Mecarbam	50	76 (72-78)	59 (51-65)
	150	85 (80-88)	75 (66-81)
Quinalphos	50	86 (83-89)	78 (72-82)
	150	95 (92-97)	92 (88-95)
Terbufos	50	88 (85-91)	81 (76-86)
	150	98 (97-99)	98 (96-99)
Disulfoton	50	63 (53-72)	30 (4-49)
	60	64 (56-72)	34 (13-50)
	75	67 (60-73)	39 (22-52)
	100	69 (63-75)	44 (30-55)
	150	72 (66-78)	51 (37-62)
	180	74 (67-80)	54 (38-65)
	225	75 (67-82)	57 (40-69)
	300	77 (68-84)	61 (41-74)
Untreated	-	51.2	-

with disulfoton gave more than 90% protection of the radish and all except mecarbam decreased numbers of cabbage root fly larvae by more than 90%. The expected and observed performances of the mixtures, shown in Table 2, were very similar; only the expected toxicities of the low rates of fonofos and quinalphos were outside the 95% confidence limits for the observed values of the dual-component granules.

DISCUSSION

The experiment confirmed that disulfoton performs moderately well against cabbage root fly. The presence of the insecticide, although applied at differing rates depending on the formulation, increased the efficacy of the other insecticides in the dual-component granules against cabbage root fly compared with that of the single-component products. The results of the experiment appear to satisfy the conditions distinguished by Bliss (1939) for detecting the independent joint action of two poisons having different modes of toxic action, implying that the enhanced control of cabbage root fly achieved by the mixtures did not involve similar joint action between disulfoton and the other insecticides or synergism of one of the components by the other. Further study will be necessary to elucidate why the joint action of disulfoton and the other insecticides used in this experiment should be independent.

Table 2

The protection of radish from cabbage root fly damage by insecticides in combination with disulfoton in granular products and a comparison of observed and expected control on the basis of independent joint action of the components

Insecticide combinations and doses at which responses were interpolated (mg a.i./m row)				% undamaged radish (95% confidence limits)	% decrease in no. cabbage root fly larvae	
					Observed (95% confidence limits)	Expected (assuming independent joint action of constituents)
Chlorfenvinphos	50	disulfoton	75	94 (90-96)	90 (84-93)	84
	150		225	99 (98-99.8)	99 (97-99.7)	99
Fonofos	50	disulfoton	75	86 (82-88)	77 (71-81)	82
	150		225	97 (95-98)	95 (92-97)	94
Mecarbam	50	disulfoton	50	82 (75-88)	70 (56-80)	71
	150		150	92 (84-96)	88 (74-94)	88
Quinalphos	50	disulfoton	100	96 (94-97)	93 (91-55)	88
	150		300	99 (98-99.6)	98 (97-99.3)	97
Terbufos	50	disulfoton	60	93 (89-95)	88 (82-92)	88
	150		180	99 (97-99.6)	98 (96-99.4)	99
Untreated				51.2		

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