The development of a grain protectant, containing the pyrethroid bifenthrin, which has the potential for lower terminal residues

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Abstract

Grain protectants are effective in preventing damage and loss by insects in stored grain but there is international pressure to reduce residues arising from such treatments. The objective of this work was to develop a grain protectant giving adequate control but resulting in lower levels of residue than the commonly available alternatives.

Bifenthrin was tested under laboratory conditions against a range of pests of stored grain at doses of between 0.2 and 1.0 mg/kg. It was very active against the grain borers, *Prostephanus truncatus* and *Rhyzopertha dominica*, and also against *Oryzaephilus surinamensis* and *Sitophilus oryzae*. However, it was less active against *Tribolium castaneum*. The activity of the compound when applied to grain was maintained over a 3-month period.

Further work concentrated on the development of a commercial grain protectant based on a mixture of bifenthrin plus malathion. Trials have been carried out in three European countries to establish the pattern of residues on treated grain, and biological studies have been completed demonstrating the activity of the mixture against different pests and the period of protection offered by a single treatment. This confirmed that, at a dose of 0.3 mg/kg bifenthrin + 6.0 mg/kg malathion, the mixture was effective against all major pests and that this dose gave at least 6 months protection from reinfestation under conditions approximating normal temperate storage. At the end of this period, total residues had declined by more than 60% from the dose detected at day 1. The mixture was also active when tested at 5 and 10°C.

Introduction

Throughout the world insects infesting stored grain represent a threat to quality, and pose problems for farmers, storekeepers, and consumers. Dealing with infestation adds to the costs of grain handling and the methods used may disrupt trade or put workers at some risk. A range of options is available to control pests but, in many cases, the direct admixture of a contact insecticide with the grain can provide the most convenient and cost-effective method.

The requirements of a grain protectant will vary between countries and may also depend on specific commercial constraints. In Europe, for example, all grain is inspected on delivery to a silo, to the premises of the end user and during loading onto a ship for export. Discovery of a single insect during any of these inspections will result in the supplier being penalised by up to 10% of the value of the grain. For farmers or co-operative storage, treating grain with a contact insecticide at the start of, or during, storage, is an extremely cost-effective method of preventing this loss and disruption to trade. Such treatments are expected to disinfest the grain and provide a period of protection against reinfestation. Alternatively, grain exporters use admixture to ensure that, when a cargo is unloaded at its destination, it contains no live insects. Their requirements are for rapid disinfestation, including kill of insect larvae within grains.

Admixture can also offer a valuable aid to food conservation in developing countries. Here the requirement is for a simple, safe, inexpensive, easy-to-use system of pest control.

Currently, there are only about nine pesticides which are registered either nationally or internationally for the direct application to grain. The reasons for this small number are: firstly, the efficacy and safety requirements that must be met; and secondly, the relatively limited and unattractive nature of the market for such compounds.

Most of the pesticides currently used as grain protectants throughout the world, are organophosphorous compounds. They are very active against many key pests but generally will only control *Rhyzopertha dominica* at rates of application close to or exceeding the MRL. Some synthetic pyrethroids are active against *R. dominica* at very low doses but few are registered and generally these compounds have only limited activity against other pests. Therefore, synthetic pyrethroids do not provide a complete answer to grain protection.

This paper describes development work on a new grain protectant containing a mixture of a synthetic pyrethroid and an organophosphorous compound. The aim was to produce a pesticide that would control all major pest species but which would leave lower residues at the end of storage than do most current pesticides.

Materials and Methods

Materials

The synthetic pyrethroid used was bifenthrin, a new synthetic pyrethroid developed by FMC Corporation. General details of the chemical are given in Table 1. This compound has a number of worldwide agricultural uses but this work represents the first potential use of bifenthrin as a grain protectant.

Malathion was chosen as the partner compound for bifenthrin as this organophosphorous compound has very well researched toxicology, is widely registered with established MRLs, and was available. It has the added advantage of a shorter half-life than many of the other OPs used as grain protectants and, therefore, fitted with the objective of producing a pesticide that would result in lower terminal residues.

Bifenthrin alone was tested as an emulsifiable concentrate (EC) containing 100 g/L a.i. The mixtures of bifenthrin/-

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Table 1. Properties of the synthetic pyrethroid pesticide, bifenthrin.

Chemical name	(2-methyl [1,1'biphenyl]-3-yl) methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl) 2,2-dimethyl-cyclopropanecarboxylate.
Vapour pressure	1.81×10^{-7} at 25°C.
Solubility	0.1 ppb in water.
Activity	Broad spectrum insecticide/acaricide.
Toxicity	Acute oral LD_{50} 55 mg/kg in rat. Non-irritating to skin or eyes.

malathion were prepared as emulsifiable concentrates or oil-based, ready-to-use formulations, each containing 20 g/L bifenthrin and 400 g/L Malathion. Both of these formulations were used in the trial but only the work with the EC is reported here.

Treated grain was bioassayed against a range of species of adult, grain beetles (details of species are given in the Results section). The insects came from laboratory cultures maintained in either England or Belgium but only in the case of the insects from England was their resistance status known. All English strains were susceptible, except one strain of *Oryzaephilus surinamensis*, which was resistant to organophosphorous compounds.

All efficacy testing was done with the pesticides applied to English or Belgian wheat. In addition, one residue study was done using English barley as a substrate and a further residue study was done in France using French wheat.

Methods

The grain was treated by one of two methods: during tumbling in a concrete mixer or while being moved along a conventional farm grain conveying system. All treatments for efficacy testing were done by spraying diluted pesticide with a hand-held spray gun onto 25 kg batches of grain as it was tumbled in a cement mixer. This technique offers a convenient way of mimicking practical treatments and should deposit the majority of the applied dose evenly over the grain. After treatment, the grain was held in plastic or metal containers.

In the case of one trial aimed at measuring the decline in residues, barley was sprayed with diluted pesticide as it was moved along a farm conveying system. The treated grain was then held in 1 tonne bags. All other grain used in residue studies was treated with a hand sprayer during tumbling in a cement mixer.

All treatments were replicated and, in the case of efficacy work, an appropriate standard pesticide was included in the trials. The treated grain was stored either at ambient temperature, in the case of two of the residue trials, or at 20°C in the case of the efficacy work and the other residue trials.

Samples of grain were collected for assessment 1 day, 1 month, 3 months, 6 months and 12 months after treatment. Residues were determined at each of these dates but efficacy tests were stopped after 6 months.

Bioassays were carried out using standard laboratory practice. Batches of between 25 and 50 insects were exposed to the treated grain for 1 or 7 days at 25°C. Either 3 or 5 replicates were used and insects were exposed on untreated grain as controls. Some additional tests were done at low temperatures to examine the action of the mixture under such conditions. With these the methodology was changed to take account of the slower action of pesticides at low temperatures.

Residues were determined by blending the grain with acetone and partitioning and cleaning up the extract. The residues of both pesticides in this cleaned-up extract were then determined by gas chromatography with electron capture detection. The recovery, repeatability and accuracy of the method was confirmed at intervals during the trials by analysing spiked samples.

Results

Initial testing of bifenthrin-treated grain demonstrated that this compound had a wide spectrum of efficacy against some stored-grain pests. However, a dose of at least 1 mg/kg of bifenthrin would be needed to allow the compound to be used alone. The results are summarised in Table 2.

A compilation of results from grain bioassayed at intervals over a 6-month period at two laboratories is given is Table 3. Assessments made during this work also showed that bifenthrin/malathion at 0.3 + 6.0 mg/kg gave 100% knockdown of *O. surinamensis, S. oryzae, S. granarius* and *R. dominica* after 24 hours exposure, with freshly treated grain. Additional testing confirmed that the dose of 0.3 + 6.0 mg/kg bifenthrin/malathion gave complete control of *Ahasverus advena, Cryptolestes ferrugineus* and a U.K. resistant strain of *O. surinamensis* with both freshly treated grain and after it had been aged for 3 months. Complete control of *Tribolium*

Table 2. The percentage mortality of four species of stored- grain beetle bioassayed on grain treated with bifenthrin, pirimiphos-methyl or deltamethrin.

Pesticide	Dose (mg/kg)	Time after treatment (months)							
		OS		TC		SO		RD	
		0	3	0	3	0	3	0	3
Bifenthrin	0.2	100	99	3	0	25	15	100	100
	0.5	100	100	3	0	99	96	100	100
	1.0	100	100	7	4	100	100	100	100
Pirimiphos methyl	0.2	96	4	3	0	56	2	0	4
	1.0	100	100	100	72	100	95	3	4
	4.0	100	100	100	100	100	100	22	4
Deltamethrin	0.2	92	15	0	4	5	1	81	86
	0.5	100	95	5	9	64	19	72	100
	1.0	100	100	4	16	95	61	91	100

OS = *Oryzaephilus surinamensis*, TC = *Tribolium castaneum*, SO = *Sitophilus oryzae*, RD = *Rhyzopertha dominica*

Table 3. The percentage mortality of species of stored-grain beetles bioassayed, over a 6-month period, on grain treated with bifenthrin/-malathion or pirimiphos-methyl.

Pesticide	Dose (mg/kg)	Time after treatment (months)								
		OS			SG			RD		
		0	3	6	0	3	6	0	3	6
Bifenthrin +malathion	0.3+6.0	100	100	100	100	100	100	100	100	100
Pirimiphos-methyl	4.0	100	100	100	100	100	100	7	0	0

OS = *Oryzaephilus surinamensis*, SG = *Sitophilus granarius*, RD = *Rhyzopertha dominica*

castaneum was obtained with freshly treated grain but this fell to 95% when the grain was aged for 3 months.

The bifenthrin/malathion mixture was very active at temperatures of 5 and 10°C against *O. surinamensis* and *S. oryzae*. The results are summarised in Table 4. These temperatures are normal during the treatment of grain during the winter in temperate climates and are also common during the disinfestation of export cargoes.

The residues determined in samples of grain stored at four sites in northern Europe are shown graphically in Figures 1 and 2. These results confirm that the overall level of residue declines with time so that the amount remaining after 6 months storage was less than half the original dose. All the decline was accounted for by the malathion fraction; there was no breakdown of bifenthrin.

Discussion

These trials confirm the value of using mixtures of a synthetic pyrethroid and an organophosphorous compound as grain protectants. The advantages of such mixtures have been demonstrated previously by several workers (Crampton et al. 1991; Duguet et al. 1991). The principal benefits identified were the extension of the range of species controlled and a reduction in the cost of a treatment compared with the pyrethroid alone. The results given in this paper support these claims and suggest that the use of a mixture may also allow lower application rates and lower residues at the end of treatment.

Several of the insecticides currently registered as grain protectants in Europe (chlorpyrifos-methyl, etrimfos and pirimiphos-methyl) are relatively stable when applied to grain under temperate storage conditions (Thomas et al. 1987). This may result in a residue in the treated grain close to the level of the initial dose, even after several months of storage. The use of a mixture allows both the possibility of extending the range of species controlled by a single treatment and using lower rates of application. Bifenthrin has a relatively wide spectrum of activity against stored grain pests when used alone at doses of up to 1.0 mg/kg. Malathion is also active against some grain pest when applied at doses of 10–20 mg/kg. By using these chemicals in combination some additive effect was obtained and a dose of 0.3 mg/k bifenthrin + 6.0 mg/kg malathion was effective against a wider range of pests than either compound used individually at much higher doses. This dose of the mixture also gave an adequate period of protection.

Table 4. The percentage mortality of two species of grain beetle exposed at 5 and 10°C to grain treated with bifenthrin/malathion or pirimiphos-methyl. Insects were exposed to the treated grain for 5 days.

Pesticide	Dose (mg/kg)	Temperature of exposure (°C)			
		5		10	
		OS	SO	OS	SO
Bifenthrin + malathion	0.3+ 6.0	100	100	100	100
Pirimiphos-methyl	4.0	100	64	100	100

OS = *Oryzaephilus surinamensis*, SO=*Sitophilus oryzae*

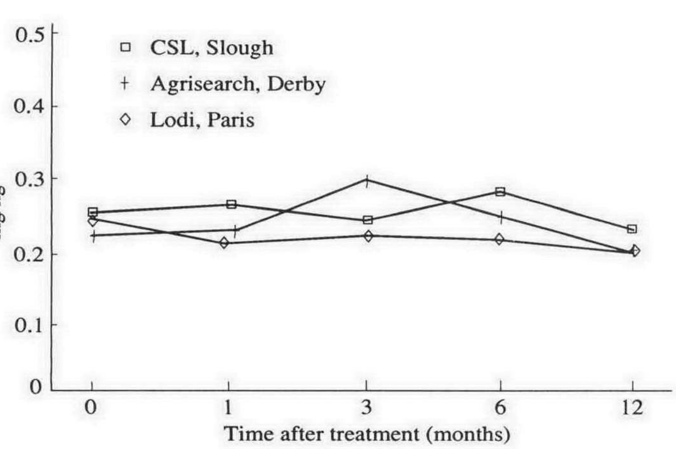

Fig. 1. Bifentrhin residues. Wheat or barley treated with emulsifiable concentrate.

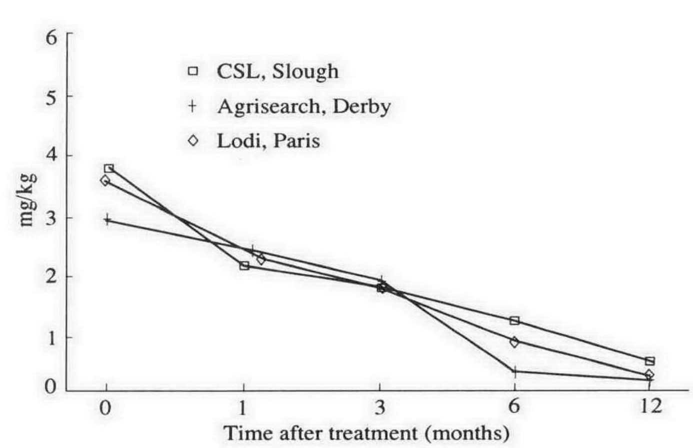

Fig. 2. Malathion residues. Wheat or barley treated with emulsifiable concentrate.

The residues arising from treatments of the bifenthrin/-malathion mixture fell by more than 60% over a 6-month storage period, yet 100% mortality was still obtained against most test insects in bioassay assessments after this period of storage. This aligns well with European storage practice where most grain is stored for less than 12 months, with 6 months being the average storage period. In northern Europe the pressures of infestation or reinfestation on grain stem mostly from insects being brought to a store in incoming grain stocks rather than active dispersal by flight. These risks are best dealt with by treating grain on intake. The decline in residues with time is also in line with consumer demands for lower levels of pesticide residues in food.

One other important use of grain protectants is their role in disinfesting cargoes of export grain. These treatments are used to make up for the inadequacies of sampling procedures in detecting insects and the opportunities for insect development offered by long sea voyages. However, under European winter conditions, grain temperatures may be below 10°C and any chemical must still be effective under these conditions. The results in Table 4 confirm that bifenthrin/malathion can meet this requirement.

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References

Crampton, P. L., Huson, A. J. and Nicholls, A. W. 1991. A new formulation liquid grain protectant based on deltamethrin and chlorpyrifos-methyl. In: Fleurat Lessard, F and Ducom, P., ed. Proceedings of the Fifth International Working Conference on Stored-product Protection, Bordeaux, France, September 1990, 1, 497–508.

Duguet, J. S., Fleurat-Lessard, F. and Peruzzi, D. 1991. The advantages of mixing deltamethrin and organophosphorus insecticides for the protection of stored cereals — a review of recent trials. In: Fleurat Lessard, F. and Ducom, P., ed., Proceedings of the Fifth International Working Conference on Stored-product Protection, Bordeaux, France, September 1990, 1, 517–526.

Thomas, K. P., Pinniger, D. B. and Wilkin, D. R. 1987. An assessment of Chlorpyrifos-methyl, etrimfos, fenitrothion and pirimiphos-methyl as grain protectants. Pesticide Science, 21, 57–72.