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Development of a sprayable slow-release formulation for the sex pheromone of the Mediterranean Corn Borer, *Sesamia nonagroides*

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Abstract In the FAIR project ''Pheromaize'', CT96-1302, the main objective is to provide European growers with a reliable, cost effective and environmentally friendly technology based on pest mating disruption. The project is mainly focused on Mediterranean Corn Borer (MCB), *Sesamia nonagroides*, the key pest of maize grown under Mediterranean conditions. TNO has developed a sprayable formulation consisting of a biodegradable matrix in which the pheromone is dissolved, together with a UV—stabilizer, an antioxidant, a surfactant and a sticker material. During outdoor exposure experiments release of pheromone was found to be high enough for more than 30 days. This formulation has been tested in large scale field experiments by helicopter spraying on 5 ha maize by field partners in Spain, Greece and France.

Keywords Slow-release formulation · Sprayable · Pheromones · Mating disruption · *Sesamia nonagroides*

1 Introduction

Use of pheromones and other semiochemicals for pest control in Europe is practically restricted nowadays to the control of moth pests in vineyards and to a less extent, in orchards. The development of pheromone-based technology more adapted to field crops and the improvement of procedures to scale up the synthesis and the sprayable slow-release formulation of blends should allow increased acreage treated with this non-chemical methodology.

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In the FAIR project ''Pheromaize'', CT96-1302, the main objective is to provide European growers with a reliable, cost effective and environmentally friendly technology based on pest mating disruption. The project is mainly focused on Mediterranean Corn Borer (MCB), *Sesamia nonagroides*, the key pest of maize grown under Mediterranean conditions (that is the European maize grown below 45°N parallel, an estimated maize area of at least 600,000 ha). The mating disruption technique has been aimed at the second generation of the MCB that emerges normally at the beginning of July.

Two general goals are envisaged in the present project. First, to provide European growers with a reliable, cost effective and environmentally friendly technology based on pest mating disruption, and second, to improve European pheromone production and marketing. Use of pheromones and other semiochemicals for pest control in Europe is mostly restricted nowadays to the control of moth pests in vineyards and, to a lesser extent, in orchards. The development of pheromone-based technology more adapted to field crops and the improvement of procedures to scale up the synthesis and formulation of blends, should allow increased acreage treated with this non chemical methodology.

2 Materials and methods

2.1 Microsphere production

Four approaches to making sprayable pheromone formulations have been examined:

a. An emulsion in water is made from a 10% pheromone/Bionolle 3001 solution in dichloromethane. After evaporating off the dichloromethane a dispersion is formed of spherical Bionolle/pheromone particles. Particle size can be adjusted accurately by the speed of stirring during emulsifying. After spraying of the resulting particles, the pheromone showed a release over more than 25 days during outdoor exposure.

b. Granules can be made by mixing Bionolle and pheromone in a twin screw extruder. After cryogenic milling of the string, particles with a predicted size distribution were obtained in a laboratory scale experiment. These particles can then be dispersed in water for spray application. Release was always found to be somewhat higher than from the particles made with method (a).
c. Controlled hydrolysis of the Bionolle to lower molecular weight material. In this way the melting point of Bionolle can be decreased to 60°C. Pheromone can be dissolved in the Bionolle and the Bionolle/pheromone can be emulsified in water at temperatures above 60°C. By lowering the temperature a dispersion of solid polymer particles with pheromone can be obtained.
d. A different matrix material, consisting of one of more polymeric compounds, can be chosen with an overall melting point below 100°C. This alternative polymer/pheromone combination can then be emulsified and dispersed in water as above. In these last two methods the pheromone is dissolved in the matrix material together with a UV stabilizer and an antioxidant. This mixture is then emulsified using a surfactant at a temperature above 80°C. After cooling sticker material(s) is/are added to the solution.

The first two methods have their disadvantages. The evaporating step of dichloromethane is quite critical. Fast irreversible coagulation can occur if conditions are not controlled carefully. Even after optimizing this method large quantities of dichloromethane are still needed for dissolving the Bionolle polymer. This makes scale-up of this method for industrial application difficult. During scale-up of the second method for field trial application milling has to be done cryogenically on a semi-technical scale. It was found that this way the particles had a flake structure and therefore a relative large surface area and consequently a release which is too fast in practice. By using method (c) it was impossible to obtain a good particle size distribution in a controlled way. The only method that could reproducibly produce microspheres and could be easily scaled-up proved to be method (d). In fact, apparatus can easily be adapted for (continuous) production of formulation at kg (based on a.i.) scale.

Trial batches were made by varying the rotation speed, the number and concentrations of adjuvants and the concentration of pheromone. First trials were made by using Z11-C14Ac instead of the pheromone mixture Z11-C16Ac/Z11-C16OH because of price and availability. Final formulations were tested with the pheromone mixture both in the laboratory and in outdoor experiments.

Release of pheromone from microspheres was followed from formulations that were sprayed onto aluminium plates. These plates were hung in a field and collected every week for analysis by GC of residual content. Release studies in the laboratory were conducted by hanging the same aluminium plates in a ventilated oven and collecting plates regularly for analysis.

2.2 Mating disruption

For mating disruption purposes, a two component blend (90/10, Z11-C16Ac/Z11-C16OH) has been in field trials in every country (Mazomenos 1989). In Spain, France and Greece two fields of each 5 ha has been sprayed by helicopter using the microsphere formulation containing 80 g pheromone per hectare. Isolated plots have been used in the field trials. The blend has been applied just before the second adult flight (Frérot et al. 1997). The final date of application was set during the first week with no catches in pheromone traps. Equipment and dosage for applications varied between 5–25 l/ha. Evaluation of every trial has been done by the field partners. Experimental field plots have been submitted to the same conditions (cultivar, sowing date, soil insecticide treatment, no insecticide treatment on foliage).

3 Results and discussion

The release from the hydrolysed Bionolle samples in a ventilated oven at 30°C (particles consisting of clusters of primary particles of 100 μm) was found to be longer than 40 days, see Fig. 1. However, with the new method of making microspheres (method d) using the new matrix material the average particle size could be adjusted by varying the stirring speed, see Table 1, with A, B and C being different samples made from the same formulation.

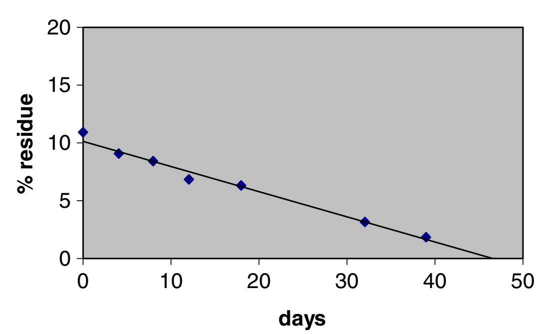

Fig. 1 Release of Z11-C14Ac from hydrolysed Bionolle at 30°C

Table 1 Effect of stirring speed on average particle size

Sample	Stirring speed (rpm)	Average particle size (μm)
A	250	200
B	750	100
C	1500	50

The effect of temperature on release seemed to be much higher than that of particle size. At 20°C the half-life of a formulation is 30 days and at 30°C the half-life has dropped to 15 days. However with some earlier formulations the release from particles of approximately 100 μm could be as long as 40 days while particles of 50 μm had a release not longer than 20 days at 30°C. Later formulations had release times in the laboratory always much longer than 40 days and half-life times of approximately 25 days, see Fig. 2.

However, the release in outdoor experiments is always much faster than in the laboratory, see Figs. 3 and 4. In the formulations tested in these experiments the 90/10 pheromone blend Z11-16Ac/Z11-C16OH has been used.

Ten formulations in total have been tested using this pheromone blend, the variations being the polymer matrix and the concentrations of the different ingredients. In addition, from most formulations different particle sizes have been produced in order to measure the effect on release of pheromone. Formulations have also been tested for rain-fastness using different concentrations of adjuvants.

The best formulation in outdoor experiments (release is shown in Fig. 4) contained 15% of the pheromone blend and had a particle size of about 100 μm. This formulation could be prepared in a reproducible way and was finally scaled-up and produced for field experiments in 1999.

The objective of this research has been to make a biodegradable, sprayable formulation with a two component blend of Z11-C16Ac/Z11-C16OH = 90/10 with a release of more than 30 days in the field. In the laboratory as well as in outdoor experiments it has been shown that such a prolonged release from a sprayable formulation is possible. During the first year of the project a very satisfactory

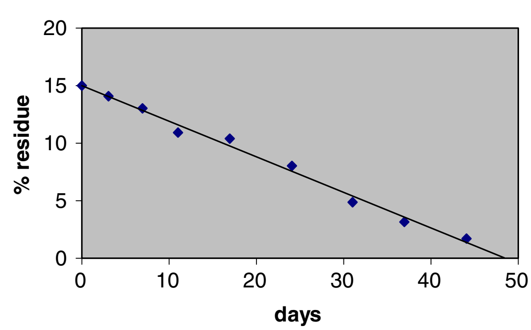

Fig. 2 Release of Z11-C14Ac at 30°C

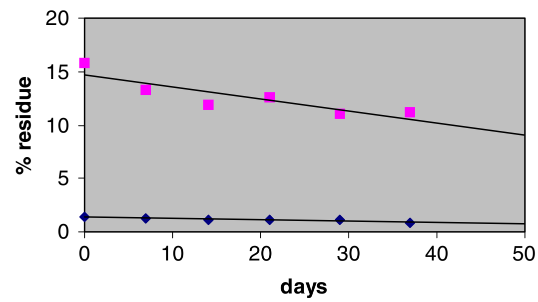

Fig. 3 Release of Z11-C16Ac (□) and Z11-C16OH (♦) at 30°C

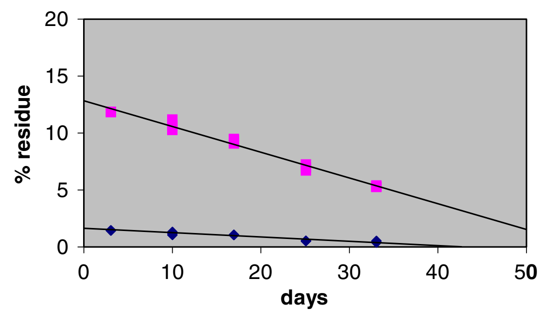

Fig. 4 Release of Z11-C16Ac (□) and Z11-C16OH (♦) during outdoor exposure in The Netherlands

formulation could be produced but this proved very difficult to scale-up. The second year formulations for the field trials were made by extrusion, milling and dispersing but these did not show the longevity found before. A different approach was used in the third year by dissolving the pheromone in the polymer melt and then making a dispersion in water. This proved to be an approach whereby release of more than 30 days could be observed, at least in small scale outdoor experiments. This technology was found to be versatile, cheap and easy to produce and scale-up.

After spraying with pheromone in the field trials it was found that in the first week after spraying the percentage of mated females were lower in the treated field than in the control field. Two weeks after the aerial treatment traps placed in the treated fields catch significantly less males than traps in control fields. The effect of mating disruption can also be found when looking at the increase of plant attack, see Table 2.

Table 2 Increase of plant attack (in percentage) of *Sesamia nonagroides* between the first and second generation and between the second and third generation

Population increase (% attacked plants) of *Sesamia nonagroides*			
	TNO 1	TNO 2	Control
2nd–1st	1.8	3.8	25.8
3rd–2nd	4.4	1.5	1.9

Although in the second sampling of attacked plants (after spraying) the attack in TNO2 has been significantly higher than in the other fields, the percentage of attacked plants increased only by 3.8% between the first and second sampling while in the control the percentage of attacked plants had increased by 25.8%.

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