

## **3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm Z-11-Tetradecenyl Acetate**

The active ingredient Z-11-tetradecenyl acetate and its associated end-use product 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm are proposed for registration under Section 13 of the Pest Control Products Regulations. This product has been reviewed under the Pest Management Regulatory Agency's (PMRA) User Requested Minor Use Registration (URMUR) program.

The product is the first pheromone that will be directly applied to a food crop (cranberries), as opposed to being used in separate lure or trap systems. The product can reduce or prevent the target pest from mating by interfering with chemical communication between males and females. The resulting decrease in the number of eggs and larvae reduces the need for conventional insecticides, making the pheromone an important addition to integrated pest management (IPM) strategies for dealing with cranberry pests.

This Proposed Regulatory Decision Document (PRDD) provides a summary of data reviewed and the rationale for the proposed Section 13 registration of these products. The PMRA will accept written comments on this proposal up to 45 days from the date of publication of this document. Please forward all comments to the Publications Coordinator at the address listed below.

***(publié aussi en français)***

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## Foreword

The submissions for the minor use registration of active ingredient Z-11-tetradecenyl acetate and its end-use product 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm were considered under the PMRA's User Requested Minor Use Registration program (URMUR). The URMUR program:

- enables sponsor or user groups to encourage pesticide companies to seek registration for products already registered in the United States (U.S.) or other Organisation for Economic Co-operation and Development (OECD) countries that, due to potential low volume of sales, might otherwise not be registered; and
- ensures the most efficient technical review of URMUR applications by making use of foreign reviews completed by reliable regulators.

Since the Pheromone for Mating Disruption of Blackheaded Fireworm had already been registered in the U.S., the PMRA was able to use the reviews completed by the U.S. Environmental Protection Agency in their assessment.

The sponsoring group for the registration of the blackheaded fireworm pheromone was the British Columbia Cranberry Growers Association. Cranberry growers from across Canada now have access to this product, which will help level the playing field with their American counterparts.

Pheromones are increasingly being investigated for use as alternatives to conventional pesticides. They control pests by modifying the mating behaviour of the pests rather than killing them. They are more target-specific than conventional insecticides, are used at concentrations close to those occurring in nature, and dissipate fairly rapidly. For these reasons, it is expected that pheromone products will pose low potential risk to human health and the environment compared with conventional pesticides.

Taking these factors into consideration, a time-limited registration has been granted by the PMRA until December 31, 1999 in order to allow users access to this low-risk product, while providing concerned Canadians an opportunity to provide input into the final decision through this PRDD.

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## 1.0 Introduction

3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm is manufactured by 3M Canada Company of London, Ontario. The technical active ingredient (a.i.) in this product, Bedoukian cis-11-Tetradecenyl Acetate Technical Pheromone, is manufactured by Bedoukian Research Inc. of Danbury, Connecticut.

3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm is a microencapsulated formulation containing 20% of the active ingredient Z-11-tetradecenyl acetate. The end-use product is proposed for use in commercial cranberry production for mating disruption of blackheaded fireworm, *Rhopobota naevana*, (Lepidoptera: Tortricidae).

Z-11 tetradecenyl acetate has been identified as the sex pheromone for the blackheaded fireworm. In nature, the sex pheromone is produced and released into the air by the female moth and is used to attract a mate. "Mating disruption" refers to the process of releasing synthetic pheromone into the air at concentrations above background levels produced by female moths, thus, disrupting communication between male and female moths. Although the exact mechanism by which disruption occurs is not known, the end result is that the male moth does not locate a female and mating does not occur, resulting in subsequent reductions in the pest population. To be effective in reducing insect damage, the product must be applied prior to the beginning of the adult moth flight season, and an ambient level of pheromone sufficient to disrupt communication must last throughout the moth mating period.

Z-11-tetradecenyl acetate is a "straight-chained lepidopteran pheromone" (SCLP) consisting of a chain of 14 carbons and an acetate group. This category of pheromone products is generally regarded to pose a low risk to human health and the environment based on available studies.

## 2.0 Product chemistry

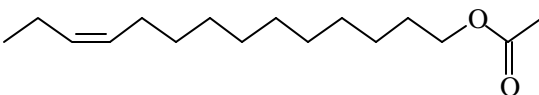
### 2.1 Identity of the active substance and preparation containing it

Active substance: Z-11-tetradecenyl acetate

Function: pheromone

Chemical name  
(International Union of Pure  
and Applied Chemistry): (Z)-tetradec-11-en-1-yl acetate

Chemical name  
(Chemical Abstracts  
Service [CAS]): (Z)-11-tetradecen-1-yl acetate

CAS Registry Number:	20711-10-8
Nominal purity of active:	96%
Identity of relevant impurities of toxicological, environmental and/or other significance:	Impurities of toxicological concerns are not expected to be present in the raw materials, nor are they expected to be generated during the manufacturing process.
Molecular formula:	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>
Molecular mass:	254.41
Structural formula:	

## 2.2 Physical and chemical properties of active substance

### Technical product: Bedoukian cis-11-Tetradecenyl Acetate Technical Pheromone

Property	Result
Colour and physical state	Colourless to slightly yellow liquid
Odour	Mild, waxy
Melting point/range	Not applicable
Boiling point/range	135/C at 0.3 mm Hg
Density	0.88 g/mL
Vapour pressure	$1.45 \times 10^{-4}$ mm Hg at 25/C
UV/visible spectrum at 26/C	Not expected to absorb UV at $\lambda > 350$ nm
Water solubility	$5 \times 10^{-7}$ mol/L at 25/C
Solubility in organic solvents	Completely soluble in acetone, methanol and hexane
n-Octanol/water partition coefficient	$K_{ow} = 5.4 \times 10^6$
Dissociation constant	Not applicable, there are no dissociable moieties
Stability (temperature, metals)	Expected to be stable under conditions of normal use

## End-use product: 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm

Property	Result
Colour	White
Odour	Mild
Physical state	Liquid
Formulation type	Microencapsulated suspension
Guarantee	20%
Container material and description	Plastic 887 mL, 3.78 L, 19 L
Specific gravity	1.01 g/mL
pH	7.5–8.5
Storage stability	A one-year ambient temperature testing is under way

### 2.3 Methods of analysis

#### 2.3.1 Method for analysis of the active substance as manufactured

A gas chromatography (GC) method with flame ionization detector was used for the determination of the active substance and significant impurities (content  $\geq 1\%$ ) in the technical product. The method has been shown to have satisfactory precision and accuracy. The requirement for the submission of the method linearity was waived as the flame ionization detector usually has a wide linear range.

#### 2.3.2 Method for formulation analysis

A GC method with flame ionization detector and internal quantification with dodecyl acetate was used for the determination of active substance in the formulation. The method has been shown to have satisfactory specificity, linearity, precision and accuracy.

### 3.0 Toxicology Evaluation

#### 3.1 Human health and safety

Reduced toxicological data requirements have been established for SCLPs. Straight-chained lepidopteran pheromones contain only carbon, hydrogen and oxygen and are poorly soluble in water. They are products of fatty acid metabolism and are biodegradable by enzyme systems present in most living organisms. Health studies have indicated that

these substances pose minimal risk and provide effective pest control at low concentrations, similar to those occurring in nature.<sup>1</sup>

The formulated product, 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm, is encapsulated and, so, the potential for direct human exposure to the formulation ingredients is considered to be negligible. In addition, since capsule size is ~25 microns, it is not considered to pose any hazard via the inhalation route to applicators.

A detailed review of the toxicity data base available for Bedoukian cis-11-Tetradecenyl Acetate Technical Pheromone and its formulation, 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm, has been completed. The data submitted satisfactorily addressed the current toxicological requirements for registration of a pheromone technical active ingredient and a pheromone end-use product.

### 3.2 Acute toxicity—technical and formulation

Bedoukian cis-11-Tetradecenyl Acetate Technical Pheromone was considered to be of low acute toxicity by the oral, dermal and inhalation routes to laboratory animals. It was minimally irritating when applied to the skin and instilled into the eyes of rabbits. There were no reports of human dermal sensitization resulting from exposure to this product.

Based on the results of acute toxicity testing, no signal words are required to be displayed on the primary panel of the label.

3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm, containing 20% Z-11-tetradecenyl acetate, was considered to be of low acute toxicity by the oral route in Sprague Dawley rats (lethal dose 50% [LD<sub>50</sub>] > 5.0 g/kg/body weight [bw]), and of low acute toxicity by the dermal route to New Zealand White rabbits (LD<sub>50</sub> > 2.0 g/kg bw). It was slightly irritating when applied to the skin of New Zealand White rabbits, and minimally irritating when instilled into the eyes of the same species. Results of skin sensitization testing using Hartley-derived albino guinea pigs, employing the modified Buehler method, were positive.

An acute inhalation study was not conducted since the microcapsules of the 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm are between 20–25 microns; therefore, the acute inhalation hazard of this product is considered to be low.

Based on the results of acute toxicity testing, it is recommended that the signal words “POTENTIAL SKIN SENSITIZER” be displayed on the primary panel of the label.

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<sup>1</sup> Refer to “The White Paper - A Review of the Current Bases for the United States Environmental Protection Agency’s Policies for the Regulation of Pheromones and Other Semiochemicals, Together with a Review of the Available Relevant Data which may Impact the Assessment of Risk for These Classes of Chemicals”, compiled by James E. Touhey, Senior Agricultural Advisor, Field Operations Division.

### **3.3 Mutagenicity—technical**

Data provided by the applicant indicated that Bedoukian cis-11-Tetradecenyl Acetate Technical Pheromone was not a mutagenic agent.

### **3.4 Acceptable daily intake and acute reference dose determination**

Based on the chemical, physical, biological and toxicological properties of SCLP compounds, it is considered that they pose little or no risk of eliciting any adverse toxicological effects. Data indicate that SCLPs pose a minor potential impact on human/animal health due to their inherent safety and use patterns. Adverse human health effects resulting from exposure to pheromone products have never been reported. It is, therefore, not considered necessary to establish an acceptable daily intake (ADI) or an acute reference dose (ArfD) for Z-11-tetradecenyl acetate due to the inherent lack of toxicity of this compound, and since it does not pose any significant residue concerns.

### **3.5 United States *Food Quality Protection Act* considerations and endocrine disruptor potential**

Based on all of the available data for SCLPs, there is no evidence of increased susceptibility of infants and children in comparison to adults that may result from exposure to SCLPs, nor of any potential to disrupt endocrine activity in humans.

## **4.0 Occupational and bystander exposure**

### **4.1 Exposure assessment**

The proposed end-use product contains 20% Z-11-tetradecenyl acetate as the active ingredient to control blackheaded fireworm in cranberries. The proposed end-use product is a microencapsulated formulation that is to be applied at a rate of 44 g a.i./hectare (ha). The timing of application is just prior to the start of the spring and summer moth flight periods. Repeat applications are to be made at two to three week intervals during each adult flight period. The proposed methods of application are via ground boom sprayer, aerial equipment (e.g., helicopter) or through irrigation equipment (i.e., chemigation).

Based on the toxicological profile of the active ingredient, a quantitative estimate of exposure was not required for this product. Exposure to the applicator could occur during mixing, loading, application, cleanup and repair. Exposure would be predominantly dermal.

Re-entry exposure is considered to be negligible due to the rapid dissipation of the product.



## 4.2 Risk assessment

Based on the toxicological profile of the active ingredient, it is concluded that use of the proposed product is not likely to present a risk to workers provided the label specifies appropriate personal protective equipment.

The precautionary statements should read: “During mixing, loading and application, personnel should wear long-sleeved shirt, long pants, shoes and socks. In addition, chemical-resistant gloves and goggles should be worn during mixing, loading, cleanup or repair activities.”

## 5.0 Food residue exposure

The PMRA has no objections to the registration of Bedoukian cis-11-tetradecenyl acetate technical pheromone or 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm, since neither the technical grade active ingredient or the end-use product are considered to pose any significant residue concerns. Furthermore, no ADI or ARfD were established for Z-11-tetradecenyl acetate due to the inherent lack of toxicity of this compound. Therefore, it is unlikely that this pheromone will pose any dietary concerns to any segment of the population.

## 6.0 Environmental assessment

Bedoukian cis-11-Tetradecenyl Acetate Technical Pheromone is a compound proposed for use in the end-use product, 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm, to be used in cranberry fields. The product is a sprayable microencapsulated formulation (containing 20 % a.i.) to be diluted in water and applied by aerial or ground equipment or through chemigation. The rate of application is to be 44 g a.i./ha (equivalent to 222 mL product/ha).

According to the information submitted by the applicant, the area of intended use would be approximately 1671 ha. The active ingredient is currently registered in Canada under the Import for Manufacturing and Export Program (Pest Control Product Registration Number 25246). Also, the active is a component of a pheromone blend registered as Isomate-GBM Grape Berry Moth Pheromone (Pest Control Product Registration Number 25147). The subject product is registered in the U.S. (EPA Registration Number 52991-7).

The submission for the subject products encompassed a reduced data set consistent with the PMRA Regulatory Directive Dir97-02 *Guidelines for the Research and Registration of Pest Control Products Containing Pheromones and Other Semiochemicals*. Subsequently, the PMRA conditionally accepted waivers for these data.

Upon further review of these waivers, the PMRA concurs with the submitted rationales that the

subject products would not pose an appreciable risk to aquatic invertebrates and fish, based on the proposed use and an exposure assessment using an elevated rate of application, and a maximum exposure scenario in which the encapsulated pheromone was released instantly in the water body. An assessment of the potential of the end-use product to form a film and surface coverage on water (thus, reducing the transmission of oxygen) following application at an elevated rate also indicated that the product would not present a risk.

## **7.0 Value assessment**

### **7.1 Intended uses**

3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm is a microencapsulated formulation containing 20% of the active ingredient Z-11-tetradecenyl acetate. The end-use product is proposed for control of blackheaded fireworm in cranberry fields through mating disruption. The product is to be applied at a rate of 222 mL of product (44 g a.i.) per hectare just prior to the start of the spring (first generation) and summer (second generation) moth flight periods. Repeat applications are to be made at two to three week intervals during each adult flight period based on monitoring for moths with pheromone traps and routine inspection of foliage and fruit for the presence of larvae and/or damage. Application is permitted by ground boom sprayer, aerial equipment (e.g., helicopter), or through irrigation equipment (i.e., chemigation). Since 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm acts on the adult moth stage through mating disruption, the pheromone must be present in the field throughout the adult moth flight periods at sufficient levels to mask the natural pheromone produced by female moths.

### **7.2 Description of pest problem**

The blackheaded fireworm overwinters in the egg stage on the underside of cranberry leaves. Eggs hatch from mid-April to early May in western Canada, later in central and eastern Canada. Feeding by first generation larvae on the leaves and flowers of the terminal buds can affect yield by reducing the number of flowers available for pollination. Moths of the first generation emerge from late May through to the end of June in western Canada and about a month later in central and eastern Canada. Male moths locate the females through pheromone communication. Moths typically mate within a day or two after emergence and the female moths lay eggs within one to three days of mating. Second generation larvae feed on the leaves, flowers and berries. Damaged foliage dries and takes on a scorched appearance. If left untreated, second generation larvae can damage fifty percent or more of the foliage in a field, which can result in a significant reduction in fruit development and yield. A third generation of fireworm can occur if autumn temperatures are warm. The cranberry industry has a very low tolerance for larval feeding on berries destined for the fresh market. A few damaged berries can cause the entire harvest to be used for juice instead of the fresh market, resulting in a reduction in return on the crop for the grower.

### 7.3 Efficacy trials

Results were submitted from field trials conducted in 1996 and 1997 in British Columbia, Washington and Wisconsin, which assessed the efficacy of 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm in cranberry fields. Efficacy was assessed by placing pheromone-baited traps in the treated and untreated plots and recording trap catches of male moths on a weekly basis following application. The treatment is assumed to be effective if few or no male moths are caught in the traps in the treated plots and many male moths are caught in the untreated plots. A reduction in trap catches in the treated plots reflects disruption of pheromone communication by male and female moths. Results from the efficacy trials are briefly summarized below:

**1996 Trials:** Field trials were conducted in 1996 at sites located in Washington (three sites) and Wisconsin (three sites). In these trials, two to three applications of 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm were made to each treatment plot at a rate of 89 g a.i./ha/application. The treatments were applied either by helicopter, mist blower or through the irrigation system (chemigation) and were timed to coincide with the first and second moth flight periods. At the sites in Washington, weekly trap catches of male moths in the treated plots were reduced by 90–100% throughout the season compared with the untreated plots, suggesting that the treatment was effective in disrupting pheromone communication. Results were more variable at the Wisconsin sites with reductions in trap catches ranging from near zero at one site to 85–95% at another site. The variability in performance of treatments at the Wisconsin sites could be explained in part due to the treatments being applied too early at some sites (e.g, about three weeks prior to beginning of moth flight period), or possibly due to very high moth populations at some sites.

**1997 Trials:** Efficacy field trials were conducted in 1997 at sites located in British Columbia (two sites), Washington (three sites) and Wisconsin (three sites). In these trials, application rates of 89 and/or 44 g a.i./ha/application were evaluated. One to four applications were applied to coincide with the first and second moth flight periods. In seven of eight of the sites, trap catches of male moths were reduced by 75.7–100% following treatment with 3M MEC Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm compared with untreated plots. Trap catches of male moths were significantly reduced for about three weeks following application at the sites in British Columbia and Wisconsin, and for about five weeks after application at the sites in Washington. Thereafter, trap catches increased considerably in the treated plots, suggesting that the effectiveness of the treatment in disrupting pheromone communication had worn off by that time. Treatments at a rate of 44 g a.i./ha were similar in duration and effectiveness to 89 g a.i./ha in trials that directly compared the performance for both rates. Treated and untreated fields were also assessed for larval populations following the pheromone treatment. There was no significant correlation between reductions in trap catches of male moths and subsequent reductions in larval populations in the treated fields. However, the study reports stated that this may have been due to difficulties that were encountered in assessing larval populations (possibly due to limitations in sampling techniques) rather than an indication that the pheromone treatments were ineffective in disrupting mating.

#### **7.4 Adverse effects to crop (phytotoxicity)**

No adverse effects to the treated crop were observed in the efficacy field trials conducted with 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm.

#### **7.5 Alternatives**

Currently, only chemical controls are used in practice for control of blackheaded fireworm in commercial cranberry production in Canada. Chemical insecticides, primarily organophosphate and carbamate chemistries, are applied to control each generation of larvae, as necessary. Biological control with parasitoids of blackheaded fireworm has been investigated, but is not used in commercial production. There are also no cultural control practices in use for control of blackheaded fireworm.

#### **7.6 Sustainability considerations**

The mode of action of 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm is through disruption of pheromone communication rather than direct toxicity to the target pest. Pheromone pest control products are generally more target specific than conventional pesticides, are used at concentrations close to those that occur in nature, and tend to dissipate fairly rapidly. For these reasons, it is expected that most pheromone pest control products would pose a low potential risk to human health or the environment compared with conventional pesticides. Although 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm would be an alternative to chemical insecticides currently used for control of blackheaded fireworm, it is likely that its use in a pest management program would be to complement the use of insecticide treatment rather than replace chemical insecticides completely. For example, since 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm targets the adult moths, it is not be an option for control of the overwintering generation of larvae.

#### **7.7 Value conclusions and recommendations**

The available efficacy data suggest that the product is effective in disrupting pheromone communication in male moths when applied during the moth flight periods. However, due to difficulties encountered in sampling for larvae following treatment, there was no significant correlation between reductions in trap catches of male moths and reductions in subsequent larval populations in the submitted studies.

3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm is a potentially useful tool in the management of blackheaded fireworm in commercial cranberry fields. Although 3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm would be an alternative to chemical insecticides currently used for control of this pest, it is likely that its use in a pest management program would be to complement the use of insecticide treatment rather than replace chemical insecticides completely.

## **8.0 Proposed regulatory decision**

The Agency has established, pursuant to Section 13 of the Pest Control Products Regulations, interim registrations (time-limited to December 31, 1999) of the technical grade active ingredient (Bedoukian cis-11-Tetradecenyl Acetate Technical Pheromone, Registration Number 25879) and the associated end-use formulation (3M Sprayable Pheromone for Mating Disruption of Blackheaded Fireworm, Registration Number 25880), and is open to comments on their future regulatory status.