National Organic Standards Board Crops Subcommittee Pear Ester Petition August 6, 2024

Introduction:

In September 2023, the National Organic Program received a petition from Trece Incorporated requesting the addition of pear ester (i.e., Ethyl-2E,4Z-Decadienoate), a semiochemical material, to the National List as a synthetic allowed for use in crop production [§ 205.601]. Semiochemicals are bioactive molecules released by an organism to signal or provoke a behavioral or physiological response (Klassen et. al., 2023). Signaling may be between members of the same species or between two or more distinct species. Pheromones, kairomones and allomones are sub-categories of semiochemicals. Pear ester was previously allowed for use in organic crop production under the synthetic pheromone classification until its correct reclassification as a kairomone. Even though pheromones and kairomones are both semiochemicals, they differ in a couple of significant characteristics. Pheromones are volatile chemicals produced by a given species to communicate with other individuals of the same species to affect their behavior (EPA, 2011). A 2012 technical report on pheromones stated that they may signal dominance status, sexual receptivity, danger, and other information. Kairomones are chemical signals produced by plants or other organisms that are detected by a distinct species, often insects. They convey communication signals between two or more different species (Klassen et al., 2023). Detection of kairomones leads to a fitness benefit (to the receiving organism); these benefits include avoiding a predator or finding a suitable host plant. Pear ester was first isolated from ripe Bartlett pears (Jennings et al., 1964). The original experiments that identified pear ester as a kairomone used pear extracts (Light et al., 2001). Commercial pear essence contains about one-third pear ester by weight (Tucker et al., 2003). Pear ester used in commercial pest control formulations is produced by chemical synthesis (Light et al., 2017; Trécé, Inc., 2023; Tsubi et al., 1993). The high solubility of pear ester in lipid-like substances allows it to penetrate codling moth receptor structures with ease. Because of its volatility, pear ester dissipates quickly in the environment. Manufacturers encapsulate volatile components of spray formulations to limit volatilization and produce products that have a lasting effect (US EPA, 2013) [2024 TR 86-88].

The proper classification of pear ester as a kairomone instead of a pheromone rendered its continued use under the pheromone category in organic crop production, untenable (Trécé, Inc., 2023). This discussion document covers the petition to add pear ester, a kairomone, to the National List under 7 CFR 205.601 (synthetic material allowed in organic crop production). The petition is aimed at providing organic crop producers with pest management tools that were available to them prior to the reclassification of pear ester as a kairomone instead of a pheromone.

The current discussion document covers pertinent information from the <u>2024 technical report (TR)</u> on the human, environmental, and ecological health, as well as the economic impact of the synthesis and application of pear ester in organic crop production.

Synthesis of Pear Ester

Pear ester is produced by a condensation reaction between two chemicals that are by-products of petroleum processing. The prevalent process for manufacturing pear ester is the condensation reaction between the eight-carbon allyl alcohol, oct-1-yn-3-ol (CAS No. 818-72-4), and triethylorthoacetate (CAS No 78-39-7). The condensation product is heated with propanoic acid as a catalyst, and the subsequent Johnson-Claisen rearrangement gives ethyl 2E, 4Z-decadienoate. It is a convenient one-step synthesis with good yields (Trécé, Inc., 2023; Tsubi et al., 1993).

Approved Legal Uses of Pear Ester:

Pear ester appears on the FDA list of Substances Added to Food (*formerly EAFUS*) for use as a flavoring agent or adjuvant food additive (US FDA, 2024). The EPA has registered pear ester formulations for pest management. This behavior-altering chemical (i.e., semiochemical) is particularly useful in the management of the codling moth, *Cydia pomonella* – an economically significant pest that principally affects apple, pear, and walnut crops (Trécé, Inc., 2023).

The codling moth has four life stages: adults, eggs, larvae, and pupae. The life cycle is synchronized with the weather by larval diapause, a form of hibernation. Larvae go into diapause in August and over winter in this form. In late winter, they pupate, and emerge as adults in the early spring (Quarles, 1997; Steiner, 1940; Van Leeuwen, 1940; Witzgall et al., 2008) [2024 TR 101-104]. Within a week after emergence from pupae as adults, mating is complete. Females lay up to 100-130 eggs, as isolated eggs, never as clusters, near developing fruit. Most of the reproductive activity associated with this first flight of adults is over by the end of April; there are a total of three flights each year in most areas (Quarles, 1997; Steiner, 1940; Van Leeuwen, 1940; Witzgall et al., 2008) [2024 TR 106-109]. The larvae damage fruit by chewing their way inside. Once inside, the fruit is unmarketable (Caprile & Vossen, 2011).

Pear Ester and Mating Disruption

Pear ester is used as part of codling moth mating disruption treatments. Although pheromones alone are used, pheromones combined with a simultaneous release of pear ester may be more effective (Light et al., 2017) (see also *Focus Question #1*) [2024 TR 151-153]. These mating disruption treatments can be applied in two ways: via plastic dispensers or as microencapsulated cover sprays (University of California Statewide Integrated Pest Management (IPM) Program, 2015). PVC dispensers have two reservoirs, one for the codling moth sex pheromone codlemone, (E, E)-8,10-dodecadien-1-ol (CAS No. 33956-49-9), and one for pear ester. Both materials passively diffuse from the dispensers into the air. There are standard dispensers and larger, "meso" dispensers that hold more active ingredient (Trécé, Inc., 2023) [2024 TR 111-112].

Mating disruption dispensers loaded both with codling moth sex pheromone and pear ester can be more effective for mating disruption than dispensers with pheromone alone (Light et al., 2017). Microencapsulated sprays of pear ester can also improve the effectiveness of mating disruption, make some insecticides more effective (Light et al., 2017), and can even prevent fruit damage as a standalone spray [2024 TR 161-167].

Pear Ester and Monitoring/Timing

Pear ester can be used as a lure in traps to monitor populations of codling moth in orchards (Light et al., 2001). Successful monitoring can then be used to determine the timing and set action thresholds for treatments (A. L. Knight & Light, 2005) [2024 TR 115-117].

Farmers and pest control professionals hang monitoring traps in orchards each year before mating populations of the codling moth emerge from their pupae. This helps to determine the "biofix point," which is the date of the first appearance of a codling moth in a monitoring trap. The biofix point is particularly important because mating disruption programs against the pest are not effective when commenced later than the first detection of the pest. Once mating disruption has started, monitoring traps with pheromone lures are no longer useful. At this point, the air is saturated with pheromones, and moths cannot find the traps. According to Integrated Pest Management experts, traps containing pear ester, and perhaps other kairomones, are essential to determine when to apply treatments (Caprile & Vossen, 2011; University of California Statewide IPM Program, 2015). Traps baited with pear ester lures can also be used for mass trapping, to remove egg-laying females from orchards (A. L. Knight et al., 2022). It is extremely important to note that unlike pheromone traps, monitoring traps containing kairomones such as pear ester make it possible for farmers and pest control professionals to check the effectiveness of mating disruption (A. Knight, 2010; A. Knight et al., 2014; A. L. Knight et al., 2019; Trécé, Inc., 2023). The kairomone improves codling moth monitoring, enhances mating disruption, disrupts egg laying, and confuses moth larvae and thereby make it harder for them to find, infest, and damage host fruits.

Monitoring to Determine Effectiveness of Mating Disruption

When used in combination with pheromones (e.g. codlemone) in mating disruption dispensers, or in microencapsulated sprays, pear ester can enhance the effectiveness of mating disruption (Light et al., 2017). The performance of mating disruption techniques can be evaluated in many ways. Monitoring traps baited with codlemone pheromone are used most often. The fewer moths trapped, the more effective the disruption. Elevated levels of the mating disruption pheromone make it difficult for males to locate the traps, resulting in trap shutdown. Monitoring traps baited with tethered females are also used (Stelinski et al., 2013). A more conclusive result is achieved by using monitoring traps baited with pear ester to catch females. The fewer mated females caught, the more effective the mating disruption (A. L. Knight, 2006). A practical measure is the amount of fruit damage. The less damage, the more effective the mating disruption. Of all the possible measurements of effectiveness, the easiest is trap shutdown, and the most important, from a grower standpoint, is the amount of fruit damage (Kovanci, 2015) [2024 TR 342-354-117].

Limitations of Mating Disruption

Even though mating disruption treatments release substantial amounts of pheromone, which make it harder for males to find females, its effectiveness is reduced by large initial codling moth populations. In situations of high population density, males can find females with visual cues. Farmers and pest control professionals sometimes use an insecticide treatment before starting a mating disruption program (Witzgall et al., 2008) to reduce population densities, thereby rendering mating disruption interventions more effective [2024 TR 358-362].

Immigration of already mated females from a nearby orchard can also overcome mating disruption treatments. This is because these females do not release pheromones to attract males for mating purposes. A buffer zone of 400 m and border sprays of insecticides help in limiting immigration of this insect pest (Rothschild, 1982) [2024 TR 364-366].

Sex pheromone treatments need to have uniform concentration throughout an orchard. If there are dead spots in the distribution, mating can occur in that area. There can also be problems with patchy codling moth distribution. Females prefer to lay eggs on trees that have the most fruit. When larvae pupate, males are already in the area waiting for females to emerge (Light et al., 2017; Witzgall et al., 2008) [2024 TR 368-371].

It is extremely important to note that mating disruption is not equivalent to mating prevention. According to Light et al. (2017), experiments have shown untreated apple orchards have 73-90% mated females, and orchards utilizing conventional pest controls have >77% mated females. When mating disruption treatments use pheromone only, 58-85% of females are mated, whereas mating disruption with combined pheromone and pear ester results in 64-71% mated females (Light et al., 2017) (see *Combinations of the Substance*) [2024 TR 375-377]. As stated earlier, mating disruption does not signify mating prevention. A simple delay in mating can reduce pest populations and fruit damage. A delay in female mating by more than two days results in significant reduction in population density because the female is older and lays fewer eggs. Fewer eggs results in less fruit damage (Jones et al., 2008). Witzgall et al. (2008) reports damage levels of 0.03 to 0.8% for California apple orchards using area-wide pheromone mating disruption.

Pear ester is a useful addition to IPM programs because it gives another layer of protection. If moths successfully mate and start laying eggs, pear ester confuses females that prefer to lay eggs near ripening fruit. This is because the insects identify ripening fruit partly using the pear essence (i.e., pear ester). Misplaced eggs lead to less fruit damage (Hughes et al., 2003). If eggs successfully hatch, larvae are also confused by pear ester and have trouble finding their way to fruit (Light & Beck, 2012) [2024 TR 385-389].

Human Health Impacts

Pear ester is a Generally Recognized as Safe (GRAS) food additive. In 2013, the EPA exempted it from the need to establish food tolerance for residues in or on food crops at 40 CFR 180.1323. The EPA concluded that, "there is a reasonable certainty that no harm will result to the U.S. population from aggregate exposures to ethyl-2E-4Z-decadienoate (pear ester)" (78 FR 53051, August 28, 2013). [2024 TR 889-892]. Pear ester has low acute toxicity to mammals, and the oral LD₅₀ for rats is 4,027 mg/kg.¹ This number means pear ester is nearly non-toxic. Additionally, pear ester is an FDA approved food additive, and average human consumption in the U.S. is about 3 µg per day (US EPA, 2013). According to the EPA, pear ester also has low chronic toxicity, and is not a likely developmental toxicant, or a mutagen. It is not on the EPA list of carcinogens, or on the IARC carcinogen list. The EPA reported in 2013 that pear ester had not been evaluated for endocrine disruption [2024 TR 876-884].

The <u>2024 technical report</u> on pear esters found no publications indicating harm to humans from pear ester or polyamide particulates. But according to the pear ester safety data sheet, pear ester may cause allergy or asthma symptoms or breathing difficulties if inhaled. Contact with skin or eyes may cause irritation. It must be noted that the food tolerance exemption provided by the EPA does not include an evaluation for occupational exposure. The maximum label amount is about 400 µg pear ester/day, which is well below the acute toxicity of 4027 mg/kg. Pear ester vapors are not likely a health problem for orchard workers [2024 TR 910-911].

Exposure to Polyamide Particulates

Sprays of about 30 g/ha decadienoic acid (DA) ethyl ester (i.e. pear ester), commercially known as DA MEC[™], are applied to tree canopies with an air blast sprayer (Cidetrak, 2020). Even though exceedingly tiny amounts of DA MEC[™] are used, the sprays contain a large number of small polyamide particles. Each tree canopy receives about five hundred million microencapsulated pear ester particles. There might be a respiratory hazard from inhaling the plastic microparticles when the spray is applied by air blast sprayer to individual trees. However, effects of exposure to the polyamide spherical capsules in the spray has not been evaluated by the EPA. Given the 4-hr re-entry restriction, the greatest acute risk is probably during spray applications with an airblast sprayer. But the DA MEC[™] label does not require respiratory protection for workers (Cidetrak, 2020) [2024 TR 911-921]. It is important to note that the maximum 8-hr worst case chronic exposure would be about 0.0357 mg/m³ or 36 µg/m³. This exposure is below the U.S. 24-hr particulate standard of 150 µg/m³ for PM 10 (89 FR 16202, May 6, 2024) [2024 TR 941-942].

Given the fact that sprayable microecapsulated pheromone particles can be washed out of tree canopies by wind, rain, and overhead irrigation sprays, pear esters are assumed/expected to meet the same fate.

Environmental and Ecological Health Impacts

The EPA did not require testing for bird, fish, and aquatic invertebrate toxicity because pear ester is expected to quickly disperse and degrade in the environment. However, the pear ester safety data sheet from Boudakian Research (Boudakian Research, 2023) states that pear ester is "very toxic to aquatic life with long lasting effects." [2024 TR 650-653]. The substance is, however, exempt from testing for bird, fish, and aquatic invertebrate toxicity. According to the safety data sheet, pear ester is a marine toxicant and hazard (Boudakian Research, 2023) [2024 TR 862-865]. Environmental damage may be mitigated by the low application rate of 12 g DA MEC[™]/acre or 30 g/ha. That is about 0.27 mg DA MEC[™]/ft². That is a small amount, but each ml of the usual diluted field spray contains about 260,000 particles (Light & Beck, 2010). [2024 TR 864-865]. Once applied, microcapsules probably stay on the leaves until dislodged by wind and rain, which is the case for microencapsulated sprayable pheromones (A. L. Knight et al., 2004). When particles are dislodged by rain, they likely become part of runoff from an orchard (Trécé, Inc., 2023) [2024 TR 862-865]. Once the microencapsulated particles reach water, they might be ingested by fish or other aquatic creatures. No density information is given (Light & Beck, 2010), but likely the polyamide particles are less dense than water. The pear ester contained in the microparticles is an aquatic hazard (Boudakian Research, 2023) [2024 TR 869-870]. The 2024 technical report found no information on the environmental effects of pear ester polyamide microcapsules. There is no published

information of the effects of these particles on earthworms. If earthworms ingest them, birds would be exposed by eating earthworms. However, again, the amounts of pear ester involved are exceedingly small [2024 TR 865-867]. We found no information on whether the polyamide capsules are a hazard. The EPA did not require the product manufacturer to submit environmental toxicity tests of microencapsulated pear ester (US EPA, 2013) [2024 TR 872-874].

Economic Impacts

Available data and evidence show that pear ester exerts significant economic impacts on pear and apple growers. The impact is exerted through pear ester's documented direct impact on mass trapping, mating disruption, and proper timing of treatments (including pesticide applications), all of which impact the level of fruit damage. The improved effectiveness of traps and monitoring tools when pear ester is combined with pheromones is well documented. A 2015 study by Kovanci reported that more mated females (70%) were trapped with microencapsulated pear ester compared to microencapsulated pheromone DA MEC[™] than with PH MEC (57.5%). There was a 54% reduction in late season pre-harvest fruit damage due to the use of microencapsulated pear ester alone, but reduction with microencapsulated pheromone or the combo was 72%. A 93% reduction in fruit damage was recorded by Ultra love volume (ULV) combo sprays. Combo sprays were more effective than sex pheromone alone in reducing fruit damage only with ULV applications (Kovanci, 2015). The author also reported that application of microencapsulated pear ester sprays alone can reduce fruit damage and increase larval mortality in apple and pear. Reduced fruit damage has direct economic impacts on producers of these fruits [2024 TR 413-420].

Performance of Alternatives

It is important to note that codling moth management performance of natural alternatives to synthetic pear ester tend to be enhanced when combined with the synthetic product. Products such as granulosis virus, Spinosad, BT products, and the use of degree day methods are employed against the codling moth. The performance of these alternatives is, however, enhanced by pear ester in monitoring traps to determine the biofix point and, thus, the correct and most effective timing of pesticide applications.

The NOSB has deemed the 2024 TR sufficient and has used the document as a basis for the current discussion document for use in the Fall 2024 meeting. Comments received so far on pear ester have been positive.

Subcommittee Next Steps

The Crops Subcommittee (CS) will continue its deliberations on pear ester through the presentation of a discussion document at the Fall 2024 NOSB meeting. A subsequent proposal will factor in public comments received. The CS will seek additional information on the reasons behind the EPA not requiring testing for fish and aquatic invertebrate toxicity given the fact that the safety data sheet for pear ester states that it is a marine toxicant and hazard (Boudakian Research, 2023).

Questions for Stakeholders

The CS has the following specific questions for stakeholders and, as always, welcomes any additional perspectives, solutions, and information related to inert ingredients used in organic pesticides.

1. Are there any human health and environmental concerns pertaining to pear ester that the CS needs to consider in its evaluation of the petition to add it to the National List?

Subcommittee Vote:

Motion to accept the discussion document on the petition to add pear ester to the National List as a Synthetic Substance Allowed in Pesticides for use in Organic Crop Production Motion by: Franklin Quarcoo

Seconded by: Wood Turner Yes: 8 No: 0 Abstain: 0 Recuse: 0 Absent: 1