Methyl Benzoate as Insecticide

Subjects: Entomology

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The methyl benzoate is an effective pesticide against a range of different agricultural, stored product, and urban insect pests. Methyl benzoate has several important modes of action, including as a contact toxicant, a fumigant, an ovicidal toxin, an oviposition deterrent, a repellent, and an attractant.

methyl benzoate | biopesticides | biorational pesticides | natural product | environmentally-friendly | Insect pest management | sustainable agriculture

1. Introduction

The primary challenge for human societies has always been sufficient food. However, pests, diseases, and weeds have destroyed a considerable portion of the global annual crop production [1]. It has been a long time now that synthetic chemical pesticides have played an important role in controlling insect pests in crops [2][3]. Nevertheless, widespread use of these pesticides can lead to pesticide resistance, environmental degradation, contamination of underground water and soil, harming ecosystems and nontarget species, including humans [4][5][6][7][8]. Therefore, curbing synthetic pesticide use is an urgent matter [9][10][11][12][13][14][15][16].

Some botanical pesticides (BPs) are biorational pesticides as they are less harmful to human health and the environment than synthetic pesticides [17][18][19][20][21]. BPs are derived from plant species in various families. They are obtained either as plant extracts or as essential oils (EOs) [3][22]. Presently, at least four kinds of BPs are widely used for insect control: pyrethrum, rotenone, neem, and EOs. These widely used BPs are also utilized along with three others that are more limited in use. They include ryania, nicotine, and sabadilla [23][24][25]. Aromatic plants generate EOs as secondary metabolites, which are the most common forms of BPs. Thus, they are composed of complex mixtures of chemical constituents and components with various functional groups (e.g., monoterpenes, sesquiterpenes, phenylpropanoids) [10][19][26]. Different EOs have proven beneficial for pest control, and several studies have been undertaken [3][18][27][28]. The major constituents of EOs often display biological activity, such as insecticidal or ovicidal effects on insects.

Additionally, they demonstrate antibacterial effects against microbes [29][30][31][32]. Generally, EOs are less harmful to nontarget species than most conventional synthetic pesticides. Therefore, the Environmental Protection Agency (EPA) and Food and Drug Administration (FDA) of the USA accepted them as safe for human consumption [33][34][35].

Some commercially available products derived from EOs or their constituents (e.g., oil products of neem, garlic, thyme, limonene, linalool, carvacrol, nicotine, and rotenone) are used in agriculture and urban pest management. Nonetheless, these products command only 1% of the global pesticide market [10][24][36]. Therefore, a significant opportunity exists in pest management to develop BPs as environmentally friendly tools.

EOs are volatile aromatic liquids extracted from different plant materials, such as flowers, leaves, and fruits [37][38]. Hardy and Michael [39] were among the earliest scientists to identify volatile compounds in feijoa (*Feijoa sellowiana* Berg [Myrtales: Myrtaceae]). They discovered that methyl benzoate (MBe) was the dominant active component of the aroma, accounting for more than 90% of the EO in feijoa. Moreover, MBe has been found in the EOs of many other plants, including jonquil (*Narcissus jonquilla L.*), tuberose (*Polianthes tuberosa L.*), ylang-ylang (*Cananga odorata Lam.*), ginger lily (*Hedychium coronarium Koenig*), jasmine (*Jasminum grandiflorum L.*), Bakul (*Mimusops elengi L.*), champaca (*Michelia champaca L.*), and pomelo (*Citrus grandis L.*) [40][41][42][43]. Therefore, MBe occurs widely in nature [44]. Recently, studies have identified the volatile component of MBe from fermented apple juice [13][14][45]. Furthermore, MBe derived from fermented apple juice has significant pesticidal activity against several insect pests, including spotted wing drosophila (*Drosophila suzukii* Matsumura [Diptera: Drosophilidae]), marmorated stink bug (*Halyomorpha halys Stål* [Hemiptera: Pentatomidae]), tobacco hornworm (*Manduca sexta* L. [Lepidoptera: Sphingidae]), diamondback moth (*Plutella xylostella* L. [Lepidoptera: Plutellidae]), and gypsy moth (*Lymantria dispar* L. [Lepidoptera: Erebidae]) [13][14].

2. Natural Function and Sources of Methyl Benzoate

MBe ($C_8H_8O_2$; molecular weight 136.15 gm/mol) is a volatile ester that occurs naturally as a metabolite in plants [44]. Various plants release MBe as a pleasant odor in nature [46], including flowers [47][48][49] and fruits [50][51][52][53][54]. Lepidopteran insects can be attracted to the floral scent of MBe, e.g., some hawk moths [55][56]. In addition, MBe is emitted from rice plants damaged by the larvae of the fall armyworm (FAW), *Spodoptera frugiperda* (Smith) (Lepidoptera: Noctuidae) [57]. FAW-induced volatiles, including MBe, are highly attractive to females of the FAW parasitoid, *Cotesia marginiventris* (Cresson) (Hymenoptera: Braconidae) [57]. Silva et al. [58] reported that MBe occurs at significantly higher levels in the emissions of plants infested with the tomato leaf miner, *Tuta absoluta* (Meyrick) (Lepidoptera: Gelechiidae). MBe is particularly abundant in the aromas emitted from petunias (*Petunia* spp.) and snapdragons (*Antirrhinum majus* L.), functioning as a long-range attractant to lure bees such as the orchid bee, *Euglossa cybelia* (M.) (Hymenoptera: Apidae), for pollination [44][59][60][61][62][63]. In addition, MBe is a semiochemical that affects both intraspecific and interspecific interactions in a number of insect species [64].

MBe is recognized for its sweet, balsamic, and spicy floral odor. It is used as a fragrance ingredient and preservative in various personal care products, such as shampoos, shower products, face/neck products, liquid soaps, mouthwash, perfumes, hair colorants, and cosmetics [65][66]. MBe has low-to-moderate human toxicity by ingestion and inhalation. Hence, it is approved by the US FDA (21 CFR 172.515; FDA 2015) and the European Union (EU Regulation 1334/2008 & 178/2002; EU 2015) for use as a food-grade flavor ingredient. George [67] reported that MBe is used as a flavor ingredient in some chewing gums in concentrations of up to 45.63 mg/kg. Additionally, MBe biodegrades slowly in the atmosphere [68].

3. Extraction, Biosynthesis Pathway, and Chemical Properties of Methyl Benzoate

Extraction of essential oil from the peel of the aromatic fruit feijoa was done according to a procedure published by Peng et al. [37]. Extraction was optimized using steam distillation and hydro-distillation. Volatile and active aroma compounds, such as MBe, were characterized by gas chromatography-mass spectrometry and headspace solid-phase microextraction combined with gas chromatography-olfactometry-mass spectrometry. In a procedure published by Feng et al. [45], the collection of MBe from fermented apple juice was explained.

MBe is a common component of floral scents, identified in more than 80 different plant species [55]. Nevertheless, the pathway for its biosynthesis is vastly unknown in most species, especially in monocots [69]. MBe is formed through methylation of benzoic acid, the biosynthesis of which is derived from the aromatic amino acid L-phenylalanine, an end product of the shikimate pathway [70]. In plants, benzoic acid biosynthesis occurs through multiple routes that arise from the phenylpropanoid pathway. It starts with the deamination of l-phenylalanine to trans-cinnamic acid by phenylalanine ammonia-lyase [70]. The peroxisomal β-oxidation pathway plays a vital role in the catabolism of fatty acids in animals, fungi, and plants [71]. In plants, β-oxidative pathways are involved in the biosynthesis of numerous primary metabolites, including benzoic acid [72]. The flowers of *Petunia hybrida* cv (Mitchell) emit high levels of benzenoid volatiles [73][74]. Recently, the core β-oxidative pathway of benzoic acid in this species was fully explained [72][75]. First, the committed step in this pathway is converting trans-cinnamic acid to its CoA thioester, cinnamoyl-CoA, catalyzed in petunias by a peroxisomal cinnamate-CoA ligase [76]. MBe is formed via a methylation reaction with benzoic acid as a substrate, catalyzed by *S*-adenosyl-l-methionine-dependent benzoic acid methyltransferase [48] (**Figure 1**).

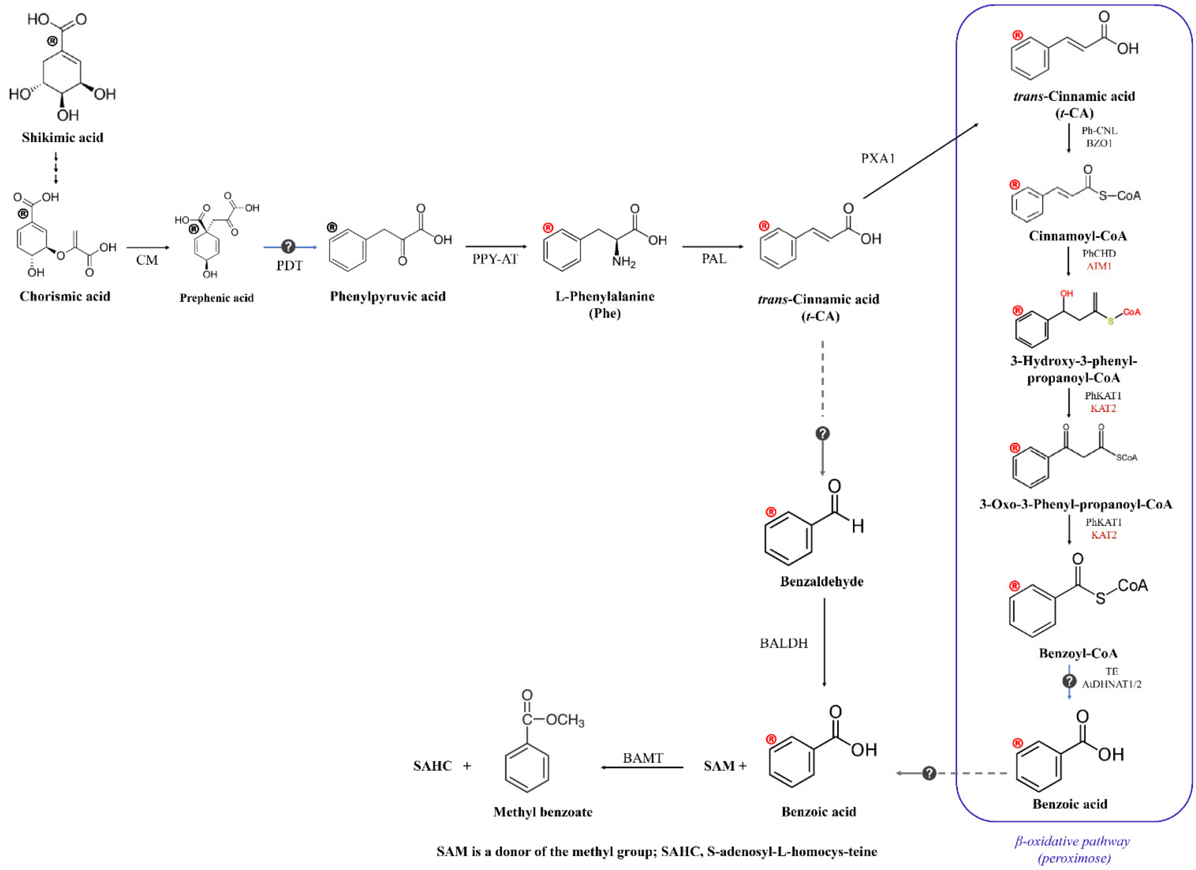

Figure 1. The biosynthesis network for plant benzoic acid. The shikimate/chorismate pathway proposed the biosynthesis of methyl benzoate in plants by the shikimate/chorismate pathway and via phenylalanine. The carboxyl carbon of shikimate is labeled (®), as is the β-carbon of phenylalanine (®). The plant enzymes involved in plant benzoic acid biosynthesis for which genes have been cloned are also indicated. Black and blue arrows show the existence and absence, respectively, of genetic evidence for a given reaction. Black and dark red enzymes indicate the presence and absence, respectively, of biochemical evidence for a given response. Question marks indicate the proposed steps with no available information. CM, chorismate mutase; PDT, prephenate dehydratase; PPY-AT, phenylpyruvate aminotransferase; PAL, l-phenylalanine ammonia-lyase; Ph-CNL, *Petunia hybrida* cinnamoyl-CoA ligase; PhCHD, *P. hybrida* cinnamoyl-CoA hydratase/dehydrogenase; PhKAT1, *P. hybrida* 3-ketoacyl thiolase 1; TE, thioesterase; BALDH, benzaldehyde dehydrogenase; SAM, *S*-adenosyl-l-methionine; BAMT, benzoic acid methyltransferase.

MBe is a colorless liquid with intense floral and cherry aromas. It is soluble in methanol and ethyl ether but insoluble in water [77].

4. Insecticidal Effects of Methyl Benzoate

The toxicity of MBe can be classified by the various ways that it may affect target and nontarget organisms. For example, MBe can act via contact toxicity, fumigant activity, attraction or repellent action, oviposition deterrence, or insect growth regulator effects.

4.1. Contact Toxicants

Contact toxicants act externally to (1) dry the insect body; (2) create a gas-tight film that blocks regular gas exchange; or (3) penetrate the skin and affect the nervous system, etc., including through ovicidal activity (that is, killing the eggs by disrupting embryonic development and preventing hatching). When used on different arthropod pests, including sap-sucking hemipterans and phytophagous mites, MBe demonstrates potent contact toxicity [13][14][78][79][80]. The contact toxicity of MBe has been assessed using different methods [13][14][78][79][80][81]. However, the direct topical application of the product to the body surface of insects with a hand-held sprayer or syringe has been the most commonly used method.

The contact toxicity of MBe has been tested against the sweet potato whitefly, *Bemisia tabaci* (Gennadius) (Hemiptera: Aleyrodidae), a primary pest of many agricultural and horticultural crops worldwide [82][83]. Mostafiz et al. [79] reported that the direct spray application of 1% MBe to adults of *B. tabaci* caused 100% mortality 24 h post-treatment (**Figure 2**).

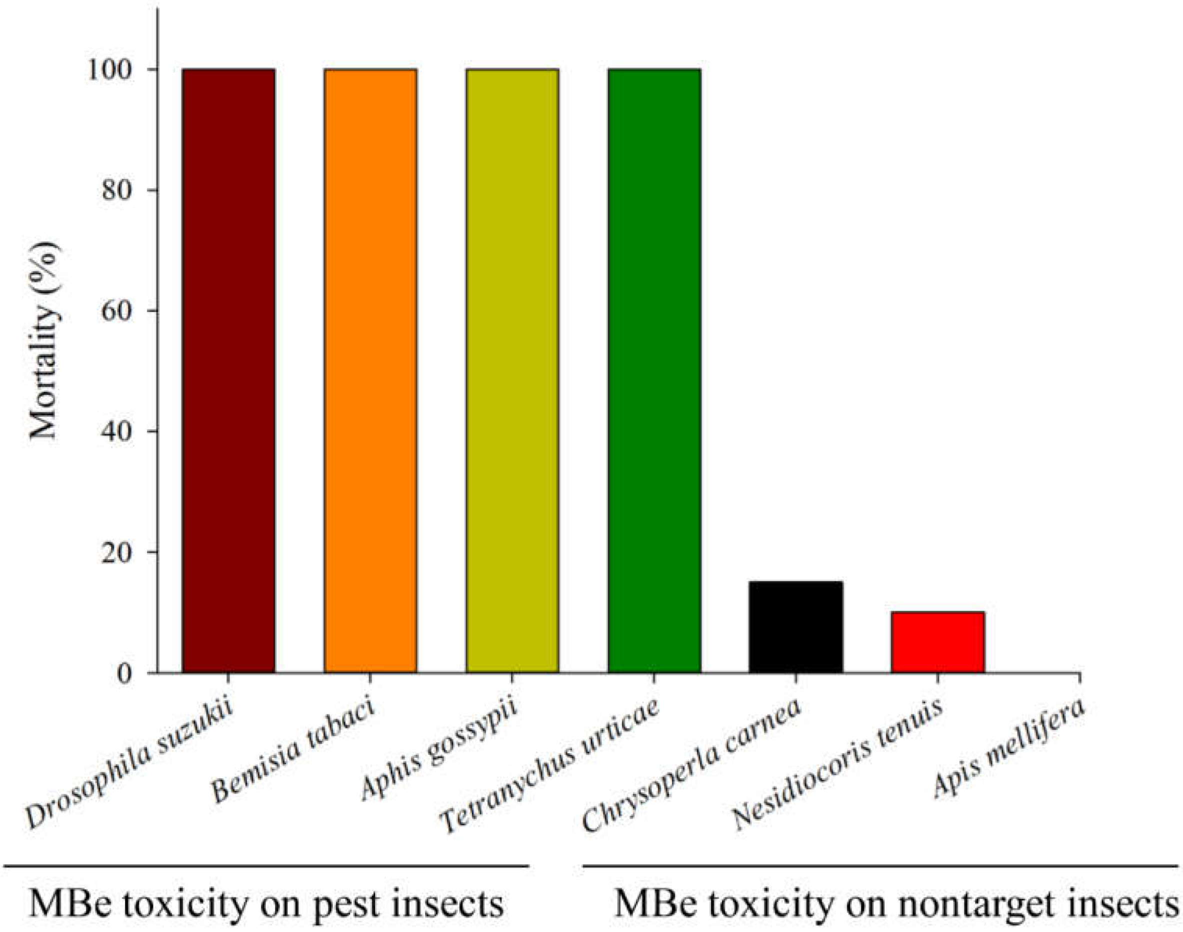

Figure 2. Toxicity differences of methyl benzoate against various arthropod pests and nontarget organisms: Mortality data from 1% MBe concentration after 48 h of exposure.

The eggs and nymphs of *B. tabaci* are found on the underside of crop leaves. Application of 1% or 2% MBe via the leaf-dipping method, which ensures good coverage of the underside, caused a 75.6% and 94.2% reduction in egg hatch rate, respectively [79]. Similarly, adult eclosion following leaf-dipping with 1% MBe was reduced by 93.2% [79]. The lethal median concentration (LC_{50}) values for MBe solutions on eggs, fourth-instar nymphs, and adults of *B. tabaci* were 0.3, 0.2, and 0.2% (*v*/*v*), respectively.

The cotton aphid, *Aphis gossypii* (Glover) (Hemiptera: Aphididae), is a polyphagous pest associated with more than 700 host plants worldwide [84][85]. Using a leaf-dipping assay, Mostafiz et al. [78] reported 100% mortality of third-instar nymphs and adults of *A. gossypii* 24 h after applying 1% MBe solution (**Figure 2**). The LC_{50} values for MBe solutions on nymphs and adults were 0.18% and 0.32% (*v*/*v*), respectively. Moreover, MBe showed acaricidal activity against the two-spotted spider mite, *Tetranychus urticae* (Koch) (Acari: Tetranychidae) [80], which is one of the most destructive pests of ornamental and horticultural plants [86][87]. Egg hatch of this mite was reduced by 76.9% and 92.5%, respectively, in leaf-dipping assays with 0.5% and 1% MBe [80]. However, 24 h after exposure to 0.5 and 1% MBe, the mortality of *T. urticae* adults was 55.3% and 81.3%, respectively. The LC_{50} values for MBe solutions on eggs and adults were 0.27% and 0.38% (*v*/*v*), respectively.

Additionally, MBe induces acute toxicity in other pests, including the invasive fruit fly *D. suzukii*, the stink bug *H. halys*, and the lepidopterans *P. xylostella*, *M. sexta*, and *L. dispar* [13][14]. For example, 100% mortality of *D. suzukii* immature stages (**Figure 2**) was caused by the direct application of 1% MBe to pre-infested blueberries, with no larvae and pupae developing or adult flies emerging after 10 d of incubation at room temperature [14]. Compared with other EOs (α-terpinene, γ-terpinene, terpineol, cineole, and α-pinene), MBe is the most toxic metabolite for *D. suzukii* [14]. Furthermore, when used on *H. halys* nymphs, MBe has shown contact toxicity [14]. For the five nymphal instars tested, the LC_{50} values of MBe ranged from 1.01 to 2.39 µL/vial. In laboratory bioassays (LC_{50} values ranged from 0.26 to 2.70, µL/vial), the toxicity of MBe against nymphs of *H. halys* is comparable to that of two commercial pesticides (acetamiprid and pyriproxyfen) [14].

Feng and Zhang [14] assessed the ovicidal toxicity of MBe in a direct spray bioassay by measuring the hatch rate of eggs of *H. halys*, *M. sexta*, and *P. xylostella*. MBe exhibited ovicidal effects, with LC_{50} values of 0.020, 0.015, and 0.001 mg/cm^2, respectively, for the three species listed. The ovicidal action of MBe was greater than that of a mixture of bifenthrin and ζ-cypermethrin. Reportedly, it was also greater than that of an EO product containing 2-phenethyl propionate and oils of clover, rosemary, and thyme [14]. Feng et al. [13] reported that MBe showed high larvicidal activity against *L. dispar* (LC_{50} = 0.114 mg/cm^2), which was 1.94 times more toxic than acetamiprid (LC_{50} = 0.221 mg/cm^2).

The red imported fire ant, *Solenopsis invicta* (Buren) (Hymenoptera: Formicidae), native to South America but invasive in North America and Asia, is considered one of the world's worst invasive species [88][89]. Recently, Chen et al. [90] demonstrated that contact toxicity to workers of *S. invicta* is due to topical application of MBe, with the highest mortality at a dose of 93.65 µg per ant. Moreover, MBe has demonstrated contact toxicity against the azuki bean weevil, *Callosobruchus chinensis* (L.) (Coleoptera: Chrysomelidae) [81]. Furthermore, Park et al. [81] reported that the topical application of MBe at a dose of 44.81 µg/beetle produced the highest mortality 24 h after treatment.

Recently, Larson et al. [91] reported that MBe displays contact toxicity against adults of *Aedes aegypti* (L.) (Diptera: Culicidae). The results showed that the LD_{50} value for MBe was 45.6 µg per adult female. Mostafiz et al. [92] found that MBe exhibits larvicidal activity against *Aedes albopictus* (Skuse) and *Culex pipiens* (L.) MBe was three times more harmful to *Ae. albopictus* than *Cx. pipiens* based on the findings.

4.2. Fumigant Toxicity

More than 100 species of insects cause significant economic losses to stored products [93][94]. Furthermore, fumigants are commonly used against these challenging pests. Fumigants enter the body as gases via the trachea and may influence the activities of different enzymes in the nervous system, muscular system, fat bodies, or other tissues. Thus, fumigant toxicity is often assessed using impregnated paper, allowing the product's release into the air of a closed experimental chamber [95][96]. The experimental setup uses a sieve or mesh to prevent insects from coming into physical contact with the impregnated paper.

MBe has been shown to possess fumigant activity against various stored product pests [81][90][97][98][99][100]. According to Park et al. [81], MBe exhibited the highest fumigation toxicity against adult weevils of *C. chinensis* at 11.76 mg/L of air. The LC_{50} value was estimated to be 5.36 mg/L.

In treating fire ant mounds, fumigants have been used [101]. Recently, MBe displayed strong fumigation toxicity against workers of the invasive species *S. invicta* [90]. The highest percent mortality of ant workers 24 h after being fumigated with MBe occurred at a dosage of 1.43 µg/mL, with an LC_{50} value of 0.77 µg/mL. Morrison et al. [97] studied MBe as a possible environmentally friendly fumigant for the control of stored product beetles, including *Rhyzopertha dominica* (Fabricius) (Coleoptera: Bostrichidae), *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae), *Sitophilus zeamais* (Motschulsky) (Coleoptera: Curculionidae), and *Trogoderma variabile* (Ballion) (Coleoptera: Dermestidae). Using 1080 mg/L of MBe, *R. dominica* was the most susceptible, followed closely by *T. castaneum*, whereas *S. zeamais* and *T. variabile* were much less susceptible to MBe [97].

The common bed bug, *Cimex lectularius* (L.) (Hemiptera: Cimicidae), whose incidence is on the rise worldwide, is a human health pest [102][103]. Larson et al. [98] reported that MBe caused 97% mortality of adult bed bugs 24 h after fumigation with 7.14 mg/L of MBe in Erlenmeyer flasks (volume ca. 280 mL).

MBe has been examined as a potential fumigant for controlling pests on apples at different temperatures and evaluated treatment effects on postharvest quality [99]. The pest species included western flower thrips, *Frankliniella occidentalis* (Pergande) (Thysanoptera: Thripidae); lettuce aphid, *Nasonovia ribisnigri* (Mosley) (Hemiptera: Aphididae); rice weevil, *Sitophilus oryzae* (L.) (Coleoptera: Curculionidae); and bulb mites, *Rhizoglyphus* spp. (Sarcoptiformes: Acaridae). *F. occidentalis* and *N. ribisnigri* were completely controlled in 8, 16, and 24 h at 25 °C, 13 °C, and 2 °C, respectively. For *S. oryzae*, complete control was achieved in 16 and 72 h with and without rice, respectively, at 25 °C. Furthermore, complete control of *Rhizoglyphus* spp. on peanuts was achieved in 64 h at 25 °C. Additionally, MBe fumigation for 24 h at 25 °C led to the full control of *F. occidentalis.* In addition, there was no negative impact on the visual quality of three varieties of apples four weeks after fumigation [99].

Most recently, Mostafiz et al. [100] reported that for controlling the Indian meal moth, *Plodia interpunctella* (Hübner) (Lepidoptera: Pyralidae), MBe is superior to other botanical fumigants. Within 4 h of exposure using 1 µL/L air, MBe demonstrated high fumigant activity against adults of *P. interpunctella*. The LC_{50} of MBe was 0.1 µL/L air.

4.3. Repellents, Oviposition Deterrents, Attractants, and Developmental Disruptors

Repellents deter organisms from getting close to treated surfaces. Oviposition deterrents, which make ovipositing females move away, are included among repellents. Attractants entice or lure insects or natural enemies, whereas developmental disruptors alter or inhibit the development of eggs, larvae/nymphs, and pupae.

The direct airborne repellent test is suitable for testing volatile compounds without a contradicting effect due to a sense of taste [104][105]. It uses a bioassay tube constructed of clear plastic pipe with two open ends and a hole midway down the tube. Small chambers are formed at each end by inserting mesh net rings. One end is left empty as the control, whereas MBe-treated filter paper is placed at the other end. Randomly collected adults are released into the pipe via the middle hole, and their position is recorded [79].

Using the test described above, MBe displayed repellent activities toward adults of *B. tabaci* under laboratory and greenhouse conditions [79]. The ability of MBe to repel *B. tabaci* was concentration- and time-dependent. At 2%, repellency was highest, MBe for 1 h, 3 h, and 6 h post-treatment, with repellencies of 78.2%, 82.1%, and 55.1%, respectively [79]. A choice test was conducted with MBe on treated tomato plants versus untreated plants; maximum repellency was found using a 2% MBe solution at 24 h (96.1%) and 48 h (89.1%) post-treatment [79]. Moreover, MBe acted as a strong oviposition deterrent against adult *B. tabaci* in a choice test. At a 2% MBe solution for 24 h (98.2% deterrence) and 48 h (94.9% deterrence) post-treatment, the most effective oviposition deterrent was observed [79].

The behavior of *T. urticae* adult females was strongly affected by MBe under greenhouse conditions [80]. At 24 h post-treatment, the highest repellent effects were observed. At this time, approximately 52%, 60%, 64%, and 84% of adult female mites were repelled at MBe concentrations of 0.1%, 0.25%, 0.5%, and 1%, respectively. Reportedly, the mites were repelled significantly by MBe-treated plants compared to water-sprayed plants throughout the 7-day experiment. The maximum observed repellencies recorded for this species were 91.9% for 1% MBe and 77.4% for 0.5% MBe at 24 h post-treatment [80].

In response to MBe in a laboratory bioassay, Larson et al. [106] determined the behavioral activity of the common bed bug. Reportedly, MBe repelled adult *C. lectularius* over a 1 h period. Furthermore, using an EthoVision video system designed to track the movement of individuals, the authors noted that MBe treatment resulted in a reduction in the time spent within the target zone. Finally, Zhang et al. [107] reported that MBe identified from ylang-ylang EO had strong repellent effects against the invasive stink bug *H. halys*. The authors found that MBe significantly reduced trap catches of *H. halys* by 72%. In particular, MBe was likely responsible for the repellency of the corresponding EO.

Conversely, the attraction of some species to MBe was demonstrated by Feng et al. [45]. They reported that a seven-component blend comprising MBe was more effective and selective for attracting *D. suzukii* under field conditions than the currently used standard apple cider vinegar bait.

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