agriculture

Review

Methyl Benzoate as a Promising, Environmentally Safe Insecticide: Current Status and Future Perspectives

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Abstract: The widespread use of synthetic chemical pesticides beginning in the late 1930s has contributed to the development of insecticide resistance of many important species of pest insects and plants. Recent trends in pesticide development have emphasized the use of more environmentally benign control methods that take into consideration environmental, food safety, and human health. Biopesticides (e.g., naturally occurring pesticidal compounds) are alternative pest management tools that normally have no negative impact on human health or the environment. Here we review methyl benzoate, a relatively new botanical insecticide that occurs naturally as a metabolite in plants, and whose odor is an attractant to some insects. Since 2016, many studies have shown that 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. In this review, we summarize various modes of action of methyl benzoate and its toxicity or control potential against various kinds of arthropods, including agricultural pests and their natural enemies, and pollinators. We conclude that methyl benzoate is a very promising candidate for use in integrated pest management under either greenhouse or field conditions.

Keywords: botanical pesticides; biorational pesticides; essential oils; integrated pest management; mode of action; sustainable agriculture

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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 [4–8]. Therefore, curbing synthetic pesticide use is an urgent matter [9–16].

Some botanical pesticides (BPs) are biorational pesticides as they are less harmful to human health and the environment than synthetic pesticides [17–21]. 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 [23–25]. 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 [29–32]. 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 [33–35].

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.) [40–43]. 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]. Generally, previous studies have demonstrated that MBe is a compelling biorational pesticide against some invasive species, especially *H. halys* and *D. suzukii*. MBe also appears to have low toxicity to nontarget organisms [46–48]. This review examined the characteristics, applications, and toxicity of MBe, stressing its significance in agriculture for insect pest control. We addressed various routes of exposure to MBe, considering its effects on nontarget arthropods and plants, and discussed the sublethal impacts of MBe and its mammalian toxicity. Our objective was to evaluate recent studies on the use of MBe as a potential biorational pesticide.

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 [49], including flowers [50–52] and fruits [53–57]. Lepidopteran insects can be attracted to the floral scent of MBe, e.g., some hawk moths [58,59]. In addition, MBe is emitted from rice plants damaged by the larvae of the fall armyworm (FAW), *Spodoptera frugiperda* (Smith) (Lepidoptera: Noctuidae) [60]. FAW-induced volatiles, including MBe, are highly attractive to females of the FAW parasitoid, *Cotesia marginiventris* (Cresson) (Hymenoptera: Braconidae) [60]. Silva et al. [61] 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 [44,62–66]. In addition, MBe is a semiochemical that affects both intraspecific and interspecific interactions in a number of insect species [67].

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 [68,69]. 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 [70] 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 [71].

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 [58]. Nevertheless, the pathway for its biosynthesis is vastly unknown in most species, especially in monocots [72]. 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 [73]. 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 [73]. The peroxisomal β-oxidation pathway plays a vital role in the catabolism of fatty acids in animals, fungi, and plants [74]. In plants, β-oxidative pathways are involved in the biosynthesis of numerous primary metabolites, including benzoic acid [75]. The flowers of *Petunia hybrida* cv (Mitchell) emit high levels of benzenoid volatiles [76,77]. Recently, the core β-oxidative pathway of benzoic acid in this species was fully explained [75,78]. 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 [79]. MBe is formed via a methylation reaction with benzoic acid as a substrate, catalyzed by *S*-adenosyl-L-methionine-dependent benzoic acid methyltransferase [51] (Figure 1).

MBe is a colorless liquid with intense floral and cherry aromas. It is soluble in methanol and ethyl ether but insoluble in water [80].

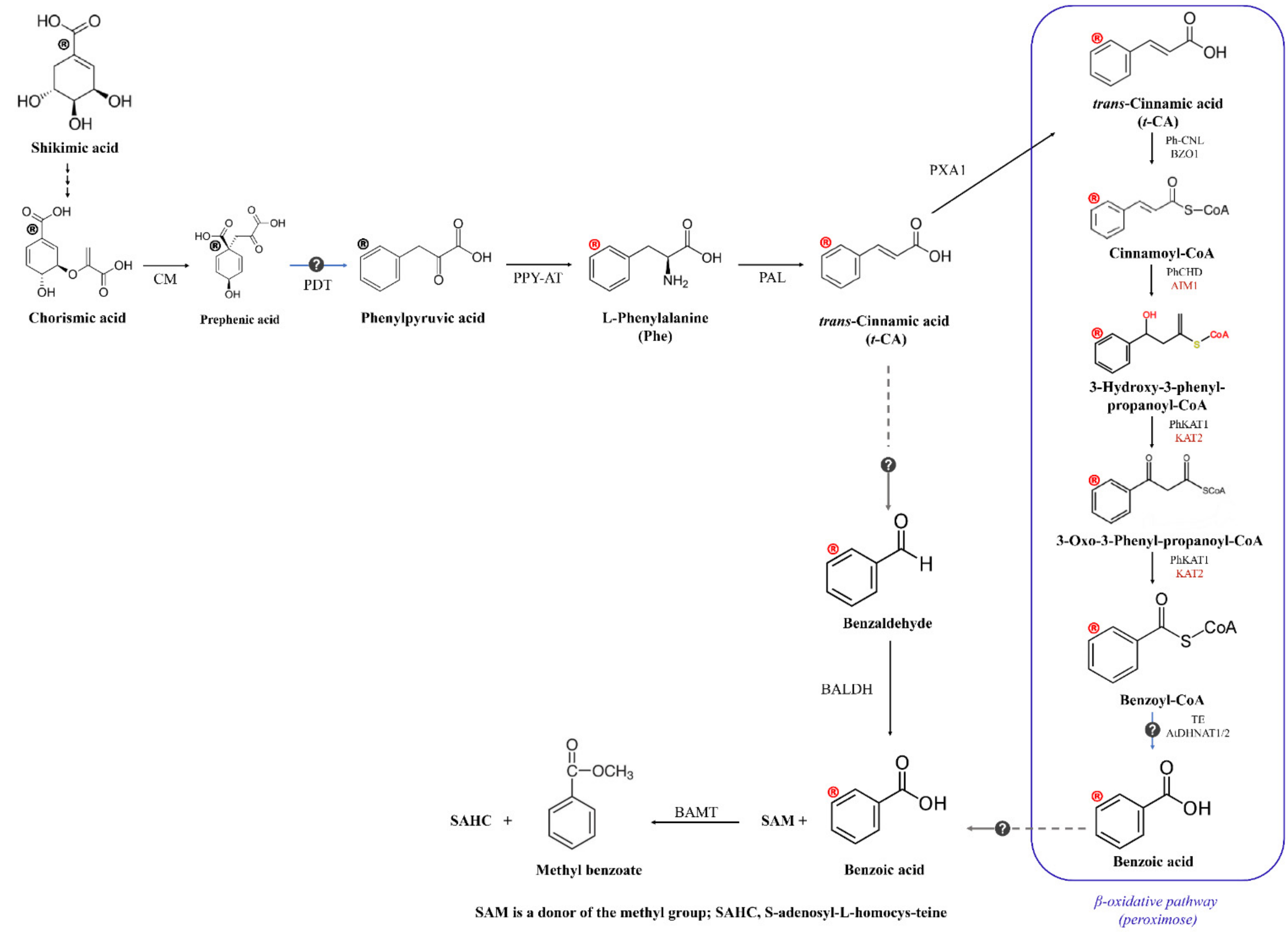

Figure 1. The biosynthesis network for plant benzoic acid. The shikimate/chorismate pathway proposed the biosynthesis of methyl benzoate in plants by the shikimate/chorismate pathway and via phenylalanine. The carboxyl carbon of shikimate is labeled (®), as is the β-carbon of phenylalanine (®). The plant 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. In proposing this pathway, we utilized data from publications by Yue et al. [72] (licensed under CC BY 4.0) and by Widhalm and Dudareva [73].

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 [13,14,48,81,82]. The contact toxicity of MBe has been assessed using different methods [13,14,48,81–83]. 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 [84,85]. Mostafiz et al. [81] reported that the direct spray application of 1% MBe to adults of *B. tabaci* caused 100% mortality 24 h post-treatment (Figure 2).

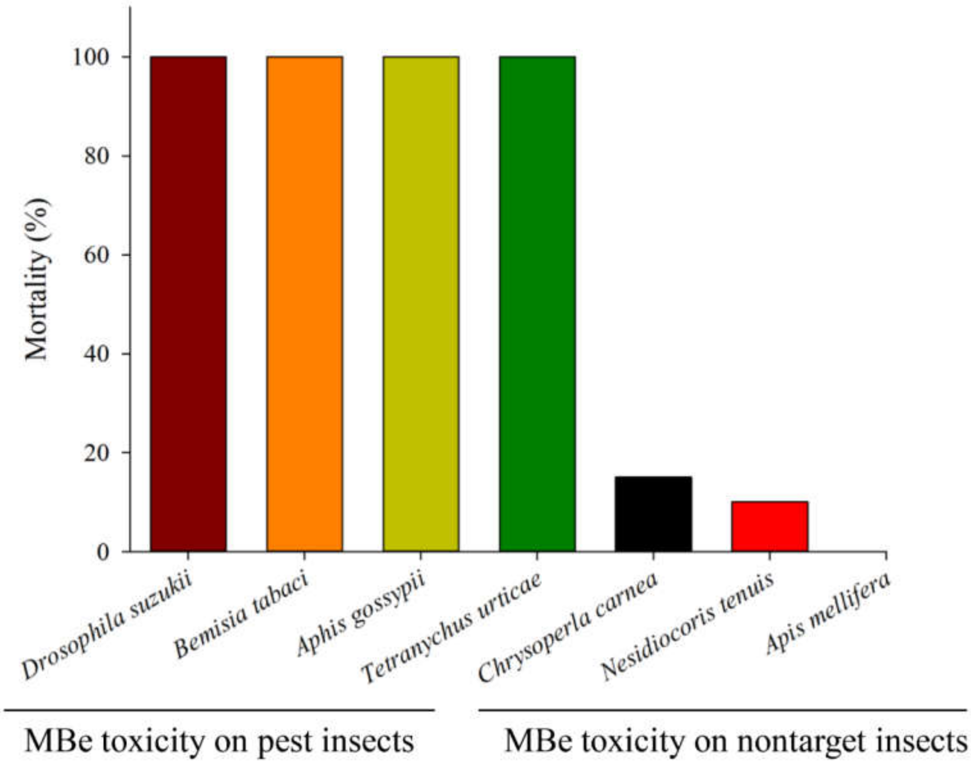

Figure 2. Toxicity differences of methyl benzoate against various arthropod pests and nontarget organisms: Mortality data from 1% MBe concentration after 48 h of exposure. The image was adapted from Feng and Zhang (licensed under CC BY 4.0), Mostafiz et al., and Zhu et al. (licensed under CC BY 4.0) [14,46–48,81,82].

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 [81]. Similarly, adult eclosion following leaf-dipping with 1% MBe was reduced by 93.2% [81]. 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 (Table 1).

Table 1. Contact toxicity of methyl benzoate for major pests and predators with LC_{50} values.

Groups	Species	Developmental Stages	LC_{50}	Units	References
Pests	*Halyomorpha halys* (Hemiptera: Pentatomidae)	Egg	0.02	mg/cm^2	Feng and Zhang [14]
		1st-instar nymph	1.03	µL/vial	
		2nd-instar nymph	1.01	µL/vial	
		3rd-instar nymph	1.23	µL/vial	
		4th-instar nymph	2.39	µL/vial	
		5th-instar nymph	1.77	µL/vial	
	Bemisia tabaci (Hemiptera: Aleyrodidae)	Egg	0.3	%	Mostafiz et al. [81]
		4th-instar nymph	0.2	%	
		Adult	0.2	%	
	Aphis gossypii (Hemiptera: Aphididae)	3rd-instar nymph	0.18	%	Mostafiz et al. [48]
		Adult	0.32	%	
	Manduca sexta (Lepidoptera: Sphingidae)	Egg	0.015	mg/cm^2	Feng and Zhang [14]
	Plutella xylostella (Lepidoptera: Plutellidae)	Egg	0.001	mg/cm^2	
	Lymantria dispar (Lepidoptera: Erebidae)	Larvae	0.114	mg/cm^2	Feng et al. [13]
	Drosophila suzukii (Diptera: Drosophilidae)	Larvae	1	%	Feng and Zhang [14]
		Pupae	1	%	
		Adult	1	%	
	Tetranychus urticae (Trombidiformes: Tetranychidae)	Egg	0.27	%	Mostafiz et al. [82]
		Adult	0.38	%	
	Solenopsis invicta (Hymenoptera: Formicidae)	Worker	93.65	µg/ant	Chen et al. [86]
	Callosobruchus chinensis (Coleoptera: Chrysomelidae)	Adult	44.81	µg/beetle	Park et al. [83]
	Aedes aegypti (Diptera: Culicidae)	Adult	45.6	µg/mosquito	Larson et al. [87]
	Aedes albopictus (Diptera: Culicidae)	4th-instar larvae	61	ppm	Mostafiz et al. [88]
	Culex pipiens (Diptera: Culicidae)	4th-instar larvae	185	ppm	
Predators	*Chrysoperla carnea* (Neuroptera: Chrysopidae)	1st-instar larvae	>1	%	Mostafiz et al. [48]
		2nd-instar larvae	>1	%	
		Adult	>1	%	
	Nesidiocoris tenuis (Hemiptera: Miridae)	Adult	>1	%	Mostafiz et al. [47]

The cotton aphid, *Aphis gossypii* (Glover) (Hemiptera: Aphididae), is a polyphagous pest associated with more than 700 host plants worldwide [89,90]. Using a leaf-dipping assay, Mostafiz et al. [48] 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 (Table 1). Moreover, MBe showed acaricidal activity against the two-spotted spider mite, *Tetranychus urticae* (Koch) (Acari: Tetranychidae) [82], which is one of the most destructive pests of ornamental and horticultural plants [91,92]. Egg hatch of this mite was reduced by 76.9% and 92.5%, respectively, in leaf-dipping assays with 0.5% and 1% MBe [82]. 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 (Table 1).

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 (Table 1). 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 (Table 1). 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) (Table 1), 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 [93,94]. Recently, Chen et al. [86] 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) [83]. Furthermore, Park et al. [83] reported that the topical application of MBe at a dose of 44.81 µg/beetle produced the highest mortality 24 h after treatment (Table 1).

Recently, Larson et al. [87] 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 (Table 1). Mostafiz et al. [88] 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 (Table 1).

4.2. Fumigant Toxicity

More than 100 species of insects cause significant economic losses to stored products [95,96]. 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 [97,98]. 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 [83,86,99–102]. According to Park et al. [83], 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 (Table 2).

Table 2. Fumigation toxicity of methyl benzoate to different stored product pests with LC_{50} values.

Species	Developmental Stages	LC_{50}	Units	References
Callosobruchus chinensis (Coleoptera: Chrysomelidae)	Adult	5.36	mg/L	Park et al. [83]
Rhyzopertha dominica (Coleoptera: Bostrichidae)	Adult	<1080	mg/L	Morrison et al. [99]
Tribolium castaneum (Coleoptera: Tenebrionidae)	Adult	<1080	mg/L	Morrison et al. [99]
Sitophilus zeamais (Coleoptera: Curculionidae)	Adult	<1080	mg/L	Morrison et al. [99]
Sitophilus oryzae (Coleoptera: Curculionidae)	Adult	-	-	Yang et al. [101]
Trogoderma variabile (Coleoptera: Dermestidae)	Larvae	>1080	mg/L	Morrison et al. [99]
Plodia interpunctella (Lepidoptera: Pyralidae)	Adult	0.1	µL/L	Mostafiz et al. [102]
Frankliniella occidentalis (Thysanoptera: Thripidae)	Larva and adult	-	-	Yang et al. [101]
Nasonovia ribisnigri (Hemiptera: Aphididae)	Nymph and adult	-	-	Yang et al. [101]
Rhizoglyphus spp. (Sarcoptiformes: Acaridae)	Adult			Yang et al. [101]
Solenopsis invicta (Hymenoptera: Formicidae)	Worker	0.77	µg/mL	Chen et al. [86]

In treating fire ant mounds, fumigants have been used [103]. Recently, MBe displayed strong fumigation toxicity against workers of the invasive species *S. invicta* [86]. 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 (Table 2). Morrison et al. [99] 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 [99].

The common bed bug, *Cimex lectularius* (L.) (Hemiptera: Cimicidae), whose incidence is on the rise worldwide, is a human health pest [104,105]. Larson et al. [100] 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 [101]. 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 [101].

Most recently, Mostafiz et al. [102] 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 (Table 2).

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 [106,107]. 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 [81].

Using the test described above, MBe displayed repellent activities toward adults of *B. tabaci* under laboratory and greenhouse conditions [81]. 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 [81]. 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 [81]. 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 [81].

The behavior of *T. urticae* adult females was strongly affected by MBe under greenhouse conditions [82]. 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 [82].

In response to MBe in a laboratory bioassay, Larson et al. [108] 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. [109] 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.

5. Toxicity of Methyl Benzoate to Natural Enemies, Pollinators, Plants, and Mammals

Integrated pest management (IPM) strategies against crop pests must consider the side effects of insecticides on nontarget organisms, including species that act as biological control agents and pollinators. The side effects of MBe have been assessed for just a few predatory insects. One study tested the contact toxicity of MBe to larvae and adults of the green lacewing *Chrysoperla carnea* (Stephens) (Neuroptera: Chrysopidae) under laboratory conditions [48]. The study results showed that 1% MBe solution killed 20% and 12% of first- and second-instar larvae, respectively, within 24 h of application. Adult mortality was 6.7% at 24 h post-treatment. In contrast, no lacewing mortality was recorded at 24 h in the residual assays (as opposed to the direct applications above) [48]. In a second study, in which the adults of the predatory bug *Nesidiocoris tenuis* (Reuter) (Hemiptera: Miridae) were exposed to plant surfaces treated with a 1% MBe solution, the observed mortality was 17.8% and 13.3%, under laboratory and greenhouse conditions, respectively [47]. Therefore, according to the rating scheme of the International Organization for Biological Control, 1% MBe can be classified as harmless to *N. tenuis* [47].

Furthermore, MBe is a component of honeybee semiochemicals. Recently, Zhu et al. [46] evaluated the potential adverse impact of MBe on *Apis mellifera* (L.) (Hymenoptera: Apidae) using two different treatment methods: (1) a spray to test for contact toxicity and (2) feeding to test for oral toxicity. The spray toxicities of imidacloprid and abamectin were 2002 and 173,163 times greater, respectively, than that of MBe. Thus, this earned MBe a toxicity ranking of 35th out of the 43 tested chemicals. This ranking was lower than all conventional insecticides [46]. Sequel to this, MBe is considered safe for honeybees (Figure 2).

The physical and chemical features of a pesticide have a significant impact on the biological activity of the pesticide against the target pest species [110]. The physical properties determine the pesticide's mode of action, dosage, mode of application, and subsequent environmental chemodynamics [110,111]. Moreover, the toxicity of a pesticide depends on the pest species' body size, developmental stage (egg, larva, or adult), and behavior [112]. From these stated facts, MBe results clearly revealed that susceptibility to MBe will be greater among pest species such as aphids, whiteflies, and two-spotted spider mites than among their natural enemies, including lacewings and predatory bugs [47,48,81,82]. Hence, we summarized that the reduced susceptibility among the predators may be related to the higher volume of the predator's body compared to the pests [113].

Pesticides are characterized by different degrees of toxicity to target and nontarget organisms [114,115]. Additionally, they may enter the body by different avenues depending on species, metabolic peculiarities, and susceptibility to toxins [116]. Differences in susceptibility to MBe between herbivorous pest species and omnivorous natural enemies are worth investigating further.

Mostafiz et al. [82], by spraying three-week-old plants with 1% MBe solution every 7 days for three weeks, examined whether MBe is phytotoxic to common spider mite host plants. The previous 1% concentration of MBe, at which more than 90% of adults of *T. urticae* were killed, was used as a worst-case scenario to search for any possible phytotoxic effects. However, none were found. Furthermore, no phytotoxic symptoms, such as wilting, vein clearing, necrosis, epinasty, or hyponasty, were observed in the tested plants. This suggests that MBe is not phytotoxic at concentrations up to 1%.

Relatively, MBe exerts relatively low toxicity to mammals. The acute oral toxicities of MBe to rats, mice, rabbits, and guinea pigs are 3.5, 3.33, 2.17, and 4.1 g/kg, respectively, based on the measured LD_{50} values [80,117,118]. The LD_{50} value of MBe for the domestic cat (applied to the skin) is 10 g/kg [117].

6. Sublethal Effects of Methyl Benzoate

Insecticides that have sublethal effects on insect biology are vital for IPM programs. Sublethal effects of pesticides may affect insect biology in different ways, such as reducing oviposition, lengthening the development time of immature stages, and decreasing their longevity [119–121]. Additionally, when insects are exposed to insecticides at sublethal levels, they exhibit changes in various behavioral characteristics such as mobility, navigation/orientation, food-seeking, oviposition site selection, and others [120]. Sublethal doses of insecticides may also potentially alter the chemical communication systems of insects, reducing their chances of reproducing in insects that depend heavily on olfactory communication [120]. Recently, Feng and Zhang [14] revealed that MBe had a significant impact on *D. suzukii* development. Mostafiz et al. [122] found that a sublethal dose of MBe (LC_{30} = 0.22%) significantly reduced the fecundity and longevity of the aphid *A. gossypii* in the treated parental generation (F0) and their untreated progeny (F1). Moreover, MBe prolonged the developmental duration of each immature instar of the F1 generation compared with the controls. In another study, Mostafiz et al. [47] investigated the sublethal effects of MBe on the feeding rates of adults of *N. tenuis* consuming eggs of the whitefly *B. tabaci*. There was no significant effect on the rate of consumption. Recently, Zhu et al. [46] discovered that MBe reduced honey bee flight ability. As MBe concentrations increased, the honeybee flying scores declined.

7. Lack of Knowledge of Molecular Target(s) and the Mode of Action of Methyl Benzoate

The method of action of plant-derived EOs has been determined in a few cases at the molecular level. Studies have found that EO compounds change the activities of various bioactive target molecules within the cells, including acetylcholinesterase (AChE), octopamine, and gamma-aminobutyric acid (GABA), in insects [123–125]. The AChE of insects is an important potential target molecule of various plant-derived EOs [123]. AChE is a cholinergic enzyme found in the muscles and nerves of both insects and mammals, especially at postsynaptic neuromuscular junctions [126–130]. EO and its constituents can inhibit AChE activity. Therefore, they can also induce hyperstimulation or paralysis of pest insect species. EO components such as carvacrol, eugenol, limonene, linalool, thymol, α-Pinene, α-Terpineol, α-Terpinene, and 1,8-Cineole inhibited AChE activity of *A. aegypti*, *D. suzukii*, and *S. oryzae* [131–133]. Octopamine is a biogenic amine that acts as a neurotransmitter, neurohormone, and neuromodulator in invertebrates [134–137]. Many previous research articles have demonstrated that EOs and their primary constituents similarly affect octopamine. For example, eugenol, α-terpineol, and their mixture with cinnamyl-alcohol induced an increase in the cAMP level in the nervous system of American cockroaches, *Periplaneta americana* (L.) (Blattodea: Blattidae) [138]. In another study, Pandey et al. [139] reported that EOs including eugenol, cinnamic alcohol, and phenyl ethyl alcohol could lead to a significant increase in octopamine levels in the central nervous system of German cockroaches, *Blattella germanica* (L.) (Blattodea: Blattidae). Plant-derived EOs can inhibit GABA found in insects by binding to specific receptors in the post-synaptic cell membranes [140–142]. In another study, Tong and Coats [143] discovered three monoterpenoids (carvacrol, pulegone, and thymol) significantly increased the Cl^- uptake induced by GABA in membranes prepared from ventral nerve cords of the American cockroach. Additionally, EOs interfere with the activities of enzymes and other vital molecules associated with xenobiotic metabolism or insect respiration, such as carboxylesterase, cytochrome P450s, and glutathione S-transferase (GSTs) [144–147]. However, at the molecular level, the role of MBe has rarely been investigated. Kravets-Beker et al., as reported by Opdyke [148] and Kravets-Bekker and Ivanova [80], found that MBe reduced the cholinesterase activity of rats at a dose of 500 mg/kg. In addition, this same study found that frequent application of high doses resulted in damage to the central nervous system [148]. However, the exact mode of action was not investigated. The study results suggested that MBe potentially acts on the nervous system in animal tissues.

Furthermore, in transmitting information between the nerve cells, AChE happens to be one of the most important enzymes. Thus, this enzyme is often designated as the target molecule for organophosphate and carbamate insecticides [126]. Most recently, Mostafiz et al. [122] revealed that AChE activity in cotton aphids, *A. gossypii*, treated with MBe (0.22%) was reduced by 65% compared to the control. A molecular-docking program was also used to simulate how MBe and AChE would interact with each other. The program found that a single MBe molecule docked at the catalytic site of the AChE molecule.

Additionally, MBe exhibited hydrophobic interactions with at least five AChE amino acids [122]. These results suggest that MBe is potentially targeting AChE at a molecular level. Recently, Zhu et al. [46] investigated the influence of MBe on the detoxifying enzyme systems of honey bees. The findings revealed that cytochrome P450 activity varied the most in response to changes in MB concentrations among the three primary enzymes studied. Conversely, MB had no influence on GST and esterase (EST) activity.

Some benzoate derivatives, such as sodium benzoate and methyl hydroxybenzoate, have bacteriostatic and fungistatic properties. They have been used as preservatives in a variety of food and cosmetic products [149,150]. These compounds have been shown to act on nervous conduction in the spinal root fibers of cats [151]. At a higher dose, sodium benzoate can induce neurotoxicity, nephrotoxicity, and teratogenicity during the early embryogenesis of zebrafish larvae [152]. This suggests that MBe also has multiple target molecules with which it reacts in different action modes. MBe acts as a contact toxin, fumigant, repellent, or attractant to different insect species.

Interestingly, the diversity of targets in a multi-site bio-insecticide will considerably lower the possibility of resistance [153]. A single compound can interact with multiple targets in the insect species, causing toxic effects on the organism. For example, Enan [138,154] Tong and Coats [143,155] found that carvacrol and pulegone had effects on both octopamine and GABA receptors in insects. Further investigations into the modes of action of MBe on various target molecules are needed to understand how MBe affects insect systems.

8. Future Perspectives

The use of plant-derived natural pesticides can: (1) prevent the accumulation of toxic chemical residues in soil; (2) reduce water pollution due to pesticides; and (3) limit the bioaccumulation of certain pesticides in food chains. EOs and their constituents generated from plants are significant sources of novel bioactive compounds with broad-spectrum insecticidal actions. However, several studies have focused on the insecticidal activity of MBe on target organisms. On the other hand, few studies have focused on the effects of MBe on nontarget organisms. Similarly, the modes of action for MBe have not been well clarified. Additionally, the efficacy of MBe as a pesticide has not yet been confirmed under open greenhouse or field conditions. In this review, this has been summarized.

Recently, many studies have confirmed that MBe demonstrates substantial fumigation toxicity against numerous postharvest storage and urban pest insects. Some pests include maize weevil, rice weevil, lesser grain borer, red flour beetle, warehouse beetle, Indian meal moth, bed bug, etc. Furthermore, phosphine has been widely used as an alternative fumigant to methyl bromide, known for its ozone-depleting property and detrimental effect on human health [156]. Excessive use of phosphine increased phosphine-resistant insect populations globally. Furthermore, the significance of phosphine in the global postharvest supply chain implies that stakeholders are likely to employ an alternative fumigant if it is effective, affordable, and does not impact product quality. MBe might be a viable alternative to conventional fumigants to manage postharvest storage insect pests in such circumstances. Thus, more studies are needed to analyze and encourage the natural evaporation of MBe in commercial-scale trials, increase control efficiency, and establish commercial-scale treatment methods.

Additionally, MBe has a high level of mosquito control effectiveness. Therefore, MBe can be evaluated for its viability as a long-term, selective, biodegradable, and ecologically friendly option as a potential mosquito control agent. A mosquito control method that uses environmentally friendly active components will help reduce our reliance on synthetic pesticides. Meanwhile, formulations for employing this chemical in vector control must be investigated and established. Sublethal doses of MBe are not toxic to natural enemies, making them excellent candidates for incorporation into IPM programs in conjunction with natural enemies to control particular greenhouse pests such as thrips, aphids, whiteflies, and mites. Therefore, more research is needed to determine the effectiveness of MBe concentrations and their compatibility with natural enemies in the field. However, MBe formulations for pest management have yet to be developed. Incorporating environmentally friendly active components into a pest control program can lessen our dependency on synthetic pesticides. Organic compounds may be colonized and metabolized by microorganisms. More information about the effects of abiotic and biotic factors on the performance of MBe is of the essence.

9. Conclusions

The environmental risks associated with the continuous use of synthetic pesticides have stimulated interest in developing plant-based insecticides with selective toxicity to insects but minimal effects on nontarget species. Biopesticides tend to be safer for nontarget organisms than synthetic alternatives. Biopesticides are frequently better with the overall ecosystem or agroecosystem, considering their lower environmental risk. In addition, their potent use often depends on understanding the interaction with the environment as a whole (e.g., soil type, moisture, temperature). Pressure to seek alternative pest control products is partly driven by the growing demand for higher food safety and quality standards. Due to its diverse pesticide activities, MBe could be a suitable product for IPM programs. A patent (US 9,629,362 B1) application has been submitted for the pesticide use of MBe to the US EPA.

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