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REVIEW ARTICLE

Bio-fumigants as grain protectants in storage - A review

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Abstract

Agriculture is a global lifeline, especially in developing nations like India, where over 70% of the population relies on it. Protecting food grains from insect pests during post-harvest storage is crucial, particularly in regions lacking advanced storage technologies, leading to significant losses. Fumigation is still a key strategy for safeguarding stored grains. Methyl bromide (MBr) and aluminium phosphide (AlP) are the widely used chemical fumigants. Phosphine is used to a greater extent today, but there are frequent reports that several storage pests have developed resistance to this fumigant. The United Nations World Meteorological Organization declared methyl bromide as an ozone-depleting chemical in 1995, and hence, most of the developed countries have phased out its use. Therefore, there is an urgent requirement to develop alternatives having a possible replacement for these fumigants. Biofumigants are organic compounds derived from various plant sources, including essential oils, botanical powders, and plant residues or from microbial volatiles. They release volatile compounds toxic to pests but safe for humans and the environment, offering a sustainable pest management approach. Plants such as mustard and radish produce glucosinolates that release isothiocyanates, known for their pesticidal properties. Essential oils from eucalyptus, clove, and mint and volatiles from certain fungi and bacteria also exhibit fumigant properties. Biofumigants disrupt insect physiological and biochemical processes, leading to mortality or reduced reproduction. Studies showed their efficacy against pests like red flour beetle, lesser grain borer, and rice weevil. Unlike chemical fumigants, biofumigants do not leave harmful residues, preserving grain quality and aligning with organic farming practices. Shifting to biofumigants offers a promising, eco-friendly, and effective alternative for post-harvest pest management, ensuring food safety and sustainability.

Keywords

Agriculture; post-harvest management; pests; essential oils; stored grains; plant quarantine; fumigation

Introduction

India's total food grain production is estimated to be 3,296.87 lakh tonnes, which is an increase of 140.71 lakh tonnes compared to the 3,156.16 lakh tonnes produced during 2021–22. The total food grain production in India has increased significantly due to advancements in new technologies, but the rate of postharvest losses remains unchanged at 10% (1). In India, it is estimated that food grains of about 14 million tonnes, valued at around 7000 crores, are lost annually due to storage issues. Notably, insects are accountable for causing damage estimated at 1300 crores of these losses (2). Post-harvest losses encompass the diminution in both the volume and integrity of agricultural products from the moment of harvest until they reach the final consumer. This decline manifests through several phases, including harvesting, sorting, transportation, processing, and storage. In less economically developed countries, the magnitude of post-harvest losses fluctuates between 20 and 50%, contrasting with more economically advanced countries, where the range is generally 10 to 20%. The impact of these losses is most acutely felt in developing nations, affecting economic stability, social well-being, and environmental sustainability, thereby exacerbating issues of food scarcity (3). It is estimated that by 2050, there will be around 9.1 billion people in the world, and there will be a need to increase food production by approximately 70% to meet the upcoming demands of the increasing global population (4).

The stored grains preserved in different storage structures are generally attacked by coleopteran and lepidopteran pests. The activity of insect pests is aggravated by storing the produce in bags and conducive weather (25–35°C and 50–80% RH) prevailing in the storage area. Since the 1970s, the only fumigant used against stored grain protection is phosphine (5). Even today, aluminium phosphide is the only fumigant recommended and being used in India. The long-term use of synthetic fumigants has led to the accumulation of residues in various environmental components (such as water, food, air, and soil), negatively impacting non-target organisms, ecosystems, and human health. Resistance of stored product insect pests to phosphine was also a major problem throughout the world.

In recent years, there has been a growing interest in studying and evaluating biofumigants for the management of stored grain pests in both developing and developed countries due to the rise of insect resistance to traditional chemical fumigants. Considering the toxic impact of chemical fumigants on non-target organisms and the environmental concerns, biofumigants are being considered as alternatives to synthetic fumigants in agriculture and public health, and the need for biofumigants arises from the shortcomings and potential dangers of conventional chemical fumigants along with the growing demand for sustainable, organic, and safer methods of food production.

Major Stored Grain Insect Pests

The majority of stored product pests that infest stored grains primarily belong to the insect-order Coleoptera and Lepidoptera, representing approximately 60 and 10% of the total species of pests affecting stored products, respectively (6, 7). Stored grains are infested by different types of insect pests (Table 1), which results in losses both qualitatively and quantitatively. In India, the pests red flour beetle, *Tribolium castaneum* (Herbst.), rice weevil, *Sitophilus oryzae* (L.), and pulse beetle, *Callosobruchus chinensis* (L.) are considered significant threats to stored grains (8). Insect infestation can also lead to changes in the amino-acid and protein composition, available carbohydrates, fats, and organoleptic characteristics of stored food (9).

Bio-fumigants

In recent years, there has been an increasing concern over the safety and sustainability of using synthetic chemicals for grain protection. Synthetic fumigants such as methyl bromide and phosphine, though effective, pose environmental and health risks, and pests have developed resistance to them. This has led to a growing interest in alternative, eco-friendly methods for grain preservation (10).

Biofumigants are natural substances derived from certain plant species, predominantly mustard, radish, and brassicas, which release volatile compounds with insecticidal properties. These compounds are found promising in controlling a range of pests, including insects and fungi, providing an eco-friendly alternative to conventional chemical fumigants. Biofumigants originating from plants typically exhibit specificity towards different insect species, are quickly biodegradable, and have a high level of acceptance (11).

Biofumigants work primarily by releasing volatile organic compounds (VOCs) that have toxic effects on grain pests. These compounds interfere with the nervous systems of insects, resulting in paralysis or death. Additionally, bio-fumigants can inhibit the growth of fungi and molds that contribute to the deterioration of grain quality. Biofumigation is considered an alternative to traditional fumigation methods and proves to be effective in pest management, particularly in the protection of stored product pests. Biofumigation involves the utilization of volatile chemicals (allelochemicals) emitted from decomposing plant matter to control a broad range of pests, insects, nematodes, bacteria, fungi, viruses, and weeds (12). Unlike synthetic chemicals, bio-fumigants degrade quickly, leaving minimal to no harmful residues in the stored grains. This rapid breakdown reduces environmental impact and ensures the safety of food products for human consumption (13).

Plant Derived Biofumigants

Plants, as natural chemical factories, produce a variety of bioactive organic compounds primarily for defense against insect pests (14). These compounds emit volatile odors, hence referred to as plant volatile organic compounds (VOCs). Traditionally, farmers globally have utilized these compounds in combating pests that attack stored grains. Numerous volatile compounds from plants and their constituents have effectively been employed as powerful fumigants to combat insect pests in stored grains (15–17).

The fumigant toxicity is from 75 different plant species across many families, including Rutaceae, Anacardiaceae, Zingiberacea, Chemopodiaceae, Graminaceae, Cupressaceae, Lamiaceae, Lauraceae, Apiaceae, Pinaceae, Asteraceae, Araceae, Myrtaceae, Brassicaceae (Cruciferae), and Liliaceae, which are demonstrated for their efficacy

Table 1. Major insect pests damaging stored grain.

Sl.No.	Common name	Scientific name	Commodity	References
1.	Lesser grain borer	*Rhyzopertha dominica* (Fabricius) (Coleoptera: Bostrichidae)	All cereal grains, corn, rice, wheat and millet	(55)
2.	Saw-toothed grain beetle	*Oryzaephilus surinamensis* (L.) (Coleoptera: Silvanidae)	Flax, wheat barley, oats, and sunflower	(56)
3.	Rice weevil	*Sitophilus oryzae* (L.) (Coleoptera: Dryophthoridae)	Sorhum, wheat, barley, rice	(57)
4.	Maize weevil	*Sitophilus zeamais* Motschulsky (Coleoptera: Curculionidae)	Pasta and grains	(58, 59)
5.	Confused flour beetle	*Tribolium confusum* (Coleoptera: Tenebrionidae)	Milled products, sunflower, peas, millets, and spices	(60)
6.	Angoumois grain moth	*Sitotroga cerealella* (Olivier) (Lepidoptera: Gelichiidae)	Corn, millet, wheat, barley, rice and sorghum	(61)
7.	Merchant grain beetle	*Oryzaephilus mercator* (Fauvel) (Coleoptera: Silvanidae)	Processed flours, and cereals	(62)
8.	Granary weevil	*Sitophilus granarius* (L.) (Coleoptera: Curculionidae)	Wheat, sorghum, barley, rye, oats, corn	(63)
9.	Long headed flour beetle	*Latheticus oryzae* Waterhouse (Coleoptera: Tenebrionidae)	Maize and Sorghum	(64)
10.	Red flour beetle	*Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae)	Rice flours, oil seeds, peas and beans	(65)
11.	Rusty grain beetle	*Cryptolestes ferrugineus* (Stephens) (Coleoptera: Laemophloeidae)	Rye, oats, flours, triticale, wheat	(65)
12.	Flour mill beetle	*Cryptolestes turcicus* (Grouvelle) (Coleoptera: Laemophloeidae)	Milled flour, and broken grains	(65)
13.	Indian meal moth	*Plodia interpunctella* (Lepidoptera: Pyralidae)	Common pest of stored grains	(66)
14.	Pulse beetle	*Callosobruchus chinensis* (L.) (Coleoptera: Chrysomelidae)	Pigeon pea, lentil cow pea, and chickpea	(67, 68)
15.	Drug stored beetle	*Stegobium paniceum* (Linnaeus) (Coleoptera: Anobiidae)	Herbs, dried fruits, spices, tobacco, processed foods and cereals	(69)
16.	Khapra beetle	*Trogoderma granarium* Everts (Coleoptera: Dermestidae)	Oil seeds	(70)
17.	Pea weevil	*Bruchus pisorum* (Linnaeus) (Coleoptera: Chrysomelidae)	Peas	(71)
18.	Cowpea beetle	*Callosobruchus maculatus* (Coleoptera:Chrysomelidae)	Beans, green gram, peas, cow pea	(72, 73)
19.	Yellow meal worm	*Tenebrio molitor* L. (Coleoptera: Tenebrionidae)	Prefers decaying grain or milled cereals	(74, 75)
20.	Ground nut bruchid	*Caryedon serratus* (Olivier)	Oilseeds	(73)
21.	Bean weevil	*Acanthoscelides obtectus* (Coleoptera: Chrysomelidae)	Lentil, soybean and chickpea	(76)
22.	Flat grain beetle	*Cryptolestes pusillus* (Schönherr) (Coleoptera: Laemophloeidae)	Cereals and pulses	(77)

against stored grain pests (17, 18). Volatile compound 2, 3-Dimethylmaleic anhydride, with a maximum yield of 0.38%, extracted from the rootstock of a taro vegetable, *Colocasia esculenta,* has been discovered to exhibit toxicity against a wide diverse insect species when utilized as a fumigant (18).

Coumaran, a biofumigant extracted from the *Lantana camara*, has been identified as toxic for adult specimens of *T. castaneum, C. chinensis,* and *S. oryzae,* exhibiting LC_{50} values of 0.27, 0.38, and 0.45 µg/L after a 24 h exposure period (15). A major component of *Illicium verum* (star anise) volatiles, trans-anethole, has shown potent fumigant toxicity against *C. ferrugineus* (rusty grain beetle) by partially inhibiting the insect's acetylcholinesterase activity. This study highlights the potential of trans-anethole as a biofumigant for controlling stored grain pests (19).

A bioactive molecule, dihydro-p-coumaric acid, has been extracted from the foliage of *Tithonia diversifolia*, exhibiting significant toxicity against *R. dominica, T. castaneum,* and *S. oryzae*. This compound has been recognized for its potent acetylcholinesterase (AChE) inhibitory properties, with the degree of inhibition directly correlating to the dosage administered, and it has no detrimental impact on the germination of seeds (13). Different plant volatiles showing fumigant toxicity are given in Table 2.

Apart from plant volatiles, essential oils from different plants like eucalyptus, lavender, and peppermint have been recorded for their toxicity against stored grain insect pests. These essential oils work by disrupting the respiratory system of insects or acting as neurotoxins. Among the different constituents of essential oil, monoterpenoids have garnered the most interest due to their potent fumigant activity against insects infesting stored products (17). Different essential oils of some plants with fumigant activity are given in Table 3.

The essential oils from a plant can consist of hundreds of distinct compounds, yet specific constituents predominate in higher amounts. The major component of essential oil in *Eucalyptus* spp. is 1,8-cineole, whereas linalool is prevalent in *Ocimum* spp., limonene is found abundantly in *Citrus* spp., myrcene (*Curcuma longa)*, carvone

Table 2. Plant volatiles showing fumigant toxicity.

Sl. No.	Plant species	Family	Plant parts used	Product	Active compound	Insect listed	References
1.	*Cinnamomum aromaticum* (Nees.)	Lauraceae	Bark	Extract	Cinnamaldehyde	*T. Castaneum, S. zeamais*	(78)
2.	*Feoniculum vulgare* (M.)	Apiaceae	Fruits	Extract	Phenylpropenes, (E)-anethole	*S. Oryzae, L. serricorne*	(55)
3.	*Thespesia populnea* (L.)	Malvaceae	Leaves	Extract	Phenol	*C. maculatus*	(79)
4.	*Baccharis salicifolia* (Ruiz & Pavón)	Asteraceae	Leaves	Extract	β-Pinene	*T. castaneum, S. zeamais*	(80)
5.	*Lantana camara* (L.)	Verbanaceae	Leaf	Extract	Coumaran	*T. Castaneum, R. dominica,* and *S. oryzae*	(15)
6.	*Colocasia esculenta* var. *esculenta* (L.) Schott	Araceae	Rhizome	Extracts	2, 3-Dimethylmaleic anhydride	*T. castaneum, C. chinensis,* and *S. oryzae*	(18)

Table 3. Essential oils with fumigant activity.

Sl. No.	Plant family	Common name	Botanical name	Plant parts used	Insect tested	References
1.	Apiaceae	Ajowan caraway	*Carum copticum*	Seed	*Sitophilus oryzae* (Coleoptera: Curculionidae)	(81)
2.	Lamiaceae	Shirazi thyme	*Zataria multiflora*	Leaves and stems	*Brevicoryne brassicae* (Hemiptera: Aphididae)	(82)
3.	Asteraceae	White wormwood	*Artemisia sieberi*			
4.		Marigold	*Tagetes minuta*			
5.	Apiaceae	Dill	*Anethum graveolens*	Fruits	*Callosobruchus chinensis* (Coleoptera: Chrysomelidae)	(83)
6.		Cumin	*Cuminum cyminum*			
7.	Labiatae	Japanese catnip	*Schizonepeta tenuifolia*	Whole plant	*Lycoriella ingenua* (Diptera: Sciaridae)	(84)
8.	Illiciaceae	Star anise	*Illicium verum*	Fruits	*Reticulitermes speratus* (Blattodea: Rhinotermitidae)	(85)
9.	Compositae	Cacalia	*Cacalia roborowskii*	Whole plant		
10.	Labiatae	Japanese catnip	*Schizonepeta tenuifolia*	Herba		
11.	Liliaceae	Onion	*Allium cepa*	Bulb		
12.		Garlic	*Allium sativum*			
13.	Apiaceae	Caraway	*Carum carvi*	Fruits	*Sitophilus zeamais* (Coleoptera: Curculionidae), *Tribolium castaneum* (Coleoptera: Tenebrionidae)	(86)
14.	Lamiaceae	Corsican mint	*Mentha microphylla*	Aerial parts	*Sitophilus oryzae* (Coleoptera:Dryophthoridae)	(87)
15.	Asteraceae	Judean wormwood	*Artemisia judaica*		*Tribolium castaneum*	
16.	Rutaceae	Mandarin orange	*Citrus reticulata*	Fruits		
17.	Lamiaceae	Russian sage	*Perovskia abrotanoides*	Flower	*Sitophilus oryzae* (Coleoptera: Dryophthoridae), *Tribolium castaneum* (Coleoptera: Tenebrionidae)	(88)
18.	Atherospermateceae	Chilean laurel	*Laurelia sempervirens*	Leaves	*Tribolium castaneum* (Coleoptera: Tenebrionidae)	(89)
19.	Winteraceae	Winter's bark	*Drimys winteri*			
20.	Asteraceae	Russian wormwood	*Artemisia vestita*	Aerial parts	*Sitophilus zeamais* (Coleoptera:Curculionidae)	(90, 91)
21.	Rutaceae	Lemon	*Citrus limonum*	Leaves	*Tenebrio molitor* (Coleoptera: Tenebrionidae)	(92)

(*Carum carvi*), asarone (*Acorus calamus*), and glucosinolates are characteristic of botanical plants in the Brassicae family. Cyanohydrins are significant in *Manihot esculenta* Crantz, thiosulphinates (*Allium* spp.), methyl salicylate (*Securidaca longepedunculata* Fers), and both carvacrol and β-thujaplicine are notably found in *Thujopsis dolabrata* (17). In the diverse experiments conducted, essential oils were primarily extracted from aerial parts of plants (71.88%) and leaves (28.51%) of the extractions. Other plant materials utilized for extracting essential oils included resin, gum, rhizomes, and roots (20).

The essential oils as fumigants, alongside the significant binding affinities of their primary components, offer considerable promise for their development into natural fumigants aimed at managing pests in stored products, particularly in maize. Compounds such as 1,6-Dioxaspiro [4,4] non-ene γ-terpinene, β-farnesene, trans-chrysanthenyl acetate, α-phellandrene bornyl tiglate, p-cymene, bornyl acetate, bornyl isovalerate, and terpinen -4-ol found in the essential oil extracted from the aerial parts of *Chrysanthemum parthenium* L. have been identified as potent fumigants effective against the maize weevil, *S. zeamais* (21).

The compounds derived from plant extracts have been evaluated for their fumigant efficacy against stored grain pests. Experiments have been conducted using pure compounds sourced commercially or synthesized in the laboratory (22, 23).

Active components exhibiting toxicity to insects in their vapor stage can be classified into five, which include sulfur-containing compounds, di-n-propyl disulfide, dimethyl disulfide, allyl disulfide, diallyl trisulfide, allyl thiosulfate, and diethyl trisulfide; monoterpenoids; alkaloids, such as Z-asarone; cyanates and cyanohydrins and others, which include terpinolene, benzene derivatives, bornyl acetate, and methyl salicylate (17).

Specific phytochemicals, such as limonene, eugenol, and thymol, found in many plants, have been identified as effective biofumigants. They exhibit strong insecticides against a range of stored grain pests by interfering with their nervous system (24).

Plants from the Brassicaceae family are predominantly used for biofumigation purposes; they control pests through the release of isothiocyanates (ITCs) like methyl, 2-propenyl, 3-butenyl, 4-pentenyl, benzyl, and methyl thio butyl, produced when myrosinase enzymes in neutral pH conditions and the presence of water, hydrolyze glucosinolates (GSLs). Glucosinolates are sulfur-containing compounds (thioglucosides) generated as secondary metabolites. In addition to brassicas, families Caricaceae, Moringaceae, Salvadoraceae, and Tropaeolaceae are also recognized for their biofumigant properties (25).

Essential oils and specific components were explored for their efficacy as potential fumigants in combating pests in stored grains. Biofumigants offer the benefit of introducing innovative mechanisms against storage insect pests, which can minimize the likelihood of developing cross-resistances and also provide a way of the creation of molecules with specific targets (8).

Through the investigation of a diverse array of Brassicaceae seed species, researchers were able to extract an unidentified isothiocyanate (ITC) from the seed oils of *Eruca sativa*, *Diplotaxis* spp., and *Sinapis arvensis* with various concentrations, *viz*., 98, 92, and 33%. This was later described as methyl thiobutyl isothiocyanate. In a space fumigation study, the efficacy of this methyl thio butyl isothiocyanate was evaluated against four conventional ITCs, which included methyl, ethyl, allyl, and butyl. The findings revealed that allyl and methyl ITCs exhibited superior effectiveness in exterminating both the adult and larval stages of stored-product pests. A concentration of 1 μL/L−1 air and exposure time of 3 h were enough to kill all the tested adult insects. The activity of methyl thio-butyl ITC was comparable to that of allyl and methyl ITCs except for *Tribolium*, which was found to be much more susceptible to the two ITCs (26).

Fungi Derived Biofumigants

Muscodor albus, identified as a fungi-derived biofumigant, possesses the capability to manage the pathogens during storage. Research findings revealed that it can generate more than 20 volatile compounds, each exhibiting bactericidal, insecticidal, and fungicidal properties. Conidia from various mycotoxin-producing fungi, namely *Fusarium culmorum, Aspergillus carbonarius*, *A. ochraceus, A. flavus, F. graminearum, Penicillium verrucosum,* and *A. niger*, were effectively neutralized or inhibited from sprouting by being subjected to volatile compounds emanating from 2 g of *M. albus* infected grains in hermetically sealed containers over 24 h at 20°C. The primary volatile substances produced by *M. albus*, 2-methyl-1-butanol (2MB) and isobutyric acid (IBA), in concentrations of 100 μL/L and 50 μL/L, exhibited varying degrees of fungicidal activity against these 7 fungi when applied separately at 20°C. A synergistic effect was observed when IBA and 2MB were combined, resulting in approximately 94% of the conidia being eradicated or their germination suppressed. The experiment was meticulously designed under a controlled atmosphere (CA) maintained at 3°C for 72 h exposure to four different concentrations of 2MB and IBA. A mixture of 100 μL/L IBA and 50 μL/L 2MB was found to destroy or inhibit the germination of conidia from all 7 fungi. The controlled atmospheric conditions did not significantly alter the viability of the conidia nor the effectiveness of the volatiles. This suggests that the key volatile compounds of *M. albus* hold considerable promise for managing plant pathogens in both ambient and controlled atmospheric storage environments, especially at temperatures below 5°C. However, to achieve a comprehensive spectrum of fungicidal efficacy, a combination of volatile compounds may be necessary rather than relying on individual substances (27).

Mode of Action of Biofumigants

AChE activity inhibition in adults of *T. granarium* by *A. sativum* essential oil was observed both *in vitro* and *in vivo*, which contains fumigant-active compounds like diallyl disulfide and diallyl trisulfide, suggesting that the insecticidal mechanism of essential oils and their components can involve multiple biochemical pathways (28). The monoterpenoids contribute to insect mortality by inhibiting the activity of the acetylcholinesterase enzyme (AChE), which is crucial for nerve impulse conduction in insects. Hence, the inhibition was observed in *in vitro* conditions and not in *in vivo* conditions (29).

The essential oil did not impact oxidative phosphorylation or the activity of cytochrome C-oxidase, either *in vitro* or *in vivo*. Utilizing pentoxyresorufin as a benchmark substrate for cytochrome P4502B1-dependent enzymes, which play a role in activating genotoxic substances like cyclophosphamide, (30) observed that β-myrcene, a monoterpenoid, competitively helps in the inhibition of pentoxyresorufin-O-depenthylase and it was also demonstrated on Earthworm, *Eisenia fetida*, and d-limonene of *Citrus* spp. (31). The principal component of peel oil exhibits neurotoxic effects. Similarly, isosafrole and safrole are key components of the essential oils from *S. albidum* and *C. odoratum,* respectively, in *T. castaneum,* which help in the inhibition of α-amylase both *in vitro* and *in vivo* conditions (32).

The fumigant toxicity investigations using monoterpenes (such as menthol, β-pinene, menthone, linalool, α-pinene, and limonene) were effective against adults of *Sitophilus oryzae* and did not find a direct link between insect toxicity and the inhibition of acetylcholinesterase (AChE). Menthone, derived from wild mint, *Mentha arvensis* L., recorded high toxicity (LC_{95} 25 mL/L) towards the adults of *S. oryzae*. On the contrary, the less toxic effect of β-pinene (LC_{95} 107 mL/L) demonstrated significant inhibition of AChE (ki = 0.0028 mM). This led to the hypothesis that monoterpenes might target additional sensitive sites beyond AChE inhibition, such as cytochrome P450-dependent monooxygenases, indicating a complex mode of action for these compounds (33).

The fumigant effects of terpenes *viz*., SEM76 and ZP51, derived from the plants of labiatae, and limonene, an essential oil, promote the inhibition of acetylcholinesterase (AChE) and octopamine receptors in adults of *R. dominica* and found that the inhibitory effect of AChE recorded a maximum (65%) with extremely toxic terpene (ZP51), while it was moderately toxic in SEM76 at about 27% and very low toxic of about 2% for (+)-limonene (2%), which was the less toxic. Furthermore, it was noted that inhibition of AChE did not correlate directly with levels of insect mortality. This suggests that while AChE inhibition is a mechanism of action for some terpenes, the overall toxicity of these compounds against insects may involve multiple pathways, including the activation of octopamine systems (34). However, the relevance of this inhibition to insect mortality remains unclear, indicating that the mechanisms by which essential oils and their components exert insecticidal effects are varied and not fully understood.

Efficacy of Biofumigants in Grain Storage

The essential oils (EOs) have demonstrated remarkable efficacy against various Coleopteran species, as evidenced by their LC_{50} values, which represent the concentration needed to achieve 50% mortality. Notably, the fumigation with *Ocimum gratissimum* EO from the Lamiaceae family exhibited significant insecticidal activity, achieving LC_{50} values of 0.50 µL/L against *S. oryzae*, 0.20 µL/L against *C. chinensis*, 0.20 µL/L against *R. dominica*, and 0.19 µL/L against saw-toothed grain beetle, though it was less effective for *T. castaneum* with an LC_{50} value of 24.9 µL/L (35–37).

The rice weevil, *S. oryzae*, the most extensively researched insect among curculionids, is especially vulnerable to *Carum copticum* (Apiaceae), with an LC_{50} value of 0.91 µL/L, indicating its significant susceptibility. The Lamiaceae family emerged as the most effective group of plants in terms of fumigation efficacy. Essential oils from *Salvia fruticosa, Thymus persicus, S. pomifera, S. officinalis, Thymbra capitata*, and *O. vulgare* demonstrated substantial toxicity against rice weevil, *S. oryzae*, LC_{50} spanning from 1.5 to 9 µL/L, highlighting their potent insecticidal properties (35).

Beyond the Lamiaceae, specific plants from other families also demonstrated notable effectiveness against *S. oryzae* adults when used as fumigants. *L. nobilis* from the Lauraceae family exhibited an LC_{50} value of 8.0 µL/L; *Eucalyptus* spp. showed LC_{50} values ranging from 7 to 8.5 µL/L (38, 39); and *C. limon* had an LC_{50} value of 9.89 µL/L, indicating their significant insecticidal efficacy (40).

Essential oil extracted from the fruits of *L. salicifolia*, a plant within the Lauraceae family, also demonstrated strong insecticidal properties against *S. zeamais* in fumigation experiments, with an LC_{50} value of 4.4 µL/L, highlighting its potential as an effective biofumigant. It was observed that essential oil from *Allium sativum* (Amaryllidaceae) is considered the most potent against *T. castaneum*, showcasing an LC_{50} value of 1.52 µL/L, indicating its superior efficacy as a fumigant (41).

Similar to their impact on Curculionidae, essential oils (EOs) from the Lamiaceae family exhibit significant toxicity towards *T. castaneum*. Specifically, *Rosmarinus officinalis*, with an LC_{50} of 1.17 µg/mL and LC_{50} of *Mentha* spp., ranging between 12 and 13 µL/L after a 24h exposure, have shown the highest insecticidal efficacy when used as fumigant agents (42). Moreover, essential oils from other plant families also display notable knockdown capabilities. For example, *Achillea wilhelmsii* from the Asteraceae family achieved an LC_{50} of 10.02 µL/L against *T. castaneum* (43), while *Eucalyptus* spp. from the Myrtaceae family showed LC_{50} ranging from 11 to 14 µL/L (42). *Citrus reticulata* from the Rutaceae family demonstrated an LC_{50} of 3.49 µL/L , and *Pistacia lentiscus* from the Anacardiaceae family had an LC_{50} of 8.44 µL/L, underscoring the broad potential of essential oils as fumigants across various plant families (44). While a significant portion of essential oils (EOs) have demonstrated effectiveness against the target storage insects when used as fumigants, some essential oils exhibited very low or no insecticidal activity toward stored product pests (45).

Impact of Food Grains After Biofumigation in Storage

The impacts of essential oils for biofumigation and their constituents for the nutritional quality of food grains and the persistence of fumigant residues are notably scarce. Wheat grains essential oils exposed to fumigations of *Mentha piperita* at an insecticidal dosage of 200 mL/L for about 48 h have not observed any notable changes in germination (46). It was found that the nutritional quality and germination rate of 500 g red gram, fumigated for more than 6 months with essential oil of *M. arvensis* (0.1 mL) in 1l of desiccator, remained unchanged (47). Similarly, there was observed no alteration in the nutritional quality of sorghum treated with 167 mL/L of *M. arvensis* oil for 3 months (48). It was reported that wheat fumigated with 1,8-cineole had residue levels of 85 ppm and 62 ppm after 1 and 6 days of aeration, respectively (49).

The potential issue of strong odors from essential oils transferring to treated commodities suggests that odor tainting could be a significant drawback of using plant-based fumigants. This underscores the necessity for further research into the potential effects of odor tainting, impacts on nutritional value, and residue presence in stored grains treated with essential oils (50). The effect of 47 different monoterpenoids using the seeds of *Lactuca sativa* L. of various chemical groups on germination was studied and recorded that 50% of the monoterpenoids inhibited the growth of seedlings, and germination was affected for 5% (51). The wheat flour, derived from wheat fumigated with monoterpenoids at a dosage of 200 mL/kg at temperatures between 5 and 10°C, showed no change in rheological properties, though a persistent carvacrol odor was detected in the flour (52).

Discussion

Plant-based fumigants often fall short of an ideal fumigant's critical attribute, namely, the requisite vapor pressure necessary for effective diffusion and penetration into materials to eradicate pests. The variability in evaporation rates among monoterpenoids at a temperature of 26 ± 1°C. For example, 1,8-cineole exhibited rapid evaporation within 2.5 h, limonene evaporated at a moderate pace taking 4 h, while menthol, α-terpineol, and linalool demonstrated significantly slower evaporation rates, requiring up to 4 h. The vapor phase of 1,8-cineole is notably minimum, registering below 1 mm Hg at 20°C, a stark contrast to synthetic fumigants like phosphine (with a vapor pressure of 31,920 mm Hg at 23°C), methyl bromide (1,250 mm Hg at 20°C), and sulphuryl fluoride (12,087 mm Hg at 20°C), which exhibit considerably higher vapor pressures for effective pest control (53).

Many essential oils exhibiting fume properties will have less toxicity to mammals. LD_{50} values, measured in milligrams per kilogram of body weight for rats, highlight this low toxicity for various essential oils, including *A. calamus* oil at 0.78 mg/kg, caraway oil at 3.50 mg/kg, eucalyptus oil at 4.44 mg/kg, thyme oil at 2.84 mg/kg, and peppermint oil at 4.41 mg/kg. Similarly, key constituents of these oils demonstrate low toxicity levels: anethole at 2.09 mg/kg, carvacrol at 0.81 mg/kg, 1,8-cineole at 2.48 mg/kg, p-cymene at 4.75 mg/kg, limonene at 4.60 mg/kg, linalool at 2.79 mg/kg, and terpineol at 4.3 mg/kg. However, it is crucial to mention that not every plant compound in essential oils is beneficial. Specifically, (+)- fenchone and estragole in *F. vulgare*, an essential oil that has proven highly effective against pests like *S. oryzae, C. chinensis*, and *L. serricorne*, have been identified as carcinogenic substances (54).

Regulatory authorities have established acceptable daily intake (ADI) guidelines for specific plant-derived compounds, with anethole having an ADI range of 0 to 9.6 mg and others like citral, linalool, and methyl salicylate being set at a range of 0 to 0.5 mg, while menthol's ADI is determined to be between 0 to 0.2 mg. Despite these specifications, a considerable number of plant products known for their fumigant properties currently lack designated ADI levels.

Conclusion

The use of biofumigants as grain protectants in storage is a promising and sustainable approach to addressing the global challenges of post-harvest losses. The natural origin of these substances offers significant advantages over conventional chemical methods, including reduced toxicity to non-target organisms and minimal environmental impact. However, the practical application of biofumigants is not without challenges. Issues such as variability in efficacy, the need for optimized application techniques, and regulatory hurdles must be addressed to realize their full potential. Despite these challenges, the future of biofumigants in grain storage is optimistic. With continued research and development, coupled with supportive policy frameworks, biofumigants could revolutionize the way we protect our stored grains. They could provide an effective, eco-friendly solution that not only ensures food security but also contributes to the broader goal of sustainable agriculture.

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Authors' contributions

DSK: Wrote the first draft of the paper. GP and BK: Conceptualized, reviewed, and edited the review paper holistically. MS, NC, and KR: Reviewed the paper and shared their inputs for upscaling. All authors read and approved the final manuscript.

Compliance with ethical standards

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