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BROAD SPECTRUM ACTIVITY OF ESSENTIAL OILS IN MANAGING STORED GRAIN PESTS

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ABSTRACT

The essential oils have broad-spectrum use over the world as non-chemical alternatives over the chemical fumigation in managing different stored grain insect pests. Exceptions are for organic products where use of fumigants is not possible then application of essential oils is the best preferred choice. However, their general commercial use needs to be explored over the world. The perusal of literature on essential oils indicated that the use of most effective natural products needs to be fully exploited for their potential use in the context of pest management in household and large scale grain storage.

Key words: Essential oils, broad-spectrum use, management, stored grain insect pests, management

Global population may increase to approximately 9.8 billion in 2050 than the existing 7.6 billion (Singh et al., 2021). The world may face a huge scarcity of food if the total world food production is not increased by 70% by the year 2050 (Anonymous 2017). Food grains and pulses constitute most consumed and the most common stored food products in the world, especially in the tropical and sub-tropical regions, hence occupying a crucial position in the resolution of food insecurity problems. Unfortunately, more than 70% of the produced grains are stored in villages in traditional structures such as earthen pots, silos, gunny bags, steel drums, and baskets (Mobolade et al., 2019). This often leads to loss of food grains and pulses, particularly in less developed countries where the need is the greatest (Kesavan and Swaminathan, 2008). There are various factors which cause postharvest losses of food grains and pulses, and damage inflicted by insects represents the highest threat. It has been reported that there is a wide range of losses of approximately 5-30% of the world's total agricultural production due to insect infestation alone on stored food grains (Prusky, 2011; Rajashekar et al., 2012). This wide variation in the estimation is partly due to different geographical zones, different climatic conditions, also the disparity in the major crops grown. There is also no concrete method to accurately estimate the losses (Singh et al., 2021). About 10% of post-harvest losses are incurred in food grains due to insects, rodents, micro-organisms, improper storage etc. In India, about 14 million tonnes (MT) of food grains worth Rs. 7000 crores have been lost annually. Among these, insects alone are responsible for losses of about Rs. 1300 crores (Banga et al., 2020).

The post-harvest losses due to storage and insect account for 2.0-4.2% (Kumar and Kalta, 2017). Insects not cause the losses in economic terms by consumption alone but also by spreading contamination. About 600 species of insects are occurred in stored grains and among these, about 100 species caused economic losses in stored grains (Patel et al., 1993). Several types of insects occurs which cause the infestation in stored food grains- primary, secondary and tertiary ones. Some insects behave as free-living, visualized to the eye during the first examination and hidden insects are those insects which exist in individual grains during their immature stage or due to their development in the grains. Insect's response to various natural and simulated features, classified into behavioral and metabolic responses. Movement of insects in stored grains in storage structures lies on environmental conditions. In the summer season, insect infestation occurs on the grain surface and disseminated in clumps throughout the mass, while in the winter season, insects flock in the lower and center portions of the storage structure. Attraction towards supportive conditions and evasion from fumigants, or treated surfaces comes into behavioral aspects whereas metabolic response includes the responses, which are used to promote or demote the development of insects (Bell, 2014). Primary insects are those which have the ability to bite or pierce intact and sound grains e.g. grain weevils (Curculionidae). They have the ability to break down the hard seed coat of the whole grain and laid the eggs inside the kernel, and the growing larvae cause the infestation inside the kernel. Primary insects often develop and reproduce very quickly in the optimal conditions, which allows for large populations. They are usually more destructive than secondary pests, especially in short-term storage of food grains (Banga et al., 2018). Secondary insects follow the primary insects. They feed the grains that are broken by the primary insects, processed into products viz. flour, dal etc. or damaged by poor threshing, drying and handling e.g. red flour beetle, *Tribolium castaneum* (Herbst), one of the common secondary pests that eat wheat grains from the outside first. The presence of secondary pests often indicates that the grain is not in superlative condition and that measures should be implemented to protect the grain from a further decline in quality. Tertiary insects feed on broken grains, grain dust, and powder left by the primary and secondary insects. Confused flour beetle is a tertiary insect of whole grains. Also, it is a secondary insect of milled grains such as flour (Banga et al., 2019).

Singh et al. (2016a) evaluated different plant powers against rice weevil, *Sitophilus oryzae* (L.) on stored wheat and revealed neem and dharek kernel powders as the best. Chahal et al. (2016) studied the chemistry and insecticidal activity of bay leaf oil, its fractions and isolated compounds against red rust flour beetle, *Tribolium castaneum* (Herbst.) and revealed the adults of *T. castaneum* as more susceptible to eugenol. Their results also indicated that bay leaf essential oil may have potential to control *T. castaneum*. Singh et al. (2016b) evaluated the efficacy of three plant oils and revealed neem and eucalyptus oils as the most effective against lesser grain borer, *Rhyzopertha dominica* (L.) in stored wheat. Singla et al. (2018) used ajwain seed (*Trachyspermum ammi*) oil and some other derivatives as stored grain protectant against *S. oryzae*. Mohan et al. (2020) at TNAU developed some eco-friendly methods for stored grain/seed insect management.

Essential oils (EOs)

Widespread use of chemical insecticides in agriculture causing ecotoxicological, environmental and social consequences have led researchers to find out some more reliable and environmental friendly alternatives over the synthetic chemicals. In this context, the use of botanical extracts is attracting considerable interest both among the researchers and consumers. Among botanical extracts used as insecticides, EOs prove most promising alternative because of their worldwide availability and relative cost-effectiveness (Compolo *et al.* 2018). EOs are secondary metabolites synthesized by plants, and they play very important roles in plant defense (both against biotic and abiotic stresses) and signaling processes, including the attraction of pollinators and beneficial insects (Pavela 2015; Zurate & Salgueiro 2015). EOs are synthesized by plants both internally (secretory glands allocated inside the plants) as well as externally (secretory glands placed on the plant surface) (Svoboda & Greenaway 2003). They are produced by different plant organs such as trademark owners, herbs, buds, leaves, fruits, twigs, barks, seeds, woods, rhizomes, roots and can be accumulated in specific histological structures (glandular trichomes, secretory cavities, and resin ducts) (Asbahani *et al.* 2015; Fahn 2000). Plant species that produce EOs are called aromatic plants and are distributed worldwide; these plants (over 17,000 species) belong to a limited number of families: Asteraceae, Cupressaceae, Lamiaceae, Lauraceae, Rutaceae, Myrtaceae, Piperaceae, and Poaceae (Bruneton 1999). EOs are mainly constituted by monoterpenes and sesquiterpenes synthesized in the cytoplasm and plastids. All terpenes are synthetized via either the methylerythritol 4-phosphate (MEP) pathway or the mevalonate-dependent (MVA) pathway. Two (C5) isoprene precursors, isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP), are involved in the terpene synthesis and the isoprene units determine their class (monoterpenes, C10; sesquiterpenes, C15) (Zebec *et al.* 2016). Sesquiterpenes contain 15 carbon atoms, and they are less volatile and have a higher boiling point than monoterpenes. As a consequence, fewer of them contribute to the fragrance of EOs (Husnu & Buchbauer 2015).

The EOs are constituted by a blend of 20 to 70 organic compounds, some of which represent more than 80% of the constituents as append, e.g., in Sweet Orange EO, the main compound, limonene reaches 88- 97% of the whole oil (Campolo *et al.* 2014). Generally, the main components characterize the biological activity of the EOs. The EOs are hydrophobic and generally lipophilic, and their density is often lower than that of water and they are soluble in organic solvents. Despite the numerous extraction methods used to obtain EOs from natural raw plant material, only four methods, such as (i) hydro distillation, (ii) steam distillation, (iii) dry distillation, and (iv) mechanical processes are considered in the European Pharmacopoeia and the International Standard Organization on EOs (Zurate and Slguerio 2015). The EOs can undergo physical treatments, which do not result in any significant change in its composition (e.g., filtration, decantation, and centrifugation) but the resulted products consist of a blend of volatile compounds with a strong odor (Bakkali et al., 2008).

Extraction methods

Hydro distillation: It is one of the recent the standard EO extraction methods from plant materials like wood or flower, which is often used to isolate non water-soluble natural products with high boiling point. It involves the complete immersion of plant materials in water, followed by boiling. This method protects the oils extracted to a certain degree since the surrounding water acts as a barrier to prevent it from overheating. The advantage of this technique is that the required material can be distilled at a temperature below 100 °C. Okoh et al. (2010) studied the different extraction processes on yield and properties of EO from rosemary (*Rosmarinus officinalis* L.) by HD and solvent-free microwave extraction (SFME). The total yields of the volatile fractions obtained through HD and SFME were 0.31% and 0.39%, respectively. HD oil contained more monoterpene hydrocarbons (32.95%) than SFME-extracted oil (25.77%), while higher amounts of oxygenated monoterpenes (28.6%) were present in the oil extracted by SFME in comparison with HD (26.98%). Golmakani and Rezaei (2008) studied the microwave-assisted HD (MAHD), which is an advanced HD technique utilizing a microwave oven in the extraction process. MAHD was superior in terms of saving energy and extraction time 75 min, compared to 4 h in HD). Ohmic-assisted HD (OAHD) is another advanced HD technique (Gavahian *et al.* 2012). OAHD method had the extraction time of 24.75 min, while HD took 1 hour for extraction of EO from thyme. No changes in the compounds of the EOs obtained by OAHD were found in comparison with HD. Hydro distillation method is considered the simplest one to obtain EOs from the plant material by immersion of biomass in boiling water. The oil contained in the oil cells diffuses by means of osmosis in the hot water; then the steam, produced by boiling water, carries the oil vapors in a condenser. The condensed EOs are separated from water by decantation.

Steam distillation: In this, the vapor is supplied in such a way that liquid water does not come into contact with the vegetable raw material. In the simplest version, steam is generated by water added in the lower part of the distiller; the plant raw material is separated from the liquid water by a perforated grid. The steam that passes through the plant material carries the oil vapors, and after passing through a condenser, EO is separated from water by decantation. It is the most widely used method for plant EO extraction (Reverchon and Senatore, 1992). The proportion of EOs extracted by steam distillation is 93% and the remaining 7% can be further extracted by other methods (Masango, 2005). The heat applied is the main cause of burst and break down of cell structure of plant material. As a consequence, the aromatic compounds or essential oils from plant material are released (Perineau et al., 1992; Babu and Kaul, 2005). The temperature of heating must be enough to break down the plant material and release aromatic compound or essential oil. A new process design and operation for steam distillation of EOs to increase oil yield and reduce the loss of polar compounds in wastewater was developed by Masango (2005). The system consists of a packed bed of the plant materials which sits above the steam source. Only the steam passes through it and the boiling water is not mixed with plant material. Thus, the process requires the minimum amount of steam in the process and the amount of water in the distillate is reduced. Also, water soluble compounds are dissolved into the aqueous fraction of the condensate at a lower extent (Masango, 2005). Yildirim et al. (2004) reported that the 2, 2-diphenyl-1-picryl hydrazyl (DPPH) radical scavenging activities of EOs from steam distillation process were markedly higher than those of oils extracted using hydro distillation (HD).

Solvent extraction: This method employs food grade solvents like hexane and ethanol to isolate EOs from plant material. It is best suited for plant materials that yield low amounts of essential oil, that are largely resinous, or that are delicate aromatics unable to withstand the pressure and distress of steam distillation. This method also produces a finer fragrance than any type of distillation method. Through this process, the non-volatile plant material such as waxes and pigments, are also extracted and sometimes removed through other processes. Once the plant material has been treated with the solvent, it produces a waxy aromatic compound called a "concrete." When this concrete substance is mixed with alcohol, the oil particles are released. The aforementioned chemicals used in the process then remain in the oil and the oil is used in perfumes by the perfume industry or for aromatherapy purposes.

Conventional solvent extraction has been implemented for fragile or delicate flower materials, which are not tolerant to the heat of steam distillation. Different solvents including acetone, hexane, petroleum ether, methanol, or ethanol can be used for extraction (Areias et al., 2000; Pizzale et al., 2002; Kosar et al., 2005). For general practice, the solvent is mixed with the plant material and then heated to extract the essential oil, followed by filtration. Subsequently, the filtrate is concentrated by solvent evaporation. The concentrate is resin (resinoid), or concrete (a combination of wax, fragrance, and essential oil). From the concentrate, it is then mixed with pure alcohol to extract the oil and distilled at low temperatures. The alcohol absorbs the fragrance and when the alcohol is evaporated, the aromatic absolute oil is remained. However, this method is a relatively time-consuming process, thus making the oils more expensive than other methods (Li et al., 2009). Essential oil with antioxidant activity from *Ptychotis verticillata* was extracted using solvent extraction method by El Ouariachi et al. (2011). The oil was dominated by phenolic compounds (48.0%) with carvacrol (44.6%) and thymol (3.4%) as the main compounds. Ozen et al. (2011) studied the chemical composition and antioxidant activity of separated EOs from *Thymus praecox* subsp. *skorpilii* var. *skorpilii* (TPS) extracted using different solvents. TPS essential oil was found to contain thymol (40.31%) and o-cymene (13.66%) as the major components. The ethanol, methanol, and water extracts exerted significant free-radical scavenging activity. The water extract has the highest total phenolics (6.211 mg gallic acid/g dry weight) and flavonoids (0.809 mg quercetin/g dry weight). Moreover, Sarikurkcu et al. (2009) reported that the water extract exhibited higher antioxidant activity than other extracts (hexane, dichloromethane, ethyl acetate, and methanol). However, solvent residue could be retained in the final produc due to incomplete removal. This may cause allergies, toxicity, and affect the immune system (Ferhat et al., 2007).

Cold-press extraction: This method is also called expression or scarification and is used for citrus peels in particular. In this the whole fruit is placed in a device that mechanically pierces it to rupture the essential oil sacs, which are located on the underside of the rind. The whole fruit is pressed to squeeze out the juice and the oil. The oil and juice that are produced still contain solids from the fruits, such as the peel, and must be centrifuged to filter the solids from the liquids. The oil separates from the juice layer and is siphoned off into another receptacle. The essential oil and pigments run down into the device's collection area (Benjakul and Tongnuanchan, 2014).

Plant volatiles as alternative

Plants being one of nature's chemical producers provide several bioactive organic chemicals whose major role in plants was found to be defensive, especially against insect pests (Isman, 2006). Those organic bioactive compounds provide an odor that is typically volatile in nature and hence termed as PVOC (plant volatile organic compounds). However, considering the dangers associated along with the chemical insecticides, use of plant components with no or fewer threats forms the most viable option for the effective control measures against the various pests of tropical agricultural systems (Rajashekar et al., 2016). There are various plant species which embody a rich source of phytochemicals that could be explored for use as insecticides (Green et al., 2015). The secondary metabolites of plants were once considered to be waste products. However, the important role played by them in the plant defense mechanisms make them as one of the most interesting aspects of crop protection (Bennett and Wallsgrove, 1994). In addition, they also act as attractant or repellent in insect-pest management. Secondary metabolites are known to influence the growth and development, ecdysis, mating behavior, fertility, and adult emergence of insect pests. Numerous defensive chemicals of plant origin have already been identified. Plant volatiles organic compounds are generally much safer to human beings and to the environment. There is also less chance of developing resistance to the different botanical pesticide by the insect pests since these botanical pesticides possess a mixture of chemical components of a complex nature. Hence, plant-derived molecules could thrive in the fight against insecticide-resistant insect pests. It is well documented that farmers, especially in the developing countries like Asia, Africa, and other parts of the world are using botanicals as a measure to protect stored grains from bruchid infestation with varying degrees of success (Rajashekar et al., 2010) The secondary metabolites are often involved in plant defense mechanism, but not directly involved in growth, development, or reproduction of plant. Secondary metabolites include terpenoids, phenolics and alkaloids and these phytochemicals possess enormous potential to act as biopesticides. Over 2000 plant species boast pesticidal properties against several stored grain pests. Several authors also set forth various plant products along with their efficacy against the stored grain pests. These plant-derived botanicals are generally used in the form of aqueous/solvent extracts, powders, slurries, volatiles and oils, or as shredded segments. Hence, plant-derived botanicals hold promise as an alternative to synthetic insecticides to lessen the negative impact of the pesticide on the environment.

Chemistry of EOs

The EOs are naturally found in plants as secondary metabolites which play an important role in plant defense system against microorganisms, insects, herbivores and allelopathic interactions (Bakkali et al., 2008). Previous studies have reported that volatile compounds of EOs can be classified into four groups: (a) Terpenes, (b) Benzene derivatives, (c) Hydrocarbons and (d) Other miscellaneous compounds. Based on the number of isoprene units in the chemical structures of terpenes, EOs are classified into (a) Hemiterpenes (1 unit, C5), (b) Monoterpenes (2 units, C10), (c) Sesquiterpenes (3 units, C15), (d) Diterpenes (4 units, C20) and consequently, it has been found that most terpenes in EOs are monoterpenes (C10H16) and sesquiterpenes (C15H24). However, monoterpenoids are the most terpenes and represented by 90% of EOs (Zuzarte and Salgueiro, 2015). Monoterpenes have a chemical structure which varies greatly along with various functions. Monoterpenes and their related chemical structure compounds have 10-carbone hydrocarbon. These chemical structures divided into (1) Acyclic alcohols such as linalool, geraniol and citronellol, (2) Cyclic alcohols such as menthol, isopulegol and terpeniol, (3) Bicyclic alcohols such as borneol and verbenol, (4) Phenolic compounds such as thymol, carvacrol, (5) Ketones such as carvone, menthone and thujone, (6) Aldehydes such as citronellal, citral, (7) Acids such as chrysanthemic acid and (8) Oxides such as cineole (Tripathi et al., 2009).

Biopesticides

For two decades, EOs are used as insecticides to control insects, however, they have not reached their full potential because they are highly volatile and bearing low residual activity (Orlando et al., 2018). They are considered safe, eco-friendly and compatible with biological control programs and have low mammalian toxicity. Also, EOs available worldwide have their low to moderate cost. The main active constituents with insecticidal activity are monoterpenes, sesquiterpenes and related phenyl propenes. The EOs can be applied as pesticides as they are or as their active components "Active ingredient" or as co-adjutants in pesticide formulations. However, they can be acted as a contact insecticide, causing changes in the pathways of biochemical metabolism of the insect, knockdown and rapid death (Saxena et al., 1992), fumigants (Shaaya et al., 1997), repellents and antifeedant.

Toxicity and mode of action

The plant products with potent insecticidal activity could be used for the control of stored beetles. Many authors have reported that plant volatiles are toxic and effective in enhancing the mortality of adult beetles infesting stored grains. The plants are known to produce diverse secondary phenolic compounds which could have played a major role in inflicting the contact toxicity and mortality effect to these stored grain insects (Lattanzio et al., 2006). Kim et al. (2003) reported that the extract from the Chinese cinnamon, *Cinnamomum cassia* (L.); Lauraceae bark and oil; scurvy grass, *Cocholeria auracaria* (L.); mustard oil, *Brassica juncea* (L.) showed potent insecticidal activity against pests like *C. chinensis*. The fumigation is one of the methods in stored products pest management and it is done for killing the insects or to avoid further damage to the infested commodities. Fumigants are substances that vaporize at the temperature above 5^0C. They act in gaseous or smoke form with high penetration power and usually applied in an enclosed/airtight system. In the vapor phase, plant volatile organic compounds can penetrate through the insect's respiratory system and exhibit its toxic effect (Choi et al., 2003). The fumigant activity of plant products may be due to different functional groups attached to these volatile chemicals which enable them to persist in a closed environment for a longer time (Zang et al., 2011). One of the advantages of bio-fumigants is that it has the potential to provide a novel mode of action against insects that could nullify the danger of cross-resistance as well as offering a new lead for the design of target-specific molecules. PVOC from many plant extracts and essential oil consists of alkanes, alcohols, aldehydes, terpenes and terpenoids especially monoterpenoids. Phytochemicals which exhibit effect on insects in terms of their toxicity, repellency, antifeedant, fumigant, growth inhibitors, suppression of reproduction and reduction of fecundity.

Phytochemicals are known to affect growth, development, and metamorphosis of insect. These cause irreversible changes in the physiology and behavior of insect, such as reduction in weight of larvae, pupae and adult, as well as prolonged larval and pupal periods (Rosenthal et al., 1995). Several plant volatiles with potential insect growth regulator and sterilant characteristics have been assessed in this respect. Various plant extracts showed inhibition in percentage pupation upon larval treatment. The EOs from *Cymbopogon schoenanthus* (Spreng) (Poaceae) show inhibition of growth and development in all life stages of *C. maculatus*. The Plant-derived botanicals were also found to inhibit the development of eggs and immature stages inside grain kernels. Aqueous extracts of common cocklebur *(Xanthium strumarium*

(L.) (Asteraceae) leaf was also reported to show several insecticidal properties including toxicity, repellency, inhibition of fecundity and adult emergence of the insects and grain protection against *C. chinensis* (Roy et al., 2014).

Several investigations have been carried out to screen various plant extracts for their juvenilizing effect. Rani and Jamil (1989) discovered that plant extracts of water hyacinth containing a juvenile hormone analogue that causes abnormal moulting and metamorphosis of stored grain insects. Their role in regulating the reproduction of insect is also well studied. Lingampally et al. (2012) reported Solasodine @ 1 μg/μl to inhibit moulting and induce several morphogenetic abnormalities leading to the death of 5th instar larvae of *Tribolium confusum* (Jacquelin du Val) (Tenebrionidae) during moulting and could affect adult emergence. Oviposition deterrents are chemicals which prevent or avoid insect from egg laying. Oviposition deterrents have huge potential to prevent insect infestation and can offer the first line of defense against insect pests. Plant volatiles are generally used as cues by ovipositing females for locating host plant or substrates. Many experts have reported the involvement of PVOC in part or completely preventing egg laying as well as the emergence from the laid eggs on stored grains by different families of insect pests. The chemical compound, 1, 8 cineole isolated from EOs and their volatile component of various plants within Lamiaceae family was found to affect the oviposition rate of various insects (Koschier and Sedy, 2001). Used of garlic oil as an oviposition deterrent is also common (Yang et al., 2012). EOs of *Eucalyptus citriodora* (Hook.), *E. globulus* (Labill.) and *E. staigeriana* (F. Muell.) showed severe effects on the oviposition thereby reducing the viability of eggs and insect's emergence of *Zabrotes subfasciatus* (Chrysomelidae) and *C. maculatus* (Tapondjou et al., 2005). The EOs of other plants, viz., *Trachyspermum ammi* (L.), *Anethum graveolens* (L.) and *Nigella sativa* (L.) have affected the oviposition potential and delayed the developmental period of *T. castaneum*. It also caused deformities in insect metamorphosis. *Laurus nobilis* (L.) (Lauraceae) and *Rosmarinus officinale* (L.) (Lamiaceae) are known to cause egg mortality (Isikbe*r* et al., 2006). In a study, the effect of finely powdered and intact dried leaves of *Ocimum canum* Sims (Lamiaceae) on adults of *Zabrotes subfasciatus* (Roheman) in dried Pinto beans were determined. It was reported that the finely powdered dried leaves completely suppressed the oviposition at 2% W/W, with an EC50, of 0.45% W/W and also there was no effect of intact dried leaves reported on the insect's population. In a similar report, powdered and intact dried leaves from four locally grown plant species, i.e., *Chenopodium ambrosioides* (L.) (Amaranthaceae), *Tagetes minuta* L. (Asteraceae), *Azadirachta indica* A. Juss (Meliaceae), *C. lusitanica*, applied at a rate of 1.5 kg per 100 kg beans (*Phaseolus vulgaris*) against *A. obtectus* and *Z. subfasciatus* was compared under laboratory conditions. *C. ambrosioides* was found to be the most effective with 100% mortality of adult insects in less than three days and no progeny. *T. minuta* applied as powder also increased mortality and reduced oviposition and progeny production significantly. While *A. indica* or *C. lusitanica* applied as powder or as whole leaves showed no significant effects upon mortalities, oviposition rate, or progeny production compared with control treatments (Paul et al., 2009).

The feeding deterrents are the chemical substances that disrupt the feeding behavior of insect by making the treated food unappealing or unpalatable. Antifeedants can also induce cessation of feeding either temporarily or permanently. The presence of certain chemicals in plants prevents insects from feeding on them, thus leads to starvation of the insects and, eventual mortality. A very distinctive feature of antifeedants is the way it inflicts effect on insects when in contact with such substances. Antifeedant attempts to eliminate insects without ever disturbing the ecological balance. Antifeedant don't kill the target insect, rather it allows them to be available for their natural enemies. The deleterious effects could be activated to serve a novel role in the management of stored grain insect pest. The identification of azadirachtin and neem seed extracts, during 1970s and 1980s, as potent feeding deterrent pave the way for natural antifeedant (Casida 2012). The EOs from *Gaultheria procumbens* (L.) (Ericaceae) show potent antifeedant properties against Coleopteran insects S. *oryzae* and *R. dominica* (Kiran & Prakash 2015). The feeding behavior of three stored grain insects, *S. oryzae, R. dominica* and *T. castaneum* were reported to change significantly when flavanoids compounds, Isoglabratephrin, (þ)-glabratephrin, tephroapollin-F and lanceolatin-A isolated from *Tephrosia apollinea* (Delile), were treated at different test concentrations of 0.65, 1.3 and 2.6 mg g^{-1}. The relative growth rate and efficiency of conversion of ingested food were also significantly reduced by all the treated insects.

These are the chemical substances that protect plants or stored grain products from insect's damage by rendering the stored grains as unattractive, unpalatable or offensive to the infesting insect pests. PVOC mostly affect adult beetles causing them to flee from treated grains, or not to invade it at all. The properties of repellency of plant volatiles could have an important implication in the traditional postharvest storage system. Generally, they are available locally and it makes them further an attractive candidate in the management of stored-grain insect pests. The α-terpineol, pulegol and germacrol volatile compounds isolated from *Baccharis salicifolia* Ruiz & Pav. (Asteraceae) showed potent repellent properties against *T. castaneum*. The ar-turmerone isolated from *Curcuma longa* (L.) (Zingiberaceae) rhizomes were reported to show effective repellent activity against *S. zeamais*. Different solvent extracts (Hexane, chloroform, ethyl acetate) of three widely grown plants like *Sphaeranthus indicus* (L.) (Asteraceae), *Tephrosia purpurea* L. (Fabaceae) and *Prosopis juliflora* (Sw.) DC. (Fabaceae) were reported to show repellent activity against *T. castaneum*. Repellent activity of hexane extract of *P. juliflora* were reported with EPI value in 2.5% 0.11 and 0.33 at 1 hours and 6 hours, respectively, while the EPI value of chloroform extract of *T. purpurea* 2.5% at 6 h was 0.17. For *S. indicus* the EPI value was 0.65 at 2.5% and 6 hours (Pugazhvendan et al., 2012). (Z)-asarone is an active constituent isolated from the ethanolic extract of *Acorus calamus* (L.) (Acoraceae). This compound is reported to have strong repellency against *S. zeamais* (Yao et al., 2008). The repellent property of EOs of *Callistemon lanceolatus* (Sm.) Sweet (Myrtaceae) and *Lippia alba* (Mill.) (Verbenaceae) against *C. chinensis* is also well documented. The EOs of aromatic plants such as *Cymbopogon fexuosus* (Paoceae), *C. winterianus* (Paoceae) and *C. martini* (Paoceae) @ 1.41 µL/ cm^2 were reported to have strong repellent effect against *T. castaneum.*

Substance or agent that has the potential to kill eggs especially the eggs of insects, mites etc. are considered to have ovicidal effect. Many plants are known to possess the ovicidal property. This property of plants is of great importance in the management of insect-pests at every stages of their life cycle, thereby preventing the damage caused by other stages (Hong et al., 2018). Application of botanicals on eggs could tremendously reduce the number of adult emergence which is probably due to either chemical toxicity and/ or physical properties, which cause changes in surface tension within the egg similar to those of oils. Salunke et al. (2005) revealed that flavonoids which were isolated from *Calotropis procera* (Ait.) were toxic to the eggs of *C. chinensis* with 100% progeny suppression at 10 mg/mL concentration. The EOs of Indian dill, *Anethum sowa* (L.) (Apiaceae) were also reported to show ovicidal effect on eggs of C. maculates. L-menthol is an active component, isolated from the essential oil of *Mentha arvensi* L. (Lamiaceae), which has high ovicidal effect on eggs of *T. castaneum* (Aggarwal et al., 2001). The EOs of cardamom (*Elletaria cardamomum*) L. (Zingiberaceae), *Cinnamomum zeylanicum* Blume (Lauraceae), *Sygium aromaticum* L. Merrill. et. Perry) (Myrtaceae), *Eucalyptus* spp. and *Azadirectica indica* A. juss (Meliaceae) were also found to have ovicidal effects on eggs of *T. castaneum.*

Chemosterilants are the substances which deprive insects of their ability to reproduce. Such substances produce irreversible sterility without affecting their mating behavior or its life span but only prevent the production of F1 progeny. In some cases, eggs may not be laid, fail to hatch, larvae may not pupate, or the pupal development will be incomplete. Chemosterilants cause damage to the ovaries resulting in inhibition of egg formation (Beroza and LaBrecque, 1967) Thus, ovarian development is prevented, and it leads to sterility. Chemosterilants has proven to be an important aspect of integrated pest management programs as it reduces the occurrence of pest-resistant. Saxena et al. (1977) found that asarone isolated from the rhizomes of *A. calamus* possessed insect chemosterilant properties, causing inhibition of insect's interstitial cell activity. The active principle, 1, 3, 7-trimethylxanthine isolate from seed extract proved effective as chemosterilant for *C. chinensis.*

Like other toxic compounds, plant derived insecticides may also induce changes in the behaviour of insects. They either stimulate or reduce the insect's mobility or flight patterns, and even cause physiological alterations. Naturally, insects will tend to move away from the insecticide exposed area as soon as the presence of toxic compounds is detected. Besides EOs are known to inhibit acetylcholine esterases enzyme on insect's nervous system while also disrupting the GABAergic (Bloomquist et al., 2008) and aminergic transmissions (Kostyukovsky et al., 2002). However, EOs when given in sub lethal dose on insects can contribute to the development of resistance against traditional insecticides that could also compromise the management strategy of insect-pests. In an experiment, Haddi et al. (2015) investigated the toxicity and locomotory as well as respiration responses induced by EOs of clove and cinnamon on *S. zeamais*. It was reported that *S. zeamais* populations gave stimulatory response in median survival time when exposed to sublethal dose. The respiratory rates of *S. zeamais* (i.e., CO_2 production) were significantly reduced under low concentrations of the EOs.

The mechanism of toxicity, site of action of EOs and their chemical compounds as bio-insecticides were investigated (Bakkali et al., 2008). They have insecticidal, repellent, antifeedant and IGR activities. This fact shows that the EOs can disrupt insect physiology in different ways. However, the activity of EOs as insecticides caused the inhibition of acetylcholinesterase (AChE) or by blocking the octopamine receptors (Enan, 2001). Also, γ-aminobutyric acid (GABA) receptor was suggested as one of the mechanisms of EOs induced toxicity in insects. They can interfere with GABA-gated chloride channels in insect. For example, some monoterpenes such as thujone can induce the neurotoxic effects by acting on GABA receptors in insects (Ratra & Casida 2001). Besides, these modes of action of EOs on insects, some effects on the hormone and pheromone system and cytochrome P450 mono oxygenase were reported. Infact, octopamine is a neurotransmitter, neurohormone and circulating neurohormone-neuromodulator. Its disruption affects working of the nervous system in insects. The octopamine receptor was not found in vertebrates. Therefore, EOs as bioinsecticides has selective toxicity to mammalian. Concerning the anti-cholinesterase effect of EOs, the mechanism of neurotoxic action and symptoms are similar to that induced by organophosphates and carbamate insecticides (Isman, 2000). The symptoms shown are hyperactivity, convulsions, tremors and then paralysis (Enan, 2001). Several studies point out that EOs and monoterpenoids induce mortality by inhibiting AChE activity in insects. The neurotoxic effect of EOs may be due to the inhibition of AChE at the hydrophobic site168. However, some monoterpenoids are anticholinesterasic e.g., pulegone, 1, 8-cineole169, fenchone, carvone and linalool (Lopez *et al* 2010). In addition, the toxicity of EOs constitutions has resulted in the octopaminergic nervous system of insects. In contrast, Emekci et al. (2004) reported that monoterpenes can have effect on many targets in insects with numerous mechanism of toxicity.

Nanoinsecticides: Although, the promising activities of EOs against many insects, some problems were also registered, e.g., EOs volatility, water solubility and oxidation, that playing an important role in the EOs activity, application and persistence. Therefore, these problems must be resolved before using the EOs as an alternative to synthetic pesticides for pest control (Marrio et al., 2002). New formulations with nanotechnology "Nano-formulation" can resolve these problems. The new trends for using nano formulation lead to protect the Eos' from degradation, increase their residue half-life by reducing the evaporation. They can achieve a controlled release of EOs and ease of application and handling. These nano-formulations can enhance EOs activity due to the small particle size. It had a high surface area, solubility and mobility. Due to their solvent elimination, they have low toxicity to mammals (Kah et al., 2013). However, polymeric nanoparticles are the most promising for EOs nano-formulations. Anjali et al. (2010) reported that the insecticidal activity of neem oil was increased in nano-emulision formulation. This effect can be due to the smallest droplet size of EO nano-emulision (31.03 nm). Yang et al. (2009) showed that loaded nanoparticles with garlic EOs are active to control *T. castaneum*. New nanotechnology methods were planned to control *H. armigera*. As a result of this new method EO *of Artemisia arborescens* was stable. This stability can be due to formulation of EO with solid lipid nanoparticles and developed an emulsion. This emulsion has got better stability and insecticidal activity. The nano-encapsulation shown high repellent activity than EOs, e.g. nano-encapsulation of *Artemisia* oil and show more activity than normal oils at concentration of 1.9 ppm. The activity of nano-capsule was 80, whereas 62% for pure oil against *P. xylostella* (Negahban et al., 2014). Ebrahimifar et al. (2020) evaluated the effects of essential oil from *Ferulago angulata* (Schlecht.) The essential oil from *F. angulata* could be used for reducing *T. castaneum* and *R. dominica* populations without adverse effects on seed viability. Giunti et al. (2021) studied bioactivity of essential oil-based nano-biopesticides towards *R. dominica*. The results demonstrated that habituation could occur for repellent EO-based formulations, thus this behavioral process can reduce the effectiveness of these kind of treatments against *R. dominica* and should be considered to articulate adequate IPM programs against stored product pests.

AUTHOR CONTRIBUTION STATEMENT

All authors equally contributed.

CONFLICT OF INTEREST

No conflict of interest.

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