



Essential Oils and Their Formulations for the Control of Curculionidae Pests

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Pesticides are widely used in producing food to control pests. However, it has been determined that synthetic pesticides present severe toxicity (residual), while they also result in environmental contamination and development of high-level resistance in some insect species. Due to this, some of these substances have been banned or restricted in many countries, which has reduced the number of agrochemicals that can be used for pest control, particularly in the case of crops exported to green markets such as Europe and Asia. Under this scenario, essential oils (EOs) are being increasingly studied as bioinsecticides because they are renewable, natural, biodegradable, non-persistent in the environment and safe to non-target organism and humans. It has been determined that EOs have repellent, ovicidal, larvicidal, and insecticidal effects against different types of pests, but they also have some drawbacks due to their high volatility and low aqueous solubility. This mini-review focusses on EOs used as bioinsecticides for the control of Curculionidae and on current stabilization techniques, such as nanoencapsulation, to prolong the biocidal effect of EOs against these pests.

Keywords: essential oils, curculionidae, bioinsecticide, nanoencapsulation, pest

INTRODUCTION

Curculionids (Curculionidae), known as weevils, are a family of herbivorous phytophagous coleopterans. Some species of weevil are harmful to agriculture, affecting plantations and stored products (Tewari et al., 2014). The life cycle of this pest passes through the stages of egg, larva, pupa, and adult (Fiaboe et al., 2012). When they are in the larval stage, they attack plantations, causing damage to the neck and crown of the plants (Espinoza et al., 2018). Adults have a mouthpart with powerful jaws that allow them to consume the laminae of leaves, shoots, twigs, and fruits, causing deep gouges in lignified tissues of trees and woody shrubs (Espinoza et al., 2016). Some subspecies of this group are classified as quarantine pests requiring phytosanitary treatments to ensure that exported products are free of these pests.

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Insect damage on *Brassica* (*Brassica napus* L, *Brassica oleracea* var. *botrytis*, *Brassica oleracea* var. *capitata*) crops ranges from 10 to 90%, with an average of 35 to 45% (Pavela, 2016), varying significantly depending on the type of pest and crop, climatic conditions, and incidence of natural enemies (Grzywacz et al., 2014). Even though traditional methods used to control pests with synthetic insecticides have successfully counteracted such damage, their use and excessive application have harmed human health and the environment (Nicolopoulou-Stamati et al., 2016). Because of this, some synthetic insecticides have been banned or their use has been restricted and regulated, with maximum residue limits (MRLs) being lowered in some countries. As a result, producers have higher costs, while their products may not have access to some international markets (Rodríguez-Saona et al., 2019; Wahab et al., 2022). Under this scenario, the need to reduce or replace the use of synthetic insecticides with natural products has led to the search for eco-friendly methods of pest control. In recent years, essential oils (EOs) have gained popularity because they are readily available in different plants, and they also present low toxicity for mammals and high degradation patterns.

EOs have been tested as botanical insecticides against a wide range of pests that attack crops such as lettuce, coffee, soybean, cereal grains, legumes, and maize. (Boulogne et al., 2012; Menossi et al., 2021). Carvacrol, linalool, alpha-pinene, menthol, cinnamaldehyde, eugenol, 1-8 cineole, geraniol, and limonene are some of the components of EOs that have shown insecticidal activity against different pests (Regnault-Roger et al., 2012; de Oliveira et al., 2014; Singh et al., 2021). However, the main disadvantage of EOs is that they are highly volatile and susceptible to degradation by factors such as moisture, light, or air (Menossi et al., 2021). In this sense, nanoencapsulation can improve the effectiveness and stability of EOs, preventing fast volatilization and degradation.

This mini-review focusses on EOs used as bioinsecticides for the control of Curculionidae and on current encapsulation techniques to prolong the biocidal effect of EOs against these pests.

PESTS

Globally, the Curculionidae is the largest family of insects, with about 60,000 species (Anderson, 2002), but not all of them are considered pests. In terms of natural pest control, only a limited number of these species has been managed using EOs.

The most important Curculionidae pests are described in **Table 1**. *Sitophilus zeamais*, commonly known as corn weevil or rice weevil, is one of the most important pests that attack grains and stored seeds, resulting in both quantitative and qualitative losses (Romani et al., 2019). Larvae and adults cause the most significant damage, affecting nutritional levels, weight loss, taste, odor, and decrease in the germination capacity of the grains such as wheat, rice, sorghum, maize, and others (Patiño-Bayona et al., 2021b). *Sitophilus zeamais* and *Sitophilus oryzae* are very closely related species that are difficult to differentiate, and thus morphological or DNA tests are required (Moon, 2015). *Sitophilus oryzae* is also one

of the most destructive pests of grains, causing weight loss and affecting the nutritional value of grains, and finally resulting in significant economic losses (Maazoun et al., 2017).

Sitophilus granarius or wheat weevil attacks stored grains, also causing significant damage. Unfortunately, this insect is difficult to detect, and once it has infested a facility, all stored products must be destroyed (Plata-Rueda et al., 2018). The most effective control method for this type of pest, which specifically attacks stored products, is fumigation (Abdelgaleil et al., 2016).

Rhynchophorus ferrugineus, known as the red palm weevil, attacks coconut, date, and oil palm crops, resulting in significant damage (Antony et al., 2016). The larva is the most damaging stage of the pest, specifically attacking the heart of the palm, where it can live between 25 and 105 days before turning into a pupa. When the damage caused by the pest is visible, it means that the palm tree is already critically infested with high population levels, resulting in palm trees being felled and transported to a safe place to prevent further propagation (Al Dawsari Mona, 2020). Adults do not cause the highest level of damage, but they can fly 900 m in a single flight and travel up to 7 km, infesting quickly (Fiaboe et al., 2012).

Other important curculionid pests are *Aegorhinus superciliosus* and *Aegorhinus nodipennis*, which mainly attack hazelnut, blueberry, and raspberry plantations. These pests are found mainly in Chile and Argentina (Espinoza et al., 2016). The larval stage of both *Aegorhinus* species causes damage to the collar or crown of plants, causing premature reddening, yellowing, reduction of new twigs, and even death of plants when the attack is severe. Adults have mouthparts with powerful mandibles that allow them to consume leaf laminae, shoots, twigs, and fruits, causing deep gouges in lignified tissues of trees and woody shrubs (Tampe et al., 2015; Tampe et al., 2016; Tampe et al., 2020).

There is little information on the use of EOs for the control of *Hylastinus obscurus*, *Hypothenemus hampei*, *Listronotus oregonensis*, and *Xylosandrus germanus*, known as ambrosia beetles. The most common exotic ambrosia beetle is *Xylosandrus germanus*, attacking ornamental nursery plants. Unlike other pests, *X. germanus* bores holes to cultivate the fungus *Ambrosiella grosmanniae*, which serves as food for larvae and adults (Ranger et al., 2011; Ranger et al., 2012; Galko et al., 2018). On the other hand, *Hylastinus obscurus*, significantly affects red clover yields (Parra et al., 2013; Quiroz et al., 2017; Espinoza et al., 2018). *Hypothenemus hampei* reduces coffee production and compromises the quality of stored coffee beans (Reyes et al., 2019). In fact, *H.hampei* attacks coffee plantations, ovipositing inside coffee berries or stored green coffee so that larvae feed on them. Finally, *Listronotus oregonensis*, or carrot weevil, causes damage to *Apiaceae* (parsley, carrot, celery, and dill) plantations since larvae feed on their roots, reducing crop yield by up to 50% (Gagnon et al., 2021).

ESSENTIAL OILS FOR CURCULIONIDAE PEST CONTROL

EOs are aromatic and volatile substances with an oily consistency. They are extracted from different plant parts (leaf,

TABLE 1 | Important Cuculionidae pests (Tewari et al., 2014; Barkai-Golan and Follett, 2017; Bandeira et al., 2021).

Species	Common name	Affected crops	References
<i>Rhynchophorus ferrugineus</i>	Red palm weevil	Palm trees	(Mazza et al., 2014)
<i>Rhynchophorus palmarum</i>	Black palm weevil	Coconut palm	(Hoddle et al., 2020)
<i>Sitophilus oryzae</i>	Rice weevil	Seeds	(Wu and Yan, 2018)
<i>Sitophilus zeamais</i>	Maize weevil	Maize	
<i>Sitophilus granarius</i>	Rice weevil	Rice	(Lemic et al., 2020)
<i>Aegorhinus superciliosus</i>	Raspberry weevil	Berries	(Zavala et al., 2011)
<i>Aegorhinus nodipennis</i>	Fruit weevil	Hazelnut	
<i>Diocalandra frumenti</i>	Coconut weevil	Coconut	(Vacas et al., 2017)
<i>Cosmopolites sordidus</i> Germar	Banana corm weevil	Banana	(Alpizar et al., 2012)
<i>Diaprepes abbreviatus</i>	Root weevil	Citrus fruits	(Lapointe et al., 2012)
<i>Sitona lineatus</i>	Pea leaf weevil	Leguminous	(Vankosky et al., 2011)
<i>Sternechus subsignatus</i>	Soybean stalk weevil	Soybean	(Socias et al., 2014)
<i>Heilipus lauri</i>	Avocado seed weevil	Avocado	(Romero-Frías et al., 2019)
<i>Rhabdoscelus obscurus</i>	Sugarcane weevil	Sugar Cane	(Reddy et al., 2011)
<i>Scyphophorus acupunctatus</i>	Agave weevil	Agaves	(Cuervo-Parra et al., 2019)
<i>Hypothenemus hampei</i>	Coffe berry borer	Coffe	(Ruiz-Díaz and Rodrigues, 2021)
<i>Sternochetus Mangiferae</i>	Mango seed weevil	Mango	(Abdulla et al., 2016)
<i>Eusepeus postfasciatus</i>	West Indian sweet potato weevil	Potato	(Okada et al., 2014)
<i>Cylas formicarius Elegantulus</i>	Sweet potato weevil	Potato	
<i>Anthonomus grandis grandis</i> Boheman	Boll weevil	Cotton	(Burbano-Figueroa et al., 2021)
<i>Anthonomus eugenii</i> Cano	Pepper weevil	Pepper	(Rossini et al., 2020)
<i>Anthonomus musculus</i> Say	Cranberry weevil	Blueberry, Cranberry	(Szendrei et al., 2011)
<i>Anthonomus rubi</i> Herbst	Strawberry blossom weevil	Strawberry	(Tonina et al., 2021)

stem, flower, bark and fruit) using conventional methods such as hydrodistillation, steam distillation, dry distillation, or environmentally friendly methods like supercritical fluid extraction, microwave-assisted extraction, ultrasound-assisted extraction, and others (Regnault-Roger et al., 2012; Boukroufa et al., 2015). EOs are mainly composed of terpenoids and phenylpropanoids, which provide them with unique properties (antioxidant, antibacterial, and insecticidal), and can therefore be applied in areas such as pharmaceuticals, food and agriculture (Pavela, 2015; Plata-Rueda et al., 2018).

Research on the use of EOs as insecticides has increased considerably because sustainable agriculture has gained great acceptance, while preference to organic or ecological crops is increasingly becoming popular worldwide. On the other hand, the FDA (Food and Drug Administration) of the United States has recognized that EOs are safer than synthetic insecticides (Hikal et al., 2017). Given the interest in EOs, several research studies have shown that EOs have repellent, insecticidal, ovicidal, and growth inhibitory effects (Hikal et al., 2017; Ikbali and Pavela, 2019; Isman, 2020; Chaudhari et al., 2021). Insecticidal activity can be evaluated by methods such as: a) fumigation, in which EOs can be absorbed, ingested, or inhaled; b) contact, in which EOs should penetrate the cuticle of the insects; and c) ingestion (Nenaah, 2014; de Lira et al., 2015).

One of the essential oils that excels in controlling a wide range of insects of the Curculionidae family is eugenol, which is extracted from cloves, nutmeg, and cinnamon. Contact toxicity tests against different curculionids, such as *S. zeamais* (Gonzales Correa et al., 2015) and *S. granarius* (Plata-Rueda et al., 2018), have reported lethal concentrations to eliminate 50% (LC₅₀) of insects of 0.69 (μL/cm²) for cinnamon against *S. zeamais*, and 2.765 (μL/mL) for eugenol against *S. granarius*. Furthermore, its

contact and fumigant toxicity has also been studied against *S. oryzae* (rice weevil), where two LC₅₀ were reported; 0.376 (μL/cm²) and 963.3 (μL/L) of *Ocimum tenuiflorum* oil (eugenol is the major component of this oil) (Bhavya et al., 2018). On the other hand, a study conducted by Al Dawsari Mona (2020) determined that the application of 0.7 mL of clove essential oil extract (high concentration of eugenol) and 7 mg of clove powder caused 100% of mortality in the *R. ferrugineus* pest, on the first and third day of exposure, respectively.

The presence of α-pinene in the composition of different essential oils allows for insecticidal effects. The α-pinene is found in more significant quantities in plants such as: *Azilia eryngioides* (Apiaceae, endemic to Iran), accounting for 63.8% (Ebadollahi and Mahboubi, 2011); *Hypericum myricariifolium* (found in high mountain regions of the Andes in Central and South America), accounting for 45.52% (Patiño-Bayona et al., 2021b); *Cupressus sempervirens* (Mediterranean cypress), accounting for 37.88% (Abdelgaleil et al., 2016); and *Rosmarinus officinalis*, accounting 23.52% of the total composition. Ebadollahi and Mahboubi (2011) determined that the essential oil of *A. eryngioides* presented a toxic fumigant activity against *S. granarius* in the adult stage, with an LC₅₀ of 20.05 (μL/L) (Ebadollahi and Mahboubi, 2011). Patiño-Bayona et al. (2021b) found that *H. myricariifolium* essential oil showed fumigant toxicity against adult *Sitophilus zeamais* with an LC₅₀ of 463.1 (μL/L) The essential oil of *C. lusitanica* showed contact toxicity against *Sitophilus zeamais* in the adult stage, reaching a mortality rate of 59.2% at a concentration of 2% v/w (Bett et al., 2016).

Limonene is an essential oil that has also been studied for pest control. It comes from citrus species such as *Citrus sinensis*, *Citrus lemon*, *Citrus aurantifolia*, and *Citrus reticulata*, as well as other plants such as *Aegle marmelos* (originally from Asia) and

Lippia alba (Mishra et al., 2013; Abdelgaleil et al., 2016; Fouad and da Camara, 2017; Patiño-Bayona et al., 2021a). A study on its insecticidal activity against adults of *S. zeamais* (Fouad and da Camara, 2017) showed that the oil of *C. reticulata* had a lower mean lethal concentration than that of *C. aurantifolia*, which recorded values of 51.29 $\mu\text{L/mL}$, 1.52 $\mu\text{L/g}$ and 41.92 $\mu\text{L/L}$ in the air when tested for toxicity by contact, ingestion, and fumigant effects, respectively. **Table 2** shows the most recent studies related to the effectiveness of EOs against Curculionidae pests.

MODES OF ACTION: INSECTICIDAL ESSENTIAL OILS

The modes of action (insecticidal effects) of EOs against curculionidae have not been fully described. In general terms, it has been described that EOs inhibit some physiological functions of gamma-aminobutyric acid (GABA) receptors, which is the primary inhibitory neurotransmitter of the central nervous system of insects (Tampe et al., 2015). It has also been determined that plant metabolites can inhibit the actions of acetylcholinesterase (AChE), which hydrolyzes acetylcholine, a neurotransmitter responsible for signal transmission in the central nervous system (López and Pascual-Villalobos, 2010). Bhavya et al. (2018) analyzed the effect of eugenol and *Ocimum tenuiflorum* essential oil on AChE activity in *S. oryzae* (*in vivo*), and reported that eugenol reaches a higher percentage of AChE inhibition after two hours, while both EOs inhibit approximately 40% of AChE only after 4 h of contact. These values are related to the high insecticidal activity of eugenol and *O. tenuiflorum* since inhibiting AChE produces neurotoxic effects against *S. oryzae*, which finally results in the death of the pest (Bhavya et al., 2018).

Another neurotransmitter affected by EOs is octopamine. This substance acts as a neurohormone and neuromodulator, which means that it is involved in several biological processes (Pavela and Benelli, 2016; Upadhyay et al., 2018; Chaudhari et al., 2021). This effect was analyzed by Plata-Rueda et al. (2018), who determined that eugenol, α -pinene, α -humulene, and α -phellandrene produce muscle contractions in the legs and abdomen of the insect, along with an impairment in locomotor behavior associated with the fact that these EOs would cause blockage of octopamine receptor binding sites, which would be related to a modulatory influence on the nervous-muscular system (Plata-Rueda et al., 2018). Furthermore, this neurotoxic effect is responsible for the rapid death of *S. granarius* when in contact with EOs above mentioned.

Hussain et al. (2017) analyzed the insecticidal activity of *Piper nigrum* extract against *R. ferrugineus*, and determined that piperine, which is the main component of the extract, increased the expression of the cytochrome P450 gene, being responsible for the metabolism leading to the release of toxins in insects. Furthermore, when piperine was used in the diet of *R. ferrugineus* larvae, cytochrome P450 expression increased 35-fold, resulting in larval death within six days when using a concentration of 500 mg/L of piperine (Hussain et al., 2017).

ENCAPSULATION FOR PROLONGED EFFECT

Essential oil-based insecticides have several advantages and have proven effective against some Curculionidae species, but they are highly volatile under certain environmental conditions of temperature and pressure conditions. Nanoencapsulation is one of the techniques that can help solve this problem. Nanoencapsulation is based on encapsulating EOs in materials that have some of their dimensions in the nanometer range (between 1-100 nm), including nanoemulsions, lipid nanomaterials, polymeric nanoparticles, and clay nanomaterials (Kumar et al., 2019; Chaudhari et al., 2021; Esmaili et al., 2021).

Nanoemulsions

A nanoemulsion is produced when two phases are mixed, water in oil (W/O) or oil in water (O/W). To properly stabilize these mixtures, surfactants are used to reduce the surface tension between water and oil. It should be noted that O/W nanoemulsions are used to encapsulate EOs (Singh et al., 2017; Heydari et al., 2020; Mohd Narawi et al., 2020). The nanometric size of the droplets produced allows them to have physical stability over time, as it protects EOs from environmental factors.

Nanoemulsions are obtained by two types of techniques: a) high-energy methods and b) low-energy methods. Both techniques are expected to obtain a monomodal droplet size distribution (Espitia et al., 2019). High-energy methods use mechanical devices, which use disruptive forces to obtain smaller droplets; their disadvantages are the high acquisition values of each device and the temperature increases associated with the friction generated by the emulsions. Some of the equipment used include ultrasonic, high-pressure valve homogenization (HPVH), and microfluidization (Sneha and Kumar, 2021). Low-energy methods include phase inversion composition (PIC), phase inversion temperature (PIT), solvent displacement, emulsion inversion point (EIP), bubble bursting, and spontaneous nanoemulsion, which is the most commonly used method to encapsulate EOs (Kupikowska-Stobba and Kasprzak, 2021).

The use of EOs-based nanoemulsions for Curculionidae control has been analyzed in two studies in the literature. Adak et al. (2020) reported 100% and 80% mortality rates for eucalyptus nanoemulsion and eucalyptus oil against *Sitophilus oryzae* (adult) at a concentration of 1.5 $\mu\text{L/cm}^2$ (Adak et al., 2020). Oliveira et al. (2017) analyzed the lethal time (LT_{50}) of thymol nanoemulsion and thymol oil against *Sitophilus zeamais* populations from Maracaju. They found an LT_{50} of 47.5 hours for thymol nanoemulsion versus an LT_{50} of 26.3 hours for thymol oil (Oliveira et al., 2017). Both studies reported that EO-based nanoemulsions resulted in higher insecticidal activity compared to oils, while mortality rates were maintained over time.

Polymeric Nanoparticles

Polymeric nanoparticles can be obtained using biodegradable polymers (obtained from renewable resources) or synthetic

TABLE 2 | Current research on the effectiveness of EOs against Curculionidae pests.

Essential Oils	Major constituents	Mode of toxicity	LC ₅₀	Target Curculionidae	State	References
<i>Illicium pachyphyllum</i>	trans-p-mentha-1(7),8-dien-2-ol	Fumigant Contact	11.49 mg/L 17.33 µg/adult	<i>Sitophilus zeamais</i>	Adult Adult	(Liu et al., 2012)
<i>Lippia alba</i> <i>R. officinalis</i> <i>H. mexicanum</i>	Limonene 1,8-Cineole, α-Pinene nonane	Fumigant	254.1 (µL/L) 243.7 (µL/L) 223.5 (µL/L)	<i>Sitophilus zeamais</i>	Adult	(Patiño-Bayona et al., 2021a)
<i>Eucalyptus sp</i> <i>Laurelia sempervirens</i>	1,8-cineole undetermined	Contact Fumigant	184.3 (µL/L) 2.3 (mL/kg) 177 (µL/L air)	<i>Sitophilus zeamais</i>	Adult	(Torres et al., 2014)
<i>Alpinia purpurata</i> <i>Lippia alba</i>	β-pinene, α-Pinene Carvone Citral	Fumigant Contact	41.4 (µL/L air) 15.2 (µL/mL) 16.7 (µL/mL)	<i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i>	Adult Adult	(de Lira et al., 2015) (Peixoto et al., 2015)
<i>Clove</i> <i>Cinnamon</i> <i>Pimenta</i>	Eugenol Eugenol Chavibetol	Contact Contact	0.45 (µL/cm ²) 0.69 (µL/cm ²) 1522 (mg/kg)	<i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i>	Adult Adult	(Gonzales Correa et al., 2015) (Ribeiro et al., 2015)
<i>pseudocaryophyllus</i> <i>Cupressus lusitanica</i>	Umbellulone, α-pinene, sabinene, limonene	Contact Fumigant	0.21 (%v/w) 29.11 (µL/L air)	<i>Sitophilus zeamais</i>	Adult	(Bett et al., 2016)
<i>Eucalyptus saligna</i>	1,8-Cineole, α-Pinene	Contact Fumigant	17.0 (%v/w) 26.85 (µL/L air)	<i>Sitophilus zeamais</i>	Adult	(de Araújo et al., 2017)
<i>Ocimum basilicum</i> <i>Piper hispidinervum</i> <i>Citrus aurantifolia</i>	Linalool, Methylchavicol Safrole (S)-Limonene	Fumigant Contact Fumigant	7.42 (µL/L air) 58.51 (µL/L air) 2.75 (µL/g)	<i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i>	Adult Adult	(Fouad and da Camara, 2017)
<i>Citrus reticulata</i>	(R)-Limonene	Contact Fumigant Ingestion	51.29 (µL/mL) 41.92 (µL/L air) 1.52 (µL/g)	<i>Sitophilus zeamais</i>	Adult	(Oliveira et al., 2017)
<i>Lippia sidoides (NFs)</i> <i>Lippia sidoides</i> <i>Mustard</i> <i>Lippia sidoides</i> <i>Cupressus sempervirens</i>	Thymol Thymol Allyl isothiocyanate (AITC) thymol and p-cymene α-pinene 3-carene	Contact Contact Fumigant Fumigant Contact Fumigant	26.44 (µg/mg) 7.10 (µg/mg) 4.03 (µL/L) 86.55 (µL/L air) 13.394 ppm 1.402 ppm 6.348 ppm 0.610 ppm	<i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i>	Adult Adult Adult Adult Adult	(de Souza et al., 2018) (Oliveira et al., 2018) (Langsi et al., 2020)
<i>Hypericum mexicanum</i> <i>Hypericum myricariifolium</i> <i>Ocimum basilicum</i> <i>Lavandula dentata</i> <i>Syzygium aromaticum</i>	n-nonane α-pinene Linalool and estragole eucalyptol Eugenol	Fumigant Fumigant Fumigant	223.5 (µL/L) 463.1 (µL/L) 25.4 (µL/L air) 26.9 (µL/L air) 17.326 (µL/2 cm ²)	<i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i> <i>Sitophilus zeamais</i>	Adult Adult Adult	(Patiño-Bayona et al., 2021b) (Moura et al., 2021) (Wagner et al., 2021) (Mishra et al., 2013)
<i>Aegle marmelos</i> <i>Origanum vulgare</i>	Limonene Pulegone	Fumigant Contact	18.488 (µL/2 cm ²) 1.64 (mg/L air) 0.11 (mg/cm ²)	<i>Sitophilus oryzae</i>	Adult	(Abdelgaleil et al., 2016)
<i>Citrus lemon</i> <i>Callistemon viminalis</i>	Limonene 1,8-Cineole	Fumigant Fumigant	9.89 (mg/L air) 0.20 (mg/cm ²) 16.17 (mg/L air)	<i>Sitophilus oryzae</i>	Adult	
<i>Cupressus sempervirens</i> <i>Citrus sinensis</i>	α-Pinene Limonene	Contact Fumigant	0.09 (mg/cm ²) 17.16 (mg/L air) 0.6 (mg/cm ²) 19.65 (mg/L air)	<i>Sitophilus oryzae</i>	Adult	(Khani et al., 2017)
<i>Mentha piperita</i> <i>Rosmarinus officinalis</i> <i>Hyssopus officinalis</i>	Menthol α-pinene cis-pinocamphone	Contact Fumigant	0.27 (mg/cm ²) 299.51 (µL/L air) 115.63 (µL/L air) 78.16 (µL/L air)	<i>Sitophilus oryzae</i>	Adult	

(Continued)

TABLE 2 | Continued

Essential Oils	Major constituents	Mode of toxicity	LC ₅₀	Target Curculionidae	State	References
Ocimum tenuiflorum	Eugenol	Fumigant	963.3 (µL/L)	<i>Sitophilus oryzae</i>	Adult	(Bhavaya et al., 2018)
Agave americana	undetermined	Contact	0.376 (µL/cm ²)			
Mentha piperita	menthone	Contact	8.99 (µg/cm ²)	<i>Sitophilus oryzae</i>	Adult	(Maazoun et al., 2019)
		Fumigant	3.79 (µL/L)	<i>Sitophilus oryzae</i>	Adult	(Mackled et al., 2019)
		Contact	0.036 (mg/cm ²)			
Pinus roxburghii	longifolene	Fumigant	21.31 (µL/L)			
		Contact	0.076 (mg/cm ²)			
Rosa	methyl eugenol	Fumigant	>100 (µL/L)			
		Contact	0.52 (mg/cm ²)			
Melaleuca bracteata	methyl eugenol	Contact	20.4 (µg/adult)	<i>Sitophilus oryzae</i>	Adult	(Zhang et al., 2021)
Cinnamon	eugenol, trans-3-carene-2-ol and benzyl benzoate	Contact	13.80 (w/v)	<i>Sitophilus granarius</i>	Adult	(Plata-Rueda et al., 2018)
Clove	eugenol and caryophyllene		11.95 (w/v)			
Comercial	Eugenol		2.765 (µL/mL)			
	Caryophyllene oxide		2.784 (µL/mL)			
	α-pineno		4.235 (µL/mL)			
Humulus lupulus	undetermined	Contact	16.17 (µg/adult)	<i>Sitophilus granarius</i>	Adult	(Paventi et al., 2021)
Piper nigrum	piperine	Ingestion	342.62 (mg/l)	<i>Rhynchophorus ferrugineus</i>	Larval	(Hussain et al., 2017)
Thymus vulgaris	p- cimeno	Contact	11.4 (µg/mL)	<i>Rhynchophorus ferrugineus</i>	Larval	(Darrag et al., 2021)
			1032 (µL/mL)		Adult	
Ocimum basilicum	thymol		14.6 (µg/mL)		Larval	
			1246 (µL/mL)		Adult	
Eucalyptus resinifera	1,8-cineole	Fumigant	64.72 (µL/L)	<i>Hypothenemus hampei</i>	Adult	(Reyes et al., 2019)

polymers, also working with a blend of polymers. Some of the most used polymers are chitosan, pectin, cellulose, alginate, cyclodextrin, starch, polycaprolactone, and polyethylene glycol (Esmaili et al., 2021; Ramachandraiah and Hong, 2021). Biodegradable polymers from renewable resources are inexpensive and readily available in nature (Campos et al., 2015).

EOs can be encapsulated in different forms in the polymer (Figure 1). For example, they can be adsorbed on the nanoparticle's surface, coupled to the nanoparticle *via* linkers, encapsulated by a hydrophilic or hydrophobic polymer shell, or trapped in a polymer matrix (Kumar et al., 2019). In addition, polymeric nanoparticles can be obtained by electrospray, supercritical fluid, solvent evaporation, ionotropic gelation, nanoprecipitation, and salinization (Sagiri et al., 2016; George et al., 2019).

Unfortunately, there are no reports of essential oils encapsulated in polymeric nanoparticles evaluated against Curculionidae. However, the efficiency of polymeric nanoparticles-EOs against other pests has been demonstrated. For instance, Werdin González et al. (2014) determined that polyethylene glycol (PEG) 6000 nanoparticles can stabilize geranium or bergamot EOs, as their volatility and degradation were significantly decreased. The obtained results demonstrated that only 25% of the encapsulated EOs were volatilized in a 6-month-period. Furthermore, PEG-EOs nanoparticles may control and effectively release the oil against *Tribolium castaneum* and *Rhizopertha dominica*, since their toxicity by contact increased from 4 weeks to 24 weeks (Werdin González et al., 2014). de Oliveira et al. (2019) evaluated the effect of nanoparticles of zein containing blends of the EOs-geraniol, -eugenol, and -cinnamaldehyde against *Chrysodeixis includes*

and *Tetranychus urticae*. Nanoencapsulation prevented a decrease in acute toxicity and the rapid degradation of EOs, while it also increased the effectiveness against the target pest over 120 days (de Oliveira et al., 2019). These results demonstrate the potentiality of the polymeric nanoparticles to improve the effectiveness of EOs, highlighting the need for further research on Curculionidae pests.

Clay Nanomaterials

Nanoclays are nanoparticles with a high specific surface area and ion exchange capacity, which enables them to change their nature from hydrophobic to hydrophilic or vice versa, while they are also economically viable and biocompatible (de Oliveira et al., 2022). Furthermore, most clays are lamellar aggregates, with the presence of interlamellar cations (Na⁺), which allow ion exchange to make clays more compatible with EOs, facilitating their adsorption and then controlling their release through the "tortuous path" produced by the clay lamellae and by the interactions that occur (Garrido-Miranda et al., 2018). Furthermore, surfactants such as ammonium salts are used to alter the hydrophobicity of clays, which change the net charge of the solid, facilitating the interaction between molecular species such as EOs, and increasing the interlamellar space (Brito et al., 2018). Finally, montmorillonite and kaolinite are the most commonly used clays for encapsulating EOs as insecticides (Goletti et al., 2015). An example of this is the encapsulation of *Ocimum gratissimum* in montmorillonite. This formulation resulted in *S. zeamais* mortality rates of 100% in the first days and 75% after 30 days, proving the effectiveness of clays in the gradual release of EOs (Nguemtchouin et al., 2013).

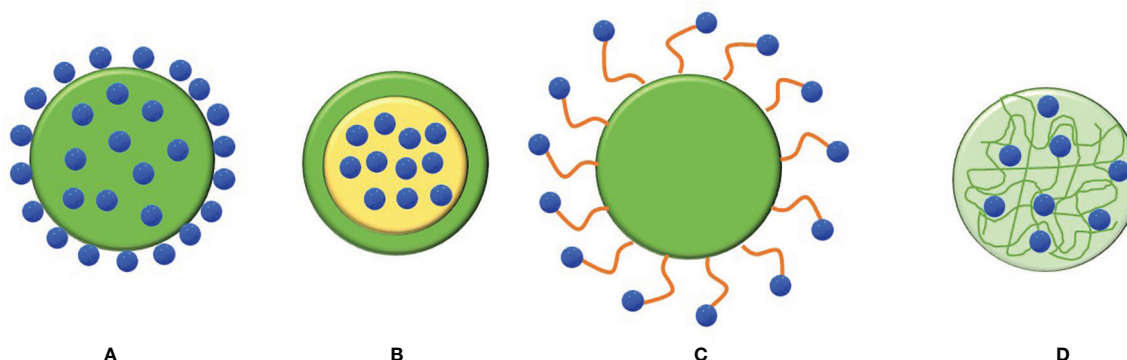


FIGURE 1 | Schematic forms of nanomaterials with essential oils, **(A)** adsorbed on the nanoparticle's surface, **(B)** encapsulated by a hydrophilic or hydrophobic polymer shell, **(C)** attachment to nanoparticle using different linkers, and **(D)** entrapment inside the polymer matrix.

CONCLUSION

Essential oils have a great potential as natural insecticides against curculionids or other species. In fact, they can play an important role in pest management and organic farming because they do not generate toxic residues and are environmentally friendly. The disadvantages they present, which are related to their high volatility and degradation, can be minimized by using current encapsulation methods. Therefore, future research should focus on determining how encapsulation of EOs or mixtures of EOs can increase the effectiveness in controlling different life stages of pests under changing environmental conditions.

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