



New Insights Into Biopesticides: Solid and Liquid Formulations of Essential Oils and Derivatives

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Essential oils and derivatives have shown effective insecticidal activity against different agricultural pests. However, the use of these bioactive compounds can result in negative effects due to their high volatility and difficult handling. Both solid and liquid formulations of essential oils have been developed in recent years. Currently, there are some commercial products available in the market, but they are still scarce and mainly based on liquid formulations. Solid formulations developed through spray-drying, including complex or micro/nanospheres, present differences in encapsulation efficiency, particle size, and controlled release, depending mainly on the wall material or surfactant content. Spray-dried essential oils have clear advantages over liquid formulations in terms of biological protection and storage. However, liquid formulations are usually easier scaled and applied. This review focuses on the advances of essential oils in both solid and liquid formulations (focusing on nanoemulsions) and derivatives to allow for their proper use in agriculture.

Keywords: monoterpenes, nanoemulsions, beads, spray-drying, controlled release

INTRODUCTION

Synthetic organic pesticides have been widely used in recent decades to control pests in agriculture, allowing for higher yields due to their high toxicity against insects. However, its intensive use has led to resistance in many insect species and poses a threat to non-target organisms (Isman, 2006). Because temperature is the most important environmental factor affecting insect populations, it is expected that the projected temperature increase due to climate change will have a major impact on the relative importance of agricultural pests (Skendžić et al., 2021). In this context, insect populations will respond differently to the effects of rising temperatures and atmospheric carbon dioxide (CO₂) levels, or precipitation and water stress, expanding their geographic places, improving survival, and more invasive insects and insect-transmitted plant diseases. Similarly, it could produce changes in their interaction with host plants and natural enemies (Skendžić et al., 2021). Therefore, pest management will require other alternatives, such as the use of phytochemicals, pheromones, biological control, or physical treatments.

Plants synthesize volatile compounds such as essential oils (EOs) that are released into the environment. Most EOs are a complex mixture of monoterpenes, phenols, and sesquiterpenes (Isman, 2006). Extracts and EOs obtained from plants can frequently present toxicity and repellency/deterrence against pests. Rosemary essential oil has shown high repellency against the aphid *Neotoxoptera formosana* (Takahashi) (Hemiptera: Aphididae) or linalool (Hori and Komatsu, 1997), while a monoterpene found in abundant EOs has shown to be an effective insecticide against

some pests (Lopez et al., 2012). In fact, the toxicity and repellent or deterrent effects of EOs and their main pure compounds have been reported on insects of different taxonomic groups since the 1990s. However, even though the number of studies on the use of EOs as botanical insecticides has increased in the last two decades, the formulations that are currently available as bioinsecticides or repellents are scarce (Isman, 2020b). One of the main problems limiting the production of EOs for agricultural use is the standardization of plant material, i.e., content, and the stable availability of the bioactive compounds. In addition, the use of EOs presents disadvantages, mainly due to their volatility as well as other chemical and physical characteristics involving low stability, high evaporation, and losses. Therefore, there is a great interest in developing formulations that improve the handling of EOs, prevent the degradation of their active ingredients, and control the release of these volatiles through micro/nanospheres or capsules in solid or liquid forms. This review focuses on the latest advances in both solid and liquid formulations (mainly nanoemulsions) of EOs and derivatives in order to allow for their proper use in agriculture.

The recent development of natural plant protection products has been successful, being approved for pest control and integrated into agricultural practice with the support of organizations authorized to market these products (Bohinc et al., 2020). The most commonly used commercial EOs include eugenol (e.g., clove and laurel oils), pine, anise, eucalyptus, and thyme oils (Lubbe and Verpoorte, 2011). There are some commercial insecticides based on plant EOs such as EcoTrol™ (KeyPlex, United States), Cinnerate (Seipasa, Spain), TetraCURB™ (Kemin, United States), Requiem® (Bayer, United States), Prev-Am® (Oro Agri, South Africa), Eco-oil® (Organic Crop Protectants, Australia), and Akabrown® (Green Corp Biorganiks, Mexico), which are being marketed in liquid form, mainly as emulsifiable concentrates (Isman, 2020a). Other products can also be found, such as clove EO (trade name: Matran EC, Burnout II, Bioorganic Lawn), which is used as an insecticide and a herbicide (neurotoxic, interference with the neuromodulator octopamine) (Karimi et al., 2018). The use of Jojoba EO (trade name: Detur, E-Rasem, Eco E-Rase, Permatrol, Erase™), cinnamon EO (trade name: Weed Zap™, Repellex, Ecosmart), and lemongrass EO (trade name: GreenMatch EXTM, EcoPCO) as insecticides and herbicides has also been recently reported (Suteu et al., 2020). However, the development and approval of new products based on EOs and derivatives (pure compounds) are still limited in the industry (Figure 1).

Volatility, persistence, phytotoxicity, and handling are the main concerns in the use of EOs or derivatives (Pascual-Villalobos et al., 2019). Consequently, formulations in solid and liquid forms are essential to control their release into the environment.

NOVEL SOLID PRODUCTS FROM ESSENTIAL OILS

The practical use of chemical plant protection products involves their direct application, in relatively low doses (in liquid form

and mixtures), to soil/plants. Particular attention is paid to the stabilization of these compounds, which involves mixing the active substance with various solid ingredients (talc, kaolin, clays, calcium carbonate, etc.) or liquids (water, organic solvents, mineral, and/or EOs) to allow for a uniform spread over large areas of active substance, improving adhesion to plants and ensuring an optimal biological effect (Soldea and Mocanu, 2009). However, they are sometimes formulated in solid form because of their longer shelf life. Both forms and formulas help increase the effectiveness of bioactive plant protection treatments and reduce the risk of pollution and phytotoxicity. The use of other chemical products such as solvents or surfactants is also of great importance in product conditioning, which should be based on the intended purpose and final properties of the commercial product (Suteu et al., 2020).

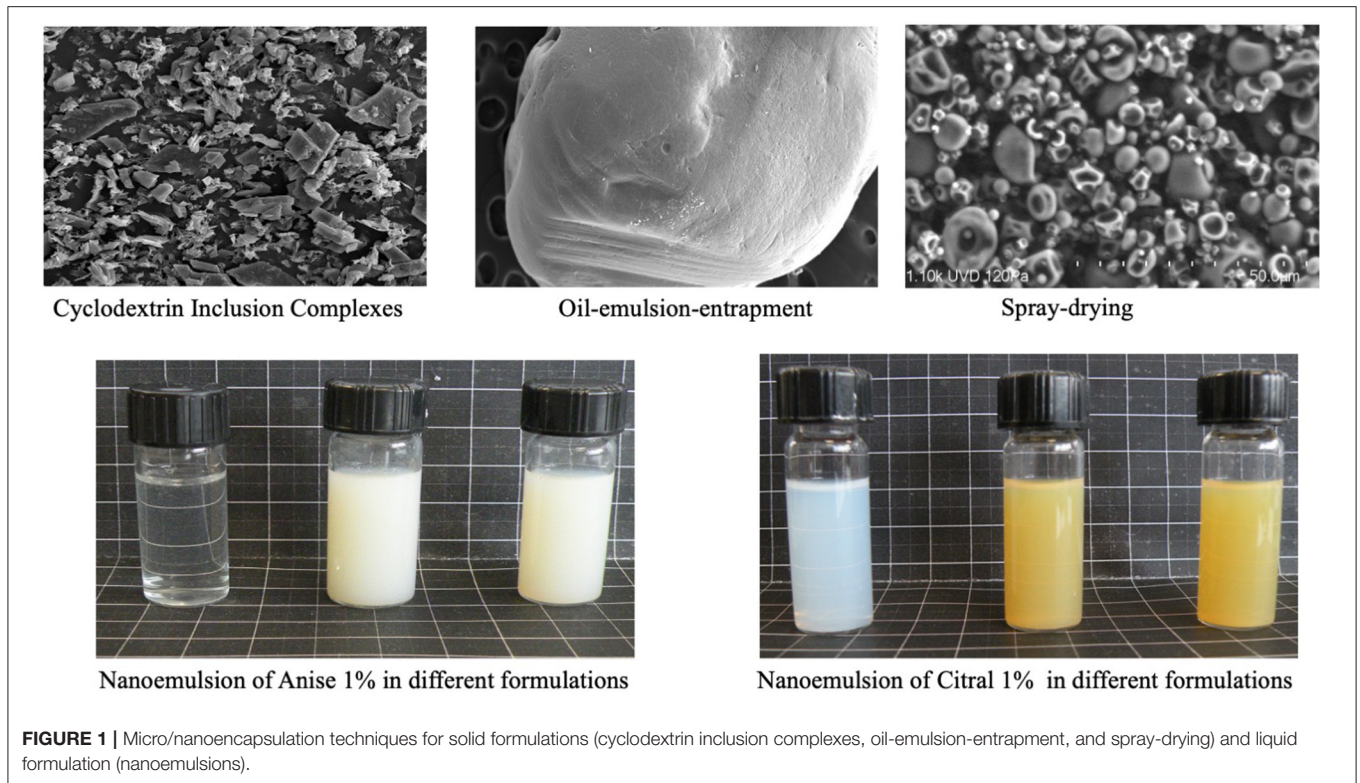
Solid products are often applied as powders, wettable powders, granules, impregnated strips, solid fertilizer mixtures, and others. Microencapsulation and the immobilization of macromolecular carriers is a modern conditioning process with advantages over classical methods, which can be applied depending on the structure and properties of the active derivatives.

From a practical point of view, different solid forms have been designed to protect EO bioactive compounds in the last 10 years. Regarding the longer controlled release, a recent study reported four encapsulation techniques for a monoterpene such as linalool (Lopez et al., 2012). In this study, chemical precipitation was performed with linalool and cyclodextrins. At the same time, it was compared with inverse gelation with alginate, a coacervation with alginate and chitosan, and finally with an oil-entrapped-emulsion with alginate, starch, and glycerol. In the cases where linalool was encapsulated with cyclodextrin and by inverse gelation only with alginate, the controlled release of the terpene was relatively fast. However, when the coacervation with chitosan and alginate was performed, a much longer release time was obtained. Even when the encapsulation technique used was an oil-entrapped emulsion with the addition of alginate, starch, and glycerol, the time to release half of the linalool content was too long.

Another study on nanoparticles was prepared using polycaprolactone and chitosan enhanced encapsulation of *Rosmarinus officinalis* and *Zataria multiflora* EOs (Ahsaei et al., 2020). In this case, a higher chitosan content increased the zeta potential, mean size, and encapsulation efficiency of the nanoparticles. The authors indicated that even though surfactant concentration might provide additional suspension stability due to the positive charge of chitosan, polymer concentration was more important than surfactant concentration in the particle size and zeta potential determination. They obtained an optimal encapsulation efficiency between 75.8 and 84.4%.

All these results provide information to design the type of capsule, powder, or solid formulation depending on whether a fast release is needed, or if the product is required to be stored for much longer.

One of the main advantages of solid formulations is that they can have a longer shelf life and be applied in solid form or even mixed with water and sprayed. In addition, these solid encapsulants can be an alternative to insecticides



that could be banned or severely restricted in the future. In this sense, a study on the use of basil and coriander EOs as alternatives to banned insecticides as dichlorvos against adult moths *Plodia interpunctella* (Hübner) and *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae) (Pascual-Villalobos et al., 2015) showed that the oils, when applied in funnel traps, were able to act as insecticides once moths entered the trap. In addition, it has been suggested that both EOs produced repellency where the traps were placed, thus repelling the pests while exerting their activity as insecticides once the insect is trapped inside the funnel. These specific trials were conducted in grain warehouses with remarkable success. However, the use of these solid encapsulants is not limited to warehouse or stored pests. Their effectiveness in insects such as *Myzus persicae* Sulzer (Hemiptera: Aphididae) has also been demonstrated in a recent study that evaluated three encapsulation methods: oil emulsion entrapment, spray-drying, and the encapsulation of (*E*)-anethole monoterpene in β -cyclodextrins (Pascual-Villalobos et al., 2020). It was concluded that most of the free (*E*)-anethole vapors were available within 2 days of application, whereas the preparations prolonged the release period for several weeks and required at least a week to release 20% of the bioactive compounds, depending on the temperature and formulation. In fact, (*E*)-anethole complexed with β -cyclodextrin required temperatures over 25°C to release the product. This highlights the importance of the application form and the environmental conditions where the pest is developing, such as temperature. Another study on the nanoencapsulation of *Eucalyptus globulus* Labill

and *Zataria multiflora* Boiss EOs against the larvae of *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae) reported that the encapsulation of the bioactive compounds reduced environmental degradation and prolonged the biological activity of their ingredients (Emamjomeh et al., 2021).

LIQUID ESSENTIAL OILS

One of the inexpensive solvent-free ways of applying plant protection or nutrition products (fertilizers) in agriculture is through liquid formulations diluted in water and applied via foliar spray or irrigation.

One of the main limitations of EOs is their low persistence due to their high volatility, but an adequate formulation can improve their performance. Essential oils are non-polar and require considerable volumes of solvents and emulsifiers to achieve stable aqueous emulsions. Nanoencapsulation can improve its stability so that nanoformulations can enhance the efficacy or persistence of oils or terpenoids (Isman, 2020b). Microemulsions and nanoemulsions are widely used to encapsulate compounds as they are relatively simple and inexpensive to manufacture (Pavoni et al., 2020). The formulation of EOs as nanoparticles allows an increase in water solubility and interface area between the components so that the oil spreads over the entire surface, increasing biological activity (Pascual-Villalobos et al., 2019). The present review will mainly focus on nanoemulsions. Nanoemulsions are colloidal systems of oil, surfactant, and water that are not thermodynamically stable (free energy of the system

is negative), but they are kinetically stable, and thus, high external energy inputs must be applied (McClements, 2012).

Some products based on EOs, monoterpenes, or sesquiterpenes are currently available in the market. However, products based on EOs and pure compounds are composed of few active ingredients. In the last two decades, the number of studies on the use of EOs as botanical insecticides has increased, but the availability of commercial products is still scarce (Isman, 2020b). The literature provides evidence of the repellent and toxic effects of formulations of aniseed, basil, peppermint, and lavender EOs and pure compounds (*E*)-anethole, citral, geraniol, linalool, farnesol, and (*Z*)-jasmone against the aphids *Rhopalosiphum padi* L. (Pascual-Villalobos et al., 2015, 2017), *M. persicae*, and *Macrosiphum euphorbiae* Thomas (Hemiptera: Aphididae) (Pascual-Villalobos et al., 2017; Cantó-Tejero et al., 2021).

Surfactants are a fundamental component of nanoemulsions, and their proper choice is essential to obtain a stable formulation over time. Tween (20, 40, 60, or 80) (MERCK, Darmstadt, Germany), modified starch, soy lecithin, sodium alginate, sodium caseinate, maltodextrin, acacia gum, and whey protein are the most common surfactants (Pascual-Villalobos et al., 2019). In the case of EO formulations, polysorbates (Tween 80 and 20) are two of the most commonly used surfactants because they form stable formulations without other cosurfactants (Pavoni et al., 2020). In previous studies, Tween 80 has been referred to as one of the principal surfactants used to prepare aqueous nanoformulations of EOs at a ratio of 1:1 or 1:2 (oil: surfactant) (Pascual-Villalobos et al., 2017, 2019). Nanoemulsions of different EOs (stored at temperatures of 4 and 25°C) were evaluated using a settling inhibition bioassay and characterized over time, measuring the Z-potential, and particle size. Other substances, like soy lecithin (1:2) or soy lecithin + glycerol (1:2:1), have also been tested as surfactants. Lecithins are a mixture of phospholipids with glycolipids and oils with a polar head and esterified lipophilic chains of fatty acids (Pascual-Villalobos et al., 2019). The literature has also described that the negative charge of the phosphate groups results in the improved stability of the formulation by causing important repulsive electrostatic interactions (Pavoni et al., 2020).

A study carried out on *R. padi* showed the repellent effect of nanoemulsions of anise and peppermint and the pure compounds (*E*)-anethole, citral, estragole, geraniol, farnesol, (*Z*)-jasmone, and others (Pascual-Villalobos et al., 2017). The effect of nanoemulsions vs. macroemulsions of the same dose of citral was also compared, resulting in a higher repellency for citral nanoemulsions due to the smaller particle size. In nanoemulsions prepared with Tween 80 at a ratio of 1:2, smaller particle sizes were obtained (<100 nm), similar to those of soy lecithin or soy lecithin + glycerol. However, formulations with soy lecithin were more stable than Tween 80 (potential Z-values between -30 and -50 mV). Due to their high efficiency, small size, and ability to penetrate the insect body, nanoemulsions have shown higher toxicity against cowpea aphid *A. craccivora* Koch (Hemiptera: Aphididae), resulting in higher mortality rates compared with essential oils or synthetic insecticides (Abdelaal et al., 2021).

The repellent effects of the pure compounds geraniol, (*E*)-anethole, and farnesol against *M. persicae* were compared with those of the nanoemulsions stored for 6 months and freshly prepared. Stored nanoemulsions with soy lecithin showed a similar repellent effect with freshly prepared nanoemulsions, e.g., stored (RI = 60.8) and freshly prepared farnesol (RI = 67.5). Nanoemulsions formulated with soy lecithin showed lower values of Z potential (≈ 40 mV) than the freshly prepared formulations (> -2.2 mV) (Pascual-Villalobos et al., 2019).

Few studies have evaluated formulations of EOs under field conditions. Foliar applications of anise and/or citral nanoformulations at 0.1–0.2% in pepper plants under greenhouse conditions reduced the populations of *M. persicae* and *Aphis gossypii* Glover (Hemiptera: Aphididae) (Pascual-Villalobos et al., 2019). Another work studied the effect of pure compounds such as (*Z*)-jasmone against the aphid *Sitobion avenae* (Fabricius) (Hemiptera: Aphididae) using previously treated barley plants under field conditions (Bruce et al., 2003). In addition, the repellent activity of EOs of rosemary, peppermint, and geraniol was evaluated in bean plants under greenhouse conditions (Isman, 2020a). Hashem et al. (2018) reduced *T. castaneum* (Herbst) (Coleoptera: Tenebrionidae) populations (81.33% mortality rate) and offspring by exposing wheat grains with a 10% anise EO nanoemulsion with particle sizes around 200 nm and good stability values (Z potential -25 mV). There is a need for characterization to allow for the proper comparison of data and, consequently, further understanding of this field.

PERSPECTIVES

The search for new insecticides for pest control, particularly, encapsulated insecticides, will continue to increase. The Food and Drug Administration (FDA) and Environmental Protection Agency (EPA) labels essential oils as generally recognized as safe (GRAS) (Pavoni et al., 2020), which indicates that they can serve as substitutes for hazardous synthetic insecticides in the future.

Further research is required for the development of more suitable matrices for pest control and to improve product application and protection. Advances in nano/microcapsules and nanoemulsions will contribute to the faster commercialization of these insecticidal products (Isman, 2017). However, factors such as the availability of EOs or derivatives, costs, and regulatory approval by institutions will have to be considered (Marrone, 2019).

The first element to consider is the type of EO or derivative to be used. In this sense, the synthesis of some synthetic compounds based on terpenoids is an option (Isman, 2016). In fact, the insecticide Requiem[®] is a good example of how synthetic compounds can be used in a way that emulates a natural product. Thus, the focus should be on the target pest, stage, or desired effect (repellency/insecticide). Once this barrier is overcome, storage or application will need to be defined. In this sense, solid formulations are quite attractive (Pascual-Villalobos et al., 2015, 2020, 2021).

Emulsions (micro/nanoemulsions) are simple and easy to obtain, achieving stable systems for their application and

TABLE 1 | Recent research in the development of essential oil formulations (solid or liquid) against pests.

Essential oil/natural compound	Encapsulation (solid/liquid)	Target insect	References
Coriander and basil essential oils	Solid	<i>Plodia interpunctella</i> and <i>Ephestia kuehniella</i>	Pascual-Villalobos et al., 2015
Linalool	Solid	Stored product pests	Lopez et al., 2012
(E)-anethole	Solid	<i>Myzus persicae</i>	Pascual-Villalobos et al., 2020
<i>Rosmarinus officinalis</i> and <i>Zataria multiflora</i>	Solid	<i>Tribolium confusum</i>	Ahsaei et al., 2020
<i>Eucalyptus globulus</i> Labill, <i>Zataria multiflora</i> Boiss	Solid	<i>Ephestia kuehniella</i>	Emamjomeh et al., 2021
(E)-anethole	Solid	<i>Plodia interpunctella</i> and <i>Ephestia kuehniella</i>	Pascual-Villalobos et al., 2021
(Z)-jasmone	Liquid	<i>Sitobion avenae</i>	Bruce et al., 2003
Orange essential oil, (E)-anethole, carvone, and limonene	Liquid	<i>Rhopalosiphum padi</i>	Zarrad and Pascual-Villalobos, 2015
Aniseed and peppermint essential oils, (E)-anethole, citral, geraniol, linalool, farnesol, (Z)-jasmone, carvone, estragole, menthone, pulegone, (Z)-hexenol, and β -caryophyllene	Liquid	<i>Rhopalosiphum padi</i>	Pascual-Villalobos et al., 2017
Aniseed	Liquid	<i>Tribolium castaneum</i>	Hashem et al., 2018
Aniseed essential oil, (E)-anethole, citral, geraniol, farnesol, and (Z)-jasmone	Liquid	<i>Myzus persicae</i> and <i>Aphis gossypii</i>	Pascual-Villalobos et al., 2019
<i>Carlina acaulis</i> and <i>Trachyspermum ammi</i>	Liquid	<i>Ceratitis capitata</i>	Benelli et al., 2021
(E)-anethole, farnesol, and (Z)-jasmone	Liquid	<i>Myzus persicae</i> and <i>Macrosiphum euphorbiae</i>	Cantó-Tejero et al., 2021
<i>Ocimum basilicum</i> , <i>Cuminum cyminum</i> , <i>Origanum majorana</i> , and <i>Matricaria chamomilla</i>	Liquid	<i>Aphis craccivora</i>	Abdelal et al., 2021

handling (Pavoni et al., 2020) while improving the ability or persistence of EOs or derivatives (Isman, 2020a). This occurs because nanoparticles expand in water due to their solubility and interface area between constituents so that the EO spreads over the entire surface, increasing the bioactivity (Pascual-Villalobos et al., 2019). In this sense, micro or nanoemulsions could have higher phytotoxicity than solid formulations.

The results of the use of nano/microemulsions in field trials are very promising, showing that products have high bioactivity and ease of application. **Table 1** lists scientific publications on solid and liquid formulations of EOs and their reported bioactivity against pests.

Table 1 shows diverse pests, which are frequently found in grain warehouses, or under greenhouses or field conditions, so that both solid and liquid formulations of essential oils are likely to reach the market in the near future. Nevertheless, the use of new formulations (solid or liquids) requires the assessment of the promising behavioral changes in natural enemies. Furthermore, lethal and sublethal concentrations of active ingredients can exert repellent effects (Benelli et al., 2021).

It is important to note that new products appear every day based on EOs or natural compounds that are present in

them that have been formulated as liquids or solids. However, it will be necessary to continue researching new formulation techniques and searching for new bioactive compounds against pests to achieve more efficient formulations and more widespread use, especially in countries where this market has not yet been established.

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ML, MC-T, and MP-V contributed to conceptualization and writing. ML wrote original draft preparation. All authors contributed critically to the drafts and gave final approval for publication.

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SUPPLEMENTARY MATERIAL

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