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Insecticidal activity of solid lipid nanoparticle loaded by *Ziziphora clinopodioides* Lam. against *Tribolium castaneum* (Herbst, 1797) (Coleoptera: Tenebrionidae)

Fahimeh Hosseinpour Jajarm[a], Gholamhossein Moravvej[a], Mehdi Modarres Awal[a] and Shiva Golmohammadzadeh[b]

[a]Department of Plant Protection, Faculty of Agriculture, Ferdowsi University of Mashhad, Mashhad, Iran; [b]Nanotechnology Research Center, Pharmaceutical Technology Institute, Mashhad University of Medical Sciences, Mashhad, Iran

ABSTRACT

Solid lipid nanoparticles (SLN) loaded by *Ziziphora clinopodioides* Lam. were synthesized using the method of high shear homogenization and ultra sound. The lipid phase consisted of percirol ATO5 and campritol 888 (5% w/v). Poloxamer 188 (2.5% w/v) was used as surfactant. Different amount of essential oil (1, 2, 2.5% w/v) were added to SLN. Particle size of solid lipid nanoparticle loaded by essential oil (2.5%) (SLN-EO) was 241.1 nm with poly dispersity index (PDI) of 0.312 and Zeta potential – 22.6 mv. Entrapment efficiency of SLN-EO (2.5%) was 93%. Transmission electron microscopy (TEM) study showed the spherical particles with the size under 100 nm. Based on the results of fumigant toxicity, the LC_{50} values of SLN-EO and pure oil against *Tribolium castaneum* were 30.602 and 68.303 µL. L air^{-1}, respectively. These results demonstrated that SLN-EO had higher toxicity effects on red flour beetles. The comparative assessment of persistence indicated SLN-EO formulation remained effective until 14 days, while the pure oil lost its toxicity after the 8^{th} day of application. Chemical composition of *Ziziphoraclinopodioides* showed that pulegone (51.78%), 1, 8- cineole (8.95%), p- menthone (7.74%) and piperitenone (5.7%) were the major components.

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Solid lipid nanoparticle; red flour beetle; fumigant toxicity; persistence; chemical composition

Introduction

The red flour beetle, *Tribolium castaneum* (Herbst, 1797) (Coleoptera: Tenebrionidae) is one of the most destructive pest of stored products. They are normally found on wheat flour, besides infest another materials including dried fruit, oilseeds, warehousing facilities, cacao and grain bulks. Both quality and quantity of stored food will be adversely affected by the presence of these insects (Campbell and Runnion 2003). In their serious infestations, the flour turns gray and has a sharp and distasteful odor that makes it unhealthy for human consumption (Prakash et al. 1987). Insects may be harmful to the seed embryos which causes reduced germination (Baier and Webster 1992; Moino et al. 1998). It is considered as secondary pest and only damages grains which have been infested by another pests (Mondal 1994).

Although synthetic insecticides and fumigants (methyl bromide, pyrethroids and phosphine) are used to control stored product pests, but their enormous use can have destructive effects such as resistance to insecticides, environmental pollution and poisonousness to non-target organisms (Lee et al. 2004; Isman 2006). Recently, botanical products are considered to develop as an alternative to dangerous pesticides. Essential oils have different influences on pests including ovicidal, repellant, toxic and antifeedant (Nawrot and Harmatha 1994).

Ziziphora clinopodioides belongs to family Lamiaceae which is a large plant family. Its Persian name is kakuti and widely disperses in Iran. Kakuti has been used for medical purposes including antibacterial, antioxidant and antifungal (Salehi et al. 2005; Ghafari et al. 2006). *Ziziphora clinopodioides* essential oil has been proved to have toxicity and repellent activity against pests of stored products (Lolestani and Shayesteh 2009). Moreover, chemical composition of kakuti was investigated (Sardashti et al. 2012; Kheirkhah et al. 2015).

The essential oil of *clinopodioides* as other essential oils is insoluble in water. Besides, rapid evaporation, sensitivity to oxygen, light and humidity limit its application in the fields (Pillmoor et al. 1993; Shi et al. 2012).

Nanoformulation of the essential oils could overcome their problems, protect them from environmental adverse effects, enhance their stability and toxicity,

CONTACT Gholamhossein Moravvej moravej@um.ac.ir Department of Plant Protection, Faculty of Agriculture, Ferdowsi University of Mashhad, Mashhad, Iran.

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make a controlled release of component of EOs and make their use more practical (Abreu et al. 2012).

Solid lipid nanoparticles loaded by essential oil of *Artemisia arborescens* L. have been prepared and characterized by Lai et al. (2006). In another study insecticidal activity of polyethylene glycol (PEG) nanoparticles loaded with garlic essential oil were evaluated against flour beetles (Yang et al. 2009). Kanis et al. (2012) prepared microcapsules with cellulose acetate (CA) and poly (ethylene-co-methyl acrylate) (PEMA) loaded with *Copaifera* sp. and assessed against *Aedes aegypti*. Kumar et al. (2014) prepared nanoparticle of *Mentha piperita* essential oil by melt dispersion process and applied against housefly larvae. González et al. (2015) proved toxic effect of nanoparticles prepared from PEG loaded by geranium (*Geranium* sp.) and bergamol (*Citrus reticulate* L.) essential oil against *Blattella germanica* over 1 year.

Solid lipid nanoparticles (SLN) with diameter from 10 to 1000 nm have been considered as a new delivery system. They are composed of physiological lipids with high melting points which decline both acute and chronic toxicity effects. Solid lipid nanoparticles have different advantages including high efficacy, low toxicity, enhanced stability and solubility, protection and controlled release of active compound (Ramteke et al. 2012). The materials used to produce SLN are low-cost. Moreover there is possibility of production in large scales (Hildebrand et al. 1998; Müller et al. 2000). Concerning these characteristics, it was theorized that SLN would be an ideal delivery system for the needed oil.

The objectives of present study were "1) preparation and characterization of solid lipid nanoparticle loaded *Ziziphora clinopodioides* 2) comparison of fumigant toxicity of Solid lipid nanoparticle essential oil (SLN-EO) and essential oil of *Ziziphora clinopodioides* against *Tribolium castaneum* 3) determination of chemical composition of both essential oil and oil from SLN-EO 4) investigation the effect of nanocapsulation in persistence of essential oil 5) evaluation of physical stability of SLN formulation during 6 months."

Methods and material

The survey was carried out in the laboratory of Toxicology, Department of Plant Protection, Ferdowsi University of Mashhad, Iran.

Insect rearing

In this study *T. castaneum* was maintained in the medium of wheat flour and brewer yeast (10:1 by weight). Wheat flour was kept in refrigerator for 48 h at −18 °C in order to eliminate any probable contamination. The beetles were cultured in the incubators at 27 ± 1 and relative humidity 65 ± 5%, in continuous darkness. *Tribolium castaneum* adults for bioassay were 2–4 days old of mixed sex. The insects have never been exposed to any chemicals.

Extraction of essential oil

Ziziphora clinopodioides leaves (50 g) were crushed and added to 650 ml distilled water in a flask. Essential oil was extracted by hydro distillation using a Clevenger apparatus at 100 °C. The time of extraction of essential oil was 4 h. In order to remove water, anhydrous sodium sulphate was used. Collected essential oil was maintained in refrigerator at 4 °C for our experiments (Sahaf et al. 2007).

Gas chromatography–mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry was conducted to identify the chemical constituents of the essential oil of *Ziziphora clinopodioides* and oil from SLN-EOS. GC-MS spectrometry analyses of essential oils were carried out using a thermoquest-finnigan equipped with a DB-1 fused-silica capillary column (60 m × 0.25 mm i.d., 0.25 µm film thicknesses). The temperature of oven was programmed from 60 to 250 °C at a rate of 5 °C min^{-1}. The injector and detector temperatures were held at 250 °C and 280 °C, respectively. Flame ionization detector (FID) was used as a detector and helium was the carrier gas at the constant flow of 1.1 ml min^{-1}. The voltage of ionization was 70 eV (Nasseri et al. 2016).

Preparation of SLN-EOs

For the preparation of SLN formulation, high shear homogenization and ultrasound methods were used. Briefly, the lipid phase including campritol 888 and percirol ATO5 (5%) was heated to 5 °C above the melting point of lipids (the melting points of campritol 888 and percirol ATO5 were 70 and 57 °C, respectively). At the end of melting process, different amounts of essential oil (EO) (1, 2 and 2.5%) were dissolved in lipid phase in order to prevent evaporation of essential oils. The aqueous phase was prepared by dissolving poloxamer 188 (Uniqema, Belgium) (2.5%) in double-distilled water up to 10 ml at the same temperature. The hot aqueous phase was then mixed with molten lipid phase . A Diax 900 homogenizer (Heidolph, Germany) was used to homogenize pre-emulsion. Then, hot dispersion was immediately ultrasonicated by prob sonicator (Bransonic, USA) for 30 sec by intervals of

Table 1. Chemical composition of *Ziziphora clinopodioides* EO and SLN-EO.

Constituent	EO (%)	RT*	SLN-EO (%)	RT
Pulegone	51.78	21.7	44.66	21.6
1.8-Cineole	8.95	12.15	9.98	12.11
P-Menthone	7.74	18.2	10.35	18.13
Piperitenone	5.7	26.09	5.57	26
Carvacrol	0.94	24.24	0.81	24.17
Thymol	0.45	24.63	0.51	24.55
2-ß-Pinene	1.31	9.74	1.4	9.71
Isomenthone	1.1	17.71	1.31	17.65
Cis-Ocimene	0.93	8.08	0.97	8.06
Isopulegone	0.95	18.75	0.58	18.67

*Retention time.

15 sec. Solid lipid nanoparticle loaded by essential oil was obtained after cooling at room temperature (Golmohammadzadeh et al. 2012).

Characterization of SLN-EOs

Dynamic Light Scatterig (DLS) (Zetasizer Nano-Zs; Malvern Instruments Ltd., United Kingdom) was used in order to measure particle size, zeta potential and polydispersity index of solid lipid nanoparticle loaded by *Ziziphora clinopodioides*.

Differential scanning calorimetry (DSC) experiments were conducted in a differential scanning calorimeter (Mettler DSC 821e, Germany). An empty aluminum oxide pan was used as a reference. The temperature range of DSC scans was 25 °C to 250 °C. The rate of heating was 5 °C min^{-1}. The melting points of SLN-EOs and bulk lipids were compared with each other. DSC studies were done under nitrogen flew.

The morphology characterization of SLN-EOs was observed with Transmission electron microscopy (TEM) (CEM 902 A; Zeiss, Oberkochen, Germany). Firstly, sample was thinned 50 folds. Then placed on a grid of carbon-coated copper for 30 sec. Filter paper was used to remove excess water. Subsequently, 20 µl uranyl acetate (2%) was put on SLN-EO and after 30 sec was cleaned by another filter paper. The grid was allowed to dry at room temperature and observed by TEM (Layegh et al. 2013).

The entrapment efficiency (EE) of the essential oil was demonstrated by measuring the concentration of free EO in the diffusion medium. Pulegone (52.78% in EO) was selected as the indexed constituent. Centrifugal filter tube was applied to determine the EE. To obtain the free EO , 1 ml of the SLN formulation was transferred to the upper chamber of an ultrafilter (Amicon Ultra-15, PLHK Ultracel-PL Membrane, 100 KDa, Millipore). Amicon tube was centrifuged at 14,000 rpm for 30 min. Then the isolated part at the bottom of tube was exposed to GC analysis to determine the pulegone content (Venkateswarlu and Manjunath 2004).

The evaluation of the both chemical and physical stability of SLN-EO was done at 8 °C for 6 months. Clarity, particle size and zeta potential of SLN-EO were investigated.

Toxicity and persistence evaluations

In order to determination of fumigant toxicity of *Ziziphora clinopodioides* essential oil and SLN-EO, initial concentration-setting experiments were carried out in 28 ml glass container. The concentrations which caused 10–20 to 80–90% mortalities were selected as well as two dosages in between by equal logarithmic intervals. Twenty adult beetles were put in each glass with five replications. For monitoring SLN-EO, unloaded solid lipid nanoparticles were used as control group. Concentrations were 25.92, 37.03, 51.85, 77.77, 111.111 and 162.96 µL L air^{-1} for essential oil, and in the case of SLN-EO 18.52, 22.22, 29.63, 33.33, 40.74 and 44.44 µL L air^{-1} were chosen. Subsequently, the concentrations were placed on filter papers (Whatman No.1) using sampler. After introducing adult insect, vials were covered with muslin cloth in order to prevent the contact of insect with filter papers. The mortality was counted after 24 h. Beetles with any movement in their legs or antennae were considered as dead . This experiment was carried out at 27 ± 1 °C and 65 ± 5% R.H in continuous darkness.

In order to determine persistence of the essential oil and SLN-EOs, LC_{80} values assessed from fumigant toxicity bioassay of essential oil (133.075 µL L air^{-1}) was used. The procedure of persistence test was similar to the method described for fumigant toxicity experiment. Twenty beetles were put in each container every 24 h. The mortality was investigated after 24 h. The persistence survey continued until the oil and SLN-EO lost their efficacy (Ziaee et al. 2014).

Data analysis

The values of lethal concentration were determined by probit analysis (Finney and Tattersfield 1952). The data were presented in terms of means and standard deviations and analyzed employing ANOVA. P-values less than 0.05 were regarded as significant.

Results

GC-MS analyses

Ziziphoraclinopodioides essential oil and oil collected from SLN were analyzed by GC-MS (Table 1). The results indicated that the major components of essential oil were pulegone (51.78%), 1, 8- cineole

Table 2. Particle size, zeta potential and polydispersity indices of SLN-EOs.

Formulation	Size (nm)	Zeta (mv)	PDI
SLN-EO 1%	147.93 ± 2	−29.2	0.287 ± 0.02
SLN-EO 2%	183.96 ± 1	−15.7	0.228 ± 0.01
SLN-EO 2.5%	206.66 ± 2.1	−22.6	0.259 ± 0.05

(8.95%), p- menthone (7.74%) piperitenone (5.7%), 2-ß-Pinene (1.31%) and Isomenthone (1.1%).

Characterization of nano-formulation

In this study, the particle size, zeta potential and poly dispersity index of solid lipid nanoparticle loaded by *Ziziphora clinopodioides* are shown at Table 2.

Besides, the effect of essential oil ratio in the mean diameter of SLN-EO was investigated. The particle size of SLN-EO resulted from 147.93 ± 2 to 206.66 ± 2.1 nm when the essential oil ratio was increased from 1 to 2.5 percentages. As shown in Table 1, the SLN-EO had high zeta potential value which proved that the surface of the SLN-EO was charged negatively. Therefore, using high shear homogenization and ultrasound method indicated good physical stability of SLN formulation. The values of PDI were around 0.3 showing a quite narrow size delivery of the particles.

The heating curves of percirol, campritol, and SLN-EO were displayed by DSC test. The results obtained from thermal analysis illustrate that melting point of SLN-EO was lower than bulk lipids used in SLN formulation (Figure 1). The thermaograms of Campritol 888 ATO and Percirol ATO5 appeared at 73.19 °C and 58.76 °C, respectively (Figures 2 and 3). The reduction of the melting point of the SLN-EO is related to compritol and percirol mixture.

The TEM experiment was conducted to obtain more information about morphology of SLN formulation. According to the TEM image, most of the SLN-EO were spherical and homogenous (Figure 4). The particle size as given by TEM was not at odd with what was found using DLS.

In the present experiment, ultrafiltration method was conducted to determine EE. The quality of SLNs is extremely depends on EE. As mention previously, pulegone is the major ingredient of *Ziziphora clinopodioides* essential oil. Therefore, pulegone was chosen as index component to assay the EE. The results of gas chromatography mass spectrometry indicated high encapsulation efficacy (93%). So, high lipophility of the essential oil caused a high incorporation capacity of SLN formulation.

Figure 5 illustrates SLN-EO particle size during 6 months after production at the storage temperature of 4 °C. There were no significant differences between them and the diameters determined at the first day of production ($p > 0.05$).

Fumigant toxicity and persistence

The results from fumigant toxicity of *Ziziphora clinopodioides* essential oil and SLN-EO are presented in Table 3. According to the results of the calculated LC_{50} ratio, the toxicity of EO against *Tribolium castaneum* was 2.23 times lower than that of SLN-EO (95% confidence limit: 1.76–2.78, $p < 0.05$).

Persistence of essential oil of *Ziziphora clinopodioides* and Solid lipid nanoparticle loaded by oil during the experiment time is illustrated in Figure 6. The mortality caused by SLN-EO remained 100% even after 8 days and reached 95% in 10th day of persistence test, while the essential oil lost its influence in the early days.

Discussion

The purpose of this study was to prepare and characterize SLN-EO and evaluate its insecticidal activity in comparison of pure oil. By high shear homogenization and ultrasound method we were able to make appropriate SLN-EO. Based on the obtained result of DLS, the particle size of SLN-EOs were chiefly between 147.8 and 241.1 nm.

Ekambaram et al. (2012) explained that the size of solid lipid nanoparticle is influenced by different frameworks including composition of the formulation, production technique and circumstances. Zeta potential of SLN-EOs was negative. By measuring the zeta potential, stability of SLN-EO can be predicted. Generally, charged particles because of electric repulsion present less aggregation. It can be concluded that prepared formulations were physically stable. Particle size of our prepared formulations (1, 2, and 2.5%) did not change significantly during stored period (6 months) and for all SLN-EOs, the outcomes displayed particle size less than 200 nm.

According to Lai et al. (2006), the particle size of solid lipid nanoparticles loaded by *Artemisia arborescence* (199- 207 nm) was not in micrometer span and reported zeta potential was −36 ± 0.5 mv. In addition, they reported that zeta potential values of SLN did not changed during 2 months indicating good stability of prepared formulation.

Further, this study scrutinized the impact of EO incorporation on particle size. The findings showed that an increase in the EO concentration results in an increase in particle size. The smallest formulation was the one containing %1 EO (147 nm). The particle size increased to 241.1 nm in SLN-EO loaded by 2.5% essential oil. Ziaee et al. (2014) showed that size of nanogel loaded by 2% *Cuminum cyminum*

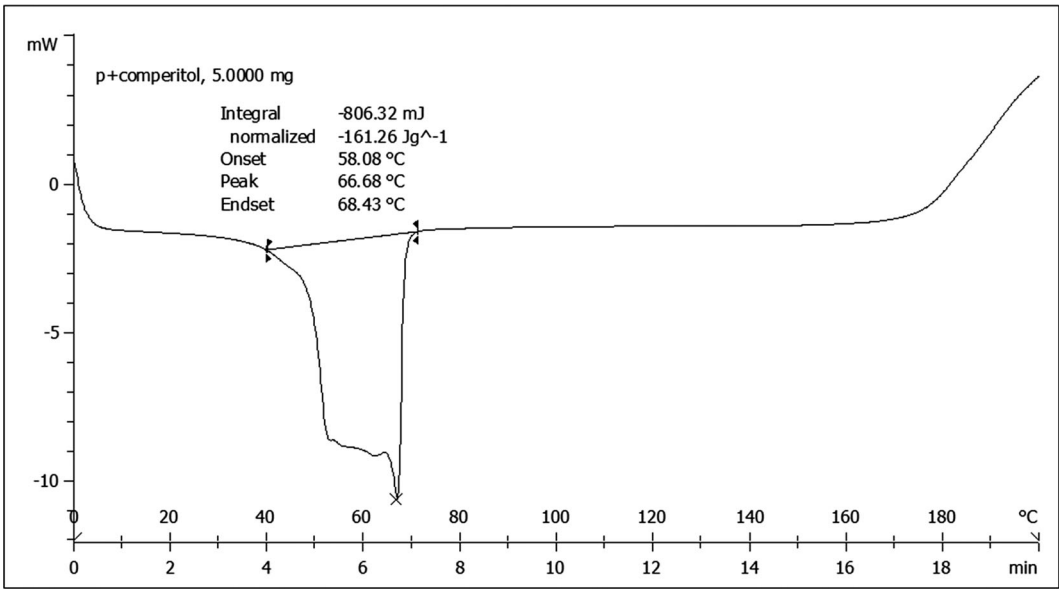

Figure 1. DSC thermogram of solid lipid nanoparticle loaded by *Ziziphora clinopodioides* essential oil.

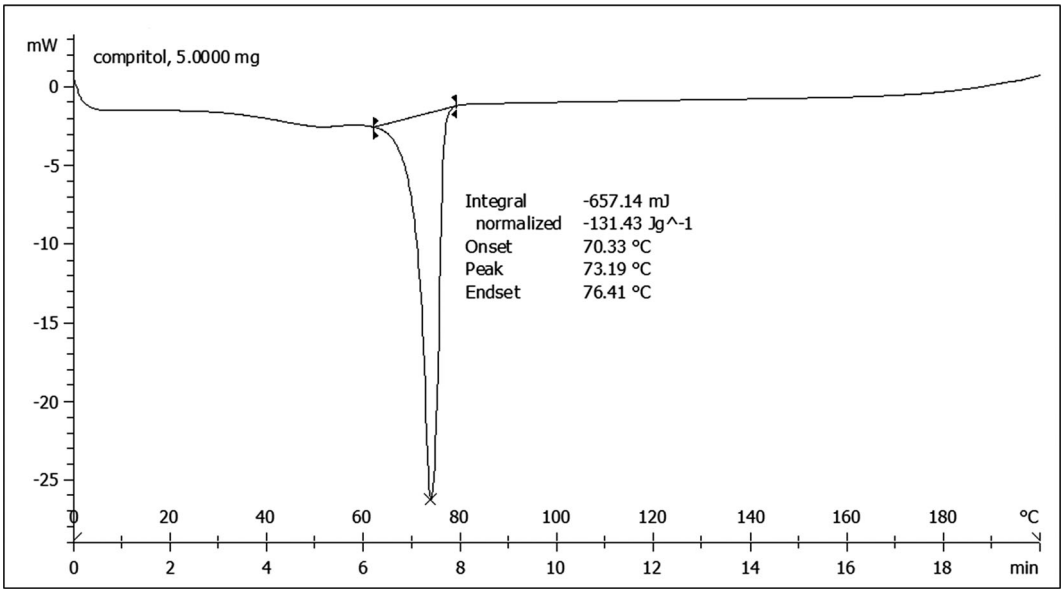

Figure 2. DSC thermogram of bulk campritol.

essential oil was less than 50 nm, while it increased to 250 nm when 6% EO was used. Chen et al. (2003) stated that particle size is affected by amount of active component.

The high encapsulation efficacy of *Ziziphora clinopodioides* was seen for prepared formulation (93%). It was known that essential oil is a lipid soluble molecule that could disperse in lipid mixture easily. Likewise, Nasseri et al. (2016) reported 84 ± 0.22% encapsulation efficacy for solid lipid nanoparticle loaded by *Zataria multiflora*.

The obtained image of TEM indicated that SLN-EO had spherical appearance. High capability of SLN for conservation of pure oil and controlled-release depend on spherical shape. This form possesses the lengthful path for the motion of encapsulated EO. Besides, in comparison to another form of nanoparticles, globular shape has less contact area with aqueous medium (Layegh et al. 2013).

The DSC experiment was carried out to evaluate the extent of crystallinity. In conclusion, the melting point of SLN dispersion was about 66.68 °C. The SLN-EO heating curved was less than bulk lipid. Similarly, Shi et al. (2012) detected that making solid lipid nanoparticle altered the lipid structure and formed a novel distorted shape.

In the chemical analysis of *Ziziphora clinopodioides* essential oils, pulegone, 1, 8- cineole, p-menthone and piperitenone were the most abundant ingredients as previously reported by other authors (Ghafari et al. 2006; Sonboli et al. 2006; Kheirkhah et al. 2015). Pulegone was determined as main component of *Ziziphora clinopodioides*. According to our results, components of essential

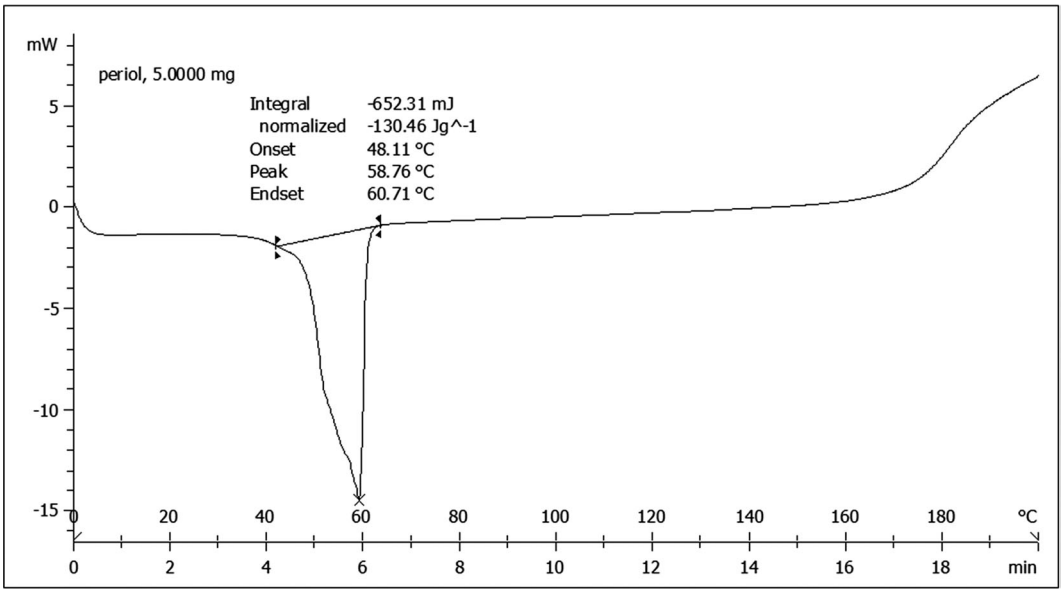

Figure 3. DSC thermogram of bulk percirol.

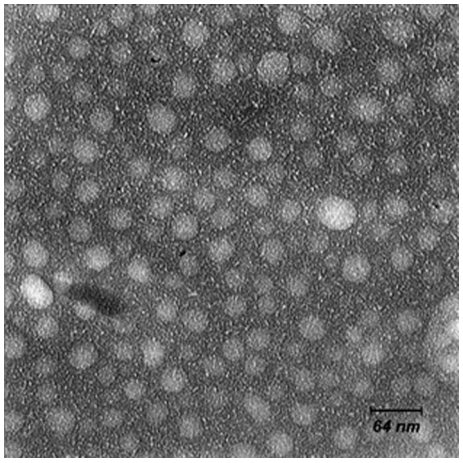

Figure 4. TEM image of solid lipid nanoparticle loaded by *Ziziphora clinopodioides* essential oil.

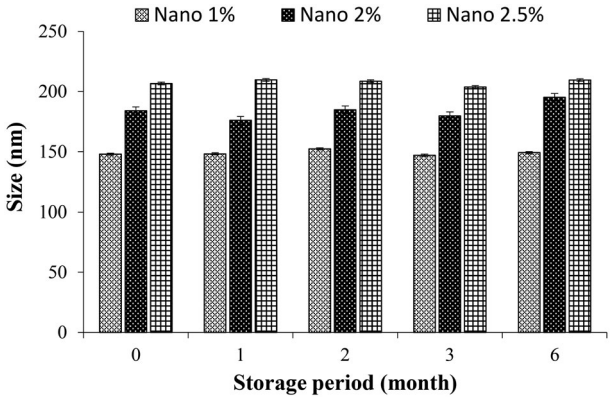

Figure 5. Solid lipid nanoparticle loaded by*Ziziphora clinopodioides* essential oil particle size through 6 months of storage at 4 °C.

oil before and after encapsulation did not change significantly indicating a more constituent stability of the nanoformulation. Similar findings were reported by González et al. (2015) who stated that the encapsulation of geranium and bergamot essential oil enhanced stability of pure oil. The percentage of major constituents of essential oil did not show any differences after formulation production.

Due to the high surface area, the chemical activity of nanoparticles is higher than the bulk form. Thus, the biological activity, mobility, and bioavailability will be increased (Margulis-Goshen and Magdassi 2013).

Nanoparticles can penetrate into insects tissues, so nanocapsulation enhances insecticidal activity of essential oil (Prates et al. 1998).

Our finding showed that SLN-EO had higher insecticidal toxicity than pure oil against red flour beetles. The LC_{50} of SLN-EO which was hardly effective against tested insects was 30.6 (μL L^{-1} air), while achieved LC_{50} of pure oil was 68.3 (μL L^{-1} air).

These results are in line with Yang et al. (2009) who reported that fumigant toxicity of garlic essential oil against *Tribolium castaneum* was lower than encapsulated oil. Also Adel et al. (2014) reported that SLN-EO of *Pelargonium graveolens* was stable under field conditions and gave high percentage of mortality on *Phthorimaea operaculella*.

GC-MS results showed that the main components of *Ziziphora clinopodioides* are monoterpene. They are high lipophilic and can enter to insect body rapidly. Therefore, physical functions of insects may be interfered by these materials (Haouas et al. 2012).

Based on the results of this study, while *Ziziphora clinopodioides* essential oil lost its insecticidal potential in a short period of time, the oil-loaded one was more efficient over time. Moreover, the SLN was able to protect the essential oil active ingredient remaining effective for up to 14 days. In vitro experiments done by Lai et al. (2006), it was shown that SLN could decrease the evaporation of

Table 3. LC_{50} and LC_{80} values of *Ziziphora clinopodioides* essential oil and SLN-EO (2.5%) after 24 h against *Tribolium castaneum* adults.

		Lethal concentration (μL L^{-1} air)			
Treatment	n	LC_{50} CL (lower-upper)	LC_{80} CL (lower-upper)	Slope ± SE	X^2 (df)
EO	700	68.303 (62.495–74.812)	133.075 (117.291–156.272)	2.906 ± 0.228	1.178 (4)
SLN-EO	700	30.602 (29.217–32.047)	43.305 (40.628–46.99)	5.582 ± 0.453	2.323 (4)

CL, 95% confidence limits; SE, standard error.

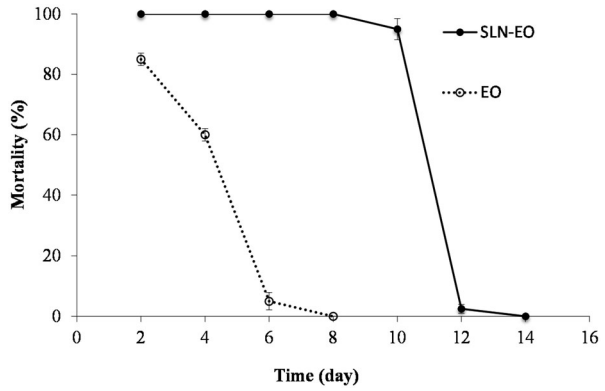

Figure 6. Mortality percentage of *Tribolium castaneum* by essential oil and solid lipid nanoparticle loaded by oil during bioassay.

essential oil too. Similarly, Specos et al. (2010) reported stronger and longer conservation of microcapsulated EO incomparison of pure oil. More surveys are required to investigate the efficiency of SLN-EO in stored places such as warehouses.

Conclusion

The obtained results of current study confirmed that SLN-EO formulations can reduce evaporation of *Ziziphora clinopodioides* and can increase the efficacy of essential oil. All prepared formulations showed good physical stability during 6 months storage time. These findings indicated that SLN-EO can be suitable carrier for application of EO as a pesticide against stored product pests. Although, more field surveys are required to evaluate SLN-EO as an alternative pesticide in management of stored product pests.

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The present research was a part of PhD thesis of the first author.

Authors'contribution

FHPJ as a PhD student conducted experiments and wrote the first draft of the manuscript. GM as the supervisor conceived and designed the research, edited and completed the final draft. MMA and SG helped for chemical analyses. All authors contributed to writing the manuscript and approved the final version.

Disclosure statement

No potential conflict of interest was reported by the authors.

Ethical approval

This article does not contain any studies with human participants or animals (vertebrates) performed by any of the authors.

Informed consent

Informed consent was obtained from all individual participants included in the study.

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References

Abreu FOMS, Oliveira EF, Paula HCB, de Paula RCM. 2012. Chitosan/cashew gum nanogels for essential oil encapsulation. Carbohydr Polym. 89(4):1277–1282.

Adel M, Atwa W, Hassan ML, Salem NY, Farghaly DS, Ibrahim SS. 2014. Biological activity and field persistence of *Pelargonium graveolens* (Geraniales: Geraniaceae) loaded solid lipid nanoparticles (SLNs) on *Phthorimaea operculella* (Zeller) (PTM) (Lepidoptera: Gelechiidae). Int J Sci Res. 4(11):514–520.

Baier AH, Webster BD. 1992. Control of *Acanthoscelides obtectus* Say (Coleoptera: Bruchidae) in *Phaseolus vulgaris* L. seed stored on small farms—I. Evaluation of damage. J Store Prod Res. 28(4):289–293.

Campbell J, Runnion C. 2003. Patch exploitation by female red flour beetles, *Tribolium castaneum*. J Insect Sci. 3(1):8.

Chen X-G, Lee CM, Park H-J. 2003. O/W emulsification for the self-aggregation and nanoparticle formation of linoleic acid modified chitosan in the aqueous system. J Agric Food Chem. 51(10):3135–3139.

Ekambaram P, Sathali AAH, Priyanka K. 2012. Solid lipid nanoparticles: a review. Sci Rev Chem Commun. 2(1): 80–102.

Finney DJ, Tattersfield F. 1952. Probit analysis. Cambridge (UK): Cambridge University Press.

Ghafari H, Yasa N, Mohammadirad A, Dehghan G, Zamani MJ, Nikfar S, Khorasani R, Minaie B, Abdollahi M. 2006. Protection by *Ziziphora clinopoides* of acetic acid-induced toxic bowel inflammation through reduction of cellular lipid peroxidation and

myeloperoxidase activity. Hum Exp Toxicol. 25(6): 325–332.
Golmohammadzadeh S, Mokhtari M, Jaafari MR. 2012. Preparation, characterization and evaluation of moisturizing and UV protecting effects of topical solid lipid nanoparticles. Braz J Pharm Sci. 48(4):683–690.
González JOW, Stefanazzi N, Murray AP, Ferrero AA, Band BF. 2015. Novel nanoinsecticides based on essential oils to control the German cockroach. J Pest Sci. 88(2):393–404.
Haouas D, Cioni PL, Ben Halima-Kamel M, Flamini G, Ben Hamouda MH. 2012. Chemical composition and bioactivities of three Chrysanthemum essential oils against *Tribolium confusum* (du Val)(Coleoptera: Tenebrionidae). J Pest Sci. 85(3):367–379.
Hildebrand GE, Dingler A, Runge SA, Müller RH. 1998. Medium scale production of solid lipid nanoparticles. Proc Int Symp Control Rel Bioact Mater. 968–969.
Isman MB. 2006. Botanical insecticides, deterrents, and repellents in modern agriculture and an increasingly regulated world. Annu Rev Entomol. 51(1):45–66.
Kanis LA, Prophiro JS, da Silva Vieira E, do Nascimento MP, Zepon KM, Kulkamp-Guerreiro IC, da Silva OS. 2012. Larvicidal activity of *Copaifera* sp. (Leguminosae) oleoresin microcapsules against *Aedes aegypti* (Diptera: Culicidae) larvae. Parasitol Res. 110(3):1173–1178.
Kheirkhah M, Ghasemi V, Yazdi AK, Rahban S. 2015. Chemical composition and insecticidal activity of essential oil from *Ziziphora clinopodioides* Lam. used against the Mediterranean flour moth, *Ephestia kuehniella* Zeller. J Plant Protect Res. 55(3):260–265.
Kumar P, Mishra S, Malik A, Satya S. 2014. Preparation and characterization of PEG-Mentha oil nanoparticles for housefly control. Colloids Surf B: Biointerf. 116: 707–713.
Lai F, Wissing SA, Müller RH, Fadda AM. 2006. *Artemisia arborescens* L essential oil-loaded solid lipid nanoparticles for potential agricultural application: preparation and characterization. Aaps Pharmscitech. 7(1):E1–E10.
Layegh P, Mosallaei N, Bagheri D, Jaafari MR, Golmohammadzadeh S. 2013. The efficacy of isotretinoin-loaded solid lipid nanoparticles in comparison to Isotrex® on acne treatment. Nanomed J. 1(1):38–47.
Lee B-H, Annis PC, Tumaalii F, Choi W-S. 2004. Fumigant toxicity of essential oils from the Myrtaceae family and 1, 8-cineole against 3 major stored-grain insects. J Store Prod Res. 40(5):553–564.
Lolestani F, Shayesteh N. 2009. Fumigant toxicity of *Ziziphora clinopodioides* (Boiss.)(Lamiaceae) against adults and eggs of *Callosobruchus maculatus* (Fab.)(Coleoptera: Bruchidae). J Biol Sci. 9(1):92–95.
Margulis-Goshen K, Magdassi S. 2013. Nanotechnology: An advanced approach to the development of potent insecticides. Can J Microbiol. 56(3):247–253.
Moino A, Alves SB, Pereira RM. 1998. Efficacy of *Beauveria bassiana* (Balsamo) Vuillemin isolates for control of stored-grain pests. J Appl Entomol. 122(1–5):301–305.
Mondal K. 1994. Flour beetles *Tribolium* spp. (Coleoptera: Tenebrionidae) as pests and their control. Agric Zool Rev. 6:95–119.
Müller R, Dingler A, Schneppe T, Gohla S. 2000. Large scale production of solid lipid nanoparticles (SLN^{TM}) and nanosuspensions (DissoCubes^{TM}). In: Wise D, editor. Handbook of pharmaceutical controlled release technology. Boca Raton (FL): CRC Press. p. 359–376.
Nasseri M, Golmohammadzadeh S, Arouiee H, Jaafari MR, Neamati H. 2016. Antifungal activity of *Zataria multiflora* essential oil-loaded solid lipid nanoparticles in-vitro condition. Iran J Basic Med Sci. 19(11): 1231–1236.
Nawrot J, Harmatha J. 1994. Natural products as antifeedants against stored products insects. Postharvest News Info. 5(2):17–21.
Pillmoor J B, Wright K, Terry A S. 1993. Natural products as a source of agrochemicals and leads for chemical synthesis. Pestic Sci. 39(2):131–140.
Prakash A, Rao J, Pasalu IC, Mathur KC. 1987. Rice storage and insect pest management. Delhi (India): BR Publishing Corporation.
Prates HT, Santos JP, Waquil JM, Fabris JD, Oliveira AB, Foster JE. 1998. Insecticidal activity of monoterpenes against *Rhyzopertha dominica* (F.) and *Tribolium castaneum* (Herbst). J Store Prod Res. 34(4):243–249.
Ramteke K, Joshi S, Dhole SN. 2012. Solid lipid nanoparticle: a review. IOSR J Pharma. 2(6):34–44.
Sahaf BZ, Moharramipour S, Meshkatalsadat MH. 2007. Chemical constituents and fumigant toxicity of essential oil from *Carum copticum* against two stored product beetles. Insect Sci. 14(3):213–218.
Salehi P, Sonboli A, Eftekhar F, Nejad-Ebrahimi S, Yousefzadi M. 2005. Essential oil composition, antibacterial and antioxidant activity of the oil and various extracts of *Ziziphora clinopodioides* subsp. rigida (BOISS.) RECH. f. from Iran. Biol Pharm Bull. 28(10): 1892–1896.
Sardashti A, Valizadeh J, Adhami Y. 2012. Chemical composition of the essential oil from *Ziziphora clinopodioids* Lam. from Iran by means of gas chromatography-mass spectrometry (GC-MS). J Hortic Forestry. 4(10): 169–171.
Shi F, Zhao J-H, Liu Y, Wang Z, Zhang Y-T, Feng N-P. 2012. Preparation and characterization of solid lipid nanoparticles loaded with frankincense and myrrh oil. Int J Nanomedicine. 7:2033–2043.
Sonboli A, Mirjalili MH, Hadian J, Ebrahimi SN, Yousefzadi M. 2006. Antibacterial activity and composition of the essential oil of *Ziziphora clinopodioides* subsp. bungeana (Juz.) Rech. f. from Iran. Zeitschrift für Naturforschung C. 61(9–10):677–680.
Specos MMM, García JJ, Tornesello J, Marino P, Vecchia MD, Tesoriero MVD, Hermida LG. 2010. Microencapsulated citronella oil for mosquito repellent finishing of cotton textiles. Trans R Soc Trop Med Hygiene. 104(10):653–658.
Venkateswarlu V, Manjunath K. 2004. Preparation, characterization and in vitro release kinetics of clozapine solid lipid nanoparticles. J Control Rel. 95(3):627–638.
Yang F-L, Li X-G, Zhu F, Lei C-L. 2009. Structural characterization of nanoparticles loaded with garlic essential oil and their insecticidal activity against *Tribolium castaneum* (Herbst)(Coleoptera: Tenebrionidae). J Agric Food Chem. 57(21):10156–10162.
Ziaee M, Moharramipour S, Mohsenifar A. 2014. Toxicity of *Carum copticum* essential oil-loaded nanogel against *Sitophilus granarius* and *Tribolium confusum*. J Appl Entomol. 138(10):763–771.