Advances in Crop Science and Technology

Adel et al., Adv Crop Sci Tech 2018, 6:6
DOI: 10.4172/2329-8863.1000409

Research Article | Open Access

New Nano-Biopesticide Formulation of *Mentha piperita* L. (Lamiaceae) Essential Oil Against Stored Product Red Flour Beetle *Tribolium castaneum* Herbs and its Effect on Storage

Manal M Adel[1*], Magdy A Massoud[2], Magdy IE Mohamed[3], Khaled H Abdel-Rheim[3] and Shimaa SI Abd El-Naby[4]

[1]*Department of Pests and Plant Protection, National Research Center, Cairo, Egypt*

[2]*Faculty of Agriculture-Saba Basha, Department of Plant Protection, Alexandria University, Egypt*

[3]*Department of Stored Products and Grains Pests, Agricultural Research Center, Plant Protection Research Institute, Al-Sabahia, Alexandria, Egypt*

[4]*Department of Pesticide Formulation Research, Central Agriculture Pesticides Laboratory, Agricultural Research Center, Al-Sabahia, Alexandria, Egypt*

[*]**Corresponding author:** Manal M Adel, Department of Pests and Plant Protection, National Research Center, Cairo, Egypt, Tel: 01224214021; E-mail: mhassanein11@hotmail.com

Rec date: November 04, 2018; **Acc date:** December 22, 2018; **Pub date:** December 29, 2018

Abstract

In recent years, providing new formulations such as nano-emulsions have been widely used for the target delivery, and enhanced biological functions of pesticides combinations. In this study, contact toxicity of *Mentha piperita* L. essential oil compared with its nano-emulsion on *Tribolium castaneum* herbs as well as its effect on wheat grain storage has been investigated. The results indicated that, production of nano-emulsion with this new technique results in considerable decrease of the required EO concentrations. The results concluded that by using nano-emulsion formulation, the effect of essential oil contact toxicity and its durability increases. Hence, the nano-emulsion formulation may represent a new category of biopesticide and this should be considered in the integrated pest management program.

Keywords: *Mentha piperita*; Essential oils; *Tribolium castaneum*; Red flour beetle; Germination; Wheat grain; Nano-emulsion formulation

Introduction

Nano-emulsion formulation system is a recent favorable method to improve botanical insecticide characteristics and effectiveness for commercial use [1]. Nano-emulsion formulations have good storage stability under a broad range of temperatures (-10 to 55°C). In nano-emulsion formulation system, the biological performance of the pesticides is improved by using adjuvants and surfactants [2]. Non-ionic surfactants are considered safe to be used in chemical, cosmetic, food, and pharmaceutical industries [3]. Formulating essential oils (EOs) into nano-emulsion can be used in food and beverage products, thereby, decreasing the amount of EOs required [4].

Nano-emulsions can be formulated by two kinds of methods such as high-energy and low-energy emulsification methods. High-energy emulsification method comprises high-pressure homogenization and ultra-sonication [5-7]. Ultra-sonication is the most widely used method because it is economical and easy to use. Recent studies have shown that the ultrasound technique has developed as a powerful energy-efficient tool for the emulsification process. Ultrasonic emulsification provides reduced droplet diameter and narrow size distribution as compared to other mechanical devices [8,9].

Currently, new trend is started for using the natural plant extracts as well as EOs as natural pesticides to control pests with nano-formulation [1,10] in green pest management [11]. These green and nano-pesticides are safe, low to no mammalian toxicity and have many sites of toxic actions in pests, which lead to high selectivity and low resistance development [12,13]. Essential oils proved to have significant effects against a large number of stored grain insects, acting through ingestion [14] and by contact as well [15,16].

The red flour beetle, *Tribolium castaneum* (Herbst) is a globally distributed crop pest, infesting a wide variety of stored products worldwide [17]. It is considered a primary pest of flour and other milled products of cereals, and a secondary pest of stored wheat, causing severe damages to these food grains [18,19]. Indeed, heavy losses of grain weight and nutritive contents, reduction of commercial value and frequency of germination were resulted from this insect pest [20].

Many plants may provide potential alternatives to currently used insect-control agents because they constitute a rich source of bioactive chemicals [21], in which active substances extracted from plants may not only act as toxicants, but also as insect growth regulators, repellents, synergists or as phagodeterrents. These substances include a large group of the so-called essential oils (EOS). Essential oils (EOS) are defined as any volatile oils that have strong aromatic components and give a distinctive odor or flavor to a plant [22]. Biopesticides based on essential oils (EOS) appear to be complementary or alternative method in crop production and integrated pest management [23].

The essential oils extracted from *M. piperita* have also been reported as a source of botanical insecticides [24]. Efficiency of volatile oils derived from *M. piperata*, *Mentha arvensis*, *M. spicata* and *Cymbopogon nardus* on Adult *C. maculatus* (F.) were introduced into cowpea seeds.

The toxicity of essential oils to stored-product insects is influenced by the chemical composition of the oil, which in turn depends on the

Citation: Adel MM, Massoud MA, Mohamed MIE, Abdel-Rheim KH, El-Naby SSA (2018) New Nano-Biopesticide Formulation of *Mentha piperita* L. (Lamiaceae) Essential Oil Against Stored Product Red Flour Beetle *Tribolium castaneum* Herbs and its Effect on Storage. Adv Crop Sci Tech 6: 409. doi:10.4172/2329-8863.1000409

source, season and ecological conditions, method of extraction, time of extraction and plant part used [25-28].

Our study evaluates the efficiency of *M. piperita* (EO nano-emulsion) in water was formulated using nonionic surfactants such as Tween® 80 by ultrasonic emulsification method, at several concentrations comparing with *M. piperita* (EO) as possible protecting agents of wheat grains against infestation by the red flour beetle *Tribolium castaneum* herbs without negative effect on germination of wheat grains. Which may lead to the discovery of new agents for pest control, it may be an effective alternative to conventional synthetic insecticides and encourage the use of these natural oils in nano-emulsion and participate in programs of integrated pest management (IPM).

Materials and Methods

Compounds

The Peppermint essential oil extraction was used in this study. The non-ionic surfactants Tween 80 (Polysorbate 80) nonionic surfactant was purchased from Al-Nasr Pharmaceutical Chemicals Co. (ADWIC) (Egypt). Acetone was purchased from Al-Nasr Pharmaceutical Chemicals Co. (ADWIC) (Egypt).

Nano-emulsion preparation

The oil-in-water nano-emulsion was formulated using peppermint essential oil, non-ionic surfactant (tween 80) and deionized water. The concentration of *M. piperita* (EO) (4%, v/v). The preparation method was used as described in a previous study of Massoud et al. [29].

Bioassay technique

Contact toxicity bioassay using thin film residue: The insecticidal efficacy of the *M. piperita* free EO and its formulation (nano-emulsion) was carried out by residual film technique against the adults of *T. castaneum*. The residual film was done directly on petri dish (9 cm) without any grains according to Qi and Burkholder [30] Broussalis et al. [31].

M. piperita free EO and its formulation (nano-emulsion) concentrations were (10, 15 and 30 µl) to *T. castaneum* every concentration were mixed with 1 ml acetone by using micropipette, for each concentration in petri-dish. The dilutions were spread uniformly along the whole surface of the petri dishes. The solvent was allowed to evaporate leaving thin film on the floor of the dishes. After evaporation of acetone, 20 adults were placed in each petri-dish.

Three replicates were carried out of each concentration and control. Mortality percentages were recorded after 24, 48, and 72 hours of treatment and LC_{50} values were calculated according to Finney [32]. The toxicity index (TI) of nano-emulsion or free EO calculated by the equation according to Sun, [33] and Yamamoto et al., [34]:

- Toxicity index (TI)=(LC_{50} of nano-emulsion or EO)/(LC_{50} of EO).
- Based on LC_{50} calculated after 72 hrs.
- The compound has TI less than 1 (TI<1) have high toxicity.
- Toxicity increase (%)=(TI of EO-TI of nano-emulsion) × 100.

Wheat grain treatment: The essential oils were admixed with grains according to Qi and Burkholder, [30]. Wheat grains were treated with different concentrates of *M. piperita* (EO) (100, 200, 800, 1000 and 2000 µl) and its formulated nano-emulsion (100, 200, 500 and 800 µl). By using micropipette each concentration were dissolved in acetone (2 ml), and then mixed manually with grains.

Sixty gram of grains were used in each concentration and then divided into three equal replicates in 0.4 Litter glass jars. After evaporation of acetone, the treated grains were infested by newly emerged adults (10 pairs). Mortality was recorded every week for two weeks. The number of progeny was recorded after six weeks of infestation. Notably, it has been previously elucidated that when the solvent evaporates, the nano-emulsion retains its properties [35].

Germination tests: Germination test were done for the treated wheat grains with *M. piperita* free EO and its formulation (EO nano-emulsion), after one month of storage, accomplished for wheat according to Qi and Burkholder [30] with slight modification. Sixty seeds from each treatment with essential oils were divided into three replicates, placed on petri dishes containing cotton layer instead of (filter paper) soaked with tap water and covered with tissue paper. Germinant seed were recorded after 4 days for wheat. The obtained results of germination test were recorded for all treatment and control.

Statistical analysis

The toxicity data was analyzed using probit analysis to estimate the LC_{50} (Ldp line). All data were analyzed using one-way ANOVA. Significant differences between treatments were determined using Duncan's test ($p<0.05$).

Mortality rate was estimated and corrected according to formula [36] as follows:

Corrected Mortality=((Mortality% of treated insects-Mortality% of control)/(100-Mortality% of control)) × 100

Results

Contact toxicity bioassay of the *M. piperita* free EO and (EO nano-emulsion) against adults of *T. castaneum* using thin film residue

The insecticidal activity of the nano-emulsion *M. piperita* and free *M. piperita* EO was evaluated by direct contact toxicity (Film residue) against *T. castaneum*. The results presented in Table 1 and Figure 1 indicated that after 24 hr, 48 hr, 72 hr from exposure the lethal concentration LC_{50} recorded 0.332, 0.304 and 0.290 µl/cm² of EO against *T. castaneum*, respectively.

Time	LC_{50} µl/cm²	Confidence Limits		Slope	X^2	Toxicity Index (TI)
		Lower	Upper			
24 hr	0.332	0.298	0.376	3.534 ± 0.419	0.219	
48 hr	0.304	0.277	0.338	3.953 ± 0.43	0.321	
72 hr	0.29	0.265	0.32	4.168 ± 0.438	0.705	1

Table 1: Insecticidal effect of *M. piperita* free EO on *T. castaneum* adults using thin film residue after 24, 48, and 72 h post-exposure.

While it was recorded 0.192, 0.167 and 0.132 µl/cm² after exposure time 24, 48 and 72 of EO nano-emulsion against *T. castaneum*, respectively as shown in Table 2 and Figure 2. The results pointed to

Citation: Adel MM, Massoud MA, Mohamed MIE, Abdel-Rheim KH, El-Naby SSA (2018) New Nano-Biopesticide Formulation of *Mentha piperita* L. (Lamiaceae) Essential Oil Against Stored Product Red Flour Beetle *Tribolium castaneum* Herbs and its Effect on Storage. Adv Crop Sci Tech 6: 409. doi:10.4172/2329-8863.1000409

the direct contact toxicity of nano-emulsion of *M. piperita* against *T. castaneum* adults was higher than free EO with lower LC_{50} values concentration 0.132 µl/cm^2 compared to the free EO 0.290 µl/cm^2 after exposure time 72 hr as show in Tables 1 and 2 and Figures 1 and 2. The Values of LC_{50} of the nano-emulsion and free EO decreased with increasing the exposure time.

Time	LC_{50} µl/cm^2	Confidence Limits		Slope	X^2	Toxicity Index (TI)	Toxicity Increase (%)
		Lower	Upper				
24 hr	0.192	--	--	3.782 ± 0.472	12.216		
48 hr	0.167	--	--	3.88 ± 0.533	6.493		
72 hr	0.132	0.104	0.152	4.065 ± 0.693	3.088	0.455	54.5

Table 2: Insecticidal effect of *M. piperita* nano-emulsion 4% on *T. castaneum* adults using thin film residue after 24, 48 and 72 h post-exposure.

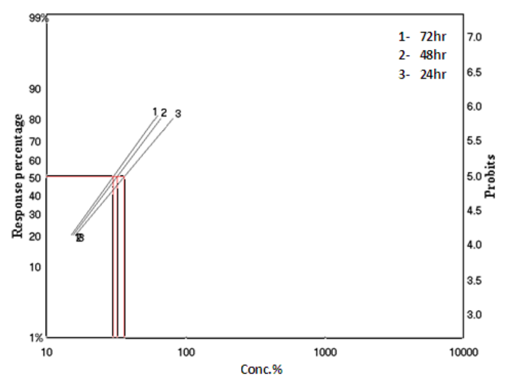

Figure 1: Efficacy of the *M. piperita* free EO against *T. castaneum* adults.

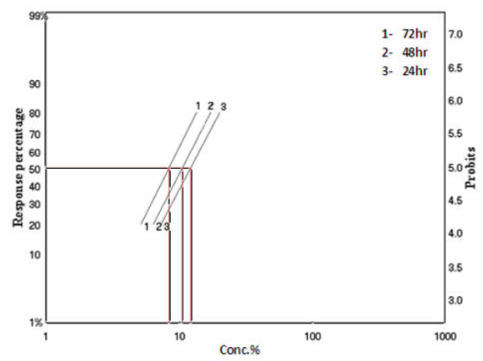

Figure 2: Efficacy of the *M. piperita* nano-emulsion against *T. castaneum* adults after 24, 48 and 72 h.

The toxicity index (TI) for *T. castaneum* accounted 0.455 based on LC_{50} after 72 hr of exposure as show in Table 2 while for free was EO 1.00 as show in Table 1.

However, the mortality in *T. castaneum* was increased with increasing exposure time and concentration of nano-emulsion or free EO in a concentration-dependent manner. A significant difference ($p<0.05$) between *M. piperita* nano-emulsion and free EO at the concentration 10 µl was observed (Table 3).

It is observed that *M. piperita* nano-emulsion was more effective on the adult of *T. castaneum* as shown in Table 3 after 24 hr of application which caused 45.00% death compared to free EO 11.67% at the same concentration 10 µl. While the concentration of 15 µl caused 50.00% mortality compared to the free EO 31.67% after 24 hr of application. And also conc. 30 µl after 24 h of application which caused 96.67% death compared to free EO 70.00% at the same concentration and time.

Conc. µl	Mortality (%)						p	$LSD_{0.05}$
	24 h		48 h		72 h			
	EO Nano-Emulsion 4%	EO	EO Nano-Emulsion 4%	EO	EO Nano-Emulsion 4%	EO		
10	45 ± 1.7	11.67 ± 1.3	51.67 ± 0.58	11.67 ± 1.3	65 ± 2.0	11.67 ± 5.8	0.03*	1.63
15	50 ± 7.0	31.67 ± 3.2	63.33 ± 5.1	35 ± 3.6	80 ± 4.0	38.33 ± 6.0	0.84 ns	4.17
30	96.67 ± 1.6	70 ± 2.0	98.33 ± 0.58	76.67 ± 2.5	100 ± 0.0	80 ± 3.0	0.3 ns	2.53

Table 3: Insecticidal effect of *M. piperita* free EO and nano-emulsion on *T. castaneum* adults using thin film residue after 24, 48, and 72 h post-exposure. *=Significant, ns=non-significant.

The residual effect of *M. piperita* oil (nano-emulsion and free EO) against the adult of *T. castaneum* was tested at intervals after 48 h and

72 hr (Table 3). After 48 hr, the calculated data indicated that the nano-emulsion at 10 µl conc. was more efficient showing 51.67% compared with 11.67% mortality for the free oil.

Moreover, the concentrations 15 µl and 30 µl of the nano-emulsion gave 63.33 and 98.33% mortality versus 35.00 and 76.67% mortality for the free oil, respectively. Furthermore, the nano-emulsion showed more residual effect than among the three used concentrations 10, 15 and 30 µl resulting adult mortality of 65.00, 80.00 and 100% compared with 11.67, 38.33 and 80.00% in the free oil, successively.

Efficacy effect *M. piperita* free EO and EO nano-emulsion upon adults of *T. castaneum* and wheat grain storage

In this study the mortality of *T. castaneum* was evaluated throughout 1,2 weeks and subsequently the adult's emergence post treating wheat grain with *M. piperita* nano-emulsion formulation and the free (EO) of the tested oil (Table 4).

Essential Oil	Conc. µl	Mortality (%) After		Mean	Mean of Emerged Adults After		Mean
		1 week ± SD	2 weeks ± SD		6 weeks ± SD	3 Months ± SD	
M. piperita (EO nano-emulsion) 4%	100	40 ± 1.73	70 ± 4.58	84.79	1.67 ± 0.71	8.33 ± 0.94	2.27
	200	80 ± 2.64	90 ± 2.00		0.0 ± 0.0	1.67 ± 0.71	
	500	98.33 ± 0.58	100 ± 0.0		0.0 ± 0.0	0.0 ± 0.0	
	800	100 ± 0.0	100 ± 0.0		0.0 ± 0.0	0.0 ± 0.0	
M. piperita free EO	100	10 ± 3.46	60 ± 2.83	68.97	8.33	13.33 ± 0.58	2.63
	200	10 ± 1.73	70 ± 4.89		1.67	3.0 ± 0.71	
	800	80 ± 2.0	81.67 ± 2.52		0	0.0 ± 0.0	
	1000	88 ± 2.08	90 ± 2.64		0	0.0 ± 0.0	
	2000	100 ± 0.0	100 ± 0.00		0	0.0 ± 0.0	
Control	0	0	0		115 ± 20.0	220 ± 15.5	
p				0.15 ns	--		0.032*
$LSD_{0.05}$				15.62	--		15.85

Table 4: Effect of *M. piperita* (EO nano-emulsion) and *M. piperita* free EO on mortality and emergence of *T. castaneum* adults.

The results indicated that the highest percentage of *T. castaneum* adult mortality (100%) was obtained post the exposure to the treated wheat grains with nano-emulsion concentration 800 and 500 µl after one week and two weeks, respectively. Meanwhile, this highest mortalities, 90 and 100% needed high concentrations amounted to 1000 µl and 2000 µl with *M. piperita* free (EO) after one and two weeks of exposure, consequently. The results in Table 4 showed that significant differences (p<0.05) in the emergence of *T. castaneum* adult between concentrations of *M. piperita* free EO, *M. piperita* nano-emulsion and control after 6 weeks and 3 months.

The number of emerged *T. castaneum* adult decreased with increasing concentration gradient of the *M. piperita* nano-emulsion and the free EO. After 6 weeks, concentration 200, 500 and 800 µl of nano-emulsion, gave no adult emergence, while after 3 months concentration 500 and 800 µl gave no adult emergence was observed (Table 4). Meanwhile, free EO concentration 800, 1000 and 2000 µl gave no adult emergence, for 6 weeks and 3 months.

Germination

The effect of nano-emulsion on germination of wheat grains was evaluated at different concentrations (100, 200, 500 and 800 µl) to study the adverse effect response.

The results in Table 5 showed non-signi icant differences (p>0.05) in seed germination between *M. piperita* nano-emulsion, free EO treatments and control. Results showed that *M. piperita* nano-emulsion concentrations (100, 200, 500 and 800 µl) gave germination percentages respectively (98.33, 96.67, 95.00 and 93.33%).

Materials	Conc. µl	Germination After 4 days (%) ± SD
M. piperita (nano-emulsion) 4%	100	98.33 ± 0.57
	200	96.67 0.57
	500	95.00 ± 0.60
	800	93.33 ± 1.00
M. piperita free EO	100	68.00 ± 1.94
	200	66.67 ± 1.94
	800	42.00 ± 1.73
	1000	30.00 ± 1.00
	2000	25.10 ± 2.35
Control	0	100 ± 0.0

p	0.26 ns
$LSD_{0.05}$	10.43

Table 5: Germination of wheat grains with *M. piperita* nano-emulsion and *M. piperita* free EO after storage one month of treatment.

While that the effect of free EO on germination at different concentrations (100, 200, 800, 1000 and 2000 µl) gave germination percentages (68.00, 66.67, 42.00, 30.00 and 25.10%), respectively.

The germination percentages slightly decreased with increasing the concentration of *M. piperita* nano-emulsion. These results indicated that the *M. piperita* nano-emulsion had a slight effect on the germination as compared to the control. While that free EO reduced the germination percentage of wheat grains, especially with high concentrations, compared to the control and/or *M. piperita* nano-emulsion formulation.

Discussion

In the present study laboratory experiments were carried out to evaluate the effect of *M. piperita* essential oil and its nano-emulsion formulation against the most common stored grain pest's adult of *T. castaneum*. Two methods of application (thin film residue and mixing with the grains) were used in this evaluation, and their effect on germination and storage. It is an attempt to control these stored grain pests and avoid the environmental risks and mammalian toxicity arose from chemical insecticides.

The bioassay of the nano-emulsion formulations of *M. piperita* demonstrated toxicity effects on adult of *T. castaneum*. The insecticidal effects of the formulations varied with the insect species, concentration of the formulations, exposure time and the method of application. As far as we know, there are no studies on *M. piperita* essential oil nano-emulsions in simulated field conditions. However, several researchers have evaluated other oils stabilized as nano-emulsions.

The results of contact toxicity in thin film residue method using glass Petri dish and contact toxicity using treatment with wheat grains method, showed that with increasing concentration and the exposure time for both insects, increased the mortality agreed with results are similar to those obtained by researches using other essential oils studies [37-40]. And the effect in a long-term agreed with Sabbour and Abd El-Aziz [41].

They found that oils (Bulk and Nano) had bio-residual efficacy against *E. kuehniella* moths. The percentage of emerged moths was extremely significantly decreased with Purslane oil in Bulk phase (10%) in comparison with untreated control (57%) during tested storage interval (120 days). While, Purslane oil in Nano phase completely suppressed the percentage of emerged moths (zero%) comparing with untreated control (66%).

Certainly, when the essential oil formulated as a nano-emulsion leads to smaller particle size and increase biological activity due to increased surface area therefore more opportunity of the formulation to come in contact with the target insect. Whereas, the lower mortality caused by *M. piperita* EO with the biggest particle size indicates that the smaller the particle size, the greater the probability of higher efficacy.

This finding is consistent with the results are similar to those obtained by researches using other essential oils studies of Yang et al. [42]. The nanoparticles and bulk of garlic essential oil were tested against *Tribolium castaneum* adults. The control efficacy of both nanoparticles and free garlic essential oil were recorded 80% and 11%, respectively. And Anjali et al. [1]; Nenaah [43]; Pant et al. [44]; Sugumar et al. [45]; Abouelkassem et al. [46]; Nenaah et al. [35]; Oliveira et al. [47,48]; Choupanian et al. [49]; Mossa et al. [50]; Choupanian et al. [51] and Louni et al. [52]. The study showed that *M. piperita* essential oil based nano-emulsion formulations were able to increase the mean mortality rate of *T. castaneum* compared to the *M. piperita* EO, in addition to this nano-emulsion method can improve performance of *M. piperita* oil and maintains its properties in a long-term.

The study has also shown that significantly more effective against adult of *T. castaneum* with respect to adult mortality and emergence between concentrations of *M. piperita* free EO, *M. piperita* nano-emulsion and control after 6 weeks and 3 months. It has been reported that one of the main mechanisms of plant oil action is their ability to penetrate the chorion of eggs via the micropyle and cause the death of developing embryos through sphyxiation [53].

The possible explanation for these results caused considerably higher reductions of adult emergence to smaller particle size and increase biological activity due to increased surface area when the essential oil formulated as a nano-emulsion therefore more opportunity of the formulation to come in contact with the eggs and the higher ability to penetrate into the insect's body. Reduction of adult's emergence may have been achieved through a combination of high mortality of eggs and larvae immediately a ter eclosion and contact with essential oil [54-58].

Conclusion

In our results showed that *M. piperita* EO had effect on germination of wheat grains, so *M. piperita* EO was the highest treatment that reduced germination percentages of wheat grains. The international germination threshold required by seed exportation is 90%, so the *M. piperita* nano-emulsion could be used to protect wheat used as seed. The obtained results are in line with Zayed, reported that *M. piperita* nano-emulsion had a slight effect on the germination as compared with *M. piperita* EO.

However, these results are similar to those obtained by researches using other essential oils found that both nano-emulsion and camphor EO did not show any effect on germination especially at the concentration of LC_{50} and LC_{90}. Derbalah and Ahmed, found that the spearmint oil was the highest treatment that reduced the germination percentage of wheat grains. Arya and Tiwari, found that mustard oil at 2% concentration clearly reduced the wheat grains germination.

References

1. Anjali CH, Sharma Y, Mukherjee A, Chandrasekaran N (2012) Neem oil (*Azadirachta indica*) nanoemulsion: A potent larvicidal agent against *Culex quinquefasciatus*. Pest Manage Sci 68: 158-163.
2. Green JM, Beestman GB (2007) Recently patented and commercialized formulation and adjuvant technology. Crop Prot 26: 320-327.
3. Solans C, Izquierdo P, Nolla J, Azemar N, Garcia-Celma MJ (2005) Nano-emulsions. Curr Opin Colloid Interface Sci 10: 102-110.
4. Qian C, Decker EA, Xiao H, McClements DJ (2012) Physical and chemical stability of β-carotene-enriched nanoemulsions: Influence of

pH, ionic strength, temperature, and emulsi ier type. Food Chem 132: 1221-1229.

5. Yilmaz E, Borchert HH (2005) Design of a phytosphingosine-containing, positively-charged nanoemulsion as a colloidal carrier system for dermal application of ceramides. Eur J Pharm Biopharm 60: 91-98.
6. Takegami S, Kitamura K, Kawada H, Matsumoto Y, Kitade T, et al. (2008) Preparation and characterization of a new lipid nano-emulsion containing two cosurfactants, sodium palmitate for droplet size reduction and sucrose palmitate for stability enhancement. Chem Pharm Bull 56: 1097-1102.
7. Klang V, Matsko NB, Valenta C, Hofer F (2012) Electron microscopy of nanoemulsions: An essential tool for characterisation and stability assessment. Micron 43: 85-103.
8. Abismaıl B, Canselier JP, Wilhelm AM, Delmas H, Gourdon C (1999) Emulsification by ultrasound: Drop size distribution and stability. Ultrasonics Sonochemistry 6: 75-83.
9. Kentish S, Wooster TJ, Ashokkumar M, Balachandran S, Mawson R, et al. (2008) The use of ultrasonics for nanoemulsion preparation. Innov Food Sci Emerg Technol 9: 170-175.
10. Ghosh V, Mukherjee A, Chandrasekaran N (2014) Optimization of process parameters to formulate nanoemulsion by spontaneous emulsi ication: evaluation of larvicidal activity against Culex quinquefasciatus larva. Bio Nano-Sci 4: 157-165.
11. Mossa ATH (2016) Green pesticides: Essential oils as biopesticides in insect-pest management. J Environ Sci Technol 9: 354.
12. Dover MJ, Cro t BA (1986) Pesticide resistance and public policy. Biosci 36: 78-85.
13. Isman MB, Miresmailli S (2011) Plant essential oils as repellents and deterrents to agricultural pests. In: Recent developments in invertebrate repellents, ACS Symposium Series, USA 1090: 67-77.
14. Fabres A, Da Silva JDCM, Fernandes KV, Xavier-Filho J, Rezende GL, et al. (2014) Comparative performance of the red flour beetle *Tribolium castaneum* (Coleoptera: Tenebrionidae) on different plant diets. J Pest Sci 87: 495-506.
15. Bossou AD, Ahoussi E, Ruysbergh E, Adams A, Smagghe G, et al. (2015) Characterization of volatile compounds from three *Cymbopogon* species and *Eucalyptus citriodora* from Benin and their insecticidal activities against *Tribolium castaneum*. Industrial Crops and Products 76: 306-317.
16. Lee HK, Lee HS (2016) Toxicities of active constituent isolated from *Thymus vulgaris* lowers and its structural derivatives against *Tribolium castaneum* (Herbst). Appl Biol Chem 59: 821-826.
17. Opit GP, Phillips TW, Aikins MJ, Hasan MM (2012) Phosphine resistance in *Tribolium castaneum* and *Rhyzopertha dominica* from stored wheat in Oklahoma. J Econ Entomol 105: 1107-1114.
18. Smith JLW, Pratt JJJ, Nii I, Umina AP (1971) Baking and taste properties of bread made from hard wheat flour infested with species of *Tribolium, Tenebrio, Trogoderma* and *Oryzaephilus*. J Stored Prod Res 6: 307-316.
19. Iram N, Arshad M, Akhter N (2013) Evaluation of botanical and synthetic insecticide for the control of *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). Bio Assay 8: 1-10.
20. Tefera T, Kanampiu F, De Groote H, Hellin J, Mugo S, et al. (2011) The metal silo: An effective grain storage technology for reducing post-harvest insect and pathogen losses in maize while improving smallholder farmers' food security in developing countries. Crop Protection 30: 240-245.
21. Wink M (1993) Production and application of phytochemicals from an agricultural perspective. Phytochem Agri 34: 171-213.
22. Pavela R (2014) Acute, synergistic and antagonistic effects of some aromatic compounds on the *Spodoptera littoralis* Boisd.(Lep., Noctuidae) larvae. Industrial Crops and Products 60: 247-258.
23. González JOW, Gutiérrez MM, Ferrero AA, Band BF (2014) Essential oils nanoformulations for stored-product pest control: Characterization and biological properties. Chemosphere 100: 130-138.
24. Aflatuni A (2005) The yield and essential oil content of mint (Mentha spp.) in Northern Ostrobothnia. PhD Thesis, University of Oulu.
25. DonPedro KN (1996) Fumigant toxicity of citruspeel oils against adult and immature stages of storage insect pests. Pesticide Science 47: 213-223.
26. Lee BH, Annis PC, Lee SE (2004) Fumigant toxicity of *Eucalyptus blakelyi* and *Melaleuca fulgens* essential oils and 1,8-cineole against different development stages of the rice weevil *Sitophilus oryzae*. Phytoparasitica 32: 498.
27. Latha C, Ammini J (2000) *Curcuma raktakanda* is a potential larvicide for mosquito control. Pharm Biol 38: 167-170.
28. You CX, Jiang HY, Zhang WJ, Guo SS, Yang K, et al. (2015) Contact toxicity and repellency of the main components from the essential oil of *Clausena anisum-olens* against two stored product insects. Int J Insect Sci 2: 1.
29. Massoud MA, Adel MM, Zaghloul OA, Mohamed MIE, Abdel-Rheim KH (2018) Eco-friendly nano-emulsion formulation of *Mentha piperita* against stored product pest *Sitophilus oryzae*. Adv Crop Sci Tech.
30. Qi YT, Burkholder WE (1981) Protection of stored wheat from the granary weevil by vegetable oils. J Econ Entomol 74: 502-505.
31. Broussalis AM, Ferraro GE, Martino VS, Pinzón R, Coussio JD, et al. (1999) Argentine plants as potential source of insecticidal compounds. J Ethnopharmacol 67: 219-223.
32. Finney DJ (1971) Probit analysis. Cambridge University Press, London, UK, p: 318.
33. Sun YP (1950) Toxicity Index-an improved method of comparing the relative 378 toxicity of insecticides. J Econ Entomol 2: 1.
34. Yamamoto I, Casida JE (1999) Nicotinoid insecticides and the nicotinic acetylcholine receptor.
35. Nenaah GE, Ibrahim SI, Al-Assiuty BA (2015) Chemical composition, insecticidal activity and persistence of three *Asteraceae* essential oils and their nanoemulsions against *Callosobruchus maculatus* (F.). J Stored Prod Res 61: 9-16.
36. Abbott WS (1925) A method of computing the effectiveness of an insecticide. J Econ Entomol 18: 265-267.
37. Scott IM, Jensen H, Scott JG, Isman MB, Arnason JT, et al. (2003) Botanical insecticides for controlling agricultural pests: Piperamides and the *Colorado potato* beetle *Leptinotarsa decemlineata* Say (Coleoptera: Chrysomelidae). Archives of Insect Biochemistry and Physiology: Published in Collaboration with the Entomological Society of America 54: 212-225.
38. Upadhyay RK, Jaiswal G (2007) Evaluation of biological activities of Piper nigrum oil against *Tribolium castaneum.* Bull Insectology 60: 57.
39. Arabi M, Frankenberger JR, Engel BA, Arnold JG (2008) Representation of agricultural conservation practices with SWAT. Hydrological Processes: An International Journal 22: 3042-3055.
40. Kraikrathok C, Ngamsaengi S, Bullangpoti V, Pluempanupat W, Koul O (2013) Bio efficacy of some piperaceae plant extracts against *Plutella xylostella* L.(Lepidoptera: Plutellidae). Communications in Agricultural and Applied Biological Sciences 78: 305-309.
41. Sabbour MM, Abd El-Aziz SES (2017) Screening effects of three natural oils and their nano against *Ephestia kuehniella* (Lepidoptera-Pyralidae) in laboratory and store. Biosci Res 14: 408-416.
42. Yang FL, Li XG, Zhu F, Lei CL (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: 10156-10162.
43. Nenaah GE (2014) Chemical composition, toxicity and growth inhibitory activities of essential oils of three *Achillea* species and their nano-emulsions against *Tribolium castaneum* (Herbst). Industrial Crops and Products 53: 252-260.
44. Pant M, Dubey S, Patanjali PK, Naik SN, Sharma S (2014) Insecticidal activity of eucalyptus oil nanoemulsion with karanja and jatropha aqueous iltrates. Int Biodeterior Biodegradation 91: 119-127.

45. Sugumar S, Clarke SK, Nirmala MJ, Tyagi BK, Mukherjee A, et al. (2014) Nanoemulsion of eucalyptus oil and its larvicidal activity against *Culex quinquefasciatus.* Bull Entomol Res 104: 393-402.

46. Sh A, Abdelrazeik AB, Rakha OM (2015) Nanoemulsion of jojoba oil, preparation, characterization and insecticidal activity against *Sitophilus oryzae* (Coleoptera: Curculionidae) on wheat.

47. Oliveira AE, Duarte JL, Amado JR, Cruz RA, Rocha CF, et al. (2016) Development of a larvicidal nanoemulsion with *Pterodon emarginatus* Vogel Oil. PloS One 11: e0145835.

48. Oliveira AP, Santana AS, Santana ED, Lima APS, Faro RR, et al. (2017) Nanoformulation prototype of the essential oil of *Lippia sidoides* and thymol to population management of *Sitophilus zeamais* (Coleoptera: Curculionidae). Industrial Crops and Products 107: 198-205.

49. Choupanian M, Omar D, Basri M, Asib N (2017) Preparation and characterization of neem oil nanoemulsion formulations against *Sitophilus oryzae* and *Tribolium castaneum* adults. J Pest Sci 42: 158-165.

50. Mossa ATH, Afia SI, Mohafrash SMM, Abou-Awad BA (2017) Nano-emulsion of camphor (Eucalyptus globulus) essential oil, formulation, characterization and insecticidal activity against wheat weevil, *Sitophilus granarius.* Asian J Crop Sci 9: 50-62.

51. Choupanian M, Dzolkhifli O (2018) *Sitophilus oryzae* L., (Coleoptera: Curculionidae) ve *Tribolium castaneum* (Coleoptera: Tenebrionidae)'un kontrolünde neem yağının nano emülsiyonlarının ve fizikokimyasal tanımlaması ve formülasyonu. Türkiye Entomoloji Dergisi 42: 127-139.

52. Louni M, Shakarami J, Negahban M (2018) Insecticidal efficacy of nanoemulsion containing *Mentha longifolia* essential oil against *Ephestia kuehniella* (Lepidoptera: Pyralidae). J Crop Prot 7: 171-182.

53. Credland PF (1992) The structure of bruchid eggs may explain the ovicidal effect of oils. J Stored Prod 28: 1-9.

54. Lale NES, Abdulrahman HT (1999) Evaluation of neem (*Azadirachta indica* A. Juss) seed oil obtained by different methods and neem powder for the management of *Callosobruchus maculatus* (F.) (Coleoptera: Bruchidae) in stored cowpea. J Stored Prod Res 35: 135-143.

55. González U (1995) El maíz y su conservación. Trillas, México DF, México, p: 399.

56. Zayed GMM (2018) Efficacy of marjoram (*Origanum majorana*) on *Rhizopertha dominica* and identification of its chemical components. Academia J Agri Res 6: 163-170.

57. Derbalah A, Ahmed S (2011) Oil and powder of spearmint as an alternative to Sitophilus oryzae chemical control of wheat grains. J Plant Prot Res 51: 145-150.

58. Arya M, Tiwari R (2013) Efficacy of plant and animal origin bioproducts against lesser grain borer, *Rhyzopertha dominica* (fab.) in stored wheat. IJRSR 4: 649-653.