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Nanoemulsions of Chamomile and Cumin Essential Oils: As an Alternative Bio-rational Control Approach against the Red Flour Beetle, *Tribolium castaneum*

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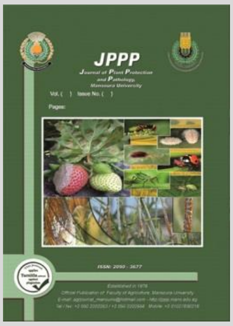

ABSTRACT

Essential oil (EO) nanoemulsion is a new approach to formulate and convey insecticides and to minimize some of the common shortcomings associated with the conventional formulations of synthetic insecticides and also of essential oils. The aim of the present was to develop an oil-in-water (O/W) nanoemulsion of the essential oils of chamomile (*Matricaria chamomilla* L.) and cumin (*Cuminum cyminum* L.), and assess their lethal and sublethal toxicity to the red flour beetle *Tribolium castaneum* (Hersbt). The nanoemulsions of EO were characterized by droplet sizes of 341.4 and 387.1 nm for the chamomile and cumin, respectively. The polydispersivity (PDI), viscosity (cP), zeta potential (mV) and conductivity (mS/cm) of the nanoemulsions were also characterized. The cumin nanoemulsion exhibited higher lethal toxicity to the flour beetle, besides of compromising the insect weight gain while impairing their food consumption and conversion rate in sublethal exposure. Cumin EO nanoemulstion also sparked anti-feeding activity, reduced progeny production and prevented grain weight loss by the red flour beetle indicating its potential for stored product protection.

Keywords: Essential oils; Nanopesticides; Stored product beetles; Insecticidal activity

INTRODUCTION

Food production is key to food security and thus issues concerning pest management are crucial. This has become more so as the world is trying to produce more food to feed a growing population (Hagstrum and Phillips, 2017). One of the main ways to increase food production is to improve pest control and management minimizing potential adverse environmental and human health impacts (Lusk and McCluskey 2018). Nowdays alternative control methods are received more attention than conventional synthetic pesticides (Athanassiou *et al*., 2018). Among these methods, biopesticides, and more particularly naturally occurring insecticides that obtained from plants, are targets of particular attention (Walia *et al*., 2017).

Large quantities of cereal crops are yearly lost in temperate (5–10%) and tropical regions (> 20%) by pest infestations in the stone (Rajendran, 2002). The red flour beetle, *Tribolium castaneum* Herbst (Coleoptera: Tenebrionidae), is one of the most cerious insects of stored grains. Both adults and larvae of the red flour beetle feed on a wide variety of stored products, including milled cereal products and causing extensive losses in both the quality and quantity of these products (Rees, 2004). Besides losses due to grain consumption, the infestations also resulted in elevation of temperature and moisture conditions leading to mold development, including that of toxigenic species (Magan *et al*., 2003).

The necessary management of the red flour beetle is usually achieved with the use of traditional grain protectants and fumigants, which are cost-effective in many storage systems and also against several insect pest species (Boyer *et al*., 2012). However, the use of these compounds does impose intrinsic risks to environmental and human health (Abbassy *et al*., 2014). In addition, stored-grain insects and the red flour beetle, in particular exhibit widespread problems of insecticide resistance (Opit *et al*., 2012). Therefore, the demand for alternative control methods with improved safety profile is in high demand for stored product protection.

In recent years, natural plant products have been a focus of intensive research as environmentally safer pest control materials (Saad *et al*., 2018). Further, their low mammalian toxicity, and insect selectivity and resistance profiles are promising frequently requiring longer time and larger populations for the development of insecticide resistance (Jindal *et al*., 2013). Essential oils from higher plants are considered one of the most efficient alternative bio-rational control methods against stored product insects (Regnault-Roger *et al*., 2012). These natural compounds are active against a wide range of pests like mites, insects, nematodes, weeds, and fungi (Çalmaşur *et al*., 2006). They also exhibit a wide range of distinct modes of action leading to divergent expression of toxicity (Mossa, 2016). These characteristics reinforce the perception of the potential of essential oils as pest management tools, particularly for organic farming (Adil *et al*., 2015). However, the field use of essential oils requires suitable formulations to allow the expression of their potential (Benelli *et al*., 2017).

Nanotechnology is currently considered a novel approach in diverse fields of research and also has potential

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for the development of improved insecticide formulations through exhibiting small particle sizes ranging from 50 to 200 nm (Tadros *et al*., 2004). This interest in nanotechnology for the development of pesticide formulations, including nanoemulsions, is due to their promising applications in material science, medicine, pharmacology and agriculture (Singh *et al*., 2018). Nano-size materials show general and biological properties that include large increase of surface/area and hence increased ability to reach the target site, in addition to fast penetration and selective accumulation in various types of cells (Hashem *et al*., 2018; Madhyastha and Daima, 2018). A nanoemulsion is an example of these nanoformulations, which exhibits droplet sizes ranging from 20 to 200 nm (Sugumar *et al*., 2014).

An alleged advantage of nanoemulsions is their solubility of natural pesticides such as essential oils without using any organic solvent, which increases their environmental safety profile (Wang *et al*., 2007). Therefore, essential oil nanoemulsions seem to solve the inconvenient of the rather frequent low water solubility of (organic) pesticides (Fernandes *et al*., 2014). Here the development of nanoemulsions of essential oils from two plant species - the German chamomile and the cumin, which were prepared as oil-in-water two-phase nanoemulsion formulations were reported. The chemical components of the essential oils, the nanoemulsion characterization and their lethal and sublethal toxicity to the red flour beetle were also assessed and here reported.

MATERIALS AND METHODS

Insects

The red flour beetles were obtained from stock colonies that maintained at the laboratory of Stored Product Insects of the Sakha Agricultural Research Station, Agriculture Research Center (ARC), Egypt. Cultures were kept at $28^{O} \pm 2^{O}$ C, 65 ± 5% R.H., and 16: 8 (L:D) photoperiod. The insects were reared in 250 ml jars and the adults were obtained by sieving the feeding substrate. The adult insects (unsexed; 4-7 days old) that sieved out of the stock colony were used in the experiments on the following day.

Essential oils

Essential oils of German chamomile (*Matricaria chamomilla* L.) and cumin (*Cuminum cyminum* L.) are available in Egypt and were provided, as a gift, from Hashem Brothers Company for Essential Oils and Aromatic Products (Kafr-Elsohby, Kalyoubeya, Egypt).

Chemical constituents of the essential oils

Chemical components of essential oils were identified with gas chromatography-mass spectrometry (GC/MS) using the HP5890 system with a HP column (60 meter X 0.25 millimeter, 0.25 μm film thickess) (Hewlett Packard, Palo Alto, CA, USA). The oils were detected using flame ionization detector (FID); nitrogen and hydrogen formed the stationary phase. The initial temperature was 60 °C, the maximum temperature was 250 °C, and the injector temperature was 240 °C. The relative amounts of the oil components were calculated from the total area of the detected peak obtained using the equipment. All of the steps of sample preparation, extraction and analysis procedures were carried out in the Laboratory of the Hashem Brothers Company (Abdel Moneim Riad St., Giza, Egypt).

Chemicals

Polysorbate 80 (Tween 80) and ethanol were obtained from El-Gomhouria for Trading Chemicals and Medical Appliances (Egypt).

Nanoemulsion preparation

Oil-in-water nanoemulsions of the two oils (14%) were prepared according to Hamouda *et al.* (1999), which were further detailed by Joe *et al.* (2012). Tween 80 was used as a non-ionic surfactant. The oil phase of the nanoemulsion consisted of the selected essential oil representing 14% of the total emulsion; ethanol (3%) and biosurfactant (Surfactin, Tween 80; final concentration 3%) representing 20% (v/v) of the emulsion (Hashem *et al*., 2018)**.** The oil phase was mixed and kept for 1 h at 86 °C, and subsequently mixed with distilled water (80% v/v), kept for 3 min and finally centrifuged at 10,000 rpm for 15 min.

Nanoemulsion characterization

The nanoemulsion physicochemical properties the average droplet size, viscosity (cP), polydispersivity (PDI), zeta Potential (mV) and conductivity (mS/cm) were characterized. The droplet size and viscosity were determined by the dynamic laser scattering method (Zetasizer Nano ZS90) (Jun *et al*., 2015). The zeta potential and polydispersivity index were determined by photon correlation spectroscopy using the kit ZetaPlus (Zhermack, Badia Polesine, Italy), (Arancibia *et al*., 2017). All characterization analyses were performed at the Electron Microscopy Unit of the Faculty of Agriculture at Mansoura University (Egypt).

Nanoemulsion toxicity

Acute concentration-mortality bioassay

Acute toxicity of both nanoemulsions was determined by concentration-mortality bioassay where 1 mL of the nanoemulsion at the concentrations of 0, 25, 50, 75 and 100 mg/mL were applied on 20 g cracked wheat grains and left to dry for 20 min. The wheat grains treated with the nanoemulsion were placed in 50 mL glass jars, which subsequently received 10 non-sexed adult flour beetles (7-14 days old). Insect mortality was recorded after 96 h exposure. All bioassays were repeated three times.

Time and concentration-dependent mortality asssessments

Adult flour beetles were exposed to cracked wheat grains treated with EO nanoemulsion as previously described for the acute toxicity bioassays. However, the bioassays were performed under different exposure times allowing mortality assessments at 3, 6, 9 and 12 days after treatment. Again, each combination of essential oil and concentration was replicated three times.

Nutritional *indices*

The insects and the cracked wheat grains were used as rearing substrate. They were initially weighted before the insect release in each experimental unit following the treatments indicated above. The insects were left on the cracked wheat for eight consecutive days, after which adult mortality and insect and grain weight were estimated. The nutritional indices were calculated following Farrar *et al.* (1989), as follow**:** relative growth rate (RGR) = (A - B)/B × day $^{-1}$; relative consumption rate (RCR) = D/B × day $^{-1}$; conversion efficiency of ingested food (ECI) (%) = (RGR) / (RCR) × 100; and feeding deterrence index (FDI) (%) = (C -

T)/C × 100; where A = weight of live insects on the investigated day (mg) / number of live insects on the investigated day, B = initial weight of insects (mg) / initial number of insects, D = biomass ingested (mg) / number of live insects on the investigated day, C = food consumption in control and T = food consumption of treatment.

Progeny production and grain loss

The adult insects released on the cracked wheat grains, as described above, were removed after eight days, and the grains were maintained for eight additional weeks under the same environmental conditions as previously described. After this period, the F_1 progeny emergence was recorded avoiding the overlapping of generations. The grain loss caused by the insects was also recorded at this time.

Statistical analyses

Toxicity of the EO nanoemulsions was estimated by probit methods using the software PcProbit (LdP Line, available at http://www.ehabsoft.com/ldpline/) and following Finney (1971). The remaining results were subjected to regression analyses with concentration and time, as independent variables (adult mortality), or only concentration (other results), and using the curve fitting procedure of the softwares TableCurve 3D (for adult mortality) and TableCurve 2D (remaining results) (Systat, San Jose, CA, USA). The regression models were selected from the simplest (linear) to more complex models based on parsimony, F-values (and error estimates), and steep increase/decrease in R2 with model complexity. وضح كيف اجريت التحليل الاحصائى لكل من

RESULTS AND DISCUSSION

Results

Chemical composition of the essential oils

The results of Gas Chromatography/ Mass Spectrometry (GC/MS) analyses of the tested oils that obtained by hydrodistillation are summarized in Table (1). The main compounds (>1%) of the tested oils were identified by matching their spectra with those available in the mass spectra digital library of the GC/MS. Thus, the main components recognized were: bisabolol oxide A (40.54%), 7,11-dimethyl-3-methylene (17.01%), and Bisabolol oxide B (7.43%) in the chamomile EO; and γ-terpinene (15.76%), benzene methanol (11.32%) and beta-pinene (10.37%) in the cumin EO.

Table 1. Composition of the chemical components of the essential oils of chamomile and cumin used as nanoemulsion.

Chemical component of essential oil	Chamomile (flowers) Retention time (min)	Chamomile (flowers) Concentration (%)	Cumin (seeds) Retention time (min)	Cumin (seeds) Concentration (%)
7,11-Dimethyl-3-methylene	28.58	17.01	-	-
Germacrene-D	29.35	1.90	-	-
Germacrene-B	29.94	1.26	-	-
3,7,11-Trimethyle	30.45	1.14	-	-
5,8-Dimethylisoquinoline	30.64	1.11	-	-
Alpha-bisabolol	36.52	6.43	-	-
Bisabolol oxide B	35.28	7.43	-	-
Chamazulen	39.23	3.52	-	-
Bisabolol oxide A	40.52	40.54	-	-
Lend-in-dicycloether	44.87	6.32	-	-
Benzene methanol	-	-	10.94	11.32
γ-Terpinene	-	-	11.23	15.76
Beta Pinene	-	-	8.56	10.37
P- cymine	-	-	12.05	7.45
1-pPhenil-1-butanol	-	-	8.25	6.45

Nanoemulsion characterization

The characterization of both nanoemulsions, from chamomile and cumin essential oils, are shown in Table (2). The average size and conductivity of chamomile and cumin NE were 341.4 nm and 0.033 mS/cm for the former, while it were 387.1 nm and 0.072 mS/cm for cumin NE. Also, the zeta potential was -3.2 ± 4.28 for the chamomile NE and -10.1 ± 4.08 for the cumin NE. However, the polydispersivity index (PDI) value was slightly higher for the cumin NE (0.628) than for the chamomile NE (0.069), both of which exhibited similarly low viscosity (0.8872 cP), which may be due to the usually low oil content of nanoemulsions.

Table 2. Physical characteristics of the nanoemulsion formulations.

Source of oil	Z-Average (nm)	Poly dispersivity (PDI)	Viscosity (cP)	Zeta Potential (mV) ± SE	Conductivity (mS/cm)
Chamomile	341.4	0.069	0.887	-3.2 ± 4.28	0.033
Cumin	387.1	0.628	0.887	-10.1 ± 4.08	0.072

Short-term contact toxicity

The NE of both essential oils were subjected to concentration-mortality bioassays with 96 hours exposure of adult flour beetles to assess their acute contact toxicity to these insects. The results of probit analyses indicated suitability of this model for the concentration-mortality curves of both NE (high $\chi 2$-values and $P > 0.05$) (Table 3)..

Table 3. Relative toxicity of nanoemulsion of the essential oils of chamomile and cumin against the red flour beetle *Tribolium castaneum*

Essential oil	Slope (± SE)	LC_{50} (95% FL) (mg/ml)	χ^2	*P*
Chamomile	1.69	685.96 (548.77-857.45)	4.37	0.39
Cumin	4.68	136.25 (108.9-170.3)	3.43	0.44

The cumin NE was 5x more toxic to adult red flour beetles than the chamomile NE based on the estimated LC50s (Table 3). The higher slope observed with cumin NE also indicated a higher homogeneity of response to this formulation when compared with the chamomile NE

Time and concentration-dependent mortality

Extended exposure of adult red flour beetles to cracked wheat grains treated with increasing concentrations of either chamomile or cumin NE in reinforced the trend observed with the short-term toxicity bioassay reported above. Mortality was increased with increasing concentration and length of exposure for both NEs, but the cumin NE exhibited higher toxicity with a steep increase in mortality at concentrations above 50 mg/mL and reaching mortality levels above 50% after 10 days exposure, unlike chamomile, which did not reach even 25% mortality at the highest concentration and longest exposure (Fig. 1).

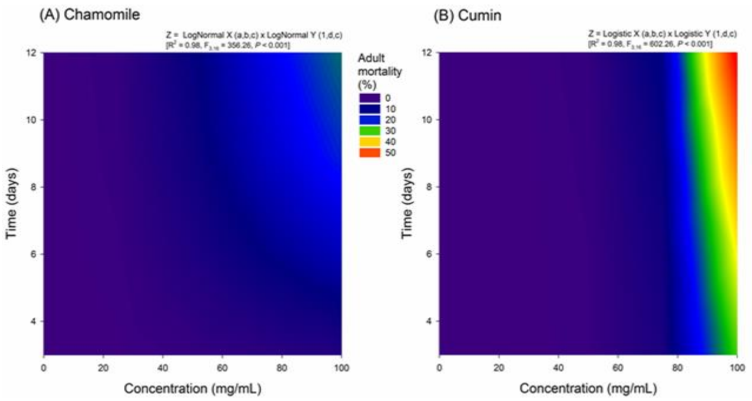

Fig. 1. Filled contour maps exhibiting the effects of concentration and exposure time on adult mortality of red flour beetles provided with cracked wheat treated with essential oil nanoemulsions of chamomile and cumin. The maps were plotted using regression models, as indicated in the figures, where Z is mortality, X is the essential oil concentration, and y is the exposure time.

Insect weight gain, food consumption, and feeding deterrence

The insects surviving were followed for eight days, after which their gain in weight (i.e., body mass) was determined, as was the food consumption during the period. The weight gain of adult insects decreased with increasing the essential oil concentration with the cumin NE exhibited higher effect in compromising insect weight gain (Fig. 2A). A similar trend was observed for food consumption, which also declined with essential oil concentration and again with cumin exhibited more drastic effect in compromising the relative rate of food consumption than chamomile (Fig. 2B).

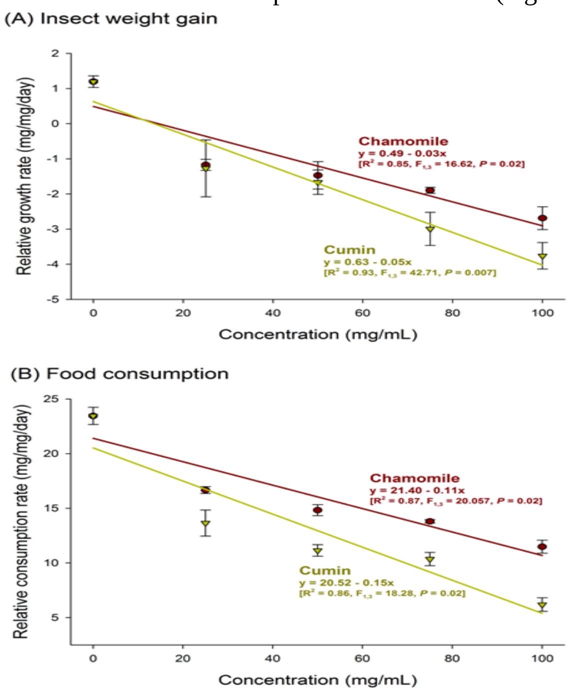

Fig. 2. Insect weight grain (± SE) (A) and food consumption (± SE) (B) of red flour beetles exposed to increasing concentrations of essential oil nanoemulsions of chamomile and cumin. The symbols represent the mean of three independent replicates.

The efficiency of food conversion was estimated based on the insect weight gain and food consumption with both essential oils compromised food conversion at concentrations as low as 25 mg/mL. The rate of such decline with increasing concentration was similar for both oils, but cumin imparted slightly higher effect than chamomile (Fig. 3A). In addition, both essential oils also deterred feeding among flour beetles with a similar rate, as indicated by the similar slopes of the curves of feeding deterrence with concentration (Fig. 3B). Feeding deterrence increased with concentration and the effect of cumin was consistently stronger than that of chamomile (Fig. 3B).

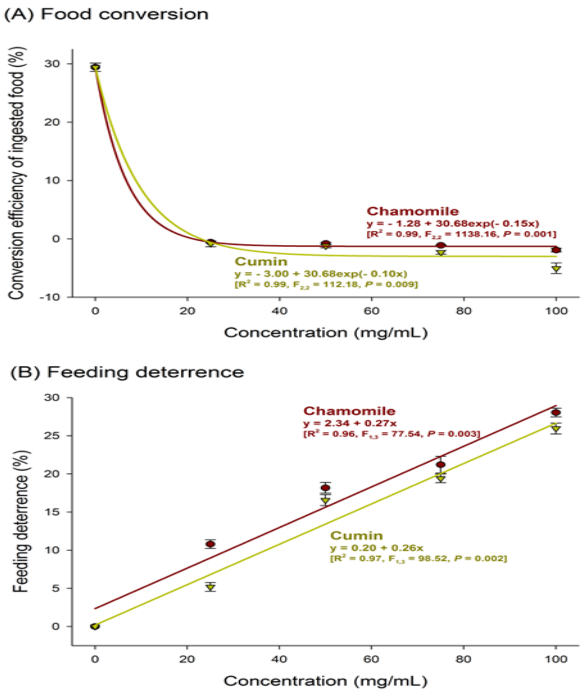

Fig. 3. Food conversion efficiency (± SE) (A) and feeding deterrence (± SE) (B) of red flour beetles exposed to increasing concentrations of essential oil nanoemulsions of chamomile and cumin. The symbols represent the mean of three independent replicates.

Progeny production and grain loss

The insects surviving with were able to reproduce while maintaining their feeding activity. Although, the progeny production of the exposed adults of the red flour beetles decreased with the concentrations of both essential oils with similar rate, the effect of the cumin NE was always stronger leading to lower progeny emergence (Fig. 4A). The cost of the feeding activity and progeny production was the decrease in grain weight with essential oil concentration (Fig. 4B). The rate of decrease was similar for both essential oils, but again cumin led to higher declines in grain weight loss with increasing in concentration than chamomile (Fig. 4B).

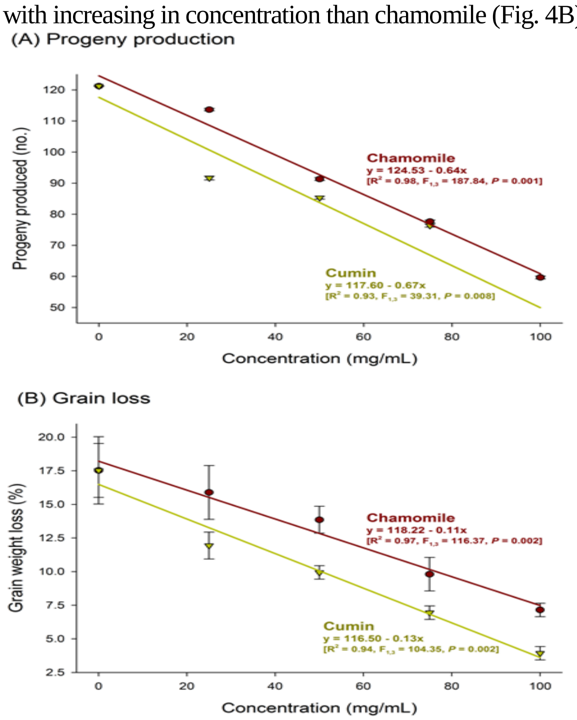

Fig. 4. Progeny production (± SE) (A) and grain loss (± SE) (B) by red flour beetles exposed to increasing concentrations of essential oil nanoemulsions of chamomile and cumin. The symbols represent the mean of three independent replicates.

Discussion

The development of nanoemulsion formulations form the essential oils of chamomile and cumin was the focus of the present study aiming their potential use as alternative insecticides against the red flour beetle. Indeed, we were able to obtain both nanoemulsions, which favors the use of essential oils as insecticides minimizing their variability while improving the physical stability of their bioactive compounds, protecting them from the interactions with food ingredients. Because of the subcellular size of the nanoformulations, their bioactivity is increased through the activation of passive mechanisms of cell absorption (Berne and Pecora, 2000).

The physicochemical properties of the nanoemulsions are mainly determined by their zeta potential (mV), poly-dispersivity (PDI), Z-average (nm), and other related characteristics (Lett 2016). Nanopesticides, including nanoemulsions, have a typical particle size range of 50-200 nm (Tadros *et al*., 2004). Emulsifiers may act as a mechanical barrier and by forming a surface potential (zeta potential), which can produce repulsive electrical forces among approaching oil droplets, thus hindering coalescence (Bordes *et al*., 2009). High zeta potentials were observed for nanoemulsions of chamomile and cumin EO (-3.2 and -10.1 mv, respectively), which results from both oil and surfactant compositions. Zeta Potential values greater than +25 mV or less than -25 mV typically have high degrees of stability, as the case with chamomile and cumin EA. Scatterings with a low zeta potential value will eventually aggregate due to Van Der Waal inter-particle attractions (Shi *et al*., 2017). Both of these effects lead to a narrow range of sample concentrations that will yield a satisfactory quality result (Hinds, 2012). In addition, a highly conductive sample (> 5mS/cm) can lead to electrode polarization and degradation (Patakangas, 2014). Other studies revealed that particle sizes of nanoemulsions of essential oils produced by high pressure homogenization and spontaneous emulsification were similar to those obtained in this study, as mentioned by Dias *et al*. (2014).

Poly-dispersity (PDI) is another important property of nanoformulations. The measurement refers to the uniformity of droplet size within the formulation (Flores *et al*., 2011). Therefore, values of PDI lower than 0.2 indicate homogenous droplet populations, while a 0.3 value represents heterogeneity (Hoeller *et al*., 2009). Our results demonstrated that the nanoemulsion of chamomile was particularly uniform compared to the nanoemulsion of cumin. Thus, added homogeneity can be achieved by increasing the viscosity of the continuous phase of the formulation preparation. However, this delays instability resulting in oil droplets of more homogeneous particle size (Arancibia *et al*., 2016), which can be further improved for the cumin oil. Regardless of whether the insecticidal effects of cumin are higher or less effective compared to chamomile

The search for bio-rational insecticides of natural origin is on the increase particularly for organic production systems, because they also consider as a means to minimize adverse effects of conventional pesticides (Aktar *et al*. 2009). In such context, preparation of nanoemulsions has emerged as a promising alternative to improve EO performance against arthropod pest species (Damalas and Koutroubas 2018). Nanoemulsions have received a great deal of attention from the pharmaceutical sector, for example as potential vehicles for transdermal delivery of hydrophobic drugs (Shakeel *et al*., 2012). Recent advances in agriculture research have also triggered great interest in the exploration of nanotechnology (Khot *et al*. 2012). The objective is usually to increase the physical stability of the essential oil bioactive compounds. Nanoemulsions of pesticidal active ingredients have often been suggested to increase the insecticide uptake, but supporting data in plant-protection products remains scarce. However, two recent studies support the hypothesis of enhanced uptake (Oberdörster *et al*., 2005). In the first of these studies, experiments on a series of nanoemulsions of neem oil showed that the LC_{50} decreased with droplet size, which was interpreted as indicating an increased uptake of smaller droplets. (Anjali *et al*., 2012).

The bioactivity and persistence of nanoemulsions of the two tested oils against the red flour beetle exhibited insecticidal activity, including lethal and sublethal effects. Increased mortality with nanoemulsions of natural insecticides were also observed in other studies with stored product insects (e.g., Nenaah *et al*. 2015; Oliveira *et al*. 2017), and mosquitoes (Oliveria *et al*., 2016). Most reports followed the same approach in controlling insect pests, but used different surfactants, like Tween (Montefuscoli *et al*., 2014) and polyethylene glycol (González *et al*., 2014), and β-cyclodextrin (Galvão *et al*., 2015), poly-β-hydroxybutyrate and poly-ε caprolactone (Carvalho *et al*., 2015), as encapsulating agents.

The main point is that the developed nanoemulsion allowed for the insecticidal use of chamomile and cumin EO. The concentration-mortality toxicity bioassays performed indicated that the acute activity of these compounds, which are not particularly high, but cumin EO seems promising for further development. Eventual fractioning of use extracts with higher concentration of main components will likely improve the short-term performance of this EO. However, insecticidal activity goes beyond short-term mortality (Guedes and Cutler, 2014; Guedes *et al*., 2016, 2017), and in our study we also assessed a range of sublethal effects of the EO nonemulsion exposure. Both essential oils and specially cumin essential oil compromised food consumption, food conversion, insect development and reproduction, minimizing grain loss. The effects were always higher for cumin EO reinforcing the potential of nanoemulsions of cumin EO for further development aiming stored product protection, wich might deserve further investigations.

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المستحلبات النانوية لزيتى البابونج والكمون كنهج بديل للتحكم البيولوجي ضد خنفساء الدقيق الصدئية

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[1]قسم افات الحبوب والمواد المخزونة ـمعهد وقاية النبات ـمركز البحوث الزراعية بسخا ـ كفر الشيخ

[2]قسم الحشرات الاقتصادية ــ كلية الزراعة ـجامعة المنصورة

يعتبر مستحلب النانو القائم على الزيوت الأساسية (EO) نهجًا جديدًا لصياغة وتركيب المبيدات الحشرية وتقليل بعض أوجه القصور الشائعة المرتبطة للمبيدات الحشرية الاصطناعية وكذلك الزيوت الأساسية. الهدف من البحث تطوير مستحلب نانوي للزيوت الأساسية للبابونج (Matricaria chamomilla L.) والكمون (Cuminum cyminum L.) ، وتقييم سميتها المميتة وشبه المميتة بالنسبة إلى خنفساء الدقيق الصدئية .(Tribolium castaneum (Hersbt تميزت مستحلبات النانو بأحجام قطيرات 341.4 و 387.1 نانومتر للبابونج والكمون على التوالي. وتم تمييز التشتت المتعدد (PDI) ، اللزوجة (cP) ، جهد الزيت (mV) والتوصيل (mS / cm) لمستحلبات النانو. أظهر مستحلب الكمون النانوي سمية مميتة أعلى لخنفساء الدقيق ، إلى جانب المساومة على زيادة وزن الحشرات مع إضعاف استهلاكها الغذائي ومعدل التحويل في التعرض شبه المميت. كما أثبت المستحلب النانوى للكمون نشاطًا مضادًا للتغذية ، وقلل من إنتاج النسل ، ومنع فقدان وزن الحبوب بواسطة خنفساء الدقيق الصدئية مما يشير إلى قدرتها على حماية المنتجات أثناء عملية التخزين