J Pest Sci (2016) 89:219–229
DOI 10.1007/s10340-015-0665-z

ORIGINAL PAPER

Chemical composition, insecticidal and biochemical effects of essential oils of different plant species from Northern Egypt on the rice weevil, *Sitophilus oryzae* L.

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Received: 5 November 2014 / Revised: 25 February 2015 / Accepted: 31 March 2015 / Published online: 9 April 2015
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Abstract The extensive use of synthetic insecticides and fumigants for control stored-product insects has led to the development of resistance. Essential oils from aromatic plants may provide proper alternatives to currently used insect control agents. Essential oils from 20 Egyptian plants were obtained by hydrodistillation. The chemical composition of the oils was identified by gas chromatograph/mass spectrometer. Fumigant and contact toxicities of the essential oils were evaluated against *Sitophilus oryzae*. The inhibitory effects of the essential oils on acetylcholinesterase and adenosine triphosphatases activities were examined. The oils were composed of monoterpene hydrocarbons (i.e., limonene, sabinene, β-pinene and γ-terpinene) and oxygenated monoterpenes (i.e., terpinen-4-ol, β–thujone, 4-terpineol, α-citral and 1,8-cineole) with the exception of the oil of *Schinus terebinthifolius* which was contained sesquiterpenes, and the oil of *Vitex agnus-castus* which contained similar amounts of monoterpenes and sesquiterpenes. In the fumigation assay, the oils of *Origanum vulgare* (LC_{50} = 1.64 mg/L air), *Citrus lemon* (LC_{50} = 9.89 mg/L air), *Callistemon viminals* (LC_{50} = 16.17 mg/L air), *Cupressus sempervirens* (LC_{50} = 17.16 mg/L air), and *Citrus sinensis* (LC_{50} = 19.65 mg/L air) showed high toxicity to *S. oryzae*. In the contact assay, the oils of *Artemisia judaica*, *C. viminals,* and *O. vulgare* caused the highest toxicity to *S. oryzae* with LC_{50} values of 0.08, 0.09, and 0.11 mg/cm^2, respectively. The oil of *A. judaica* (I_{50} = 16.1 mg/L) invoked the highest inhibitory effect on AChE activity, while the oils of *C. viminals* and *O. vulgare* were the most potent inhibitors to ATPases activity with I_{50} values of 4.69 and 6.07 mg/L, respectively. The results indicate that the essential oils of *A. Judaica, O. vulgare*, *C. limon*, *C. viminals,* and *C. sempervirens* could be applicable to the management of populations of *S. oryzae*.

Keywords Essential oils · Fumigant toxicity · Contact toxicity · Curculionidae acetylcholinesterase · Adenosine triphosphatase

Key message

- Introducing novel effective natural compounds with different mechanisms of action is essential to overcome increasing insect resistance rates.
- Twenty essential oils were isolated from Egyptian plants.
- The chemical composition of the isolated oils was identified by GC/MS.
- The isolated oils showed pronounced fumigant and contact toxicities against *Sitophilus oryzae*.
- The oils caused significant inhibition on acetylcholinesterase and adenosine triphosphatases activities.
- Some of the tested oils have potential as a control agent against *S. oryzae*.

Communicated by C. G. Athanassiou.

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Introduction

The rice weevil, *Sitophilus oryzae* L. (Coleoptera: Curculionidae), is one of the most serious and destructive pests found in stored cereals throughout the world (Park et al. 2003; Yoon et al. 2007). It causes extensive loss in cereals and affects the quantity and quality of the grains and grain products as well as deterioration of seed viability (Gupta et al. 1999). The control of stored-products insects, including *S. oryzae*, throughout the world is primarily dependent upon application of organophosphorus and pyrethroid insecticides and fumigants such as phosphine (PH_3) (Kljajic and Peric 2006; Ren et al. 2008). Fumigation is still one of the most effective methods for the control of stored-product insects. However, methyl bromide is being phased out in both developed and developing countries due to its ozone depletion effects (Rajendran and Sriranjini 2008). In addition, some stored-product insects have developed resistance to phosphine in many countries (Nayak et al. 2007). Therefore, there is an interest in developing new alternative ways for stored products protection. One of these alternatives is the use of plant natural products that are known to be less harmful to human health and the environment.

Essential oils are mixtures of volatile secondary metabolites, mainly monoterpenes and sesquiterpenes, obtained from plants by steam distillation or hydrodistillation. The term ''essential'' derives from ''essence'' which means smell or taste, and relates to the property of these substances of providing specific flavors and odors to many plants. Essential oils are used as fragrances and flavors in the perfume and food industries as well as in aromatherapy (Enan 2001; Isman et al. 2007). They are generally broad spectrum in activity because of the presence of several chemicals with different modes of action. Essential oils possess acute contact and fumigant toxicity to insects (Sahaf et al. 2008; Kim et al. 2010; Suthisut et al. 2011), repellent activity (Nerio et al. 2010; Carroll et al. 2011; Nenaah 2014), antifeedant activity (Huang et al. 1999; Stefanazzi et al. 2011), as well as development and growth inhibitory activity (Tomova et al. 2005; Waliwitiya et al. 2008).

Many plant essential oils have been reported to possess insecticidal properties against *S. oryzae* (Kim et al. 2003; Lee et al. 2003; Popović et al. 2006; Negahban and Moharramipour 2007; Ogendo et al. 2008; Rajendran and Sriranjini 2008; Sahaf et al. 2008; Stefanazzi et al. 2011; Kim et al. 2013). However, no studies had been reported on the fumigant and contact toxicities of essential oils isolated from plants growing in North coast of Egypt, except our previous study (Mohamed and Abdelgaleil 2008) in which we described the fumigant and contact toxicities of eight essential oils against *S. oryzae* and *Tribolium castaneum*. Therefore, this study was carried out to evaluate the insecticidal activity of 20 essential oils extracted from plants commonly growing in North coast of Egypt against the adults of *S. oryzae*. The chemical compositions of the oils were identified by gas chromatography–mass spectrometry (GC–MS). To determine their mode of action, we also studied their ability to inhibit acetylcholinesterase (AChE) and adenosine triphosphatases (ATPases) as common target enzymes for insect control chemicals.

Materials and methods

Culturing of insects

The stock culture of the rice weevil, *S. oryzae* (L.) (Coleoptera: Curculionidae), had been maintained in our laboratory for over 12 years without exposure to insecticides. The insect was reared on sterilized whole wheat at 26 ± 1 °C and 65 ± 5 % RH in complete darkness. The unsexed adult insects used in toxicity and biochemical studies were 2-week post-emergence.

Plant materials

Twenty plant species (Table 1) were collected during the flowering stages from different locations of Alexandria, Albehira, and Matrouh Governorates, Egypt, in April, to August, 2011. The plant materials were identified by Prof. FathAllah Zaitoon of the Plant Pathology Department, Faculty of Agriculture, Alexandria University. Voucher specimens were deposited in Department of Chemistry of Pesticides, Faculty of Agriculture, Alexandria University.

Isolation of essential oils

Essential oils were extracted by hydrodistillation in a Clevenger-type apparatus for 3 h. The leaves and aerial parts were partially dried at room temperature (26 ± 1 °C) with good ventilation for 5 days and the fruit peels were used fresh. Anhydrous sodium sulfate was used to remove water after the extraction. The extracted oils were stored in airtight glassware in a refrigerator at 4 °C.

Analysis of essential oils

Chemical analyses were performed on a gas chromatography (Hewlwett Packard 5890)/mass spectrometry (Hewlwett Packard 5989B) (GC–MS) apparatus. The essential oils were diluted in diethyl ether and 0.5 µL was injected. The GC column was a 30-m (0.25 mm i.d., film thickness 0.25 µm) HP-5MS (5 % diphenyl) dimethylpolysiloxane capillary column. The GC

Table 1 Major constituents, date of collection, place of collection, and yields of essential oils extracted from twenty Egyptian plant species

Plant name	Family	Plant part (date of collection)	Place of collection	Oil yield (%) (v/w) (color)	Major components (%)
Artemisia judaica	Asteraceae	Aerial parts 10-4-2011	Matrouh	0.2 (Pale yellow)	β-Thujone (49.83), chrysanthenone (10.88), α-thujone (8.21), 1,8-Cineole (4.91), L-Camphor (3.0), artemisia alcohol (2.20)
Artemisia monosperma	Asteraceae	Leaves 5-6-2011	Matrouh	0.8 (Pale yellow)	Capillene (36.86), capillin (14.68), γ-terpinene (12.46), β-pinene (7.85), *cis*-ocimene (3.26), 4-terpineol (2.59)
Astoma seselifolium	Apiaceae	Leaves 11-4-2011	Albehira	0.1 (Pale yellow)	Sabinene (23.02), 4-terpineol (17.83), γ-Terpinene (8.97), germacrene D (8.27), α-pinene (6.20), β-myrcene (3.64)
Citrus aurantifolia	Rutaceae	Fruit peels 22-5-2011	Alexandria	0.75 (Colorless)	Limonene (40.19), β-pinene (19.65), α-citral (8.14), γ-terpinene (6.34), α-terpineol (3.71), terpinen-4-ol (2.62)
Citrus limon	Rutaceae	Fruit peels 18-4-2011	Alexandria	0.2 (Colorless)	Limonene (56.30), β-pinene (8.81), γ-terpinene (6.42), α-citral (4.96), β-citral (3.83), α-terpineol (3.38)
Cupressus macrocarpa	Cupressaceae	Leaves 8-5-2011	Alexandria	0.45 (Colorless)	Terpinen-4-ol (20.29), sabinene (18.67), β-citronellol (13.01), γ-terpinene (7.59), camphor (6.66), α-terpinene (4.50)
Citrus paradisi	Rutaceae	Fruit peels 2-4-2011	Alexandria	0.12 (Colorless)	Limonene (74.29), linalool (4.61), linalool oxide (4.18), β-Citral (2.66), β-fenchyl alcohol (1.99), Nootkatone (1.78)
Cupressus sempervirens	Cupressaceae	Leaves 14-4-2011	Alexandria	0.14 (Colorless)	α-Pinene (37.88), δ-carene (20.05), α-terpinolene (6.91), β-myrcene (5.47), dl-limonene (4.67), β-pinene (4.29)
Citrus sinensis	Rutaceae	Fruit peels 1-5-2011	Alexandria	0.7 (Colorless)	Limonene (89.23), linalool (2.98), β-myrcene (1.77), octanal (1.28), α-terpineol (0.51), decanal (0.47)
Callistemon viminals	Myrtaceae	Leaves 15-8-2011	Alexandria	0.5 (Colorless)	1,8-Cineole (71.77), α-pinene (11.47), terpinen-4-ol (3.18), octadecanoic acid (3.08), 1-phellandrene (1.30), terpinen-4-ol (1.22)
Myrtus communis	Myrtaceae	Leaves 16-5-2011	Alexandria	0.2 (Pale yellow)	α-Pinene (26.16), 1,8-cineole (16.45), linalool (11.23), β-fenchyl alcohol (8.34), geranyl acetate (6.43), linalyl acetate (4.65)
Origanum vulgare	Lamiaceae	Aerial parts 10-7-2011	Behera	0.5 (Pale yellow)	Pulegone (77.45), menthone (4.86), *cis*-isopulegone (2.22), piperitenone (2.13), dl-limonene (1.08), β-myrcene (0.66)
Pelargonium graveolens	Geraniaceae	Leaves 31-7-2011	Alexandria	0.09 (Pale yellow)	β-Citronellol (35.92), geraniol (11.66), citronellylformate (11.40), linalool (9.63), (+)-isomenthone (6.36), σ-selinene (5.52)
Pituranthos tortuosus	Apiaceae	Aerial parts 26-4-2011	Matrouh	0.22 (Pale yellow)	Sabinene (32.09), terpinen-4-ol (20.31), myristicine (6.84), dillapiole (5.72), γ-terpinene (4.16), α-pinene (3.25)
Rosmarinus officinalis	Lamiaceae	Leaves 10-8-2011	Alexandria	0.33 (Colorless)	1,8-Cineole (19.60), camphor (17.01), α-pinene (15.12), verbenone (9.55), endo-borneol (8.17), L-linalool (5.32)
Syzygium cumini	Myrtaceae	Leaves 6-6-2011	Alexandria	0.08 (Pale yellow)	α-Pinene (17.26), α-terpineol (13.88), β-pinene (11.28), *cis*-ocimene (11.27), *trans*-caryophyllene (6.96), dl-limonene 6.79)
Schinus molle	Anacardiaceae	Leaves 24-4-2011	Alexandria	0.88 (Colorless)	α-Phellandrene (29.87), β-phellandrene (21.08), elemol (13.00), τ-muurolol (5.35), γ-eudesmol (4.48), σ-cadinene (3.99)
Schinus terebinthifolius	Anacardiaceae	Leaves 2-5-2011	Alexandria	0.25 (Colorless)	Sabinene (14.93), γ-elemene (13.18), β-elemene (6.63), α-candiol (6.61), germacrene B (4.71), β-eudesmol (3.55)
Thuja occidentalis	Cupressaceae	Leaves 23-4-2011	Alexandria	0.25 (Pale yellow)	α-Pinene (35.49), δ-3-carene (25.42), α-cedrol (9.05), α-terpinolene (6.76), limonene (4.91), β-myrcene (2.77)
Vitex agnus-castus	Lamiaceae	Leaves 12-6-2011	Alexandria	0.16 (Yellow)	*trans*-Caryophyllene (15.19), 1,8-cineole (13.04), *trans*-β-farnesene (8.35), 4-terpineol (7.45), bicyclogermacrene (7.30), sabinene (6.42)

conditions were as follows: injector temperature, 240 °C; column temperature, isothermal at 70 °C and held for 2 min, then programmed to 280 °C at 6 °C/min and held at this temperature for 2 min; ion source temperature, 200 °C; and detector temperature, 300 °C. Helium was used as the carrier gas at the rate of 1 mL/min. The effluent of the GC column was introduced directly into the ion source of the MS. Spectra were obtained in the EI mode with 70 eV ionization energy. The sector mass analyzer was set to scan from 40 to 400 amu for 5 s. The oil components were identified by comparison of their retention indices and mass spectra with the NIST Mass Spectral Library.

Fumigant toxicity assay

To determine the fumigant toxicity of the essential oils against *S. oryzae* adults, a modified fumigant assay described by Huang et al. (2000) was used. Glass jars (1 L) were used as fumigation chambers. The essential oils were applied to Whatman No.1 filter paper pieces (2 × 3 cm) attached to the undersurface of the screw caps of jars at 0.1, 0.5, 1, 2.5, 5, 7.5, 10, 15, 20, 30, 40, 50, 80, 90, and 100 mg. The inner side of the jar's neck was painted with Vaseline to prevent direct contact of insects with essential oils. The caps were screwed tightly onto the jars containing 20 adults of *S. oryzae,* and the lid was sealed with parafilm. The control insects were kept under the same conditions without essential oils. Four replicates of each treatment were set up. All the treated and untreated insects were maintained at 26 ± 1 °C, 65 ± 5 % RH, and a 12:12 h light: dark photoperiod. The number of dead insects was recorded after 24 h of treatment. Insects were considered dead when no leg or antennal movements were recorded. The lethal concentration causing 50 % mortality (LC_{50}) expressed as mg/L air was calculated from log-concentration mortality regression lines (Finney 1971).

Contact toxicity assay

A direct contact application assay (Qi and Burkholder 1981; Broussalis et al. 1999) was used to evaluate the insecticidal activity of the essential oils extracted from 20 plants against the adults of *S. oryzae*. A series of concentrations were prepared in acetone. One milliliter of each concentration was applied on the bottom of a glass Petri dish (9 cm diameter) to give the concentrations of 0.01, 0.02, 0.04, 0.08, 0.1, 0.2, 0.4, 0.8, and 1.0 mg/cm^2. The solvent was allowed to evaporate for 2 min prior to the introduction of insects. Twenty adults of *S. oryzae* were placed into each Petri dish, and the control dishes were treated with acetone alone. All the treatments were replicated four times. Malathion was used as a reference insecticide. Mortality was recorded after 24 h after treatment, and LC_{50} values were calculated.

In vitro inhibition of acetylcholinesterase (AChE) activity assay

Adults of *S. oryzae* (6 g) were homogenized in 20 mL of 50 mM ice-cold phosphate buffer (pH 7.4) using a Polytron Kinematica. The homogenates were filtered through two layers of cheesecloth. The filtrates were centrifuged under cooling (5,000 rpm for 30 min at 4 °C), and the supernatants were used as the enzyme source. The inhibition of AChE was determined by the colorimetric method of Ellman et al. (1961) using ATChI as substrate. Enzyme aliquots (50 µL) and dithiodinitrobenzoic (DTNB) (100 µL of 0.01 M) acid were added to 0.1 M phosphate buffer (pH 8.0; 2.8 mL). To this mixture, the essential oil solutions (20 µL) prepared in acetone and Triton-X 100 (at concentration of 0.01 %) were added. The essential oils were tested at a series of concentrations (5, 10, 15, 20, 30, 50, 75, 100, 150, 250, and 500 mg/L). The control treatments were prepared by adding 20 µL of acetone without essential oil. The mixtures were incubated at 37 °C for 15 min. The reactions were started by adding ATChI (30 µL) followed by incubation at 37 °C for 10 min. The change in absorption at 412 nm was monitored on Sequoia-Turner Model 340 spectrophotometer. All the experiments were done in triplicate. Specific activity of AChE (ΔOD/mg protein/min) was calculated for each concentration and control. Inhibition percentage of AChE activity was calculated as follows: AChE inhibition% = $[1 - SA_T/SA_C] \times 100$, where SA_T is specific activity of the enzyme in the treatment and SA_C is specific activity of the enzyme in the control. The concentrations of the tested essential oil that inhibited the hydrolysis of substrate by 50 % (I_{50}) were determined by a linear regression analysis (probit analysis) between the inhibition percentages against the oil concentrations.

In vitro inhibition of total adenosine triphosphatases (ATPases) activity assay

The adults of *S. oryzae* were homogenized in an appropriate volume (10 % w/v) of TSE buffer (40 mM Tris–HCl, 320 mM sucrose, 1 mM EDTA, pH 7.4). The homogenates were centrifuged at 5,000 rpm for 30 min at 4 °C using IEC-CRU 5000 cooling centrifuge. The supernatants were re-centrifuged at 15,000 rpm using Cryofuge 20-3, Heraeus Christ centrifuge for 15 min at 4 °C. The particulate pellets were re-suspended in the homogenizing TSE buffer solution to give approximately 1–2 mg protein/ml. The in vitro inhibition of total ATPases activity was determined by incubating the enzyme for 30 min at 37 °C with different

concentrations (1, 2, 4, 8, 10, 15, 20, 40, 80, and 100 mg/L) of essential oils prepared in acetone. Triton-X 100 was added to enzyme solution at concentration of 0.01 %. Then, total ATPases activity was determined as reported by Koch et al. (1969) with slight modification in which Tris–HCl buffer was used instead of imidazole buffer. Total volume of reaction mixture was 850 µL contained 40 mM Tris–HCl pH 7.4, 100 mM NaCl, 20 mM KCl, 5 mM $MgCl_2$, 5 mM ATP, and the enzyme source (10 µL), which contains the appropriate protein concentration. The mixture was incubated at 37 °C for 15 min, and the reaction was terminated by adding 150 µL of TCA (30 % w/v). The liberated inorganic phosphorus (Pi) from ATP hydrolysis was measured according to Taussky and Shorr (1953) by adding 4 mL coloring reagent (10 % Amm. Molybdate in 10 N H_2SO_2; diluted to 1:10 by GDW, and then $FeSO_4$ was added to the resultant diluted solution). The color was measured at 740 nm against blank using Sequoia-Turner Model 340 spectrophotometer. The concentration of Pi was calculated from a standard curve, and accordingly, the enzyme specific activity was computed as µmole Pi/mg protein/min. The standard curve of Pi was made using KH_2PO_4 (concentrations from 0.1 to 1.0 µmol/ml). To 1 ml of each concentration, 4 ml of the coloring reagent was added. The developed color was measured at 740 nm. The results were plotted, and a standard curve was fitted using the least squares method ($K = 0.8$). The inhibition percentage of ATPases activity and I_{50} of the tested oils were calculated as previously described.

Statistical analysis

The mortality of each concentration was calculated after 24 h as the mean of four replicates. The mortality and enzyme inhibition percentages were subjected to probit analysis (Finney 1971) to obtain the LC_{50} and I_{50} values, using SPSS 12.0 (SPSS, Chicago, IL, USA). The values of LC_{50} and I_{50} were considered significantly different if the 95 % confidence limits did not overlap.

Results

Chemical composition of the isolated essential oils

The results of GC/MS analysis of the essential oils obtained by hydrodistillation are provided in Table 1. The main components of the essential oils were limonene (40.19, 56.30, 74.29, and 89.23 %) in *Citrus aurantifolia*, *C. lemon, C. paradise,* and *C. sinensis*, respectively; β-thujone (49.83 %) in *Artemisia judaica;* α-pinene (11.47, 37.88, 26.16, 15.12, 17.26, and 35.49 %) in *Callistemon viminals, Cupressus sempervirens, Myrtus communis, Rosmarinus officinalis, Syzygium cumini,* and *Thuja occidentalis*, respectively; 1,8-cineole (71.77 % 16.45, 19.60, and 13.04 %) in *C. viminals, M. communis, Pelargonium graveolens,* and *Vitex agnus-castus*, respectively; and sabinene (32.09, 23.02, and 14.93 %) in *Pituranthos tortuosus*, *Astoma seselifolium,* and *Schinus terebinthifolius*, respectively. Other main components were capillene (36.86 %) in *Artemisia monosperma;* terpinen-4-ol (20.29 %) in *Cupressus macrocarpa;* pulegone (77.45 %) in *Origanum vulgare;* β-citronellol (35.92 % and 13.01 %) in *P. graveolens* and *C. macrocarpa,* respectively, and α-phellandrene (29.87 %) and β-Phellandrene (21.08 %) in *Schinus molle*. It can be noticed that some major components such as limonene, α-pinene, β-pinene, 1,8-cineole, β-citronellol, sabinene, and γ-terpinene were found in more than one plant, but others were specific to certain plant species. The major constituents of the essential oils mainly belonged to four chemical groups: oxygenated monoterpenes (i.e., α-thujone, β-thujone, chrysanthenone, terpinen-4-ol, linalool, pulegone, α-citral, β-citronellol, camphor, and linalool oxide); monoterpene hydrocarbons (i.e., limonene, sabinene, γ-terpinene, β-pinene, δ-3-carene, phellandrene, and α-pinene); sesquiterpene hydrocarbons (i.e., bicyclogermacrene, α-elemene, β-elemene, and *trans*-caryophyllene), and oxygenated sesquiterpenes (i.e., cedrol and elemol).

Fumigant toxicity of the oils against *S. oryzae*

The fumigant toxicity of the 20 essential oils in terms of median lethal concentration (LC_{50}) to *S. oryzae* adults is shown in Table 2. The results revealed that all essential oils had a pronounced toxic effect except the oils of *A. monosperma*, *P. graveolens,* and *S. cumini* which had no or weak toxicity with LC_{50} values greater than 50 mg/L air. The oil of *O. vulgare* ($LC_{50} = 1.64$ mg/L air) was the most potent toxicant, followed by *C. limon* ($LC_{50} = 9.89$ mg/L air), *C. viminals* ($LC_{50} = 16.17$ mg/L air), *C. sempervirens* ($LC_{50} = 17.16$ mg/L air), and *C. sinensis* ($LC_{50} = 19.65$ mg/L air). Similarly, the oils of *S. terebinthifolius*, *S. molle*, *R. officinalis*, *M. communis*, *C. paradisi*, *C. aurantifolia,* and *A. judaica* possessed strong fumigant toxicity where LC_{50} values were less than 30 mg/L air.

Contact toxicity of the oils against *S. oryzae*

The toxicity of the essential oils from Egyptian plants against adults of *S. oryzae* exposed by direct contact is recorded in Table 3. Based on LC_{50} values, the oils exhibited different levels of contact toxicity. The oils of *A. judaica*, *C. viminals,* and *O. vulgare* invoked the highest toxicity. Their LC_{50} values were 0.08, 0.09, and 0.11 mg/cm^2, respectively. In contrast, the oils of *S. cumini*

Table 2 Fumigant toxicity of essential oils against the adults of *Sitophilus oryzae*

Oil	LC_{50}^{a} (mg/L)	95 % confidence limits (mg/L)		Slope[b] ± SE	Intercept[c] ± SE	$(\chi^2)^{d}$
		Lower	Upper			
Artemisia judaica	29.97	25.21	36.14	1.72 ± 0.25	−2.54 ± 0.37	3.34
Artemisia monosperma	>50	–	–	–	–	–
Astoma seselifolium	44.43	36.36	59.77	1.99 ± 0.30	−3.29 ± 0.45	1.26
Callistemon viminals	16.17	11.72	20.14	5.55 ± 0.41	−6.72 ± 0.54	10.12
Citrus aurantifolia	29.37	19.48	88.39	4.82 ± 0.39	−7.08 ± 0.53	32.10
Citrus lemon	9.89	7.23	13.85	3.74 ± 0.28	−3.72 ± 0.28	9.57
Citrus paradisi	24.13	19.23	29.59	7.17 ± 0.59	−9.92 ± 0.83	13.97
Citrus sinensis	19.67	13.60	33.93	5.39 ± 0.44	−6.97 ± 0.57	26.31
Cupressus macrocarpa	30.34	21.03	72.37	5.94 ± 0.46	−8.80 ± 0.66	31.20
Cupressus sempervirens	17.16	15.19	19.20	3.56 ± 0.35	−4.40 ± 0.46	1.33
Myrtus communis	27.40	20.44	45.76	4.84 ± 0.37	−6.96 ± 0.52	20.19
Origanum vulgare	1.64	0.67	2.45	2.39 ± 0.24	−0.51 ± 0.12	9.29
Pelargonium graveolens	>50	–	–	–	–	–
Pituranthos tortuosus	41.01	38.49	44.36	4.97 ± 0.60	−8.01 ± 0.94	1.97
Rosmarinus officinalis	26.71	23.92	29.60	2.63 ± 0.28	−3.75 ± 0.41	1.78
Syzygium cumini	>50	–	–	–	–	–
Schinus molle	26.89	19.06	52.21	5.47 ± 0.42	−7.82 ± 0.58	27.77
Schinus terebinthifolius	28.16	25.57	31.13	2.86 ± 0.27	−4.15 ± 0.40	1.70
Thuja occidentalis	43.11	36.66	62.16	6.28 ± 0.66	−10.28 ± 1.04	4.07
Vitex agnus-castus	39.85	30.72	67.40	2.86 ± 0.31	−4.58 ± 0.46	7.76

[a] The concentration causing 50 % mortality

[b] Slope of the concentration-inhibition regression line ± SE

[c] Intercept of the regression line ± SE

[d] Chi square value

and *C. sempervirens* had the lowest toxicity with LC_{50} values higher than 0.6 mg/cm^2. Moreover, the oils of *A. seselifolium*, *A. monosperma*, *C. aurantifolia*, *P. tortuosus*, *P. graveolens*, *O. vulgare S.molle,* and *R. officinalis* showed strong toxicity, where LC_{50} values for these oils were less than 0.20 mg/cm^2. Furthermore, the oils of *C. lemon*, *C. paradisi*, *C. sinensis,* and *T. occidentalis* (LC_{50} values ranged between 0.21 and 0.30 mg/cm^2) showed moderate toxicity, while the rest of the oils (LC_{50} values ranged between 0.31 and 0.42 mg/cm^2) displayed weak toxicity. All tested essential oils were less toxic to the insect than a reference insecticide, malathion.

Inhibitory effect of essential oils on AChE activity

Table 4 shows the inhibitory effects of selected essential oils on acetylcholinesterase (AChE) in terms of I_{50}values. All of the oils caused significant AChE inhibition. The oil of *A. judaica* (I_{50} = 16.1 mg/L) was the most potent enzyme inhibitor. In addition, the oils of *C. viminals*, *C. aurantifolia,* and *C. lemon* caused strong inhibition of enzyme activity based on their I_{50} values. The oil of *O. vulgare* induced moderate inhibitory effect, while the oil of *A. monosperma* invoked the weakest enzyme inhibition.

Inhibitory effect of essential oils on ATPases activity

Based on their I_{50} values, the essential oils showed remarkable inhibition of ATPases activity (Table 5). The oils of *C. viminals*, *O. vulgare,* and *C. lemon* caused the highest enzyme inhibition with I_{50} values of 4.69, 6.07, and 9.69 mg/L, respectively. Furthermore, the oil of *C. aurantifolia* showed a moderate enzyme inhibition, while the oils of *A. judaica* and *A. monosperma* caused the weakest enzyme inhibition.

Discussion

The oil of *A. seselifolium* was analyzed for the first time in this study. The chemical compositions of the extracted essential oils from *C. aurantifolia*, *C. paradise*, *C. limon*, *C. sinensis*, *C. viminals*, *C. sempervirens*, *S. molle*, *C. macrocarpa*, *P. graveolens*, *R. officinalis,* and *M.*

Table 3 Contact toxicity of essential oils against the adults of *Sitophilus oryzae*

Oil	LC_{50}^{a} (mg/cm^2)	95 % confidence limits (mg/cm^2)		Slope[b] ± SE	Intercept[c] ± SE	$(\chi^2)^d$
		Lower	Upper			
Artemisia judaica	0.08	0.06	0.11	1.45 ± 0.13	1.56 ± 0.37	0.39
Artemisia monosperma	0.15	0.02	0.33	3.17 ± 0.25	2.60 ± 0.20	11.85
Astoma seselifolium	0.16	0.13	0.22	1.86 ± 0.31	1.47 ± 0.32	1.99
Callistemon viminals	0.09	0.08	0.10	4.37 ± 0.41	4.58 ± 0.44	0.97
Citrus aurantifolia	0.15	0.14	0.16	7.15 ± 0.70	5.86 ± 0.58	0.15
Citrus lemon	0.20	0.17	0.47	3.89 ± 0.32	2.74 ± 0.22	13.88
Citrus paradisi	0.27	0.25	0.29	6.54 ± 0.59	3.68 ± 0.33	2.03
Citrus sinensis	0.29	0.27	0.31	8.01 ± 0.70	4.29 ± 0.37	0.82
Cupressus macrocarpa	0.32	0.29	0.35	3.90 ± 0.42	1.94 ± 0.21	1.76
Cupressus sempervirens	>0.6	–	–	–	–	–
Myrtus communis	0.31	0.28	0.33	5.53 ± 0.50	2.85 ± 0.26	1.77
Origanum vulgare	0.11	0.10	0.12	5.17 ± 0.47	4.90 ± 0.46	0.02
Pelargonium graveolens	0.17	0.15	0.18	6.19 ± 0.60	4.84 ± 0.48	1.45
Pituranthos tortuosus	0.19	0.11	0.28	4.27 ± 0.35	3.08 ± 0.25	6.72
Rosmarinus officinalis	0.18	0.17	0.20	7.44 ± 0.79	5.51 ± 0.60	0.88
Syzygium cumini	>0.60	–	–	–	–	–
Schinus molle	0.16	0.15	0.17	6.71 ± 0.66	5.40 ± 0.54	0.42
Schinus terebinthifolius	0.42	0.38	0.46	3.79 ± 0.45	1.42 ± 0.20	0.76
Thuja occidentalis	0.30	0.28	0.32	7.56 ± 0.65	3.95 ± 1.04	1.77
Vitex agnus-castus	0.39	0.33	0.40	16.97 ± 6.74	6.99 ± 2.67	0.08
Malathion	0.16×10^{-3}	0.14×10^{-3}	0.17×10^{-3}	2.60 ± 0.16	9.88 ± 0.62	7.31

[a] The concentration causing 50 % mortality

[b] Slope of the concentration-inhibition regression line ± SE

[c] Intercept of the regression line ± SE

[d] Chi square value

Table 4 In vitro inhibition of acetylcholinesterase (AChE) isolated from *Sitophilus oryzae* adults by selected essential oils

Oil	I_{50}^{a} (mg/L)	95 % confidence limits (mg/L)		Slope[b] ± SE	Intercept[c] ± SE	$(\chi^2)^d$
		Lower	Upper			
Artemisia judaica	16.1	13.2	19.7	1.30 ± 0.11	−1.57 ± 0.14	0.57
Artemisia monosperma	120.0	101.3	141.4	1.61 ± 0.12	−3.35 ± 0.26	1.82
Callistemon viminals	28.5	22.9	35.2	1.19 ± 0.11	−1.72 ± 0.17	1.81
Citrus aurantifolia	29.4	24.0	36.0	1.26 ± 0.11	−1.85 ± 0.11	1.45
Citrus lemon	20.2	16.5	24.4	1.37 ± 0.11	−1.78 ± 0.17	2.83
Origanum vulgare	61.3	49.8	75.3	1.23 ± 0.11	−2.21 ± 0.20	1.05

[a] The concentration causing 50 % enzyme inhibition

[b] Slope of the concentration-inhibition regression line

[c] Intercept of the regression line ± SE

[d] Chi square value

*communis*are were similar to those previously reported (Chanegriha et al. 1997; Malizia et al. 2000; Lota et al. 2001; Srivastava et al. 2003; Tuberoso et al. 2006; Viuda-Martos et al. 2009; Bendaoud et al. 2010). On the other hand, the major constituents of the essential oils extracted from *A. monosperma*, *O. vulgare*, *T. occidentalis,* and *A. judaica* differed from those previously reported on the chemistry of these oils (Şahin et al. 2004; Mohamed and

Table 5 In vitro inhibition of adenosine triphosphatases (ATPases) isolated from *Sitophilus oryzae* adults by selected essential oils

Oil	I_{50}^{a} (mg/L)	95 % confidence limits (mg/L)		Slope[b] ± SE	Intercept[c] ± SE	$(\chi^2)^{d}$
		Lower	Upper			
Artemisia judaica	21.4	16.4	28.1	18.1 ± 0.17	−2.41 ± 0.23	6.78
Artemisia monosperma	24.6	20.6	29.0	1.58 ± 0.12	−2.19 ± 0.18	0.45
Callistemon viminals	4.69	3.92	5.55	1.49 ± 0.13	−1.00 ± 0.11	0.56
Citrus aurantifolia	11.4	9.52	13.6	1.51 ± 0.11	−1.59 ± 0.14	1.51
Citrus lemon	9.69	8.51	11.0	2.02 ± 0.17	−1.09 ± 0.19	1.21
Origanum vulgare	6.07	5.15	7.16	1.55 ± 0.13	−1.22 ± 0.12	0.94

[a] The concentration causing 50 % enzyme inhibition

[b] Slope of the concentration-inhibition regression line

[c] Intercept of the regression line ± SE

[d] Chi square value

Abdelgaleil, 2008; Tsiri et al. 2009; Khan et al. 2012). Some of the major constituents of the essential oils of *P. tortuosus*, *V. agnus-castus*, *S. terebinthifolius,* and *S. cumini* were similar to those previously reported for the oils isolated from plants growing in Egypt and other countries around the world (Singab 2003; Gundidza et al. 2009; Stojković et al. 2011). However, the percentages of constituents were differed. The differences in essential oil compositions may be due to several factors, such as geographical location, season, environmental conditions, and the nutritional status of the plants (Ozcan and Chalchat 2006; Perry et al. 1999).

Plant essential oils and their major constituents, primarily monoterpenoids, are considered to be an alternative means of controlling many insect pests (Tripathi et al. 2009). In integrated pest management of stored-product insects, phytochemicals may be used for pest prevention, early pest detection, or pest control (Lopez et al. 2008).

In this study, the different oils exhibited variable degree of toxicity. Although the fumigant toxicity of essential oils from many plant families against *S. oryzae* had been described (Shaaya et al. 1997; Kim et al. 2003; Lee et al. 2003; Negahban and Moharramipour 2007; Ogendo et al. 2008; Mohamed and Abdelgaleil 2008; Rajendran and Sriranjini 2008; Sahaf et al. 2008; Stefanazzi et al. 2011; Kim et al. 2013), there are no reports on the fumigant toxicity of the tested oils against this insect. Our results showed that the oil of *O. vulgare* (LC_{50} = 1.64 mg/L air) had strong fumigant toxicity against *S. oryzae*. This oil is among the most active natural fumigant toxicants such as the oils of *Mentha microphylla* (LC_{50} = 0.21 µl/L air) (Mohamed and Abdelgaleil 2008), ZP51 oil (LC_{50} = 0.7 µL/L air) (Shaaya et al. 1997), *Carum copticum* (LC_{50} = 0.91 µl/L air) (Sahaf et al. 2007), and *Artemisia scoperia* (1.87 µl/L air) (Negahban et al. 2006) evaluated against this insect. In addition, our results showed that the oils of *C. lemon*, *C. viminals*, *C. sinensis,* and *C. sempervirens* showed remarkable insecticidal activity as fumigants. The toxicity of these oils against the adults of *S. oryzae* was higher than those of several other plants (Lee et al. 2001, 2004; Negahban et al. 2006; Sahaf et al. 2008; Hashemi and Safavi 2012; Kim et al. 2013).

To the best of our knowledge, this is the first report on the contact toxicity of these essential oils against the adults of *S. oryzae* in Egypt. Based on LC_{50} values, the contact toxicities of isolated oils reported in this study were comparable with those of essential oils of *Tagetes terniflora*, *Cymbopogon citratus*, *Elyonorus muticus*, *Achillea santolina*, *Citrus reticulate*, *Lantana camara*, *Majorana hortensis,* and *Eucalyptus camaldulensis* (Mohamed and Abdelgaleil 2008; Stefanazzi et al. 2011).

The results of fumigant and contact toxicities indicated that the insecticidal activity of the oils was highly depended on the bioassay method. For example, *O. vulgare* oil was the most potent fumigant and the third most potent in contact toxicity. The oil of *A. judaica* exhibited the highest contact toxicity (LC_{50} = 0.08 mg/cm^2) but induced a moderate fumigant activity (LC_{50} = 29.97 mg/L). Furthermore, the oils of *A. monosperma* and *P. graveolens* were not toxic (LC_{50} > 50 mg/L) in the fumigant assay but both oils had strong contact toxicity. Similarly, García et al. (2007) stated that the essential oil of *Flourensia oolepis* showed contact toxicity but did not invoke fumigant toxicity against *T. castaneum*. In contrast, the oil of *C. sempervirens* induced strong fumigant toxicity but was not active in the contact assay. On the other hand, the oil of *C. viminals* invoked strong toxicity in both the contact and fumigant assays. These findings indicated that the assay method has effect on the insecticidal activity of the oils (Prates et al. 1998; Kim et al. 2003; Mohamed and Abdelgaleil 2008).

The inhibitory effects of essential oils (*A. judaica*, *A. monosperma*, *C. viminals*, *C. aurantifolia*, *C. lemon*, and *O. vulgare*) which had the highest insecticidal activity

against *S. oryzae* on acetylcholinesterase (AChE) and adenosine triphosphatases (ATPases) were examined in vitro. The oils caused pronounced inhibition of acetylcholinesterase (AChE). The oils also showed death symptoms on the adults of *S. oryzae* that indicated a neurotoxic mode of action. Several essential oils from aromatic plants and monoterpenes have been described as inhibitors of AChE isolated from *S. oryzae* and other insect species (Miyazawa et al. 1997; Lee et al. 2001; Kostyukovsky et al. 2002; Shaaya and Rafaeli 2007; Abdelgaleil et al. 2009; Kim et al. 2013). On the other hand, the tested oils showed strong inhibitory effect on ATPases activity. To the best of our knowledge, this is the first report on the inhibitory effect of essential oils on ATPases activity. However, Guo et al. (2009) found that a monoterpenoid, terpinen-4-ol, had strong inhibition on activity of Na^+, K^+-ATPase of housefly in vivo and in vitro. Based on the I_{50} values, the ATPases were more sensitive to essential oils than AChE, suggesting that ATPases may be the main target to the essential oils. Beside the inhibition of AChE and ATPases described in this study, the essential oils have been shown to inhibit GABA receptor (Enan 2001). It can be concluded that essential oils have broad-spectrum pesticidal activities, due to the presence of several active ingredients that operate via several modes of action.

In conclusion, the results of this study indicate that the oils of *O. vulgare*, *C. limon*, *C. viminals*, *C. sempervirens,* and *C. sinensis* had potent fumigant toxicity to *S. oryzae*. These oils might be useful for managing population of this insect in enclosed spaces such as storage bins and buildings because of their fumigant action. In addition, the oils of *A. judaica*, *C. viminals,* and *O. vulgare* possessed strong contact toxicity to *S. oryzae*. The insecticidal activity of the oils might be due to their inhibitory effects on AChE and ATPases activities. Although the fumigant toxicity of the essential oils was less than commercial fumigants, they have contact toxicity as well as repellent activity. Therefore, field trials with suitable essential oil formulations need to be carried out to assess the efficacies of the essential oils for the control of stored-product insects. Finally, the effects of essential oils on the quality of stored products, and risk to humans would need to be determined before commercial application.

Author contribution

SAMA designed the research. MIEM and HKA conducted the experiments; SAMA and MSS analyzed the data; SAMA and MSS wrote the paper; SAMA had primary responsibility for the final content. All authors have read and approved the final manuscript.

Acknowledgment This work was supported by the Alexandria University Research Fund (ALEX-REP, 2010–2013).

Conflict of interest The authors S. A. M. Abdelgaleil, M. I.E. Mohamed, M. S. Shawir, and H. K. Abou-Taleb report no conflicts of interest to be declared.

Ethical standard This article does not contain any studies with human participants or animals performed by any of the authors.

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