UNIVERSITI PUTRA MALAYSIA

INSECTICIDAL ACTIVITY OF FOUR CITRUS PEEL OILS AND OIL NANOEMULSION FORMULATION AGAINST *Sitophilus oryzae* L. AND *Corcyra cephalonica* (St.)

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By

ELMILIGY ELSAYED ELSAYED IBRAHIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Master of Science

January 2019

DEDICATION

Dedicated to:

My father (Elsayed Ibrahim Elmiligy), My mother (Zeinab Mohamed Elbezawy),
My father-in-law (Moustafa Elgendy), My mother-in-law (Amina Abdella),
My wife (Aya Moustafa Elgendy) and My son (Sohaib Elsayed Elmiligy)

For their true love, support and inspiration

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman : Professor Dzolkhifli Omar, PhD
Faculty : Agriculture

The rice weevil, *Sitophilus oryzae* and rice moth, *Corcyra cephalonica* are primary destructive insect pests. The adults and larvae of *S. oryzae* and the larvae of *C. cephalonica* feed voraciously on a wide variety of grains causing quantitative and qualitative losses. This study was conducted to evaluate the insecticidal effects of citrus peel oils of sweet orange; *Citrus sinensis*, green lemon; *Citrus aurantifolia*, Kaffir lime; *Citrus hystrix* and calamansi lime; *Citrus microcarpa* against these two major stored product insects. Essential oils from four species of citrus plants were obtained from Best Formula Industries Company (Kuala Lumpur, Malaysia). The chemical components in these essential oils were identified using gas chromatography/mass spectrometry and they were tested for their insecticidal properties against adults of the rice weevil, *S. oryzae* L. and the 4th instar larvae of rice moth, *C. cephalonica* (St.). The major compounds found in tested essential oils were limonene, β-pinene, citronellal, α-terpineol, citronellol, and geraniol. The *S. oryzae* populations treated with *C. hystrix*, *C. aurantifolia*, *C. sinensis*, *C. microcarpa* showed contact toxicity with LC_{50} values of 119.44, 149.94, 183.26, and 341.26 ppm after 72 hours, post exposure, respectively, compared to *C. cephalonica* populations with the LC_{50} values of 1176.43, 1889.24, 3965.71, and 6107.51 ppm after 72 hours, post exposure, respectively. In the case of fumigant toxicity, the *S. oryzae* populations treated with *C. hystrix*, *C. aurantifolia*, *C. sinensis*, *C. microcarpa* showed toxicity with LC_{50} values of 96.96, 192.21, 224.22, and 276.99 ppm after 72 hours, post exposure, respectively, compared to *C. cephalonica* populations with the LC_{50} values of 533.48, 752.35, 959.82, and 1082.53 ppm after 72 hours, post exposure, respectively. This variation in results and efficacy of essential oils is related to the chemical components of these essential oils. Oil nano-emulsion system was developed for insecticide formulations of the citrus peel oils by constructing ternary phase diagrams, constituted of non-ionic surfactants, carriers, water, and *C. hystrix* oil as an active ingredient. The non-ionic surfactants were Emersense AM 8025, Triton X-100, and Tween 80. Three oils were used as a carrier

(Rapeseed methyl ester, Methyl oleate, and Agnique AMD 810). All phase diagrams revealed a range of 46 to 91% isotropic region. The phase diagram of Agnique AMD 810/Triton X-100/water system gave the largest 91% one phase region, while that of Methyl oleate/Emersense/water system gave the smallest 46% one phase region. The points were selected from the isotropic regions which exhibited high proportion of oil, low proportion of water and adequate proportion of surfactant to mix with the active ingredient and to form oil-in-water (O/W) emulsion. Sixteen formulations miscible with *C. hystrix* oil were selected. In the stability study, all the selected formulations were stable under centrifugation and storage at room temperature (25°C) and at 54°C. The mean particle size of nano-emulsion ranged between 54.04 to 461.30 nm except for F2, F3, and F15 with mean particle size >500 nm. All sixteen formulations showed surface tension, lower than water. The zeta potential values of all formulations ranged from 42.16 mV to 86.66 mV, except for F2, F3, F4, F6, and F8 were lower than 30 mV. The value is related to the stability of colloidal dispersions and high zeta potential value will confer stability. In the toxicity study, the formulated oils against the two insects showed the mortality was higher than that of the nonformulated oils. The contact toxicity against the *S. oryzae* populations showed that the oil nanoemulsion formulations were more toxic with LC_{50} ranging from 43.46 to117.25 ppm after 72 hours, post exposure, compared to *C. cephalonica* populations with LC_{50} ranging from 462.63 to 916.27 ppm. Similarly, the fumigant toxicity against the *S. oryzae* populations treated with the oil nano-emulsion formulations were more toxic with LC_{50} ranging from 43.38 to 91.71 ppm after 72 hours post exposure, compared to *C. cephalonica* populations with LC_{50} ranging from 405.09 to 494.39 ppm. The findings suggested that the nano-emulsion formulations of *C. hystrix* essential oil were effective and could be used to control *S. oryzae* and *C. cephalonica*.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

AKTIVITI INSEKTISIDAL EMPAT MINYAK KULIT SITRUS DAN FORMULASI NANOEMULSI TERHADAP, *Sitophilus oryzae* L. DAN *Corcyra cephalonica* (St.)

Oleh

ELMILIGY ELSAYED ELSAYED IBRAHIM

Januari 2019

Pengerusi : Profesor Dzolkhifli Omar, PhD
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Kumbang padi, *Sitophilus oryzae* dan rama-rama padi, *Corcyra cephalonica* merupakan perosak haiwan destruktif yang utama. Kumbang dewasa dan larva *S. oryzae* serta larva *C. cephalonica* memakan secara rakus pelbagai jenis bijian yang menyebabkan kerugian secara kuantitatif dan kualitatif. Kajian ini dijalankan bagi menilai kesan insektisidal minyak kulit sitrus daripada oren manis; *Citrus sinensis*, lemon hijau; *Citrus aurantifolia*, limau purut; *Citrus hystrix* dan limau kalamansi; *Citrus microcarpa* terhadap dua serangga produk tersimpan utama. Minyak pati daripada empat spesis tumbuhan sitrus telah diperoleh daripada Syarikat Industri Best Formula (Kuala Lumpur, Malaysia). Komponen kimia dalam minyak pati tersebut telah dikenal pasti menggunakan gas kromatografi/spektrometri jisim dan komponen tersebut telah diuji bagi sifat insektisidal mereka terhadap kumbang dewasa padi, *S. oryzae* L. dan instar keempat larva rama-rama padi, *C. cephalonica* (St.). Kompaun utama yang dijumpai dalam minyak pati yang diuji ialah limonena, β-pinena, sitronelal, α-terpineol, sitronelol, dan geraniol. Populasi *S. oryzae* yang dirawat dengan *C. hystrix*, *C. aurantifolia*, *C. sinensis*, *C. microcarpa* menunjukkan ketoksikan kontak dengan nilai LC_{50}, masing-masing ialah 119.44, 149.94, 183.26, dan 341.26 ppm selepas 72 jam pascapendedahan, berbanding dengan populasi *C. cephalonica*, dengan nilai LC_{50} ialah masing-masing 1176.43, 1889.24, 3965.71 dan 6107.51 ppm selepas 72 jam pascapendedahan. Dalam kes ketoksikan fumigan, populasi *S. oryzae* yang dirawat dengan *C. hystrix*, *C. aurantifolia*, *C. sinensis*, *C. microcarpa* menunjukkan ketoksikan dengan nilai LC_{50}, masing–masing ialah 96.96, 192.21, 224.22 dan 276.99 selepas 72 jam pascapendedahan, berbanding dengan populasi *C. cephalonica*, dengan nilai LC_{50} ialah masing-masing 533.48, 752.35, 959.82 dan 1082.53 ppm selepas 72 jam pascapendedahan. Variasi tersebut dari segi dapatan dan kemujaraban minyak pati berkaitan dengan komponen kimia bagi minyak pati tersebut. Sistem minyak nanoemulsi telah dihasilkan bagi formulasi insektisid minyak kulit sitrus melalui pembinaan rajah fasa ternari yang terdiri daripada surfaktan bukan ionik, pembawa, air, dan minyak *C. hystrix* sebagai bahan aktif. Surfaktan bukan ionik ialah Emersense AM 8025, Triton X-100, dan Tween 80. Tiga jenis minyak telah digunakan sebagai pembawa (Rapeseed metil ester, Metil oleate, dan Agnique AMD 810). Semua rajah fasa menunjukkan julat antara 46 hingga 91% lingkungan isotropik. Rajah fasa Agnique AMD 810/Triton X-100/sistem air mengutarakan 91% lingkungan fasa satu terbesar, manakala Metil oleate/Emersense/sistem air memberikan 46% lingkungan fasa satu terkecil. Titik tersebut telah dipilih daripada lingkungan isotropik yang memperlihatkan kadar minyak yang tinggi, kadar air yang rendah dan kadar surfaktan yang mencukupi bagi mencampurkannya dengan bahan aktif dan bagi membentuk emulsi minyak dalam air (O/W). Enam belas formulasi larut campur dengan minyak *C. hystrix* telah dipilih. Dalam kajian stabiliti, semua formulasi yang dipilih adalah stabil di bawah pengemparan dan penyimpanan pada suhu bilik (25˚C) dan pada 54˚C. Min saiz partikel nanoemulsi berjulat antara 54.04 hingga 461.30 nm kecuali bagi F2, F3, dan F15 dengan min saiz partikel >500 nm. Semua enam belas formulasi menunjukkan tekanan permukaan yang rendah daripada air. Nilai potensi zeta bagi semua formulasi berjulat dari 42.16 mV hingga 86.66 mV, kecuali bagi F2, F3, F4, F6, dan F8 yang lebih rendah daripada 30 mV. Nilai tersebut berkaitan dengan stabiliti penyebaran koloid dan nilai potensi zeta tinggi yang akan memberikan stabiliti. Dalam kajian ketoksikan, minyak formulasi terhadap kedua-dua haiwan tersebut menunjukkan mortaliti yang lebih tinggi daripada minyak bukan formulasi. Ketoksikan kontak terhadap populasi *S. oryzae* menunjukkan bahawa formulasi minyak nanoemulsi adalah lebih toksik dengan nilai LC_{50} berjulat dari 43.46 hingga 117.25 ppm selepas 72 jam pascapendedahan, berbanding dengan populasi *C. cephalonica* dengan LC_{50} berjulat dari 462.63 hingga 916.29 ppm. Begitu juga, fumigan ketoksikan terhadap populasi *S. oryzae* yang dirawat dengan formulasi minyak nanoemulsi adalah lebih toksik dengan LC_{50} berjulat dari 43.38 hingga 91.71 ppm selepas 72 jam pascapendedahan, berbanding dengan populasi *C. cephalonica* dengan nilai LC_{50} berjulat dari 405.09 hingga 494.39 ppm. Dapatan kajian ini mengesyorkan formulasi minyak nanoemulsi minyak pati *C. hystrix* adalah efektif dan dapat digunakan bagi mengawal *S. oryzae* dan *C. cephalonica*.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

g	gram
µg	microgram(s)
g/m^3	gram per cubic meter
mg/L	milligram per liter
mg/cm^2	milligram per square centimeter
cm	centimeter
mm	millimeter
nm	nanometer
µm	micrometer
cm/sec	centimeter per second
µL	microliter(s)
µL/L	microliter per liter
ppm	parts per million
mL/min	milliliter per minute
v/v	volume over volume
w/w	weight over weight
a.i	active ingredient
$a.i/m^3$	active ingredient per cubic meter
min	minute(s)
h	hour(s)
kPa	kilopascal
β	Beta
α	Alpha

γ	Gamma
mN/m	milliNewton per meter
mV	milliVolt
AChE	Acetylcholinestrase
LD_{50}	median lethal dose
O/W	Oil-in-Water
HLE	Hydrophilic-Lipophilic Equilibriums
HLB	Hydrophile-lipophile balance
GC-MS	Gas Chromatography-Mass Spectroscopy
CMC	Critical Micelle Concentration
S.E.	Standard Error
R.H.	Relative humidity
UPM	Universiti Putra Malaysia
UK	United Kingdom
Co.	Company
˚C	degree(s) Celsius
%	percent
$	dollar sign
mΩ	Mega ohm
et al.	*et alii*, and others

CHAPTER 1

INTRODUCTION

Cereal crops are continuing to be the most fundamental food supply in the world, so they are considered as the main food for peoples in many countries (Alonso-Amelot and Avila-Nú˜nez, 2011). Rice, *Oryza sativa* is contemplated as the most important grain, as it is the second highest worldwide production, after maize (FAO, 2005). Rice is cultivated annually, mostly in countries with low labor cost and high waterfall; likewise, 90% of the world's rice is produced and consumed in Asia. In granaries, rice is suspected to be attacked by many stored-product insect pests, causing a great loss of the stored grains, then a serious problem with the national economy. It is recorded that 5−10% in the temperate regions of the world and as high as 20−30% in tropical regions of the different stored grains are lost annually by the action of insect pests attack (Haque et al., 2000). The rice weevil, *Sitophilus oryzae* (Linnaeus, 1763) and the rice moth, *Cocyra cephalonica* are the most important pests of the stored rice, causing quantitative and qualitative losses (Sartori et al., 1990).

The rice weevil, *S. oryzae* (Coleoptera; Curculionidae) is a major and severe insect pest. Insect adults and larvae feed voraciously on a wide variety of grains; especially rice (Bougherra et al., 2015). It is a widespread pest, it has been noted that about one million of *S. oryzae* can be produced by only two of its adults under suitable conditions. The adults have brown/black colored body of 2 mm long, they are can fly and live for up to two years. They feed on rice and lay their eggs inside rice kernels (Estalle and Riudavets, 1999). The larvae emerged inside the holes in rice kernels and feed on the germ of the grains. Both stages feeding can cause a severe reduction in grain weight by more than 75%, and decrease the nutritional value of the grains (Dal Bello et al., 2001). The rice moth, *C. cephalonica* (Stainton) (Lepidoptera: Pyralidae), is the major cosmopolitan and destructive pest of stored commodities in the tropics, Asia, South America, and Africa. The larvae feed on rice, corn, cocoa, dried fruits, and many other grains, causing extensive loss. They not only consume the products, but also contaminate them by weaving hard, dense webbing threads containing their fecal matter and exuviae (Huang and Subramanyam, 2004). In this study, the rice weevil, *S. oryzae* (L) and the rice moth, *C. cephalonica* (Staint.), the important pest in milled rice, were selected as the animal models for biological control by natural plant products (Sartori et al., 1990).

A constant war should be made with stored-grain pests to conserve the grains. Control of these pests depends mainly on the direct application of synthetic insecticides which include, organochlorines (lindane), organophosphates (malathion), carbamates (carbaryl), pyrethroids (deltamethrin) and fumigants including methyl bromide, phosphine, and sulfuryl fluoride; however, many organochlorine and organophosphate chemicals are already banned, while others are under restriction, regarding their drawbacks (Forget, 1993). The intensive use of synthetic insecticides has created serious environmental and health problems. The problems have been arisen from using synthetic insecticides are high toxicity, non-biodegradability of pesticides, lack of exact scientific formulations, ozone depletion, toxicity to non-target organisms, and resistance of stored-grain insects (Opit et al., 2012); consequently, research efforts have been done to search for safe, cheap, highly selective and biodegradable pesticides (Cantrell et al., 2012). In this regard, natural compounds from plants are efficient alternatives to synthetic insecticides because of their innate biodegradability, low toxicity to mammals, and regional availability (Rajendran and Sriranjini, 2008).

It has been documented that higher plants are considered as a rich source of many natural substances that can be used safely to control insect pests. The essential oils extracted from many aromatic plants revealed toxicity to stored-product insects during the last decade (Huang et al., 2002). Rutaceae is the large family containing 130 genera in seven subfamilies with many important fruits and the essential oil products, for example, *Citrus sinensis*, *Citrus aurantifolia*, *Citrus reticulate*, *Citrus hystrix*, *Citrus microcarpa*. It has been reported that the fruit peels of some citrus species, especially their essential oils have insecticidal properties against many insect pests (Elhag, 2000). The essential oils were used in a broad spectrum showing insecticidal activity against many stored-product insect pests (Mbata and Payton, 2013). Many problems evolved from the use of essential oils as insecticides, comprise: (1) short lasting of essential oils was reported by Barnard and Xue (2004), (2) Lack of persistent efficacy in the field (Chen et al., 2013), (3) hydrophobicity, reactivity, and volatility of the bioactive molecules constituting the essential oils (Huang et al., 2010), so the amount of used essential oils can be reduced by formulating them into transparent nanoemulsions.

According to the above-mentioned problems of using essential oil, there is an urgent need to provide innovative techniques to develop the use of essential oils and enhance their efficacy; hence, nanotechnology has been emerging as a new research field to strengthen the use of plant-based products. Many efforts devoted to develop, improve and use nanoscale structures for biological efficacy (Tadros et al., 2004). There is an evolution in nanostructure techniques due to the increased number of their promising applications in material science, medicine, pharmacology, and agriculture. Nanoemulsion-based pesticides have a particle size of 100−200 nm, which exhibit many properties such as stiffness, permeability, crystallinity, thermal stability, solubility, biodegradability, and large specific surface area to increase affinity to the target (Khot et al., 2012). They rapidly penetrate different types of cells like epithelial and endothelial cells by transcytosis and accumulate in them, then, traveling along the dendrites, axons, the blood, and lymph inducing oxidative stress and other consequences (Oberdörster et al., 2005).

Hence, the current study aimed to:

1- Evaluate the insecticidal activity of the peel essential oils of four citrus plants, namely, *C. hystrix* DC, *C. aurantifolia* (Cristm.) Swingle, *C. microcarpa* (Bunge) Wijnands, *C. sinensis* (L.) Osbeck, against *S. oryzae* and *C. cephalonica*,
2- Investigate the chemical composition of the four peel essential oils,
3- Prepare oil nanoemulsion formulations of the most effective essential oil and determine the physiochemical properties of the formulations, and
4- Evaluate the toxicity of oil nanoemulsion formulations against *S. oryzae* and *C. cephalonica*.

REFERENCES

Abbassy, M. A., Abdelgaleil, S. A., & Rabie, R. Y. (2009). Insecticidal and synergistic effects of *Majorana hortensis* essential oil and some of its major constituents. *Entomologia Experimentalis et Applicata*, *131*(3), 225-232.

Abbott, W. S. (1925). A Method of Computing the Effectiveness of an Insecticide. *Journal of Economic Entomology*, *18*(2), 265-267.

Abdelgaleil, S. A., Mohamed, M. I., Badawy, M. E., & El-arami, S. A. (2009). Fumigant and Contact Toxicities of Monoterpenes to *Sitophilus oryzae* (L.) and *Tribolium castaneum* (Herbst) and their Inhibitory Effects on Acetylcholinesterase Activity. *Journal of Chemical Ecology*, *35*(5), 518-525.

Allotey, J. (1991). Development and fecundity of the rice moth *Corcyra cephalonica* (Pyralidae). *Discovery and Innovation* 3:123-126.

Allotey, J., & Azalekor, W. (2000). Some aspects of the biology and control using botanicals of the rice moth, *Corcyra cephalonica* (Stainton), on some pulses. *Journal of Stored Products Research*, *36*(3), 235-243.

Alonso-Amelot, M. E., & Avila-Núñez, J. L. (2011). Comparison of seven methods for stored cereal losses to insects for their application in rural conditions. *Journal of Stored Products Research*, *47*(2), 82-87.

Alvarez-Figueroa, M., & Blanco-Méndez, J. (2001). Transdermal delivery of methotrexate: iontophoretic delivery from hydrogels and passive delivery from microemulsions. *International Journal of Pharmaceutics*, *215*(1-2), 57-65.

Anton, N., Benoit, J., & Saulnier, P. (2008). Design and production of nanoparticles formulated from nano-emulsion templates—A review. *Journal of Controlled Release*, *128*(3), 185-199.

Anton, N., & Vandamme, T. F. (2010). Nano-emulsions and Micro-emulsions: Clarifications of the Critical Differences. *Pharmaceutical Research*, *28*(5), 978-985.

Azeem, A., Rizwan, M., Ahmad, F. J., Iqbal, Z., Khar, R. K., Aqil, M., & Talegaonkar, S. (2009). Nanoemulsion Components Screening and Selection: a Technical Note. *AAPS PharmSciTech*, *10*(1), 69-76.

Baboota, S., Shakeel, F., & Kohli, K. (2006). Formulation and evaluation of once a day transdermal gels of diclofenac diethylamine. *Methods and Findings in Experimental and Clinical Pharmacology*, *28*(2), 109.

Bakkali, F., Averbeck, S., Averbeck, D., & Idaomar, M. (2008). Biological effects of essential oils–A review. *Food and Chemical Toxicology*, *46*(2), 446-475.

Barbhuiya, M. H., &Kar, D. (2002). Biology of Rice Weevil, *Sitophilus oryzae* Linn. (Coleoptera: Curculionidae) in Stored Wheat *Triticum vulgare* and Its Control: *Environment and Ecology*, 20(3): 700-702.

Barnard, D. R., & Xue, R. (2004). Laboratory Evaluation of Mosquito Repellents Against *Aedes albopictus*, *Culex nigripalpus*, and *Ochlerotatus triseriatus* (Diptera: Culicidae). *Journal of Medical Entomology*, *41*(4), 726-730.

Barry, D. W. (1996). Greenhouse Pesticide Management: Private Pesticide Applicator Training Manual: Greenhouse: Pesticide Formulations (19th edn) USA. University of Maine Cooperative Extension. New England USA.

Bernardi, D. S., Pereira, T. A., Maciel, N. R., Bortoloto, J., Viera, G. S., Oliveira, G. C., & Rocha-Filho, P. A. (2011). Formation and stability of oil-in-water nanoemulsions containing rice bran oil: in vitro and in vivo assessments. *Journal of Nanobiotechnology*, *9*(1), 44.

Bhattacharyya, A., Bhaumik, A., Usha Rani, P., Mandal, S., & Epidi, T. T. (2010). Nano-particles-A recent approach to insect pest control. *African Journal of Biotechnology*. 9(24): 3489-3493.

Bheemanna, M. (1986). Studies on biology of rice weevil *Sitophilus oryzae* Linnaeus (Curculionidae: Coleptera) and host resistance in sorghum. M.Sc. (Agri.) Thesis, University of Agricultural Sciences, Dharwad.

Bouchemal, K., Briançon, S., Perrier, E., & Fessi, H. (2004). Nano-emulsion formulation using spontaneous emulsification: solvent, oil and surfactant optimisation. *International Journal of Pharmaceutics*, *280*(1-2), 241-251.

Bougherra, H. H., Bedini, S., Flamini, G., Cosci, F., Belhamel, K., & Conti, B. (2015). *Pistacia lentiscus* essential oil has repellent effect against three major insect pests of pasta. *Industrial Crops and Products*, *63*, 249-255.

Boyer, S., Zhang, H., & Lempérière, G. (2011). A review of control methods and resistance mechanisms in stored-product insects. *Bulletin of Entomological Research*, *102*(02), 213-229.

Cantrell, C. L., Dayan, F. E., & Duke, S. O. (2012). Natural Products As Sources for New Pesticides. *Journal of Natural Products*, *75*(6), 1231-1242.

Chaubey, M. K. (2012). Biological Effects of Essential Oils Against Rice Weevil *Sitophilus oryzae* L. (Coleoptera: Curculionidae). *Journal of Essential Oil Bearing Plants*, *15*(5), 809-815.

Chen, F., Wang, Y., Zheng, F., Wu, Y., & Liang, W. (2000). Studies on cloud point of agrochemical microemulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *175*(1-2), 257-262.

Chen, G., & Tao, D. (2005). An experimental study of stability of oil–water emulsion. *Fuel Processing Technology*, *86*(5), 499-508.

Chen, K., Chen, C., Lin, Y., & Chen, M. (2013). Formulation of a novel antagonistic bacterium based biopesticide using microencapsulated techniques in fungal disease control. *Journal of Agricultural Science*, *5*(3).

Chidavaenzi, O. C., Buckton, G., & Koosha, F. (2001). The effect of co-spray drying with polyethylene glycol 4000 on the crystallinity and physical form of lactose. *International Journal of Pharmaceutics*, *216*(1-2), 43-49.

Dal Bello, G., Padin, S., López Lastra, C., & Fabrizio, M. (2001). Laboratory evaluation of chemical-biological control of the rice weevil (*Sitophilus oryzae* L.) in stored grains. *Journal of Stored Products Research*, *37*(1), 77-84.

De Oliveira, J. L., Campos, E. V., Bakshi, M., Abhilash, P., & Fraceto, L. F. (2014). Application of nanotechnology for the encapsulation of botanical insecticides for sustainable agriculture: Prospects and promises. *Biotechnology Advances*, *32*(8), 1550-1561.

Denloye, A., Makanjuola, W., Teslim, O., Alafia, O., Kasali, A., & Eshilokun, A. (2010). Toxicity of *Chenopodium Ambrosioides* L. (Chenopodiaceae) Products From Nigeria Against Three Storage Insects. *Journal of Plant Protection Research*, *50*(3).

Effiom, O. E., Avoaja, D. A., & Ohaeri, C. C. (2012). Mosquito repellent activity of phytochemical extracts from fruit peels of Citrus fruit species. *Global Journal of Science Frontier Research*, 12, 5–8.

Elhag, E. A. (2000). Deterrent effects of some botanical products on oviposition of the cowpea bruchid *Callosobruchus maculatus* (F.) (Coleoptera: Bruchidae). *International Journal of Pest Management*, *46*(2), 109-113.

El-Nahal, A., Schmidt, G., & Risha, E. (1989). Vapours of Acorus calamus oil—A space treatment for stored-product insects. *Journal of Stored Products Research*, *25*(4), 211-216.

EL Rasheed, S. L.,& EL Rasheed, A. S. (2017). Formulation of Essential Oil Pesticides Technology and their Application. *Agricultural Research and Technology*: Open Access Journal; 9(2): 555759.

Estalle E.,&Riudavets J. (1999). The rice weevil, *Sitophilus oryzae*: Data on its biology and methods of control. Catalunya Rural I Agraria, 56:29-31.

FAO (Food and Agriculture Organization of the United Nations). (2005). FAOSTAT database. FAO, Rome, Italy.

Faraone, N. W., Hillier, N. K., & Cutler, G. C. (2015). Plant Essential Oils Synergize and Antagonize Toxicity of Different Conventional Insecticides against *Myzus persicae* (Hemiptera: Aphididae). *PLOS ONE*, *10*(5), e0127774.

Felke M., Institute of Pest Control, Retrieved from: http://www.schaedlingskunde.de/Steckbriefe/htm_Seiten/Reismotte_Corcyra_cephalonica.htm

Fernandes, C. P., Mascarenhas, M. P., Zibetti, F. M., Lima, B. G., Oliveira, R. P., Rocha, L., & Falcão, D. Q. (2013). HLB value, an important parameter for the development of essential oil phytopharmaceuticals. *Revista Brasileira de Farmacognosia*, *23*(1), 108-114.

Finney, D. J. (1971). Probit Analysis. Cambridge University Press, Cambridge, 333 p.

Flamini, G., Cioni, P. L., & Morelli, I. (2003). Use of solid-phase micro-extraction as a sampling technique in the determination of volatiles emitted by flowers, isolated flower parts and pollen. *Journal of Chromatography A*, *998*(1-2), 229-233.

Ford, M. (1989). Book Reviews: Insecticides of Plant Origin. Proceedings of Symposium, Toronto, June 1988. Edited by ArnasonJ. T., PhilogèneB. J. R. and PeterMorand. Pp. 213. American Chemical Society, Washington. 1989. US$44.95 US & Canada, US$53.95 elsewhere. *Outlook on Agriculture*, *18*(4), 194-195.

Forget, G. (1993). Balancing the need for pesticides with the risk to human health. In: Impact of pesticide use on health in developing countries, (Eds.) G. Forget, T. Goodman and A. de Villiers, IDRC, Ottawa, p. 2.

Fortin, H., Vigor, C., Lohézic-Le Dévéhat, F., Robin, V., Le Bossé, B., Boustie, J., & Amoros, M. (2002). In vitro antiviral activity of thirty-six plants from La Réunion Island. *Fitoterapia*, *73*(4), 346-350.

Gi, H. J., Chen, S. N., Hwang, J. S., Tien, C., & Kuo, M. T. (1992). Studies of Formation against major insect pests of brinjal. Pestology, 21(11), 14−18.

Gianeti D., Wagemaker, M., Seixas, V., & Campos, P. (2012). The Use of Nanotechnology in Cosmetic Formulations: The Influence of Vehicle in the Vitamin A Skin Penetration. *Current Nanoscience*, *8*(4), 526-534.

Golebiowska, Z., Filipek, P., Krzymanska, J. (1968). The injuriousness of the grain weevil (*S. granarius*.L.), the rice weevil (*S. oryzae*. L.) and the lesser grain borer (*R. dominica.* F.). dla ziarma pszenicy i zyta Prac Naukowe Instytutu Ochrony Roslin, *10*(l): 31-56.

Gogos, A., Knauer, K., & Bucheli, T. D. (2012). Nanomaterials in Plant Protection and Fertilization: Current State, Foreseen Applications, and Research Priorities. *Journal of Agricultural and Food Chemistry*, *60*(39), 9781-9792.

Goudeau, D., Uratsu, S. L., Inoue, K., DaSilva, F. G., Leslie, A., Cook, D., Dandekar, A. M. (2008). Tuning the orchestra: Selective gene regulation and orange fruit quality. *Plant Science*, *174*(3), 310-320.

Gupta P., & Pandit J. (2010). Pharmaceutical Nanotechnology Novel Nanoemulsion–High Energy Emulsification Preparation, Evaluation and Application. The Pharma Research, 3:117-138.

Gutiérrez, J., González, C., Maestro, A., Solè, I., Pey, C., & Nolla, J. (2008). Nano-emulsions: New applications and optimization of their preparation. *Current Opinion in Colloid & Interface Science*, *13*(4), 245-251.

Haines, C. P. & Hodges, R. J. (1991). Insect and arachnids of tropical stored product and their Identification. A training Manual (ODA) 89-105.

Han, S. T. (1998). Medicinal plants in the South Pacific. World Health Organization (WHO) Regional Publications, Western Pacific Series N° 19. 254 p. WHO, Regional Office for Western Pacific, Manila, Philippines.

Haque, M., Nakakita, H., Ikenaga, H., & Sota, N. (2000). Development-inhibiting activity of some tropical plants against Sitophilus zeamais Motschulsky (Coleoptera: Curculionidae). *Journal of Stored Products Research*, *36*(3), 281-287.

Herzfeld D., & Sargent K. (2011). Chapter 4: Pesticide Formulations: Private Pesticide Applicator Safety Education Manual 19th Edition. Minnesota Department of Agriculture, University of Minnesota Extension, USA.

Hollingworth, R. M., Johnstone, E. M., & Wright, N. (1984). Pesticide synthesis through rational approaches. In P. S. Magee, G. K. Kohn, & J. J. Menn (Eds.), ACS symposium series No. 255 (pp. 103–125). Washington, DC: American Chemical Society.

Houghton, P. J., Ren, Y., & Howes, M. (2006). Acetylcholinesterase Inhibitors from Plants and Fungi. *ChemInform*, *37*(32).

Huang, F., & Subramanyam, B. (2004). Responses of *Corcyra cephalonica* (Stainton) to pirimiphos-methyl, spinosad, and combinations of pirimiphos-methyl and synergized pyrethrins. *Pest Management Science*, *60*(2), 191-198.

Huang, Q., Yu, H., & Ru, Q. (2010). Bioavailability and Delivery of Nutraceuticals Using Nanotechnology. *Journal of Food Science*, *75*(1), R50-R57.

Huang, Y., & Ho, S. (1998). Toxicity and antifeedant activities of cinnamaldehyde against the grain storage insects, *Tribolium castaneum* (Herbst) and *Sitophilus zeamais* Motsch. *Journal of Stored Products Research*, *34*(1), 11-17.

Huang, Y., Ho, S., Lee, H., & Yap, Y. (2002). Insecticidal properties of eugenol, isoeugenol and methyl eugenol and their effects on nutrition of *Sitophilus zeamais* Motsch. (Coleoptera: Curculionidae) and *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). *Journal of Stored Products Research*, *38*(5), 403-412.

Huang, Y., Lam, S., & Ho, S. (2000). Bioactivities of essential oil from *Elletaria cardamomum* (L.) Maton. to *Sitophilus zeamais* Motschulsky and. *Journal of Stored Products Research*, *36*(2), 107-117.

Huang, Y., Tan, J. M. W. L., Kini, R. M., Ho, S. H. (1997). Toxic and antifeedant action of nutmeg oil against *Tribolium castaneum* (Herbst) and *Sitophilus zeamais* Motsch. *Journal of Stored Product Research*, 33:289–298.

Isman, M. B. (2000). Plant essential oils for pest and disease management. *Crop Protection*, *19*(8-10), 603-608.

Isman, M. B. (2006). Botanical insecticides, deterrents, and repellents in modern agriculture and an increasingly regulated world. *Annual Review of Entomology*, *51*(1), 45-66.

Isman, M. B., & Machial, C. M. (2006). Chapter 2 Pesticides based on plant essential oils: from traditional practice to commercialization. *Advances in Phytomedicine*, 29-44.

Jadhav, K. (2006). Biology and management of rice weevil, *Sitophilus oryzae* (L.) in pop sorghum. M.Sc. (Agri.) Thesis, University Agricultural Science, Dharwad, India.

Jantan, I., Ahmad, A. S., Ahmad, A. R., Ali, N. A., & Ayop, N. (1996). Chemical Composition of Some Citrus Oils from Malaysia. *Journal of Essential Oil Research*, *8*(6), 627-632.

Jeffers, L. A., & Michael Roe, R. (2008). The movement of proteins across the insect and tick digestive system. *Journal of Insect Physiology*, *54*(2), 319-332.

Jung, W., Jang, Y., Hieu, T. T., Lee, C., & Ahn, Y. (2007). Toxicity of *Myristica fragrans* Seed Compounds Against *Blattella germanica* (Dictyoptera: Blattellidae). *Journal of Medical Entomology*, *44*(3), 524-529.

Karamaouna, F., Kimbaris, A., Michaelakis, A., Papachristos, D., Polissiou, M., Papatsakona, P., & Tsora, E. (2013). Insecticidal Activity of Plant Essential Oils Against the Vine Mealybug,*Planococcus ficus*. *Journal of Insect Science*, *13*(142), 1-13.

Karim, R. A. (2002). Limau Purut Cantikkan Kulit (Skin care by kaffir lime) Utusan Malaysia. [(accessed on 17 March 2002)]. Available online: ww1.utusan.com.my/utusan/info.asp?y=2002&dt=0317&pub=Utusan_Malaysia&sec=Kesihatan&pg=kn_06.htm.

Karr, L.L., & Coats, J. R. (1988). Insecticidal properties of d-Lemonene. *Journal of Pesticide Science*, 13: 287-290.

Khaled, N., Montent, D., Farines, M., Pina, M., & Graille, J. (1992). Syntheses de monoesters de surce par biocatalyse, Oleagineux, Vol. *47*(4):181-189.

Khan, A. A., Shah, M. A., & Majid, S. (2015). Arthropod Natural enemy- pesticife interaction. In Perspectives in Animal Ecology and Reproduction. Eds. V.K. Gupta, Anil K. Verma and G.D. Singh (Daya Publishing House, New Delhi), pp. 29-64.

Khani, M., Awang, R. M., Omar, D., Rahmani, M., & Rezazadeh, S. (2011). Tropical medicinal plant extracts against rice weevil, *Sitophilus oryzae* L. *Journal of Medicinal Plants Research*, 5 (2): 259 - 65.

Khot, L. R., Sankaran, S., Maja, J. M., Ehsani, R., & Schuster, E. W. (2012). Applications of nanomaterials in agricultural production and crop protection: A review. *Crop Protection*, *35*, 64-70.

Kim, S., Roh, J., Kim, D., Lee, H., & Ahn, Y. (2003). Insecticidal activities of aromatic plant extracts and essential oils against *Sitophilus oryzae* and *Callosobruchus chinensis*. *Journal of Stored Products Research*, *39*(3), 293-303.

Kim, S., Yoon, J., Jung, J. W., Hong, K., Ahn, Y., & Kwon, H. W. (2010). Toxicity and repellency of origanum essential oil and its components against *Tribolium castaneum* (Coleoptera: Tenebrionidae) adults. *Journal of Asia-Pacific Entomology*, *13*(4), 369-373.

Koul, O. (2004). Biological Activity of Volatile Di-*n*-Propyl Disulfide from Seeds of Neem, *Azadirachta indica* (Meliaceae), to Two Species of Stored Grain Pests, *Sitophilus oryzae*(L.) and *Tribolium castaneum* (Herbst). *Journal of Economic Entomology*, *97*(3), 1142-1147.

Koul, O., Walia, S., & Dhaliwal, G. (2008). Essential oils as green pesticides: potential and constraints. *Journal of Biopesticides*. Int. *4*, 63-84.

Knowles, A. (2005). New developments in crop protection product formulation. Agrow Reports UK: T and F Informa UK Ltd, pp. 153-156.

Kumari, K., & Pathak, P. H. (2014). Effects of citrus oil volatiles on the reproductive biology of the rice moth, *Corcyra cephalonica* (stainton) (lepidoptera: pyralidae). *Journal of Pharmaceutical & Scientific Innovation*, *3*(1), 47-51.

Kéita, S. M., Vincent, C., Schmit, J., Arnason, J. T., & Bélanger, A. (2001). Efficacy of essential oil of *Ocimum basilicum* L. and *O. gratissimum* L. applied as an insecticidal fumigant and powder to control *Callosobruchus maculatus* (Fab.) [Coleoptera: Bruchidae]. *Journal of Stored Products Research*, *37*(4), 339-349.

Lee, B., Annis, P. C., Tumaalii, F., & Lee, S. (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*(5), 498-506.

Lee, B., Lee, S., Annis, P. C., Pratt, S. J., Park, B., & Tumaalii, F. (2002). Fumigant Toxicity of Essential Oils and Monoterpenes Against the Red Flour Beetle, *Tribolium castaneum* Herbst. *Journal of Asia-Pacific Entomology*, *5*(2), 237-240.

Lin, J. J. & Lin, S. F. (2003). Size, volume fraction, and nucleation of Stober silica nanoparticles. *Journal of Colloid and Interface Science*, (258), 159.

Linnaeus, C. (1763). Vol. 2. Species Plantarum. ed. 2. Stockholm.: 785-1684 (1685-1748).

Liu, C., Mishra, A., Tan, R., Tang, C., Yang, H., & Shen, Y. (2006). Repellent and insecticidal activities of essential oils from *Artemisia princeps* and *Cinnamomum camphora* and their effect on seed germination of wheat and broad bean. *Bioresource Technology*, *97*(15), 1969-1973.

Loh, F. S., Awang, R. M., Omar, D., & Rahmani, M. (2011). Insecticidal properties of *Citrus hystrix* DC leaves essential oil against *Spodoptera litura* fabricius. *Journal of Medicinal Plants Research*, 5, 3739–3744.

Longstaff, B. C. (1981). Biology of the grain pest species of the genus Sitophilus (Coleoptera: Curculionidae): a critical review. *Protection Ecology*, 2: 83-130.

Luz, C., & Batagin, I. (2005). Potential of oil-based formulations of *Beauveria bassiana* to control *Triatoma infestans*. *Mycopathologia*, *160*(1), 51-62.

Lv, G., Wang, F., Cai, W., & Zhang, X. (2014). Characterization of the addition of lipophilic Span 80 to the hydrophilic Tween 80-stabilized emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *447*, 8-13.

Lü, J., & He, Y. (2010). Fumigant toxicity of *Ailanthus altissima* Swingle, *Atractylodes lancea* (Thunb.) DC. and Elsholtzia stauntonii Benth extracts on three major stored-grain insects. *Industrial Crops and Products*, *32*(3), 681-683.

Madrid, F. L., White, N. D. G., Loschiavo, S. R. (1990). Insects in stored cereals, and their association with farming practices in southern Manitoba. Canadian Entomologist, 122:515-523.

Manaf, Y. N., Osman, A., Lai, O. M., Long, K., & Ghazali, H. M. (2008). Characterisation of musk lime (Citrusmicrocarpa) seed oil. *Journal of the Science of Food and Agriculture*, *88*(4), 676-683.

Margulis-Goshen, K., & Magdassi, S. (2012). Nanotechnology: An Advanced Approach to the Development of Potent Insecticides. *Advanced Technologies for Managing Insect Pests*, 295-314.

Martin, A., Varona, S., Navarrete, A., & Cocero, M. J. (2010). Encapsulation and Co-Precipitation Processes with Supercritical Fluids: Applications with Essential Oils. *The Open Chemical Engineering Journal*, *4*(2), 31-41.

Mbata, G. N., & Payton, M. E. (2013). Effect of monoterpenoids on oviposition and mortality of *Callosobruchus maculatus* (F.) (Coleoptera: Bruchidae) under hermetic conditions. *Journal of Stored Products Research*, *53*, 43-47.

McClements, D. J. (2012). Nanoemulsions versus microemulsions: terminology, differences, and similarities. *Soft Matter 8*, 1719–29.

Md Othman, S., Hassan, M., Nahar, L., Basar, N., Jamil, S., & Sarker, S. (2016). Essential Oils from the Malaysian Citrus (Rutaceae) Medicinal Plants. *Medicines*, *3*(2), 13.

Mendes, R. G., Koch, B., Bachmatiuk, A., El-Gendy, A. A., Krupskaya, Y., Springer, A., Rümmeli, M. H. (2014). Synthesis and toxicity characterization of carbon coated iron oxide nanoparticles with highly defined size distributions. *Biochimica et Biophysica Acta (BBA)-General Subjects*, *1840*(1), 160-169.

Michaelraj, S., & Sharma, R. K. (2006). Fumigant toxicity of neem formulations against *Sitophilus oryzae* and *Rhyzoperthadominica*. *Journal of Agricultural Technology*, 2:1-16.

Mishra, B. B., Tripathi, S. P., & Tripathi, C. P. M. (2012). Repellent effect of leaves essential oils from *Eucalyptus globulus* (Mirtaceae) and *Ocimum basilicum* (Lamiaceae) against two major stored grain insect pests of Coleopterons. *Nature and Science*, 10(2):50-54.

Mishra, S. N., & Krishna, S. S. (1979). Influence of some specific time and age related mating schedules on oviposition and egg fertility in *Corcyra cephalonica* staint. (Lepidoptera: Galleridae) *Entomon*, 4: 197-199.

Mohamed, M. I., & Abdelgaleil, S. A. (2008). Chemical composition and insecticidal potential of essential oils from Egyptian plants against *Sitophilus oryzae* (L.) (Coleoptera: Curculionidae) and *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). *Applied Entomology and Zoology*, *43*(4), 599-607.

Moretti, M. D., Sanna-Passino, G., Demontis, S., & Bazzoni, E. (2002). Essential oil formulations useful as a new tool for insect pest control. *AAPS PharmSciTech*, *3*(2), 64-74.

Muller, R. H., & Keck, C. M. (2004). Challenges and solutions for the delivery of biotech drugs–a review of drug nanocrystal technology and lipid nanoparticles. *Journal of Biotechnology*, *113*(1-3), 151-170.

Murrell, J. N. & Jenkins, A. D. (1994). Properties of liquids and solutions. (J. Wiley & Sons, Eds.) (2^{nd} Editi., pp. 148−150). New York.

Myers, D., & John Wiley & Sons. (2006). *Surfactant science and technology*. Hoboken, NJ: J. Wiley.

Mwaiko, G. L., & Savaeli, Z. X.s (1992). Citrus peel oil extracts as mosquito larvae insecticides. *East African Medical Journal*, 69:223-227.

Negahban, M., Moharramipour, S., & Sefidkon, F. (2006). Chemical Composition and Insecticidal Activity of *Artemisia scoparia* Essential Oil against Three Coleopteran Stored-Product Insects. *Journal of Asia-Pacific Entomology*, *9*(4), 381-388.

Negahban, M., Moharramipour, S. M. Z., & Hashemi, S. A. (2014). Repellent activity of nanoencapsulated essential oil of *Artemisia sieberi* Besser on *Plutella xylostella* L. larvae. *Iranian Journal of Medicinal and Aromatic Plants*, 29: 909-924.

Nel, A. E., Mädler, L., Velegol, D., Xia, T., Hoek, E. M., Somasundaran, P., Thompson, M. (2009). Understanding biophysicochemical interactions at the nano-bio interface. *Nature Materials*, *8*(7), 543-557.

Obeng-Ofori, D., & Amiteye, S. (2005). Efficacy of mixing vegetable oils with pirimiphos-methyl against the maize weevil, *Sitophilus zeamais* Motschulsky in stored maize. *Journal of Stored Products Research*, *41*(1), 57-66.

Oberdörster, G., Oberdörster, E., & Oberdörster, J. (2005). Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles. *Environmental Health Perspectives*, *113*(7), 823-839.

Okuni, T. (1924). Insect pests of stored grains in Formosa Part I. Research Institute for Agriculture, Formosa, 6: 1-16.

Oliveira, A. E., Duarte, J. L., Amado, J. R., Cruz, R. A., Rocha, C. F., Souto, R. N., Carvalho, J. C. (2016). Development of a Larvicidal Nanoemulsion with Pterodon emarginatus Vogel Oil. *PLOS ONE*, *11*(1), e0145835.

Omar, S., Marcotte, M., Fields, P., Sanchez, P., Poveda, L., Mata, R., Philogène, B. (2007). Antifeedant activities of terpenoids isolated from tropical Rutales. *Journal of Stored Products Research*, *43*(1), 92-96.

Opit, G. P., Phillips, T. W., Aikins, M. J., & Hasan, M. M. (2012). Phosphine Resistance in *Tribolium castaneum* and *Rhyzopertha dominica* From Stored Wheat in Oklahoma. *Journal of Economic Entomology*, *105*(4), 1107-1114.

Palacios, S., Bertoni, A., Rossi, Y., Santander, R., & Urzúa, A. (2009). Efficacy of Essential Oils from Edible Plants as Insecticides Against the House Fly, *Musca Domestica* L. *Molecules*, *14*(5), 1938-1947.

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.

Perlatti, B., Souza Bergo, P. L., Fernandes da Silva, M. F., Batista, J., & Rossi, M. (2013). Polymeric Nanoparticle-Based Insecticides: A Controlled Release Purpose for Agrochemicals. *Insecticides-Development of Safer and More Effective Technologies*.

Phillips, A. K., Appel, A. G., & Sims, S. R. (2010). Topical Toxicity of Essential Oils to the German Cockroach (Dictyoptera: Blattellidae). *Journal of Economic Entomology*, *103*(2), 448-459.

Prakash, A., & Rao, J. (1997). Botanical pesticides in agriculture. CRC Lewis Publs. Boca Raton, USA.481 PP.

Prakash, B., Singh, P., Mishra, P. K., & Dubey, N. (2012). Safety assessment of *Zanthoxylum alatum* Roxb. essential oil, its antifungal, antiaflatoxin, antioxidant activity and efficacy as antimicrobial in preservation of *Piper nigrum* L. fruits. *International Journal of Food Microbiology*, *153*(1-2), 183-191.

Prakash, B., Singh, P., Yadav, S., Singh, S., & Dubey, N. (2013). Safety profile assessment and efficacy of chemically characterized *Cinnamomum glaucescens* essential oil against storage fungi, insect, aflatoxin secretion and as antioxidant. *Food and Chemical Toxicology*, *53*, 160-167.

Pratap, A. P., & Bhowmick, D. N. (2008). Pesticides as Microemulsion Formulations. *Journal of Dispersion Science and Technology*, *29*(9), 1325-1330.

Priya, S., Koland, M., & Kumari, S. (2015). Nanoemulsion components screening of quetiapine fumarate: Effect of surfactant and co surfactant (Vol. 8).

Qian, C., Decker, E. A., Xiao, H., & McClements, D. J. (2012). Physical and chemical stability of β-carotene-enriched nanoemulsions: Influence of pH, ionic strength, temperature, and emulsifier type. *Food Chemistry*, *132*(3), 1221-1229.

Rahman, A., & Talukder, F. A. (2006). Bioefficacy of some plant derivatives that protect grain against the pulse beetle, *Callosobruchus maculatus*. *Journal of Insect Science*, *6*(3), 1-10.

Rahman, M. M., & Schmidt, G. H. (1999). Effect of *Acorus calamus* (L.) (Araceae) essential oil vapours from various origins on *Callosobruchus phaseoli* (Gyllenhal) (Coleoptera: Bruchidae). *Journal of Stored Products Research*, *35*(3), 285-295.

Rajendran, S., & Hajira Parveen, K. (2005). Insect infestation in stored animal products. *Journal of Stored Products Research*, *41*(1), 1-30.

Rajendran, S., & Sriranjini, V. (2008). Plant products as fumigants for stored-product insect control. *Journal of Stored Products Research*, *44*(2), 126-135.

Rajasekaran, C., Siva R., Vijayakumar V., Meignanam E., Kalaivani T., & Jayakumararaj, R., (2008). Investigation on antimicrobial activity of leaf extract of *Azadirachta indica* A. Juss (Meliaceae): A traditional medicinal plant of India. *Ethnobotanical Leaflets*, 12: 1213-1217.

Rani, P. U. (2012). Fumigant and contact toxic potential of essential oils from plant extracts against stored product pests. *Journal of Biopesticides*, *5*(2): 120-128.

Rees, D. (2004). Insects of Stored Products. CSIRO, Collinwood, Australia.

Reza, A. (2010). Nanometric-Scaled Emulsions (Nanoemulsions).*Iranian Journal of Pharmaceutical Research*, *9*(4): 325-6.

Robertson, J. L., Russeli, R. M., Preisler, H. K., &Savin, N. E. (2007). Bioassay with Arthropods Polo Computer Programme for analysis of Bioassay data 2nd Edition, Telor and Francis, CRC, Press, PP.1-224.

Ronald, F. L. M., & Jayma, L. M. K. (2007). Bemisia tabaci (Gennadius). Retrieved January 25, 2011, from http://www.extento.hawaii.edu/kbase/crop/Type/b_tabaci.htm.

Roy, B., Amin, R., Uddin, M. N. (2005). Leaf extracts of Shiyalmutra (*Blumea lacera*) as botanical insecticides against lesser grain borser and rice weevil. *Journal of Biological Science*, *5*(2): 201-204.

Saberi, A. H., Fang, Y., & McClements, D. J. (2013). Fabrication of vitamin E-enriched nanoemulsions: Factors affecting particle size using spontaneous emulsification. *Journal of Colloid and Interface Science*, *391*, 95-102.

Salunke, B., Kotkar, H., Mendki, P., Upasani, S., & Maheshwari, V. (2005). Efficacy of flavonoids in controlling *Callosobruchus chinensis* (L.) (Coleoptera: Bruchidae), a post-harvest pest of grain legumes. *Crop Protection*, *24*(10), 888-893.

Santos, J. P. (2006). Controle de pragas durante o armazenamento de milho. Circular Técnica 84, Sete Lagoas, 20 p.

Sartori, M. R., Pacheco, I. A., Iaderosa, M. & Taylor, R. W. D. (1990). Ocorrência e especificidade de resistência ao inseticida malation em insetos-pragas de grãos armazenados no Estado de São Paulo. *Coletânea do ITAL* 20: 94–209.

Savary, S., Teng, P. S., Willocquet, L., & Nutter, F. W. (2006). Quantification and modeling of crop losses: A review of purposes. *Annual Review of Phytopathololog*y, 44: 89-12.

Shafiq, S., Shakeel, F., Talegaonkar, S., Ahmad, F. J., Khar, R. K., & Ali, M. (2007). Design and Development of Oral Oil in Water Ramipril Nanoemulsion Formulation: In Vitro and In Vivo Assessment. *Journal of Biomedical Nanotechnology*, *3*(1), 28-44.

Sharaby, A. (1988). Effect of Orange, *Citrus sinensis* (L.) Peel Oil on Reproduction in *Phthorimaea operculella* (Zell.). *International Journal of Tropical Insect Science*, *9*(02), 201-203.

Singh, G., Singh, O. P., De Lampasona, M. P., & Catalán, C. A. (2002). Studies on essential oils. Part 35: chemical and biocidal investigations onTagetes erectaleaf volatile oil. *Flavour and Fragrance Journal*, *18*(1), 62-65.

Siskos, E. P., Konstantopoulou, M. A., Mazomenos, B. E., & Jervis, M. (2007). Insecticidal Activity of *Citrus aurantium* Fruit, Leaf, and Shoot Extracts Against Adult Olive Fruit Flies (Diptera: Tephritidae). *Journal of Economic Entomology*, *100*(4), 1215-1220.

Siskos, E. P., Mazomenos, B. E., & Konstantopoulou, M. A. (2008). Isolation and Identification of Insecticidal Components from *Citrus aurantium* Fruit Peel Extract. *Journal of Agricultural and Food Chemistry*, *56*(14), 5577-5581.

Solè, I., Pey, C. M., Maestro, A., González, C., Porras, M., Solans, C., & Gutiérrez, J. M. (2010). Nano-emulsions prepared by the phase inversion composition method: Preparation variables and scale up. *Journal of Colloid and Interface Science*, *344*(2), 417-423.

Song, S., Liu, X., Jiang, J., Qian, Y., Zhang, N., & Wu, Q. (2009). Stability of triazophos in self-nanoemulsifying pesticide delivery system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *350*(1-3), 57-62.

Stone, W. W., Gilliom, R. J., & Ryberg, K. R. (2014). Pesticides in U.S. Streams and Rivers: Occurrence and Trends during 1992–2011. *Environmental Science & Technology*, *48*(19), 11025-11030.

Sparks, T. C., Dripps, J. E., Watson, G. B., & Paroonagian, D. (2012). Resistance and cross resistance to the spinosyns-A review and analysis. *Pesticide Biochemistry and Physiology*, 102: 1-10.

Suthisut, D., Fields, P. G., & Chandrapatya, A. (2011). Fumigant toxicity of essential oils from three Thai plants (Zingiberaceae) and their major compounds against *Sitophilus zeamais*, *Tribolium castaneum* and two parasitoids. *Journal of Stored Products Research*, *47*(3), 222-230.

Tadros, T., Izquierdo, P., Esquena, J., & Solans, C. (2004). Formation and stability of nano-emulsions. *Advances in Colloid and Interface Science*, *108-109*, 303-318.

Talbert, R., & Wall, R. (2012). Toxicity of essential and non-essential oils against the chewing louse, Bovicola (Werneckiella) ocellatus. *Research in Veterinary Science*, *93*(2), 831-835.

Talukder, F. A., Islam, M. S., Hossain, M. S., Rahman, M. A., & Alam, M. N. (2004). Toxicity effects of botanicals and synthetic insecticides on *Tribolium castaneum* (Herbst) and *Rhyzopertha dominica* (Fabricius). *Bangladesh Journal of Environmental Science*, *10*(2): 365–371.

Tanojo, H., Junginger, H. E., & Boddé, H. E. (1997). In vivo human skin permeability enhancement by oleic acid: transepidermal water loss and fourier-transform infrared spectroscopy studies. *Journal of Controlled Release*, *47*(1), 31-39.

Taylor, W. G., Fields, P. G., & Sutherland, D. H. (2007). Fractionation of Lentil Seeds (*Lens culinaris* Medik.) for Insecticidal and Flavonol Tetraglycoside Components. *Journal of Agricultural and Food Chemistry*, *55*(14), 5491-5498.

Tiwari, S. & A. Singh, 2004. Pesticidal activity of alcoholic extract of *Nerium indicum* leaf and their biochemical stress response on fish metabolism. *African Journal of Traditional, Complementary, and Alternative Medicines* 1: 15-29.

Tong, K., Zhao, C., & Sun, D. (2016). Formation of nanoemulsion with long chain oil by W/O microemulsion dilution method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *497*, 101-108.

Treiman, F. S. (1937). On the morphology and biology of *Calandra oryzae* (L.). Travaux Institute for Academic Sciences, 14 : 256-277.

Tripathi, A.K., Prajapati, V., & Kumar, S. (2003). Bioactivities of l-carvone, d-carvone, and dihydrocarvone toward three stored product beetles. *Journal of Economic Entomology*, 96: 1594–1601.

Udo, I. O. (2005). Evaluation of the potential of some local spices as stored grain protectants against the maize weevil *Sitophilus zeamais* Mots (Coleoptera: Curculionidae). *Journal of Applied Science and Environmental Management*. 9(1): 16.

Van Gysel, A. B., & Musin, W. (2012). Methylamines. *Ullmann's Encyclopedia of Industrial Chemistry*.

Veal, L. (1996). The potential effectiveness of essential oils as a treatment for headlice, *Pediculus humanus capitis*. *Complementary Therapies in Nursing and Midwifery*, *2*(4), 97-101.

Visarathanonth, P., & Sukprakarn, S. (1988). Current problems of pests of stored products in Thailand. Proceedings of the symposium on pests of stored products; Bogor, Indonesia. Biotrop Special Publication. 33: 45-54.

Waliwitiya, R., Isman, M. B., Vernon, R. S., & Riseman, A. (2005). Insecticidal Activity of Selected Monoterpenoids and Rosemary Oil to *Agriotes obscurus* (Coleoptera: Elateridae). *Journal of Economic Entomology*, *98*(5), 1560-1565.

Walker, K. (2006). rice weevil *(Sitophilus oryzae)* Updated on 10/8/2011 12:15:55 PM Available online: PaDIL-http://www.padil.gov.au.

Wang, C. J., & Liu, Z. Q. (2007). Foliar absorption of herbicides. Review of Weed Science, (4), 215-231.

Weaver, D. K., & Subramanyam, B. (2000). Botanicals. *Alternatives to Pesticides in Stored-Product IPM*, 303-320.

Werdin González, J. O., Stefanazzi, N., Murray, A. P., Ferrero, A. A., & Fernández Band, B. (2014). Novel nanoinsecticides based on essential oils to control the German cockroach. *Journal of Pest Science*, *88*(2), 393-404.

Westesen, K., Bunjes, H., & Koch, M. (1997). Physicochemical characterization of lipid nanoparticles and evaluation of their drug loading capacity and sustained release potential. *Journal of Controlled Release*, *48*(2-3), 223-236.

Wooster, T. J., Golding, M., & Sanguansri, P. (2008). Impact of Oil Type on Nanoemulsion Formation and Ostwald Ripening Stability. *Langmuir*, *24*(22), 12758-12765.

Wright, C., Leidy, R., & Dupree, H. (1993). Cypermethrin in the ambient air and on surfaces of rooms treated for cockroaches. *Bulletin of Environmental Contamination and Toxicology*, *51*(3).

Yang, F., Li, X., Zhu, F., & Lei, C. (2009). Structural Characterization of Nanoparticles Loaded with Garlic Essential Oil and Their Insecticidal Activity against *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). *Journal of Agricultural and Food Chemistry*, *57*(21), 10156-10162.

Zapata, N., & Smagghe, G. (2010). Repellency and toxicity of essential oils from the leaves and bark of *Laurelia sempervirens* and *Drimys winteri* against *Tribolium castaneum*. *Industrial Crops and Products*, *32*(3), 405-410.

Zewde, D., & Jembere, B. (2010). Evaluation of Orange Peel *Citrus Sinensis* (L) As a Source of Repellent, Toxicant and Protectant against *Zabrotes Subfasciatus* (Coleoptera: Bruchidae). *Momona Ethiopian Journal of Science*, *2*(1).

Zhang, L. W., Al-Suwayeh, S. A., Hung, C. F., Chen, C. C., &Fang, J. Y. (2011). Oil components modulate the skin delivery of 5-aminolevulinic acid and its ester prodrug from oil-in-water and water-in-oil nanoemulsions. *International Journal of Nanomedicine*, 693.

Zhang, Y., Gao, J., Zheng, H., Zhang, R. , Han, Y. (2011). The preparation of 3,5-dihydroxy-4-isopropylstilbene nanoemulsion and in vitro release,*International Journal of Nanomedicine*, 6, pp. 649-657

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