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Comparative Study of Insecticides Formulated from Essential Oils with Two Commercial Insecticides

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Abstract

The insecticidal activities of four formulated insecticides of plant essential oils (EOs) origin were compared with two synthetic insecticides against cowpea seed bruchid, Callosobruchus maculatus. The pesticide residues from the application of the synthetic pesticides were also investigated. The essential oils were extracted by steam distillation. The essential oil-based insecticides were formulated by mixing 0.25 g of the oil in 5 g of either calcium carbonate or clay (carrier). The various insecticides were extracted from treated cowpea seeds with dichloromethane and then clean in a column with n-hexane and analysed on auto system Gas Chromatograph (GC) with electron capture detector (ECD). The chemical composition of the oil was analysed by Gas Chromatograph-Mass Spectrometer (GC-MS). The result of the contact activities of the various insecticides against cowpea bruchid (Callosobruchus maculatus) showed that all insecticides produced 100% knockdown of Callosobruchus maculatus twelve hours after its formulation. The least effective EO-formulated insecticides was those of African nutmeg (Monodora myristica) having 90% activity after 24 hours. Aluminium phosphide and permethrin recorded twenty-one and twenty pesticides residues, respectively, while the essential oil formulated insecticides did not record any pesticide residue. Aluminium phosphide had fifteen of the residues detected above the Maximum Residual limits set by FAO/WHO, while permethrin had 13 of the pesticide's residue above the MRL. The result obtained showed that the insecticides formulated from the four essential oils have high insecticidal activity, with no record of any pesticides residues. Hence, they demonstrated potential suitability as eco-friendly biopesticides.

Keywords: Pesticide residue, Insecticide, Essential oil, Aluminium phosphide, Permethrin.

Introduction

In developing countries, the havocs which insect pests create during the cause of planting as well as during storage result in huge economic loss which is a concern to farmers (Awojide et al., 2015). Therefore, it is necessary to proffer a solution to protect farm produce from these ravaging pests to keep produce in a state of high quality.

Pesticides have been widely used to control a variety of insects that destroy crops in developing countries. They are produced from several chemicals and have been in use around the world, with a huge benefit for agricultural production. Pesticides have taken a huge place in agriculture to reduce the losses in food production caused by insects, weeds, microbial diseases and other agricultural pests (McCauley, 2006; Sanon et al., 2018). Globally, destruction of potential food crops by insects, weeds and plant pathogens has been reported to be up to 35% before harvest (Ghorab and Khalil, 2016). Although these chemicals have been widely employed in agriculture, they have become a major group of environmental contaminants that has a huge negative impact on human health. Various researchers have established that the compounds from these groups of pesticides are threatening to human health as a result of their toxic effects such as teratogenic, mutagenic and carcinogenic effects (Casas, 2004; Gupta, 2006; Osman et al., 2008; Alavanja, 2009; Ghorab and Khalil, 2015; Babarinde et al., 2016)

The metabolites that may remain in food after pesticides are applied to food crops are known as pesticide residues. These chemicals, owing to their persistent use, have been found in food products such as vegetables, vegetable oils, fruits, meat, fish and poultry (Petraitis et al., 2013). As much as pesticides are useful in the production of food and insects' control, a large percentage of them pose non-target toxicity risks. When applied on farms or during storage, they find their way into the environment and thus get accumulated in the food chain (Ghorab and Khali, 2015). Natural products have been found as an alternative to synthetic

pesticides. Plant materials have been known to contain complex secondary metabolites, some of which have been found to induce defence against insect pests. These have been utilized for insect pest's management owning to their potentiality to function as toxicants, antifeedant, repellent and insect growth regulators. They are biodegradable with little or no mammalian toxicity, which renders them safe and eco-friendly compared to synthetic pesticides (Isman, 2006). Essential oils (EO's) extracted from aromatic plants have been considerably used as insecticides. They have repellent, antifeedants, insecticidal, ovicides, oviposition inhibitors and growth-reducing effects on a variety of insects (Pereira et al., 2006; Regnault-Roger et al., 2012; Fayemiwo et al., 2014; Babarinde et al. 2017)

Despite the scale of research on natural products, only a handful of botanical insecticides are in commercial use today (Isman, 2006). In this research, we compared the insecticidal activity of four essential oil-based insecticides and two commercial insecticides against Callosobruchus maculatus. The pesticide residues of all insecticides were also determined to ascertain their ecological safety.

Materials and Methods

Materials Collection

African Nutmeg (*Monodora myristica*) seeds, the bud of clove (Eugenia caryophyllus) and seeds of cow foot leaf plant (*Piper umbellatum*) were obtained from Oja Oba Market in Oke-Baale, Osogbo, Osun State, Nigeria. Pine needle (Pinus sylvestris) was obtained from its tree at Awo Hall, Obafemi Awolowo University Ile-Ife, Osun State, Nigeria. The clay soil was collected from an undisturbed area of Osun State University Osogbo Campus which is free from agricultural activities. The samples were taken at a 0 to 15 cm depth, air-dried and ground to pass a 2 mm sieve and stored in sealed polyethene bottles in a refrigerator. All the chemicals used were of analytical grade. Aluminium phosphide and Permethrin (commercial insecticides used) were both purchased at an agrochemical store at Orisunbare Market, Osogbo, Osun State, Nigeria.

Insects Culture

The culture of bean bruchid (*Callosobruchus maculatus*) was collected from infested beans and stored in a 5-litre plastic container at room temperature (Navarro, 2006).

Essential Oil Extraction

The essential oil (EO) of E. caryophyllus, M. myristica, P. umbellatum and P. sylvestris were extracted separately using steam distillation method with the aid of a clavenger's apparatus for 6 hours. Anhydrous sodium sulphate was used to remove water after extraction. Essential oils were stored in airtight containers in a refrigerator at 4°C (Ayvaz et al., 2010).

Essential Oil-based Insecticides Formulation

Acetone ((1.5 mL) as a co-solvent was separately added to 0.25 g of EO of *E. caryophyllus, P. sylvestris, P. umbellatum and M. myristica* to form an oil-based emulsion. Clay and Calcium carbonate (5 g) was mixed with the oil-based emulsion and then mixed manually to assume a homogenous mixture (5% w/w).

Insecticidal Activity

Plastic Petri dishes were labelled and used for bioassay. Ten *C. maculatus* adults were transferred into the petri dish containing 5 g of the essential oil formulations. The control consisted of a similar setup but with 5 g of Clay or Calcium carbonate mixed with 2.0 mL of acetone. This set up was repeated with 5 g of commercial insecticides. Mortality counts were made after 60 minutes of the treatment. Six hours after the formulations, another set of 10 insects each was used to replace the initial ones and the mortality count was taken. Mortality counts were also made after 12, 24 and 48 hours after preparation. Each time, new sets of insects were being introduced to the different formulations of the essential oils and each experiment was conducted in triplicate.

Extraction of Pesticide Residue

The powdered samples were selected by coning and quartering method and 20 g of each portion was accurately weighed into a Whatman extraction thimble. As described somewhere else (Oyekunle et al., 2001), extraction was performed for 4 hours in a Soxhlet extractor apparatus using dichloromethane (DCM) as the extracting solvent. Using a distillation kit operated at 39-41°C, the extract was concentrated by distilling off the solvent (DCM) to about 3 mL and allowed to cool down to room temperature. Under a stream of high purity nitrogen (99.99%), the extract was finally concentrated further to about 2 mL and then preserved for chromatographic clean up before Gas Chromatographic analysis.

Clean-up Experiment

A slurry form of activated silica gel was prepared in n-hexane before the clean-up experiment. A column of about 15cm×1cm i.d. was then packed with about 5 g of the prepared activated silica gel. To absorb any water in the sample or the solvent, about 0.5 cm3 of anhydrous sodium sulphate was put at the top of the column (Gilles and Alain, 2015). Without exposing the sodium sulphate layer to the atmosphere to avert the adsorbent from drying up and breaking, the column was pre-eluted with 15 mL of n-hexane. The final concentrated extract was poured into the column layer where elution was performed using DCM as the extracting solvent (2 × 10 mL portions). The eluate was collected and dried with anhydrous sodium sulphate. Finally, it was evaporated to dryness under a stream of high purity nitrogen (99.99%).

Gas Chromatographic (GC) Analysis

Prior to the injection of 1µL of the purified extract into the injection part of a Hewlett Packard 5890 Series II Gas Chromatograph, the sample eluate was dissolved in 1mL n-hexane to perform the detection and determination of the insecticide residue. The Hewlett Packard 5890 Series II Gas Chromatograph was equipped with a 63Ni Electron Capture Detector (GC-ECD) and ChemStation Software which was used for the identification and integration of peaks of the analytes. The column comprised 30 m length × 0.32 mm i.d.× 0.25 µm film thickness of a DB-5 fused silica capillary column. The temperature of the column was initially programmed from 60°C to 140°C at a rate of 20°C/min, held for 1 min, and then continued at a rate of 11°C/min up to 250°C, and held for 4 min to enhance good resolution at different boiling points. The injector and the detector temperatures were 250°C and 280°C, respectively. The injection was performed at 250°C on a splitless injector and detector using activation purging time of 30 seconds. Nitrogen was used as the carrier gas at 29.2 cm3/sec measured at 150°C and the run time was 23 minutes. Reference standards and relative retention time techniques were used to identify insecticide residues while the peak areas of the samples were compared with the corresponding peak areas of a known concentrations reference standards to determine the concentration of the residues.

Gas Chromatograph-Mass Spectrometer (GC-MS) Analysis

The composition of the volatile constituents was established by gas chromatography-mass spectrometry. GC-MS equipment with model 7890A was used to carry out the analysis. A micro syringe was washed twice with acetone and 2 µL of the essential oil was pulled into the syringe and then ejected to wash away the acetone. The chart recorder was set to an appropriate flow of 40 µL/min, the temperature of the detector (flame ionization detector) at 250°C, injector at 200°C and the column at the range of 100-200°C. A duration of 60 minutes was set for the evolution to come to completion. The detector detected the various components of the essential oils at different retention time and sends a signal to the chart recorder which results in the peaks of the chart paper.

Statistical Analysis

The experiment was laid out in completely randomized design and data were subjected to analysis of variance. Significant means were separated using Duncan multiple range test at 5% level of significance. Standard deviations indicated the variations among the replicates (Babarinde et al., 2016)

Results and Discussion

Insecticidal Activities

The bud of *E. Caryophyllus, P. umbellatum, M. myristica and P. sylvestris* subjected to steam distillation yielded 0.89%, 0.52%, 0.45% and 0.34% (w/w) of essential oils respectively. Table 1 shows the major components that were determined from the essential oils of *P. sylvestris, M. myristica, P. umbellatum and E. caryophyllus*. The major compounds identified in the essential oils were terpinen-4-ol (21-82%), tri-1,3-octadecenoic acid (25.28%), aromadendrene (13.74%) and eugenol (90.45%). This is in line with what has been reported by Awojide. (Awojide et al., 2016). Tholl (2006) also reported that terpinen-4-ol; 1,8-cineole; verbenone and camphor in eucalyptus oil were active against *A. obtectus* adults. Terpinen-4-ol is a common monoterpenoids in essential oils of natural plants, they have been confirmed to possess insecticidal or repellent activities against a wide range of stored-product insects (Kamanula et al., 2017). Eugenol is the principle compound of the essential oils from basil, the essential oil has a strong repellent effect on mosquitoes and also has toxic effect to the *Bruchid zabrotes* sub *fasciatus* and other storage pests (Wu et al., 2017). The pesticidal and antifeedant activities of eucalyptus oils has been due to some components which includes aromadendrene (Chagas et al., 2002)

Table 1: Major Constituents of Four Essential Oils

Components	% In Sample			
	Piper Umbellatum	*Monodora myristica*	*Eugenia caryophyllus*	*Pinus sylvestris*
Linalool	8.55	9.11	1.73	-
Caryophyllene	10.44	-	3.35	-
Aromadendrene	13.74	-	-	-
γ Bisabolene	8.82	-	-	-
Germacrene	6.56	-	-	-
Sabinol-cis	-	17.87	-	-
tri-1,3-octadecenoic acid	-	25.28	-	-
Palmitic acid	-	7.66	-	-
β Farnescene	-	-	-	-
Terpinen-4-ol	-	-	-	21.82
β Terpineol	-	-	-	14.07
Borneol	-	-	-	6.72
α Terpineol	-	-	-	27.17
Longifolene				5.45
Eugenol			90.45	-
Eugenol acetate			5.1	

The result of the test revealed that at 1, 6 and 12 hours after treatment of the essential oil base insecticides, 100% mortality of Callosbruchus maculatus was observed (Table 2). When the insecticides were used against Callosbruchus maculatus after 24 and 48 hours of its initial formulation, essential oil-formulated insecticides of *P. sylvestris and M. myristica* recorded a decline in the mortality of *C. maculatus* (90%) while all other insecticides recorded 100% mortality of *C. maculatus*.

Table 2: Insecticidal Activity of Commercial and Essential Oil-Formulated Insecticides on Bean Bruchid

Expo-sure Time (Hr)	Aluminium phosphide	Peermethrin	CaPu	*CaEc*	*CaPs*	*CaMm*	$CaCO_3$
1	100% ±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100% ±0.00 [b]	00 ± 0.00 [a]
6	100% ±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100% ±0.00 [b]	00 ± 0.00 [a]
12	100% ±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100% ±0.00 [b]	00 ± 0.00 [a]
24	100% ±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	90%± 5.77 [b]	90% ± 5.77 [b]	00 ± 0.00 [a]
48	100% ±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	100%±0.00 [b]	90%± 5.77 [b]	90% ± 5.77 [b]	00 ± 0.00 [a]

The result shows the mean ± standard deviation of two replicates, each set up with two insects. Data within a row followed by the same letter are not significantly different at P< 0.05.
CaPu- CaCO3 formulated insecticide with P. umbellatum *CaPs- CaCO3 formulated insecticide with P. sylvestris*
CaMm- CaCO3 formulated insecticide with M. myristica *CaEc- CaCO3 formulated insecticide with E. caryophyllus*

The control experiment recorded no mortality of *C. maculatus* all through the duration of the experiment. The percentage mortality of *C. maculatus* when it was exposed to the insecticides of Aluminium phosphate, permethrin and the four (4) formulated essential oil-based insecticides using clay as the carrier is shown in Table 3. The result revealed that C. maculatus that were exposed to the different insecticides had 100% knockdown after 1, 6 and 12 h for all insecticides except in the insecticides formulated using *M. myristica* which showed a decline to 90% mortality of *C. maculatus* at 12, 24 and 48 h after treatment. Pinus sylvestris formulated insecticide likewise recorded a decline of 90% knockdown after 48 h. Some studies have also revealed that the oils of Agastache foeniculum, Anethum graveolens, *Cuminum cyminum, Foeniculum vulgare* and *Satureja hortensis* had strong effects on adults of C. maculatus (Keita et al., 2001; Ketoh et al., 2005 and Negahban et al.,

2017). It was also reported that there were differences in the insecticidal effects of these essential oils; all of them had significant fumigant activity on the *C. maculatus*. These findings clearly support the results of the present study for susceptible of *C. maculatus* to the plant essential oils. To the best of our knowledge, there are no reports on the comparison of formulated insecticides from essential oil on insects.

Table 3: Insecticidal Activity of Commercial and Formulated Insecticides with Sio_2 (Clay) on Bean Bruchid

Expo-sure Time(Hr)	Aluminium phosphide	Permethrin	ClPu	ClEc	ClPs	ClMm	Clay
1	100% ±0.00^b	100%±0.00^b	100% ±0.00^b	100%±0.00^b	100%±0.00^b	100% ±0.00^b	00 ± 0.00^a
6	100% ±0.00^b	100%±0.00^b	100% ±0.00^b	100%±0.00^b	100%±0.00^b	100% ±0.00^b	00 ± 0.00^a
12	100% ±0.00^b	100%±0.00^b	100% ±0.00^b	100%±0.00^b	100%±0.00^b	90% ±5.77^b	00 ± 0.00^a
24	100% ±0.00^b	100%±0.00^b	100% ±0.00^b	100%±0.00^b	100%±0.00^b	90% ± 5.77^b	00 ± 0.00^a
48	100% ±0.00^b	100%±0.00^b	100% ±0.00^b	100%±0.00^b	90%± 5.77^b	90% ± 5.77^b	00 ± 0.00^a

Values are mean ± standard deviation of triplicate replicates, each set up with two insects. Data within a row followed by the same letter are not significantly different at $p<0.05$.
ClPu- Clay formulated insecticide with P. umbellatum *ClPs- Clay formulated insecticide with P. sylvestris*
ClMm- Clay formulated insecticide with M. myristica *ClEc- Clay formulated insecticide with E. caryophyllus*

Pesticide Residue Analysis

Table 4 revealed the pesticide residue observed after the analysis of the various insecticides. The result showed that no pesticide residue was detected in all of the essential oil formulated insecticides. Aluminium phosphide is a highly toxic pesticide, it is known as a mitochondrial toxin, which causes death (Iyanda and Iheakanwa, 2013). For Aluminium phosphide, twenty-one pesticides residues where detected, while twenty was detected in permethrin. Phosphine (0.45 mg/Kg) was recorded in Aluminium phosphide but was not detected in Permethrin. Phosphine at low concentration can cause headache, dizziness, nausea, drowsiness and more serious exposure can cause shock, convulsion, coma, irregular heartbeat and kidney damage (Iyanda and Theakanwa, 2013).

The pesticides residues observed in Aluminium phosphide were higher than those detected in permethrin except for cypermethrin which had a value of 3.48 mg/Kg in permethrin and 2.58 mg/Kg in Aluminium phosphide. Cypermethrin has been recognized as a broad-spectrum insecticide that kills both beneficial insects and the targeted insects (WHO, 1989). Out of the twenty-one (21) pesticides residues observed in Aluminium phosphide, fifteen (15) were higher than the maximum residue limits (MRLs) while in the case of permethrin thirteen (13) of the pesticide residues were higher than the MRLs which was taken from FAO/WHO codex Alimentarium commission 1993. Some of the pesticide residues with higher values above the MRLs include cypermethrin which ranged between 3.58-3.48 mg/Kg, dichlorvos which ranges between 0.39-0.42 mg/Kg others includes Oxamyl, cyanazine, pentachlorophenol, fenoprop, alachlor, Aldrin, metolachlor. Simazine had a higher pesticide residue in aluminium phosphide (0.59 mg/Kg) but had a value lower than the MRL in permethrin (0.15 mg/Kg. Atrazine, Carbofuran, Dichlorprop, Primphosmethyl and chlorpyrifos recorded values that were lower than the MRLs in Aluminium phosphide and permethrin. Several people had worked on the pesticide residues. The presence of pesticide residues in selected varieties of mango of which cypermethrin was found in the range of 0.19-0.28 mg/Kg which was lower than the permissive limit had been reported (Hussain et al., 2002). Also, the study of Anzene et al., (2014) on organochloride pesticide residue on cereal grains showed that quiet numbers of pesticides residues were detected such as Methoxychlor (0.03 to 1.17), Aldrin (0.03 to 0.13 mg/kg), Lindane (0.25 to 1.25 mg/kg), Dieldrin (0.018 to 0.02 mg/kg). Thus, the levels of Aldrin present in all the grains were found to be above the FAO/WHO recommended MRLs value of 0.02 mg/kg for cereal grains. This is the same as reported in this work where the values of Aldrin in both insecticides of aluminium phosphide (0.28 mg/Kg) and permethrin (0.27 mg/Kg) were above the Maximum residual limits.

Table 4: Pesticide Residues in Cowpea Grains Treated with Selected Insecticides

	Synthetic Insecticides		Control		Formulated Insecticides				
Pesticide residue (compound)	**Aluminium Phosphide** (mg/kg)	**Perme-thrin** (mg/kg)	**Clay (SiO_2)** (mg/kg)	**$CaCO_3$** (mg/kg)	**CaPs** (mg/kg)	**CaEc** (mg/kg)	**CaPs** (mg/kg)	**CaMm** (mg/kg)	**MRLs** Standard level(mg/kg)[3]
Phosphine	0.45±0.01	0.10±0.02	N D	N D	N D	N D	N D	N D	0.10
Simazine	0.59±0.01	0.15±0.01	N D	N D	N D	N D	N D	N D	0.20
Atrazine	0.20±0.01	0.10±0.02	N D	N D	N D	N D	N D	N D	0.25
Dichlorvos	0.42±0.03	0.39±0.01	N D	N D	N D	N D	N D	N D	0.10
Oxamyl	0.47±0.02	0.45±0.03	N D	N D	N D	N D	N D	N D	0.01
Carbofuran	0.17±0.01	0.12±0.02	N D	N D	N D	N D	N D	N D	0.50
Dichlorprop	0.25±0.03	0.13±0.01	N D	N D	N D	N D	N D	N D	3.00
Cyanazine	0.23±0.01	0.13±0.01	N D	N D	N D	N D	N D	N D	0.05
Pentachlrophenol	0.27±0.01	0.19±0.02	N D	N D	N D	N D	N D	N D	0.20
Fenoprop	0.40±0.01	0.28±0.02	N D	N D	N D	N D	N D	N D	0.01
Alachlor	0.27±0.01	0.18±0.03	N D	N D	N D	N D	N D	N D	0.02
Fenitrothion	0.20±0.04	0.12±0.03	N D	N D	N D	N D	N D	N D	0.20
Pendimethalin	0.19±0.01	0.11±0.02	N D	N D	N D	N D	N D	N D	0.02
Metolachlor	0.42±0.01	0.34±0.01	N D	N D	N D	N D	N D	N D	0.10
Cypermethrin	2.58±0.20	3.48±0.10	N D	N D	N D	N D	N D	N D	0.30
Phosphamidon	0.19±0.02	0.14±0.01	N D	N D	N D	N D	N D	N D	0.02
Primiphosmethyl	0.22±0.01	0.17±0.01	N D	N D	N D	N D	N D	N D	7.00
Pyriproxyfen	0.31±0.01	0.28±0.01	N D	N D	N D	N D	N D	N D	0.01
Endosulfan	0.30±0.03	0.19±0.01	N D	N D	N D	N D	N D	N D	0.01
Aldrin	0.28±0.01	0.27±0.03	N D	N D	N D	N D	N D	N D	0.02
Chlorpyrifos	0.40±0.01	0.32±0.01	N D	N D	N D	N D	N D	N D	1.00

N D Stands for not detected. Source: FAO/WHO Codex Alimentarius Commission (1993).
CaPu- CaCO3 formulated insecticide with P. umbellatum
CaPs- CaCO3 formulated insecticide with P. sylvestris
CaMm- CaCO3 formulated insecticide with M. myristica
CaEc- CaCO3 formulated insecticide with E. caryophyllus
N.D- Not detected MRLs- Maximum Residual Limits

Although pesticide residues found in food or grains does not necessarily imply that it is hazardous, the people who are at a higher risk are those who are directly exposed to these chemicals either by way of being involved in the application or they live in the immediate environment where the pesticides are applied. Most at times those who are not from the area of application may also be at risk by exposure to a lower level of pesticides residues via the food chain or water bodies. To consider a pesticide unsafe, the residues detected have to be present in unacceptable quantities (Kostik et al., 2014). Often, most of these chemical residues display bioaccumulation and these could build up to an unacceptable level and becoming harmful in the body as well as in the environment (Ogah et al., 2011).

Conclusion

The insecticide formulated from the four essential oils in this study has proven to be effective like the synthetic insecticides of aluminium phosphide and permethrin. They have been found to also record high efficacy against *C. maculatus* after forty-eight hours of its formulation. The result obtained has also revealed that the insecticides formulated from the four essential oils, did not record any pesticides residue which indicates its safety concerning health effects resulting from pesticide residues.

References

Alavanja, M.C. (2009). Introduction: pesticides use and exposure extensive worldwide. Reviews on environmental health 24(4): 303–309.

Awojide, S.H., Labumi, L., Owolabi, J.B. (2015). Chemical composition and bioactivity of essential oil from Piper umbellatum against grain storage insects. Canadian Journal of Pure and Applied Sciences, 9(3): 3621-3627.

Awojide, S.H., Labumi, L., Owolabi, J.B. (2016). Chemical composition and bioactivity of four plants essential oils from Nigeria against Macrotermes subhyalinus. American Chemical Science Journal, 13(2): 1-8, 2016.

Ayvaz, A., Sagdic, O., Karaborklu, S. Ozturk, I. (2010). Insecticidal activity of the essential oils from different plants against three stored product insects. Journal of Insect Science. 10 (21):1-13.

Babarinde, S.A. Oladoye, S.O., Adesina, G.O., Adebayo, M.A. (2016). Chemical Composition and Bioactivity of Lippia adoensis Hochst ex. Walp (Verneneaceae) Leaf essential oil against Callosobruchus maculatus Fabricius (Coleoptera: Chrysomelidae). Journal of Northeast Agricultural University 23(4): 8-14.

Babarinde, S.A., Pitan, O.O.R., Olatunde, G.O., Ajala, M.O. (2017) Chemical composition of the essential oil of Nigeria grown Hoslundia opposita Vahl (Lamiaceae) dried leaves and its bioactivity against cowpea Seed Bruchid. Chemistry and Biodiversity 14 (6) DOI: 10.1002/cbdv.201600418.

Casas, A.Z.D. (2004). Bioremediation of the organophosphate methyl parathion using genetically engineered and native organisms. M.Sc. Thesis, Texas A&M University 135.

Chagas, A.C.S., Passos, W.M., Prates, H.T., Leitem, R.C., Furlong, J., Fortes, I.C.P. (2002). Acaricide effect of Eucalyptus spp. essential oils and concentrated emulsion on Boophilus microplus. Brazilian Journal of Veterinary Research and Animal Science, 39: 247–253.

FAO/WHO., 1993 Codex Alimentarius Commission, Codex Committee on Pesticide Residues, Rome, Supplement 1, Vol. 2, pg. 133.

Fayemiwo, K.A., Adeleke, M.A., Okoro, O.P., Awojide, S.H. and Awoniyi, I.O. (2014). Larvicidal efficacies and chemical composition of essential oils of Pinus sylvestris and Syzygium aromaticum against mosquitoes. Asian Pacific journal of tropical biomedicine, 4: 30-34.

Ghorab, M.A. and Khalil, M.S. (2015). Toxicological Effects of Organophosphates Pesticides. International Journal of Environmental Monitoring and Analysis 3: 218-220.

Ghorab, M.A. and Khalil, M.S. (2015). Toxicological Effects of Organophosphates Pesticides. International Journal of Environmental Monitoring and Analysis, 3: 218-220.

Ghorab, M.A. and Khalil, M.S. (2016). The effect of pesticide pollution on our life and environment. Journal of Pollution Effect and Control, 4:159.

Gilles, B. and Alain, F. (2015). Pesticide Contamination of the Coastline of Martinique, Marine Pollution Bulletin, 51:612-619.

Gupta, R.C. (2006). Toxicology of Organophosphate & Carbamate Compounds. Chapter 26, Elsevier Academic Press, Amsterdam 371-380.

Hussain, S., Masud, T. and Ahad, K. (2002). Determination of Pesticides Residues in Selected varieties of Mango. Pakistan Journal of Nutrition, 1(1): 41-42.

Isman, M.B. (2006). Botanical insecticides, deterrents, and repellents in modern agriculture and an increasingly regulated world. Annu Rev Entomol. 51:45-66.

Iyanda, A.A. and Iheakanwa, C.I. (2013). Damaging effects of phosphide- powder residue on brain, lung and heart histoarchitecture in rats. Asian Journal of Biomedical and Pharmaceutical Sciences, 3(17): 9-13.

Kamanula, J.F., Belmain, S.R., Hall, D.R., Farman, D.I., et al. (2017). Chemical variation and insecticidal activity of Lippia javanica (Burm. f.) Spreng essential oil against Sitophilus Zeamais Motschulsky. Ind Crop Prod 110:75–82

Keita, S.M., Vincent, C., Schmit, J.P., Arnason, J.T. and Langer, A.B. (2001). Efficacy of essential oil of Ocimum basilicum L. and O. gratissimum L. applied as an insecticidal fumigant and powder to control Callosobruchus maculatus F. [Coleoptera: Bruchidae]. J. Stored Prod. Res. 37: 339-349. 17.

Ketoh, G.K., Koumaglo, H.K. and Glitho, I.A. (2005). Inhibition of Callosobruchus maculatus F. (Coleoptera: Bruchidae) development with essential oil extracted from Cymbopogon schoenanthus L. Spreng. (Poaceae), and the wasp Dinarmus basalis (Rondani) (Hymenoptera: Pteromalidae). J. Stored Prod. Res. 41: 363-371

Kostik, V., Angelovska, B., Kiroska-Petreska, E. and Bauer, B. (2014). Determination of Pesticide Residues in Plant-Based Foods from the Republic of Macedonia, Journal of Food and Nutrition Sciences. 2(4):124-129.

McCauley, L.A. (2006). Organophosphates and the Gulf War Syndrome, In: Toxicology of Organophosphate and Carbamate Compounds, Editor: Ramesh C. Gupta, Academic Press, Pages 69-78, ISBN 9780120885237, https://doi.org/10.1016/B978-012088523-7/50007-7.

Navarro, S. (2006). Modified Atmospheres for the Control of Stored-Product Insects and Mites, in: Insect Management for Food Storage and Processing. Heaps, J. W. Ed., AACC International, St. Paul, MN, pp. 105–146.

Negahban, M., Moharramipour, S. and Sefidkon, F. (2007). Fumigant toxicity of essential oil from Artemisia sieberi Besser against three stored-product insects. J. Stored Prod. Res. 43: 123- 128.

Ogah, C.O., Coker, H.B. and Adepoju-Bello, A.A. (2011). Organophosphate and carbamate pesticide residues in beans from markets in Lagos State,

Nigeria. Journal of Innovative Research in Engineering and Sciences, 2(1): 50-59.

Osman, K.A., Ibrahim, G.H., Askar, A.I., Rahman, A. and Alkhail, A. (2008) Biodegradation kinetics of dicofol by selected microorganisms. Pesticide Biochemistry and Physiology 91: 180-185.

Oyekunle, J.A.O., Ogunfowokan, A.O., Torto, N. and Akanni, M.S. (2011). Determination of pesticides in the agricultural soil of Oke-Osun farm settlement, Osogbo, Nigeria. Environmental Monitoring and Assessment, 177:51-61.

Pereira, S. G., Sanaveerappanavar, V. T., and Murthy, M. S. (2006). Geographical variation in the susceptibility of the diamondback moth Ptlutella xylostella L. to Bacillus thuringiensis products and acyl urea compounds. Pest Management, 15: 26–26.

Petraitis, J., Jarmalaitė, I., Vaičiūnas, V., et al. (2013). A review of research studies into pesticide residues in food in Lithuania. Zemdirbyste-Agriculture, 100: 205-214.

Regnault-Roger, C., Vincent, C., and Arnason, J. T. (2012). Essential oils in insect control: Low-risk products in a high-stakes world. Annual Review of Entomology, 57:405–424.

Sanon, A., Zakaria, I., Clémentine L., D. B., Niango, B. M., Honora, N., 2018. Potential of Botanicals to Control Callosobruchus maculatus (Col.: Chrysomelidae, Bruchinae), a Major Pest of Stored Cowpeas in Burkina Faso: A Review. Int. J. Insect Sci., 10: 1179543318790260. https://doi.org/10.1177/1179543318790260

Tholl, D. (2006). Terpene synthases and the regulation, diversity and biological roles of terpene metabolism. Current Opinion in Plant Biology, 9:297–304.

Toloza, A.C., Zygadlo, J., Cueto, G.M., Biurrun, F., Zerba, E., and Piccolo, M.S. (2006). Fumigant and repellent properties of essential oils and component compounds against permethrin-resistant Pediculus humanus capitis (Anoplura: Pediculidae) from Argentina. Journal of Medical Entomology, 43(5), 889–895. https://doi.org/10.1093/jmedent/43.5.889

World Health Organization. (1989). Environmental Health Criteria. Cypermethrin. (Vol. 82). Geneva: United Nations.

Wu, Y., Guo, S., Huang, D., Wang, C., Wei, J., Li, Z., et al. (2017). Contact and repellant activities of zerumbone and its analogues from the essential oil of Zingiber zerumbet (L.) Smith against Lasioderma serricorne. Journal of Oleo Science, 66(4), 399–405. https://doi.org/10.5650/jos.ess16166

Zhang, Z., Pang, X., Guo, S.S., Cao, J.Q., Wang, Y., et al. (2019). Insecticidal activity of Artemisia frigida Wild. Essential oil and its constituents against three stored product insects. Rec Nat Prod 13(2):176–181.