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Assessment of the Toxicity of Natural Oils from *Mentha piperita*, *Pinus roxburghii*, and *Rosa* spp. Against Three Stored Product Insects

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Abstract: Three natural oils extracted from *Mentha piperita*, *Pinus roxburghii*, and *Rosa* spp. were assessed in order to determine their insecticidal activity against the adults of three stored product insects: the rice weevil (*Sitophilus oryzae* L.), the lesser grain borer (*Rhyzopertha dominica*, Fabricius), and the red flour beetle (*Tribolium castaneum*, Herbst.). By Gas chromatography–mass spectrometry (GC/MS) analysis, the main compounds in the n-hexane oil from *Rosa* spp. were determined to be methyl eugenol (52.17%), phenylethyl alcohol (29.92%), diphenyl ether (7.75%), and geraniol (5.72%); in the essential oil from *M. piperita*, they were menthone (20.18%), 1,8-cineole (15.48%), menthyl acetate (13.13%), caryophyllene (4.82%), β-pinene (4.37%), and D-limonene (2.81%); and from the foliage of *P. roxburghii*, they were longifolene (19.52%), caryophyllene (9.45%), Δ-3-carene (7.01%), α-terpineol (6.75%), and γ-elemene (3.88%). *S. oryzae* and *R. dominica* were reared using sterilized wheat grains, and *T. castaneum* was reared on wheat flour mixed with yeast (10:1, w/w), all under laboratory conditions (27 ± 1 °C and 65% ± 5% Relative humidity (R.H). Two toxicity bioassays were used, as well as contact using thin film residues and fumigation bioassays. The results indicated that *M. piperita* caused a high toxicity for *S. oryzae* compared to other insects. High significant variations were observed between the tested *M. piperita* doses against the stored insects, and this natural material could be used to control insects that infect the grains. Also, the data indicated that the *Rosa* spp. oil had a low-toxicity effect against these insects compared to other oils. We recommend using natural oils against the stored weevils and petals, rather than the chemical agent, so as to serve human health.

Keywords: natural plant oils; contact film; fumigation; bioassay; GC-MS analysis; *Mentha piperita*; *Rosa* spp.; *Pinus roxburghii*; stored product insects

1. Introduction

Currently, the post-harvest losses of stored cereals range from 10%–20% of the overall yearly production and are caused by insect damage, microbial deterioration, and other factors [1]. A large

part of these losses is caused by stored product insect pests, which damage the quality and quantity of grains [2].

Rice weevil *S. oryzae* L. (Coleoptera: Curculionidae) and the lesser grain borer *R. dominica* (Coleoptera: Bostrichidae) are major insects of stored grains, with both the adults and larvae feeding on whole grains. They attack wheat, corn, sorghum barley, dried beans, and cereal. They cause weight loss in grains, and they affect the quality of grains and stored products worldwide [3]. The red flour beetle, *Tribolium castaneum* (Coleoptera: Tenebrionidae), is a secondary pest of stored foods [4]. It feeds on broken grain, cereals, milled grain products, dried pet food, chocolate, nuts, and cereals previously infected with insects, and they cause serious economic losses [5].

Chemical control is most commonly used to control these insects, which include insecticides such as organophosphates, pyrethroids, and fumigants such as methyl bromide and phosphine, which are toxic to stored-grain pests [6,7]. These chemicals have several problems for the environment, although they are effective for pest control [8,9]. Besides these problems, their toxicity to nontarget organisms and human health are also of concern [10]. Therefore, we need to find new alternatives for the control methods of stored product insects, such as plant essential oils (EOs) and their constituents, which are effective and safe alternatives with low mammalian toxicity and biodegradation and are available in developing countries [11]. Several studies have described the toxicity of EOs and extracts, such as fumigants, repellents, ovicides, larvicides, insecticides, and insect growth regulators as well as their compounds, against many stored product insects [12–16]. Commercially, rose is cultivated for producing the "liquid gold" EO [17], which is confined to the fields of food, perfumes, cosmetics, and medicine. In dozens of studies, rose oil has been used for natural additives as an antibacterial, antifungal, and antioxidant agent [18,19]. There are several bioactive compounds identified in rose oil, such as citronellol, methyl eugenol geraniol, nerol, phenylethyl alcohol, nonadecane, eicosane, nonadecene, heneicosane, damascenones, and β-ionones [20–22]. Phenylethyl alcohol, abundant in rose flowers, has a rose-like odor, being one of the dominant scents emitted from the Damask rose [23]. Phenylethyl alcohol may occur in the volatile compounds of the Damask rose as phenyl ethyl alcohol-β-D-glucoside [24,25].

The EO of peppermint (*M. piperita*) is widely used in food and drink, condiments, cosmetics, pharmaceuticals, and biological activities [26,27]. The EOs of *Mentha* leaves show the presence of menthol, menthone, limonene, trans-carveol, pulegone, β-caryophyllene, pipertitinone oxide, and eucalyptol, which have been identified as the major components [28–30]. The oil has been shown to have potential antimicrobial and insecticidal activities against a wide range of pathogens [31–33].

The EOs extracted from different parts of *Pinus roxburghii*, such as wood, bark, and needles, include several bioactive chemical constituents such as caryophyllene, thunbergol, 3-carene, cembrene, α-thujene, terpinolen, α-pinene, α-caryophyllene, cembrene, longifolene, α-terpineol, caryophyllene oxide, β-pinene, and longifolene [34–37]. These EOs have been reported to have potential antimicrobial activities [35,37–39].

This study aimed to evaluate the toxicity effects of natural oils from *M. piperita*, *Rosa* spp., and *P. roxburghii*, using two methods—contact and fumigation toxicity bioassays—against three stored product insects, *S. oryzae*, *R. dominica*, and *T. castaneum*. The chemical profile of the oils was observed using Gas chromatography–mass spectrometry (GC/MS) analysis.

2. Materials and Methods

2.1. Plant Materials and Preparation of the Essential Oils

Essential oils from *M. piperita* (leaves) and *P. roxburghii* (foliage) were extracted using the Clevenger apparatus method, where about 100 g of the fresh material was subjected to 3 h of a hydro-distillation procedure. The resulting oils were separated from the aqueous phase, dried over anhydrous Na_2SO_4 (Sigma-Aldrich, Darmstadt, Germany), weighed, and the reported yield was calculated with respect

to the mass of the fresh weight of the leaves (mL/100 g fresh weight). The oil was kept dry in sealed brown bottles and stored at 4 °C before the chemical analysis [40].

The *Rosa* spp. (flowers) oil was extracted using an n-hexane solvent (Loba Chemie Pvt. Ltd., laboratory reagents & fine chemicals, Mumbai, India), according to the method of Patrascu and Radoiu [41], with minor modifications, where about 50 g of fresh flowers were extracted using a soaking method in 150 mL of n-hexane for 6 h.

2.2. GC-MS Analysis of the Oils

The chemical composition of the oils was performed using a Trace GC 1300-TSQ Quantum mass spectrometer with a direct capillary column TG–5MS (30 m × 0.25 mm × 0.25 µm film thickness) (Thermo Scientific, Austin, TX, USA). The column oven temperatures and program can be found in previous work [15]. The components were identified by comparing their retention times and mass spectra with those of the WILEY 09 and NIST 14 mass spectral databases. The Xcalibur data system (3.0, Thermo Fisher Scientific Inc., Austin, TX, USA, 2014) of GC/MS with threshold values was used to confirm that all of the mass spectra (MS) were attached to the library by measuring the standard index (SI) and reverse standard index (RSI), where a value of ≥650 was acceptable to confirm the compounds [42–45].

2.3. Insect Culture

S. oryzae (Coleoptera: Curculionidae) and *R. dominica* (Coleoptera: Bostrichidae) were reared under laboratory conditions (27 ± 1 °C and 65% ± 5% Relative humidity (R.H) using sterilized wheat grains, and *T. castaneum* (Coleoptera: Tenebrionidae) was reared on wheat flour mixed with yeast (10:1, w/w), both in 1 L glass jars that were covered with a fine mesh cloth for ventilation [46]. The adult insects used in the toxicity tests were about one to two weeks old. All of the experimental procedures were carried out under the same conditions as the culture.

2.4. Contact Toxicity Bioassay

The insecticidal activity of the different EOs was assessed using a film residue method [47]. Bioassays were done in Petri dishes (9 cm in diameter) (Adge industries, Ahmedabad, India). Then, 1 mL of the dilution was spread on the surface of the Petri dishes. The acetone solvent (El Nasr Pharmaceutical chemicals Co, Alexandria, Egypt) was allowed to evaporate for few minutes, leaving a thin film of EOs on the floor of the dishes. The control Petri dishes were treated with acetone alone. Twenty adults each of *S. oryzae*, *R. domonica*, and *T. castanium* (one to two weeks old) were released separately into each Petri dish and were covered. Three replicates of each treatment, each insect species, and control were set up. The mortality was recorded after 48 and 72 h, and the Lethal Concentration 50% (LC_{50}) values were calculated [48].

2.5. Fumigation Toxicity Bioassay

The vapor toxicity of the three evaluated oils against the adults of *S. oryzae*, *R. domonica*, and *T. castanium* were investigated by transferring twenty adults into glass jars (250 mL) (Adge industries, Ahmedabad, India) containing 10 g of wheat grains and exposing them to vapors with different doses of oils dissolved in 100 µL of acetone and applied to filter paper (9 cm diameter). The treated filter papers were attached to the inner surface of the screw lids of the jar using adhesive tape, which was made to be airtight, after allowing the solvent to evaporate for 5 min. The control jars were treated with acetone alone. All of the treatments and controls were replicated three times [47,49]. The mortality percentage (M%) was determined after 24, 48, and 72 h, and the LC_{50} values were calculated as previously described and the values were presented as mean ± standard deviation.

3. Results

3.1. Chemical Composition of the Oils

Table 1 shows the chemical composition of the n-hexane oil from *Rosa* spp., where the main compounds were methyl eugenol (52.17%), phenylethyl alcohol (29.92%), diphenyl ether (7.75%), geraniol (5.72%), and geranyl acetate (2.58%). Table 2 presents the chemical compounds identified in the EO of *M. piperita*. The main compounds were menthone (20.18%), 1,8-cineole (15.48%), menthyl acetate (13.13%), caryophyllene (4.82%), *β*-pinene (4.37%), D-limonene (2.81%), and *α*-pinene (2.25%).

The chemical composition of the EO from the foliage of *P. roxburghii* is shown in Table 3. The main compounds in the EO were longifolene (19.52%), caryophyllene (9.45%), Δ-3-carene (7.01%), *α*-terpineol (6.75%), *γ*-elemene (3.88%), aromadendrene (3.51%), *α*-caryophyllene (3.45%), pentadecane (3.35%), hexadecane (2.38%), tetradecane (2.75%), borneol (2.16%), *α*-pinene (2.12%), 3-(2-methyl-propenyl)-1H-indene (1.98%), 1,7-dimethyl-naphthalene (1.84%), 2,6,10-trimethyl tetradecane (1.83%), longicyclene (1.80%), and terpinen-4-ol (1.77%).

Table 1. Chemical composition of the oil from *Rosa* spp.

Compound Name	RT * (min.)	Relative Peak Area (%)	Molecular Formula	Molecular Weight	Standard Index	Reverse Standard Index
Methyl eugenol	13.77	52.17	$C_{11}H_{14}O_2$	178	692	766
3-O-Benzyl-d-glucose	13.98	0.99	$C_{13}H_{18}O_6$	270	639	642
Phenylethyl alcohol	14.24	29.92	$C_8H_{10}O$	122	795	833
Geraniol	14.42	5.72	$C_{10}H_{18}O$	154	874	886
Neryl acetate	18.81	0.88	$C_{12}H_{20}O_2$	196	739	837
Geranyl acetate	18.96	2.58	$C_{12}H_{20}O_2$	196	764	855
Diphenyl ether	22.03	7.75	$C_{12}H_{10}O$	170	903	917

* RT: Retention time (min).

Table 2. Chemical composition of the oil from *Mentha piperita*.

Compound Name	RT* (min)	Relative Peak Area	Molecular Formula	Molecular Weight	Standard Index	Reverse Standard Index
α-Pinene	5.31	2.25	$C_{10}H_{16}$	136	923	927
β-Pinene	6.78	4.37	$C_{10}H_{16}$	136	909	914
D-Limonene	8.12	2.81	$C_{10}H_{16}$	136	905	924
1,8-Cineole	8.94	15.48	$C_{10}H_{18}O$	154	897	933
Menthone	14.14	20.18	$C_{10}H_{18}O$	154	862	876
Neoisomenthol	14.46	0.69	$C_{10}H_{20}O$	156	838	862
Menthol	15.05	32.66	$C_{10}H_{20}O$	156	881	887
Menthyl acetate	16.75	13.13	$C_{12}H_{22}O_2$	198	888	910
Pulegone	16.99	1.09	$C_{10}H_{16}O$	152	870	870
Piperitone	17.45	0.52	$C_{10}H_{16}O$	152	797	855
Caryophyllene	19.14	4.82	$C_{15}H_{24}$	204	906	906
α-Caryophyllene	20.02	0.61	$C_{15}H_{24}$	204	861	866
Eugenol	20.31	0.13	$C_{10}H_{12}O_2$	164	839	876
α-Muurolol	20.65	0.14	$C_{15}H_{26}O$	222	859	900
α-Muurolene	21.09	0.14	$C_{15}H_{24}$	204	866	893

* RT: retention time (min).

Table 3. Chemical composition of the oil from *Pinus roxburghii*.

Compound Name	RT * (min)	Relative Peak Area (%)	Molecular Formula	Molecular Weight	Standard Index	Reverse Standard Index
α-Pinene	5.79	2.12	$C_{10}H_{16}$	136	946	947
β-Pinene	6.98	1.64	$C_{10}H_{16}$	136	935	942
Δ-3-Carene	7.78	7.01	$C_{10}H_{16}$	136	954	955
D-Limonene	8.40	1.39	$C_{10}H_{16}$	136	905	912
Terpinolene	10.00	1.02	$C_{10}H_{16}$	136	935	939
Fenchol	11.13	1.28	$C_10H_{18}O$	154	940	944
cis-4-Thujanol	12.21	0.41	$C_{10}H_{18}O$	154	789	815
Borneol	12.69	2.16	$C_{10}H_{18}O$	154	928	932
Terpinen-4-ol	12.90	1.77	$C_{10}H_{18}O$	154	937	947
α-Terpineol	13.36	6.75	$C_{10}H_{18}O$	154	937	943
2,6,10-Trimethyl tetradecane	15.06	0.22	$C_{17}H_{36}$	240	777	802
α-Fenchyl acetate	15.69	0.73	$C_{12}H_{20}O_2$	196	902	937
Tridecane	15.91	0.93	$C_{13}H_{28}$	184	837	936
Butanoic acid,3-[(1-phenylethyl-2-propynyl)oxy]	16.79	0.41	$C_{15}H_{18}O_3$	246	668	703
Terpinyl propionate	16.98	0.55	$C_{13}H_{22}O_2$	210	769	790
Hexahydrofarnesol	17.20	0.30	$C_{15}H_{32}O$	228	699	724
γ-Elemene	17.37	3.88	$C_{15}H_{24}$	204	846	865
2,6,10-Trimethyl tetradecane	17.60	0.55	$C_{17}H_{36}$	240	750	791
Geranyl isovalerate	17.77	0.18	$C_{15}H_{26}O_2$	238	701	703
Cedrol	17.86	1.21	$C_{15}H_{26}O$	222	703	768
Longicyclene	18.05	1.80	$C_{15}H_{24}$	204	902	905
Sativene	18.50	0.91	$C_{15}H_{24}$	204	882	905
Tetradecane	18.56	2.75	$C_{14}H_{30}$	198	902	951
β-Cedrene	18.75	0.29	$C_{15}H_{24}$	204	726	755
Longifolene	19.03	19.52	$C_{15}H_{24}$	204	967	967
Caryophyllene	19.22	9.45	$C_{15}H_{24}$	204	912	927
(Z,E)-2,9-Heptadecadiene-4,6-diyn-8-ol	19.36	0.75	$C_{17}H_{24}O$	244	635	683

Table 3. *Cont.*

Compound Name	RT * (min)	Relative Peak Area (%)	Molecular Formula	Molecular Weight	Standard Index	Reverse Standard Index
1,4-Dimethyl naphthalene	19.52	1.31	$C_{12}H_{12}$	156	855	944
1,7-dimethyl-Naphthalene	19.65	1.84	$C_{12}H_{12}$	156	855	947
2-Methyl-cis-7,8-epoxynonadecane	19.88	0.32	$C_{20}H_{40}O$	296	626	631
2,6,10-trimethyl tetradecane	20.01	1.83	$C_{17}H_{36}$	240	710	753
α-Caryophyllene	20.16	3.45	$C_{15}H_{24}$	204	762	897
E-8-Methyl-9-tetradecen-1-ol acetate	20.33	0.30	$C_{17}H_{32}O_2$	268	691	700
β-Cedrene	20.48	0.76	$C_{15}H_{24}$	204	674	695
Vitamin A aldehyde (Retinal)	20.85	0.18	$C_{20}H_{28}O$	284	749	859
Pentadecane	21.08	3.35	$C_{15}H_{32}$	212	888	958
6-(3-Isopropenyl-1-cyclopropen-1-yl)-6-methyl-3-hepten-2-one	21.27	0.35	$C_{14}H_{20}O$	204	710	719
3-(2-Methyl-1-propenyl)-1H-indene	21.69	0.63	$C_{13}H_{14}$	170	683	803
2,3,6-Trimethyl naphthalene	22.14	1.09	$C_{13}H_{14}$	170	786	829
cis-9,10-Epoxystearic acid	22.45	0.32	$C_{18}H_{34}O_3$	298	667	667
3-(2-Methyl-propenyl)-1H-indene	22.61	1.98	$C_{13}H_{14}$	170	734	809
Caryophyllene oxide	23.35	1.62	$C_{15}H_{24}O$	220	876	928
Hexadecane	23.47	2.38	$C_{16}H_{34}$	226	862	940
Longiborneol	23.92	0.65	$C_{15}H_{26}O$	222	780	900
1,9-Dioxacyclohexadeca-4,13-diene-2-10-dione,7,8,15,16-tetramethyl-	24.04	0.44	$C_{18}H_{28}O_4$	308	666	671
Docosane	24.48	0.58	$C_{22}H_{46}$	310	686	686
Z-5-Methyl-6-heneicosen-11-one	24.91	0.38	$C_{22}H_{42}O$	322	677	686
2-Methylene-5α-cholestan-3β-ol	25.11	0.24	$C_{28}H_{48}O$	400	682	731
Aromadendrene	25.43	3.51	$C_{15}H_{24}$	204	834	880
Heptadecane	25.75	1.53	$C_{17}H_{36}$	240	854	899
Octadecane	27.93	0.53	$C_{18}H_{38}$	254	796	813
8(14),15-Pimaradien-18-al	34.07	0.17	$C_{20}H_{30}O$	286	761	834
γ-Sitosterol	34.48	0.16	$C_{29}H_{50}O$	414	741	756

* RT: retention time (min).

3.2. Contact and Fumigant Toxicity Methods

The results of the contact toxicity of the three natural extracted oils were obtained from *M. piperita*, *Rosa* spp., and *P. roxburghii*, and their efficiency was tested against stored insects such as *S. oryzae*, *T. castaneum*, and *R. dominica*, as found in Table 1. The results of *M. piperita* by contact toxicity in Table 4 showed that with the increase of time to 72 h, the LC_{50} (mg/cm^2) values decreased from 0.036 mg/cm^2 (range of 0.030–0.042 at 48 h) to 0.022 mg/cm^2 (range of 0.019–0.026 at 72 h), 0.083 mg/cm^2 (range of 0.069–0.102) to 0.055 mg/cm^2 (range of 0.044–0.070), and from 0.088 mg/cm^2 (range of 0.088–0.099) to 0.084 mg/cm^2 (range of 0.074–0.101), respectively, for *S. oryzae, T. castaneum*, and *R. dominica.* The results indicated that *M. piperita* was highly toxic to *S. oryzae* compared to the other insects.

The mortality percentage (M%) of *S. oryzae* was 100% under high doses (0.2 and 0.4 mg/cm^2) for both exposure times (48 and 72 h) compared to the control (0.0%), and the other two insects, *T. castaneum* and *R. dominica*, had morality percentages of 70% and 90% (48 h exposure time) and 100% and 100% (72 h exposure time), respectively (Table 5). The lowest *M. piperita* dose (0.02 mg/cm^2) showed a moderate mortality percentage for *S. oryzae*, which was 36.3% and 40% after 48 and 72 h, compared with *T. castaneum*, which showed the response of 0.0% (48 h) and 30% (72 h). *R. dominica* was not affected by this dose (0.0%) for both of the exposure times (Table 5). The data showed that with the increase of *M. piperita* dose from 0.02 to 0.4 mg/cm^2, the mortality percentage increased, especially for the rice weevil *S. oryzae*. Highly significant variations were observed between the tested *M. piperita* doses against the stored insects, and this natural material could be used to control the insects that infect the grains.

Using *Rosa* spp. oil as a contact film showed a low toxicity against *S. oryzae, T. castaneum*, and *R. dominica*, with respective LC_{50} (mg/cm^2) values after 48 h of treatment of 0.520 mg/cm^2 (range of 0.381–0.995) to 0.421 (0.313–0.784, after 72 h), >1.00 mg/cm^2 (48 h) to 0.826 (range of 0.463–0.7.257, after 72 h), and 0.949 mg/cm^2 (range of 0.514–4.487, after 48 h), while after 72 h the LC_{50} was 0.706 mg/cm^2 (range of 0.428–2.192; Table 4). The results indicate clearly that *S. oryzae* was more susceptible to *Rosa* spp. oil, which resulted in a high toxicity compared to the other insects. The data in Table 5 showed no effect for the lowest concentrations of rose (from 0.02 to 0.04 mg/cm^2). The highest concentration, 0.4 mg/cm^2, showed a low mortality percentage during both exposure times of 48 and 72 h, which were 40% to 50% in *S. oryzae*, 30% to 35% in *T. castaneum*, and 35% to 40% in *R. dominica*. The concentration of 0.06 mg/cm^2 showed no mortality percentage for *S. oryzae* and *T. castaneum* under both exposure times (Table 5).

For *P. roxburghii* oil's toxicity, the data in Table 4 show that the LC_{50} (mg/cm^2) values were 0.076 mg/cm^2 (range of 0.061–0.095), 0.061 mg/cm^2 (range of 0.047–0.078), 0.383 mg/cm^2 (range of 0.317–0.516), 0.318 mg/cm^2 (range of 0.254–0.461), 0.194 mg/cm^2 (range of 0.169–0.238), and 0.156 mg/cm^2 (range of 0.128–0.196) for 48 and 72 h, recorded for the three insects *S. oryzae, T. castaneum*, and *R. dominica*, respectively. Also, the data in Table 2 for *P. roxburghii* showed no toxicity against the three tested insects at the 0.02 mg/cm^2 concentration; in addition, the previous concentration of 0.06 mg/cm^2 showed no toxicity for *T. castaneum* (Table 5). *S. oryzae* and *R. dominica* showed the highest mortality under the highest *P. roxburghii* dose (0.4 mg/cm^2), which was 80% and 70% under the two exposure times (Table 5).

The second method to test the efficiency of the three extract oils was fumigation for 72 h, as found in Tables 6 and 7. The data indicated that a very high concentration of *Rosa* spp. should be used to kill 50% of the insects, compared to the other oils. The LC_{50} (µL/L) for *Rosa* spp. oil was more than >100 µL/L. For *M. piperita*, the LC_{50} values were 3.79 µL/L (range of 2.39–5.50), 8.28 µL/L (range of 7.47–10.75), and 13.72 µL/L (range of 11.81–16.07), and for *P. roxburghii* oil, the LC_{50} values were 21.31 µL/L (range of 16.97–28.37), 24.48 µL/L (range of 19.61–32.73), and 34.63 µL/L (range of 28.21–44.04), recorded for *S. oryzae, T. castaneum*, and *R. dominica*, respectively (Table 6).

The results showed that *S. oryzae* recorded the lowest LC_{50} compared to the other two insects. Six different concentrations were used, which were 2, 4, 10, 20, 40, and 70 µL/L (Table 7), to calculate the morality percentages. From 20 to 70 µL/L, mortality was 100% in *S. oryzae*, and mortality was also

at 100% at 70 µL/L for both of the other insects. *S. oryzae* was very susceptible to all mint doses; the M% ranged from 40% (2 µL/L) to 66.6% under 10 µL/L (Table 7). On the other hand, *R. dominica* showed the lowest mortality percentage, ranging from 5% to 45% under the same concentrations. Concentrations of 20 and 40 µL/L recorded high values of M%, which were 55% and 85%.

Finally, under *M. piperita* concentrations of 20 and 40 µL/L, the mortality percentages were 65% and 90% with respect to *T. castaneum* (Table 4). Only one concentration of *P. roxburghii* (70 µL/L) showed 100% mortality for *S. oryzae* and *T. castaneum*, while *R. dominica* showed a low value (70%) under the same concentration (Table 7). No mortality was observed for *T. castaneum* and *R. dominica* under 2 and 4 µL/L of *P. roxburghii*. Only high doses of *Rosa* spp. showed mortality, although mortality was very low, ranging from 10% to 30% in *S. oryzae*, 3.3% to 16.6% in *T. castaneum*, and 5% to 35% in *R. dominica* (Table 7). These data indicate that *Rosa* spp. oil had a low-toxicity effect against these insects compared to other oils, and the data recommend using natural oil against stored weevils and petals rather than using chemical agents.

The present results agree with previous studies, which demonstrated that the toxicities of the essential oils extracted from various plant samples were mainly related to their major components.

Table 4. Contact toxicity of the isolated *M. piperita*, *Rosa* spp., and *P. roxburghii* oils using residual film assays against *Sitophilus oryzae*, *Tribolium castaneum*, and *Rhyzopertha dominica*.

Insect Species	Time Exposure (h)	Lethal Concentration 50% (LC_{50}) mg/cm^2	95% Confidence Limits (mg/cm^2)		Slope ± Stander Error	χ^2
			Lower	Upper		
M. piperita						
S. oryzae	48	0.036	0.03	0.042	1.62 ± 0.24	1.48
	72	0.022	0.019	0.026	1.98 ± 0.23	6.86
T. castaneum	48	0.083	0.069	0.102	1.58 ± 0.22	4.5
	72	0.055	0.044	0.07	1.06 ± 0.16	1.37
R. dominica	48	0.088	0.08	0.099	2.93 ± 0.24	7
	72	0.084	0.074	0.101	2.83 ± 0.36	1.04
Rosa spp.						
S. oryzae	48	0.52	0.381	0.995	1.62 ± 0.33	2.08
	72	0.421	0.313	0.784	1.41 ± 0.31	0.4
T. castaneum	48	>1.00	-	-	-	-
	72	0.826	0.463	7.257	1.04 ± 0.32	1.28
R. dominica	48	0.949	0.514	4.487	0.97 ± 0.23	1.08
	72	0.706	0.428	2.192	1.04 ± 0.22	4.13
P. roxburghii						
S. oryzae	48	0.076	0.061	0.095	1.22 ± 0.15	3.33
	72	0.061	0.047	0.078	1.22 ± 0.20	3.42
T. castaneum	48	0.383	0.317	0.516	2.23 ± 0.34	3.39
	72	0.318	0.254	0.461	1.59 ± 0.31	0.44
R. dominica	48	0.194	0.169	0.238	1.71 ± 0.17	2.64
	72	0.156	0.128	0.196	1.50 ± 0.17	0.17

Table 5. Mortality percentage and toxicities of *S. oryzae, T. castaneum*, and *R. dominica* treated using *M. piperita*, *Rosa* spp., and *P. roxburghii* as the contact methods.

Tested Oils	Concentrations (mg/cm^2)	Mortality % of *S. oryzae*		Mortality % of *T. castaneum*		Mortality % of *R. dominica*	
		Exposure Periods (h)					
		48	72	48	72	48	72
M. piperita	Control	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	3.3 ± 1.6	0.0 ± 0.0	0.0 ± 0.0 [e]
	0.02	36.3 ± 3.16	40 ± 5.00	0.0 ± 0.00	30.0 ± 10.00	0.0 ± 0.0	0.0 ± 0.0
	0.03	40.0 ± 10.00	55.0 ± 15.00	25.0 ± 7.63	40.0 ± 12.58	10.0 ± 5.77	10.0 ± 5.77
	0.04	55.0 ± 5.00	70.00 ± 15.27	25.0 ± 2.88	45.0 ± 11.54	20.0 ± 5.00	20.0 ± 7.63
	0.06	65.0 ± 7.36	80.0 ± 7.63	31.6 ± 9.27	50.0 ± 7.63	25.0 ± 7.63	30.0 ± 5.00
	0.1	76.6 ± 6.70	95.0 ± 5.00	63.0 ± 6.50	63.0 ± 12.74	50.0 ± 5.77	60.0 ± 15.74
	0.2	100 ± 0.00	100.0 ± 0.00	70.0 ± 5.00	70.0 ± 10.0	90.0 ± 5.77	100.0 ± 0.00
	0.4	100 ± 0.00	100 ± 0.00	100 ± 0.00	100.0 ± 0.00	100 ± 0.0	100.0 ± 0.00
Rosa spp.	Control	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0 [d]
	0.02	0.0 ± 0.0	0.0 ± 0.00	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	0.03	0.0 ± 0.0	0.0 ± 0.00	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	0.04	0.0 ± 0.0	0.0 ± 0.00	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	0.06	0.0 ± 0.0	0.0 ± 0.00	0.0 ± 0.0	0.0 ± 0.0	10.0 ± 2.88	10.0 ± 5.77
	0.1	10.0 ± 5.77	20.0 ± 12.58	5.00 ± 2.88	15.0 ± 7.63	20.0 ± 2.88	20.0 ± 2.88
	0.2	20.0 ± 5.77	30.0 ± 12.58	25.0 ± 7.63	30.0 ± 7.63	25.0 ± 8.66	35.0 ± 5.00
	0.4	40.0 ± 20.20	50.0 ± 11.54	30.0 ± 0.00	35 ± 12.58	35.00 ± 8.66	40.0 ± 5.00
P. roxburghii	Control	0.0 ± 0.0	0.0 ± 0.0	0.0 ±0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0 [d]
	0.02	0.0 ± 0.0	0.0 ± 0.00	0.0 ±0.0	0.0 ± 0.00	0.0 ± 0.0	0.0 ± 0.00
	0.03	25.0 ± 0.0	30.0 ± 7.63	0.0 ±0.0	0.0 ± 0.00	0.0 ± 0.0	0.0 ± 0.00
	0.04	40.0 ± 12.5	45.0 ± 12.58	0.0 ±0.0	0.0 ± 0.00	13.33 ± 8.69	15 ± 5.00
	0.06	50.0 ± 5.77	62.0 ± 13.0	0.0 ±0.0	0.0 ± 0.00	20.0 ± 0.0	30.0 ± 0.00
	0.1	55.0 ± 7.63	65.0 ± 12.58	12.33 ± 4.91	20.0 ± 10.00	25.0 ± 10.4	30 ± 7.63
	0.2	55.0 ± 10.0	70.0 ± 12.58	20.0 ± 5.77	40.0 ± 2.88	51.6 ± 11.6	60.0 ± 17.32
	0.4	80.0 ± 15.27	80.0 ± 5.00	55 ± 5	55.0 ± 12.58	70.0 ± 16.07	70.0 ± 20.00

Values are reported as mean ± standard deviation (SD).

Table 6. Fumigant toxicity of the isolated essential oils against *S. oryzae*, *T. castaneum*, and *R. dominica* after 72 h.

Essential Oils	Insect Species	LC_{50} µL/L	95% Confidence Limits (mg/cm^2)		Slope ± S.E	χ^2
			Lower	Upper		
M. piperita	*S. oryzae*	3.79	2.39	5.5	0.95 ± 0.25	0.04
	T. castaneum	8.28	7.47	10.75	1.54 ± 0.14	6.08
	R. dominica	13.72	11.81	16.07	1.97 ± 0.16	4.59
P. roxburghii	*S. oryzae*	21.31	16.97	28.37	1.31 ± 0.14	1.95
	T. castaneum	24.48	19.61	32.73	1.51 ± 0.30	21.37
	R. dominica	34.63	28.21	44.04	1.43 ± 0.21	4.71
Rosa spp.	*S. oryzae*	>100	-	-	-	-
	T. castaneum	>100	-	-	-	-
	R. dominica	>100	-	-	-	-

Table 7. Mortality percentage and toxicities of *S. oryzae, T. castaneum*, and *R. dominica* treated with *M. piperita*, *Rosa* spp., and *P. roxburghii* as a fumigation method.

Tested Oils	Concentrations µL/L	Mortality % of *S. oryzae*	Mortality % of *T. castaneum*	Mortality % of *R. dominica*
M. piperita	control	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00
	2	40.0 ± 13.22	20.0 ± 2.88	5.0 ± 5.00
	4	50.0 ± 8.66	26.6 ± 6.66	13.3 ± 6.00
	10	66.6 ± 14.52	50.0 ± 8.66	45.0 ± 7.63
	20	100 ± 0.00	65.0 ± 10.40	55.0 ± 16.07
	40	100 ± 0.00	90.0 ± 5.77	85.0 ± 8.66
	70	100 ± 0.00	100 ± 0.00	100.0 ± 0.00

Table 7. *Cont.*

Tested Oils	Concentrations µL/L	Mortality % of *S. oryzae*	Mortality % of *T. castaneum*	Mortality % of *R. dominica*
P. roxburghii	control	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00
	2	6.6 ± 1.60	0.0 ± 0.00	0.0 ± 0.00
	4	20.0 ± 7.63	0.0 ± 0.00	0.0 ± 0.00
	10	35.0 ± 13.22	30.0 ± 0.00	20.0 ± 11.54
	20	45.0 ± 8.66	40.0 ± 14.43	42.6 ± 4.33
	40	65.0 ± 10.00	65.0 ± 5.77	46.6 ± 12.01
	70	100 ± 0.00	100 ± 0.00	70.0 ± 18.92
Rosa spp.	control	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00
	2	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00
	4	0.0 ± 0.00	0.0 ± 0.00	0.0 ± 0.00
	10	0.0 ± 0.00	3.3 ± 3.33	0.0 ± 0.00
	20	10.0 ± 2.88	8.5 ± 3.5	5.0 ± 5.00
	40	25.0 ± 2.88	11.6 ± 1.66	20.0 ± 2.88
	70	30.0 ± 5.77	16.6 ± 6.66	35.0 ± 17.55

Values are reported as mean ± standard deviation (SD).

4. Discussion

Nowadays, many different types of plants are used as insecticides. Saheb and Mouhouche [50] detected that clove and thyme EOs in a fumigant method indicated the highest efficiency, showing a 100% mortality of *S. oryzae*. In addition, the results of Jairoce et al. [51] indicated that the EOs of clove caused 100% mortality after 48 h at a dose of 17.9 µL/g. Also, the peel oil reported a highly toxic effect against the rice weevil, *S. oryzae* [52]. Moreover, orange peel essential oil was also found to have an insecticide effect against *Sitophilus* spp. The fumigant toxicity was evaluated by Jayakumar et al. [53] at different concentrations of lemon oil (10 and 50 µL for 24, 48, and 72 h) and showed the highest activity of LD_{50} values (58.86, 44.90, and 40.38, respectively).

Wahba et al. [54] detected the fumigant and admixing toxicity of four monoterpenoid compounds (eugenol, isoeugenol, carvacrol, and thymol) against the cowpea weevil, *Callosobruchus maculatus.* They found that the fumigant toxicities of eugenol and carvacrol were high, with LC_{50} values of 34.58 and 37.34 mg/L, respectively, after 72 h of exposure time. Many studies have evaluated EO compounds to demonstrate their efficacy against a variety of stored product insects, including studies by Rastegar et al. [55], Tandorost and Karimpour [56], Saglam and Ozder [57], Abdelgaleil et al. [14], and Jarrahi et al. [58]. Brari and Thakur [59] showed that eugenol and thymol have potent fumigant toxicities against *C. analis*, *S. oryzae*, *Stegobium paniceum*, and *T. castaneum.*

Rose oil is one of the essential oils that contains methyl eugenol at a relatively high percentage. Methyl eugenol has been identified in high amounts, which is in agreement with previous studies [60–62]. In addition, in the present work, phenylethyl alcohol was found at a high level in the oil, which agreed with Ulusoy et al. [63], who reported that rose oil's main constituent is phenylethyl alcohol. Bulgarian rose oil (*Rosa damascena* mill.) showed the main compounds of *β*-citronellol, trans-geraniol, n-heneicosane, n-nonadecane, nonadecene, and phenylethyl alcohol [64]. *R. damascena* EO and its two major constituents, geraniol and citronellol, had contact, repellent, and ovicidal effects on the different life stages of *Tetranychus urticae* [65].

The main compounds identified in the EO of *M. piperita* were menthone, 1,8-cineole, menthyl acetate, caryophyllene, *β*-pinene, D-limonene, and *α*-pinene. The Iranian *M. piperita* contained *α*-terpinene, isomenthone, *trans*-carveol, pipertitinone oxide, and *β*-caryophyllene as the major compounds, respectively, with a high antimicrobial activity [30]. The major constituents of the EO from the Algerian plant were menthol, menthone, and menthyl acetate [66]. Limonene and eucalyptol were found in the plant from Girona (Spain), while menthone and menthol were found in the plant from

Barcelona (Spain) [67]. The plants grown in Norway showed the presence of menthol and menthone as the main compounds [68].

The present study showed that the *M. piperita* oil has potential insecticidal activity against *S. oryzae*, *R. dominica*, and *T. castaneum*. Previously, the application of EOs in 3 mL/m^2 of water observed a 100% mortality within 24 h for *Culex quinquefasciatus*, 90% for *Aedes aegypti*, and 85% for *Anopheles stephensi*. For *A. aegypti*, 100% mortality was achieved at 3 mL/m^2 in 48 h, or 4 mL/m^2 in 24 h, and for *A. stephensi*, 100% mortality was observed at 4 mL/m^2 in 72 h [69]. The EO extracted from *M. piperita* leaves possessed LC_{50} and LC_{90} values of 111.9 and 295.18 ppm, respectively, after 24 h of exposure, with an excellent larvicidal efficiency against the dengue vector of adult *A. aegypti* [70].

The EO from the foliage of *P. roxburghii* contained longifolene, caryophyllene, Δ-3-carene, α-terpineol, γ-elemene, aromadendrene, α-caryophyllene, and pentadecane as the main compounds. Salem et al. [37] reported that the major chemical constituents of EO in the wood were caryophyllene, thunbergol, 3-carene, cembrene, α-thujene, terpinolen, α-pinene, and α-caryophyllene; in the bark, they were α-pinene, 3-carene, cembrene, and longifolene; and in the needles, they were α-pinene, 3-carene, β-pinene, and longifolene. The main compounds of essential oil in needles were α-pinene, caryophyllene, 3-carene (14.2%), α-terpineol, and caryophyllene oxide, as reported by Zafar et al. [35]; in the stem, they were α-pinene, 3-carene, and caryophyllene [34]; and in the bark, they were (*E*)-caryophyllene, α-humulene, terpinen-4-ol, and α-terpineol [36].

For the LC_{50} values from the oils from *M. piperita*, *Rosa* spp., and *P. roxburghii*, which were calculated against *S. oryzae*, *T. castaneum*, and *R. dominica*, these results were in agreement with the authors of [14], who also worked with *S. oryzae*.

5. Conclusions

In the present work, the natural oils extracted from *M. piperita* (leaves), *P. roxburghii* (foliage), and *Rosa* spp. (flowers) were studied for their toxicity and insecticidal activities against three stored product insects, *S. oryzae*, *T. castaneum*, and *R. dominica*. *P. roxburghii* oil was shown to be a moderate insecticide, while the *Rosa* spp. oil had a low-toxicity effect against these insects. The results indicated that *M. piperita* was highly toxic to *S. oryzae* compared to the other insects. The M% of *S. oryzae* was 100% under high doses (0.2 and 0.4 mg/cm^2) for both of the exposure times (48 and 72 h) compared to the control, and the other two insects, *T. castaneum* and *R. dominica*, had mortalities of 70% and 90% (48 h) and 100% and 100% (72 h), respectively. Our results show that with the increase of *M. piperita* dose from 0.02 to 0.4 mg/cm^2, the mortality percentage increased, especially for the rice weevil, *S. oryzae*. Highly significant variations were observed between the tested *M. piperita* doses against the stored insects, and this natural material could be used to control insects that infect grains. This means that the essential oil from *M. piperita* had the highest toxic effects against the three stored product insects, and it could be considered as a good alternative to the production of commercial insecticidal agents.

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