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Research Article

Identification of Insecticidal Constituents from the Essential Oil of *Valeriana jatamansi* Jones against *Liposcelis bostrychophila* Badonnel

Xin Chao Liu,[1] Ligang Zhou,[2] and Zhi Long Liu[1]

[1] *Department of Entomology, China Agricultural University, 2 Yuanmingyuan West Road, Haidian District, Beijing 100193, China*
[2] *Department of Plant Pathology, China Agricultural University, 2 Yuanmingyuan West Road, Haidian District, Beijing 100193, China*

Correspondence should be addressed to Zhi Long Liu; zhilongliu@cau.edu.cn

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The aim of this research was to determine chemical composition and insecticidal activities of the essential oil of *Valeriana jatamansi* Jones roots against booklice, *Liposcelis bostrychophila* Badonnel, and to isolate insecticidal constituents from the oil. Essential oil of *V. jatamansi* was obtained by hydrodistillation and analyzed by GC-MS. A total of 27 components in the essential oil were identified. The major compounds were patchoulol (24.3%), α-bulnesene (13.8%), isovaleric acid (12.9%), α-guaiene (8.7%), and 3-methylvaleric acid (8.4%). Based on bioactivity-guided fractionation, isovaleric acid, 3-methylvaleric acid, and patchoulol were isolated and identified as the active constituents. The essential oil exhibited contact toxicity against *L. bostrychophila* with an LC_{50} value of 236.4 μg/cm^2. Patchoulol (LC_{50} = 61.35 μg/cm^2) exhibited stronger acute toxicity than 3-methylvaleric acid (LC_{50} = 210.69 μg/cm^2) against the booklice. The essential oil also possessed fumigant toxicity against *L. bostrychophila* with an LC_{50} value of 6.0 mg/L, while 3-methylvaleric acid and isovaleric acid had LC_{50} values of 5.53 mg/L and 5.67 mg/L against the booklice, respectively. The results indicated that the essential oil and its constituent compounds have potential to develop into natural insecticides or fumigants for control of insects in stored grains.

1. Introduction

Botanical pesticides have the advantage of providing novel modes of action against insects that can reduce the risk of cross-resistance as well as offering new leads for design of target-specific molecules. During the screening program for new agrochemicals from Chinese medicinal herbs and wild plants, essential oil of *Valeriana jatamansi* Jones (syn. *V. wallichii* DC) (Family: Valerianaceae) roots was found to possess strong insecticidal toxicity against the booklice, *Liposcelis bostrychophila* Badonnel (Psocoptera: Liposcelidae). The roots of *V. jatamansi*, as an important substitute for those of European *V. officinalis*, have been traditionally employed for the treatment of sleep disorder, nervous disorders, obesity, and so forth [1]. In the previous reports, various sesquiterpenoids, iridoids (valepotriates), flavonoids, and lignans have been isolated and identified in the plant [2–13]. Chemical composition of essential oil of *V. jatamansi* has been analyzed previously [14–18]. The methanol extract of *V. jatamansi* roots exhibited larvicidal and adulticidal activity against 5 species of mosquitoes [19]. The essential oil of *V. jatamansi* whole plants exhibited insecticidal activity against *Aphis craccivora* adults with a 24 h LC_{50} value of 90.75 ppm [20]. However, a literature survey has shown that there is no report on insecticidal activity of the essential oil of *V. jatamansi* against grain storage insects. The present research was therefore undertaken to investigate the chemical constituents and insecticidal activities of the essential oil against the two grain storage insects for the first time and to isolate active constituent compounds from the essential oil.

2. Materials and Methods

2.1. Plant and Essential Oil Extract. Dried *V. jatamansi* roots (5 Kg) were purchased from the Anguo Medicinal

Herb Market, Hebei, China. A voucher specimen (CMH-ZhiZhuXiang-Henan-2011-06) was deposited at the Department of Entomology, China Agricultural University, Beijing, China. The sample was ground to powder using a grinding mill (Retsch Muhle, Haan, Germany) and was subjected to hydrodistillation using a modified Clevenger-type apparatus for 6 h and extracted with *n*-hexane. Anhydrous sodium sulphate was used to remove water after extraction. Essential oils were stored in airtight containers in a refrigerator at 4°C for subsequent experiments.

2.2. Oil Isolation and Fractionation. The essential oil (25 mL) was chromatographed on a silica gel (Merck 9385, 1,000 g) column by gradient elution with a mixture of solvents (*n*-hexane, *n*-hexane-ethyl acetate, and acetone). Fractions of 500 mL were collected and concentrated at 40°C, and similar fractions according to TLC profiles were combined to yield 15 fractions. Fractions (2–4, 10) that possessed contact toxicity, with similar TLC profiles, were pooled and further purified by preparative silica gel column chromatography (PTLC GF254, 300–400 mesh, Qingdao Haiyang Chemical Group Corp., China) with petroleum etheracetone (50 : 1, v/v) until obtaining the pure compound for determining structure as isovaleric acid (**1**, 1.1 g), 3-methylvaleric acid (**2**, 0.7 g), and patchoulol (**3**, 0.5 g).

2.3. Gas Chromatography-Mass Spectrometry (GC-MS). Analyses of volatile constituents were determined using an Agilent 5973 GC-MS system operating in the EI mode at 70 eV (equipped with a 30 m HP-5MS column (0.25 mm × 30 m × 0.25 μm) and coated with 5% phenyl-methylpolysiloxane using a HP-5MS (df = 0.25 μm) (Agilent J&W Scientific, USA)). The temperature program used for the analysis was as follows: initial temperature at 60°C, held for 1 min, ramped at 4°C/min to 290°C and held for 0.5 min. Helium was the carrier gas at 1.0 mL/min; the sample (1 μL 1/100, v/v, in acetone) was injected in the split mode (1 : 10). The injector and detector temperatures were performed at 230°C, and 300°C, respectively. Most constituents were identified by gas chromatography by comparison of their retention indices with those of the literature or with those of authentic compounds available in our laboratories. The retention indices were determined in relation to a homologous series of n-alkanes (C_8–C_{24}) under the same operating conditions. Further identification was made by comparison of their mass spectra on both columns with those stored in NIST 05 and Wiley 275 libraries or with mass spectra from literature [21].

2.4. NMR Analysis. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Bruker ACF300 (300 MHz (^{1}H)) and AMX500 (500 MHz (^{1}H)) instruments using deuterochloroform ($CDCl_3$) as the solvent with tetramethylsilane (TMS) as the internal standard. Electron impact mass spectra (EIMS) were determined on a Micromass VG7035 mass spectrometer at 70 eV (probe).

*2.5. Isolated Constituent Compounds. Isovaleric acid (**1**)*: EI-MS m/z (%): 87 (17), 60 (100), 45 (17), 43 (32), 42 (33), and 27 (16). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.77 (s, –OH), 2.22 (2H, d, J = 6 Hz), 2.12–2.06 (1 H, m), and 0.99 (6 H, d, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 179.96, 43.32, 25.58, 22.62, and 22.30. The data matched with previous report [22].

*3-Methylvaleric acid (**2**)*: EI-MS m/z (%): 87 (17), 60 (100), 57 (24), 56 (16), 41 (27), and 29 (18). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.77 (s, –OH), 2.36 (1 H, m, J = 15 Hz, J = 6 Hz), 2.15 (1 H, d, J = 8.2 Hz), 1.90 (1 H, m), 1.40 (2 H, d), 1.26 (2 H, m), and 0.91–0.97 (6 H, d, J = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 179.96, 43.32, 25.58, and 22.62, 22.30. The data matched with previous report [23].

*Patchoulol (**3**)*: EI-MS m/z (%): 222 (100), 204 (25), 161 (28), 138 (55), 98 (61), 81 (63), and 41 (78). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 0.80 (3 H, d, J = 6.5 Hz), 0.86 (3 H, s), 1.29 (3 H, s), 1.31 (3 H, s), and 1.20–2.10 (m); ^{13}C-NMR ($CDCl_3$) δ 75.57, 43.72, 40.10, 39.11, 37.64, 32.68, 28.85, 28.61, 28.10, 26.85, 24.58, 24.31, 24.29, 20.63, and 18.58. The data matched with previous report [24].

2.6. Insects. *L. bostrychophila* was obtained from laboratory cultures in the dark in incubators at 28–30°C and 70–80% r.h. and was reared on a 1 : 1 : 1 mixture, by mass, of milk powder, active yeast, and flour. All containers housing insects and the Petri dishes used in experiments were made escape proof with a coating of polytetrafluoroethylene (Fluon, Blades Biological, UK). Adult insects used in all the experiments were about one-week old.

2.7. Contact Toxicity. Contact toxicity of the oil against the booklice was measured as described by Zhao et al. [25]. The filter paper with 3.5 cm in diameter (Whatman) was treated with 150 μL of the solution (2.0%, 2.4%, 2.9%, 3.5%, 4.2%, and 5.0% in acetone). The treated filter paper after treated with solid glue (Glue Stick, Jong Ie Nara Co., Ltd. Hong Kong) was placed in a petri dish (3.5 cm in diameter) and 10 booklice were put on the filter paper. The plastic cover with holes was put and all the Petri dishes were kept in incubators at 27–29°C, 70–80% r.h., for 24 h and mortality of insects was observed. Acetone was used as controls and pyrethrum extract was used as a positive control. Pyrethrum extract (25% pyrethrin I and pyrethrin II) was purchased from Fluka Chemie (Buchs, Switzerland).

2.8. Fumigant Toxicity. Fumigant toxicity of the oil against the booklice was determined as described by Zhao et al. [25]. A filter paper strip (3.5 cm × 1.5 cm) was treated with 10 μL of an appropriate concentration (3.1%, 3.3%, 3.5%, 3.6%, 3.8%, and 4.0% in acetone) of the essential oil. The impregnated filter paper was then placed in the bottom cover of glass bottle of 250 mL. The insects, 10 adults with undefined sex in a small glass bottle (8 mL), were exposed for 24 h and five repetitions for each concentration were performed. Dichlorvos was used as a positive control. Mortality of insects was observed and

Table 1: GC-MS analysis of essential oil derived from *Valeriana jatamansi* roots.

No.	Compounds	RI	Peak area (%)
1	Isovaleric acid*	875	12.9
2	3-Methylvaleric acid*	902	8.4
3	Valeric acid*	912	2.2
4	α-Pinene*	931	0.6
5	Camphene	945	1.3
6	β-Pinene*	981	0.6
7	1,8-Cineol*	1032	1.6
8	Camphor*	1143	0.2
9	α-Terpineol*	1191	0.3
10	Methyl thymol ether	1225	1.1
11	Bornyl acetate*	1285	1.4
12	Copaene	1374	0.5
13	β-Patchoulene	1382	4.0
14	β-Elemene	1393	2.4
15	α-Gurjunene	1406	0.2
16	Caryophyllene*	1420	0.4
17	Calarene	1432	0.8
18	α-Guaiene	1437	8.7
19	α-Caryophyllene	1454	0.2
20	Seychellene	1458	2.3
21	α-Bulnesene	1503	13.8
22	δ-Cadinene	1520	2.1
23	Selina-3,7(11)-dien	1534	0.6
24	Viridiflorol	1592	1.5
25	Guaiol	1601	0.9
26	Patchoulol	1660	24.3
27	Valeranone	1679	1.5
	Total identified		94.8
	Monoterpenoids		7.1
	Sesquiterpenoids		64.2
	Others		23.5

RI: retention index on a HP-5MS column. *Identification by coinjection of authentic compounds.

dichlorvos (99.9%) was purchased from Aladdin-Reagent Company (Shanghai, China).

2.9. Data Analysis. The observed mortality data were corrected for control mortality using Abbott's formula. The results from all replicates in fumigant and contact toxicity were subjected to Probit analysis using PriProbit Program V1.6.3 to determine LC_{50} and LD_{50} values, respectively [26].

3. Results and Discussion

3.1. Essential Chemical Composition. The yellow essential oil yield of *V. jatamansi* was 0.86% (v/w based on dry weight), while the density of the concentrated essential oil was 0.87 g/mL. A total of 27 components from the essential oil of *V. jatamansi* were identified, accounting for 94.8% of the total oil. Monoterpenoids only represented 8 of the 27 compounds, corresponding to 7.1% of the whole oil, while 16 of the 27 constituents were sesquiterpenoids (64.2% of the crude essential oil) (Table 1). The major constituents of *V. jatamansi* essential oil were patchoul (24.3%), α-bulnesene (13.8%), isovaleric acid (12.9%), α-guaiene (8.7%), and 3-methylvaleric acid (8.4%). Great variations in the chemical profiles of the *V. jatamansi* essential oil in this study were observed from those of previous reports [14–20]. For example, Verma et al. [17] measured chemical composition of *V. jatamansi* oils derived from 17 populations and found that the major components of these essential oils were patchouol (13.4–66.7%), α-bulnesene (0.05–23.5%), α-guaiene (0.2–13.3%), guaiol (0.05–12.2%), seychellene (0.2–9.9%), viridiflorol (0.05–7.3%), and β-gurjunene (0.0–7.1%). Singh et al. [18] determined the chemical composition of the essential oils derived from 13 populations of *V. jatamansi* and three distinct groups were suggested. Group I characterized by high contents of patchouol (48.47–65.04%), seychellene (2.97–5.29%) and pogostol (2.1–2.39%), whereas, Group II had moderate contents of patchoulol (30.16–38.52%)

Table 2: Contact and fumigant toxicity of the essential oil of *Valeriana jatamansi* and its isolated compounds against *Liposcelis bostrychophila*.

	Treatments	LC_{50}	95% FL*	Slope ± SE	Chi square (χ^2)
Contact ($\mu g/cm^2$)	*V. jatamansi*	236.39	217.43–255.89	12.78 ± 1.33	7.92
	Isovaleric acid	426.34	391.76–476.43	8.63 ± 0.82	9.88
	3-Methylvaleric acid	210.69	289.91–230.14	12.40 ± 1.31	11.76
	Patchoulol	61.35	56.53–66.06	16.63 ± 1.96	10.36
	Pyrethrum extract	18.99	17.56–20.06	7.64 ± 1.05	—
Fumigant (mg/L)	*V. jatamansi*	5.98	5.37–6.41	11.72 ± 1.60	12.88
	Isovaleric acid	5.67	5.23–6.27	11.66 ± 1.38	7.12
	3-Methylvaleric acid	5.53	5.01–5.98	14.12 ± 1.58	11.56
	Patchoulol	>7.00	—	—	—
	Dichlorvos	1.35×10^{-3}	$1.25–1.47 \times 10^{-3}$	6.87 ± 0.77	—

*Fiducial limits.

and veridiflorol (24.41–25.23%). Group III had high contents of vridiflorol (29.88–50.29%) along with calarene (10.41–24.21%).

3.2. Contact Toxicity. The essential oil of *V. jatamansi* roots exhibited contact toxicity against *L. bostrychophila* with a LC_{50} value of 236.39 $\mu g/cm^2$ (Table 2). Patchoulol (LC_{50} = 61.35 $\mu g/cm^2$) possessed stronger acute toxicity to the booklice than 3-methylvaleric acid (LC_{50} = 210.69 g/cm^2) and isovaleric acid (LC_{50} = 426.34 g/cm^2). Patchoulol shows 4 times stronger toxicity than the oil and it seems that contact toxicity of the oil may be mainly attributed to patchoulol. However, compared with the positive control, pyrethrum extract (LC_{50} = 18.99 $\mu g/cm^2$), *V. jatamansi* essential oil, and patchoulol showed 12 and 3 times less toxicity to *L. bostrychophila*, respectively. When compared with the other essential oils in the previous studies using the same bioassay, the essential oil of *V. jatamansi* exhibited stronger or the same level of acute toxicity against the booklice, for example, essential oils of *Artemisia rupestris* [27] and *Curcuma wenyujin* [28], but was less toxic than the essential oils of *Acorus calamus* [29] and *Foeniculum vulgare* [25].

3.3. Fumigant Toxicity. The essential oil of *V. jatamansi* possessed fumigant toxicity with an LC_{50} value of 5.98 mg/L against the booklice (Table 2). Isovaleric acid and 3-methylvaleric acid exhibited fumigant toxicity against the booklice with LC_{50} values of 5.53 mg/L and 5.67 mg/L, respectively, and patchoulol did not show fumigant toxicity at tested concentrations (Table 2). Compared with dichlorvos (LC_{50} = 1.35 $\mu g/L$), the essential oil of *V. jatamansi* and the two isolated compounds showed only 4000 times less toxicity against *L. bostrychophila*. However, considering that the commercial fumigants are synthetic insecticides and the most effective fumigants (e.g., phosphine and MeBr) are also highly toxic to humans and other nontarget organisms, fumigant activity of the essential oil of *V. jatamansi* and two isolated compounds is quite promising.

This study demonstrates that the essential oil of *V. jatamansi* had contact and fumigant toxicities to the booklice. Furthermore, the two isolated constituent compounds, isovaleric acid and 3-methylvaleric acid, exhibited contact and fumigant toxicities against *L. bostrychophila*. Patchoulol exhibited strong acute toxicity to the booklice, but no fumigant toxicity was observed. In the previous study, patchoulol was demonstrated to exhibit toxic and repellency against Formosan subterranean termites (*Coptotermes formosanus*) [30] and also exhibited pupicidal and repellent activities against three important vector mosquitoes (*Aedes aegypti*, *Anopheles stephensi*, and *Culex quinquefasciatus* [31]. Weak larvical activity of patchoulol against *Culex pipiens pallens* was also observed [32]. However, there is no report on insecticidal activity of other two isolated constituent compounds against insects. The above findings suggest that the essential oil and the three isolated constituent compounds show potential to be developed as possible natural insecticides/fumigants for the control of grain storage insects.

It seems that this medicinal herb is quite safe to human consumption because it has been used as a medicinal herb for the treatment of sleep disorder, nervous disorders, obesity, and so forth for hundreds of years [1]. Moreover, constituent compounds, 3-methylvaleric acid and isovaleric acid, have been used commercially in a variety of drugs, perfumes, and flavourings. Another active constituent, patchouli alcohol, has been used in decorative cosmetics, fine fragrances, shampoos, toilet soaps, and other toiletries as well as in non-cosmetic products such as household cleaners and detergents. The maximum skin level that results from the use of patchouol in formulae that go into fine fragrances has been reported to be 0.02% [33]. However, no information on toxicity of the essential oil and the isolated constituents to human was available. Thus, to develop a practical application for the essential oil and the isolated constituents as novel fumigants/insecticides, further research into the safety of the essential oil/compounds to humans is needed. Additional studies on the development of formulations are also necessary to improve the efficacy and stability and to reduce cost.

4. Conclusion

The study indicates that the essential oil of *V. jatamansi* roots and its isolated constituent compounds have potential to develop into natural insecticides and fumigants for control of insects in stored grains.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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