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Primary study of volatiles composition of *Rhodiola sachalinensis* by using gas chromatography and mass spectrometry (GC/MS)

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Abstract−To determine the volatile compounds in *Rhodiola sachalinensis,* hydro-distillation (HD) and headspace liquid-phase micro-extraction (HS-LPME) were used to extract 75 and 68 volatiles, respectively. Geraniol (24.73%), *n*-octanol (15.56%), and linalool (14.51%) were the most abundant essential oils detected in the HD samples, while geraniol (24.17%) and *n*-octanol (15.81%) were also detected at high levels in the HS-LPME samples. The main chemical classes of the essential oils were monoterpene alcohols in both the HD and HS-LPME samples at 59.02% and 37.64%, respectively. The *O*-heterocyclic (8.52%) and aromatic (5.92%) compounds were more abundant in the HS-LPME samples than in the HD samples.

Key words: Volatiles, HD, HS-LPME, *Rhodiola sachalinensis*, GC/MS

INTRODUCTION

Rhodiola sachalinensis is a medicinal plant mainly used in Asia. It is a member of the Crassulaceae family, a perennial herbaceous plant growing in northern areas [1]. This herb has a reputation for stimulating the nervous system, decreasing depression, enhancing work performance, resisting anoxia, microwave radiation, eliminating fatigue, preventing high altitude sickness and improving sleep [2-4]. Many other biological activities have also been reported for *Rhodiola* species, such as antioxidant activity, visceral organ protection, antidiabetic activity, anticancer, adaptogenic activity and enhancement of learning and memory [5-7]. The major bioactive components in the *Rhodiola* species are phenylethanol derivatives (rhodioloside or salidroside, tyrosol), flavones (quercetin, hyperoside, kaempferol, rhodiolin, rhodionin, tricin, acetylrodalgin, catechins and proanthocyanins), phenylpropanoids (rosavin, rosin and rosarin) and others, including phenolic acids, ethyl gallate, ethereal oil, organic acids and lipids, *etc*. [8]. The crude plant extracts are relatively important for the development of new medicines as a basis resource. Therefore, it has become more important to investigate how to extract the active material from crude plants [9].

Essential oils (also called volatile or ethereal oils) are aromatic oily liquids obtained from plant materials. The greatest use of essential oils is in food (as flavorings), perfumes and pharmaceuticals (for their functional properties) [10,11]. To achieve the best possible separation performance for essential oil analysis, many researchers use the most effective available technology. Supercritical fluid extraction [12-16] and the Headspace method [17-23] were used for identification of the volatile compounds compared with steam distillation (SD) or hydrodistillation.

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Jens Rohloff identified 86 volatile compounds from rhizomes of *Rhodiola rosea* L. by both SD and headspace solid-phase microextraction (HS-SPME) coupled with gas chromatography and mass spectrometry (GC/MS) analysis [24]. Yidong Lei et al. identified some essential oils from rhizomes of *Rhodiola crenulata* and *Rhodiola fastigiata* by GC/MS [25,26]. Bai et al. identified twenty-three volatiles from *Rhodiola quadrifida* by GC/MS [27]. Tashi Tsering et al. identified 45 volatiles from rhizomes of *Rhodiola sacra*, *Rhodiola calliantha*, and *Rhodiola himalensis* [28].

The determination of the volatiles from *Rhodiola sachalinensis* was first reported in this paper. In this study, HD, headspace liquid-phase micro-extraction (HS-LPME), and GC/MS technique were used to determine the essential oils from *Rhodiola sachalinensis*.

EXPERIMENT

1. Chemicals and Reagents

The *Rhodiola sachalinensis* samples used in this study were collected from the Yanji Food and Drug Administration, Jilin province, China in July of 2007. Hexane and dichloromethane were all of HPLC grade and purchased from Aldrich (St. Louis MO, USA). Anhydrous sodium sulfate and all glassware were burned at 400 °C for 12 hr and washed with solvent before use.

2. Instrumental Analysis for HD

The volatile compounds were separated using a Shimadzu GC2010 (Tokyo, Japan) with DB-5MS capillary column (30 m×0.32 mm i.d.; coated film thickness: 25 μm). One microliter of sample was introduced by split mode using an autoinjector AOC-5000 from Shimadzu. The temperature of the injection port was 280 °C. The oven temperature was held at 50 °C, then elevated to 100 °C at 5 °C/min, from 100 to 200 °C at 7 °C/min, and from 200 to 280 °C at 10 °C/min, and finally held at 280 °C for 3 min. A Shimadzu QPMS 2010 mass spectrometer was interfaced with the chromatographic sys-

tem at an interface temperature of 280 °C. Helium was used as the carrier gas at a flow rate of 1.69 mL/min. Electron ionization mode was applied to the MS analysis. The ion source temperature was 200 °C. The electron multiplier voltage was 1,250 kV and the energy of ionizing electron was 70 eV.

3. Instrumental Analysis for HS-LPME

Except for the temperature program, the procedure of the instrumental analysis for essential oils by HS-LPME was similar to that described in the above section. One microliter of sample was introduced by splitless mode using an autoinjector AOC-5000 from Shimadzu. The temperature of the injection port was 300 °C. The oven temperature was held at 50 °C for 1 min, then elevated to 140 °C at 5 °C/min, held at 140 °C for 1 min, elevated from 140 to 300 °C at 10 °C/min, and finally held at 300 °C for 5 min. The flow rate of the helium carrier gas was 1.55 mL/min.

4. Extraction of Essential Oils (HD)

The powder of *Rhodiola sachalinensis* (100 g dry) was put into a 1,000 mL distillation flask, 500 mL of distilled water was added and a volatile oil distillation extraction apparatus was set up and then used to conduct the distillation extraction. The mixture was distilled for 3 hr. The volatile and semi-volatile chemicals in the plant were dissociated by water vapor. After cooling, the targets were collected with a 1 mL *n*-hexane solvent layer, and then dried over anhydrous sodium sulfate. The targets were directly subjected to GC-MS analysis.

5. Extraction of Essential Oils (HS-LPME)

HS-LPME was conducted via the following steps. (i) A clean 10 μL micro-syringe was rinsed at least seven times with the extract solvent to ensure that no air bubble was left in the barrel or the needle. (ii) A specified volume of extract solvent was drawn into the micro-syringe. (iii) The micro-syringe needle was pierced into the sample vial through the septum, and the needle tip was fixed in the headspace of the sample. (iv) The plunger was slowly depressed to expose a drop of extract solvent in the headspace. (v) The magnetic stirrer was used to agitate the sample solution and extract for a prescribed time. (vi) A drop of the extract solvent was retracted into the micro-syringe and removed from the sample vial. (vii) The target analysts in the micro-syringe were injected into the GC for analysis. A sample of 0.5 g of *Rhodiola sachalinensis* was first ground to powder and sealed in a vial, after which the syringe was suspended in the headspace and equilibrated for 5 min at 70 °C, 80 °C and 90 °C before injection. For exact identification of the volatiles, they were further extracted for 20 min at 80 °C. The volatiles were collected using octane.

RESULTS AND DISCUSSIONS

1. Identification of Volatiles

In total, 75 compounds were identified in the essential oil from

Table 1. Chemical constituents of the volatiles from *Rhodiola sachalinensis*

No.	Compound	Chemical formula	Molecular weight	Retention time (min)		Relative area (%)		Appearance (total n=6)		Type
				HD	LPME	HD	LPME	HD	LPME	
1	2,6,6-trimethyl-6-vinyl-2H-pyran	$C_{10}H_{18}O$	154	5.976	-	0.19	-	6	-	(11)
2	3-heptanone[24](2-*heptanone*)	$C_7H_{14}O$	114	-	6.102	-	1.56	-	3	(7)
3	2-ethyl-5-methyltetrahydrofuran	$C_7H_{14}O$	114	-	6.142	-	1.84	-	4	(11)
4	5-isopropyl-2,2-dimethyltetrahydrofuran	$C_9H_{18}O$	142	-	6.212	-	1.12	-	5	(11)
5	Tetrahydro-2H-pyran-2-methanol	$C_6H_{12}O_2$	116	-	6.241	-	1.64	-	4	(11)
6	1-octen-3-ol[24,25,26]	$C_8H_{16}O$	128	6.302	7.992	0.62	0.50	6	6	(5)
7	β-myrcene[24,26,28]	$C_{10}H_{16}$	136	6.327	7.508	1.29	0.22	5	6	(1)
8	6-methyl-5-hepten-2-one[24]	$C_8H_{14}O$	126	6.368	-	1.08	-	4	-	(7)
9	2,5-diethyltetrahydro-furan	$C_8H_{16}O$	128	-	6.399	-	0.05	-	4	(11)
10	3-methyl-1-heptene	C_8H_{16}	112	-	6.470	-	0.08	-	3	-
11	6-methyl-5-hepten-2-ol	$C_8H_{16}O$	128	6.622	7.623	0.98	0.19	6	6	(5)
12	3,7-diemthyl-1-octanol	$C_{10}H_{22}O$	158	-	6.623	-	0.08	-	4	(2)
13	α-phellandrene[24] (α-*phellandrene*)	$C_{10}H_{16}$	136	-	6.659	-	0.07	-	3	(1)
14	3-methyl-1-pentanol	$C_6H_{14}O$	102	-	6.634	-	0.07	-	4	(5)
15	α-thujene	$C_{10}H_{16}$	136	-	6.710	-	0.04	-	4	(1)
16	2,6,6-trimethyl-bicyclo[3,1,1]hept-2-ene	$C_{10}H_{16}$	136	-	6.791	-	0.61	-	4	(1)
17	Octanal[24,25,26]	$C_8H_{16}O$	128	6.857	8.122	0.58	0.73	6	6	(6)
18	Pantolactone	$C_6H_{10}O_3$	130	-	7.151	-	0.06	-	3	(11)
19	Vinyl 2,2-dimethylbutanoate	$C_8H_{14}O_2$	142	-	7.301	-	0.45	-	4	(8)
20	Sabine[24]	$C_{10}H_{16}$	136	-	7.480	-	2.16	-	3	(1)
21	Limonene[24,27,28]	$C_{10}H_{16}$	136	7.524	8.425	0.21	0.39	6	6	(1)
22	2,6,6-trimethyl-bicyclo[3.1.1]heptene-2,3-diol	$C_{10}H_{18}O_2$	170	-	7.578	-	0.76	-	4	(2)
23	4,4-dimethyl-2-cyclohexen-1-ol	$C_8H_{14}O$	126	-	7.692	-	1.38	-	4	-
24	2-(3,3-dimethylbutyl)-oxirane	$C_8H_{16}O$	128	-	7.750	-	0.91	-	4	(11)
25	3,7-dimethyl-1-octanol	$C_{10}H_{22}O$	158	7.807	-	0.03	-	6	-	(2)

Table 1. Continued

No.	Compound	Chemical formula	Molecular weight	Retention time (min)		Relative area (%)		Appearance (total n=6)		Type
				HD	LPME	HD	LPME	HD	LPME	
26	Ocimene[24,28]	$C_{10}H_{16}$	136	7.842	8.817	0.48	0.10	5	6	(1)
27	2,4-dimethylcyclohexanol	$C_8H_{16}O$	128	-	7.891	-	0.75	-	5	-
28	3,7-dimethyl-1,3,6-octatriene	$C_{10}H_{16}$	136	7.986	-	0.11	-	6	-	(1)
29	5-isopropeny-3,3-dimethyl-1-cyclopentene	$C_{10}H_{16}$	136	8.164	8.243	0.08	0.53	5	6	(1)
30	α-terpinen[24]	$C_{10}H_{16}$	136	-	8.437	-	0.38	-	4	(1)
31	2-octenal[24]	$C_8H_{14}O$	126	8.439	-	0.04	-	4	-	(6)
32	1-ethyl-2,4-dimethyl-benzene	$C_{10}H_{14}$	134	-	8.615	-	0.45	-	4	(9)
33	1-methyl-2-(1-methylethyl)-benzene	$C_{10}H_{14}$	134	-	8.632	-	0.63	-	5	(9)
34	5-ethyltetrahydro-α-2-furanmethanol	$C_{10}H_{18}O_2$	170	8.680	-	1.79	-	4	-	(2)
35	*n*-octanol[24,25,26,27,28]	$C_8H_{18}O$	130	8.824	9.509	15.56	15.81	6	6	(5)
36	5-isopropenyl-2-methylcyclohexanol	$C_{10}H_{18}O$	154	8.903	-	0.14	-	5	-	(2)
37	Isooctanol	$C_8H_{18}O$	130	8.954	13.073	0.16	0.16	5	5	(5)
38	4-carene[24 (3-*carene*), 25(*carene*)]	$C_{10}H_{16}$	136	9.085	-	0.01	-	4	-	(1)
39	1-methyl-4-(1-methylethenyl)-benzene	$C_{10}H_{12}$	132	9.279	-	0.21	-	6	-	(9)
40	2,7-dimethyl-1,7-octadiene	$C_{10}H_{18}$	138	9.454	-	0.07	-	4	-	(1)
41	Linalool[24,25,26,27]	$C_{10}H_{18}O$	154	9.621	10.174	14.51	5.12	6	6	(2)
42	Tetrahydro-4-methyl-2-(2-methyl-1-propyl)-2H-pyran	$C_{10}H_{18}O$	154	9.807	-	0.05	-	4	-	(11)
43	Linalool oxide[24,28]	$C_{10}H_{18}O_2$	170	-	10.126	-	1.89	-	5	(11)
44	Phenylethyl alcohol[24]	$C_8H_{10}O$	122	10.131	10.560	0.11	2.16	4	5	(9)
45	Nonanal[24]	$C_9H_{18}O$	142	-	10.300	-	0.22	-	6	(6)
46	Decanal[24]	$C_{10}H_{20}O$	156	10.698	13.323	0.09	0.21	5	5	(6)
47	Methyl caprylate	$C_9H_{18}O_2$	158	-	10.758	-	0.61	-	4	(8)
48	Pinocarveol	$C_{10}H_{16}O$	152	10.762	11.260	1.05	0.69	6	3	(2)
49	2,6-diemthyl-2,4,6-octatriene	$C_{10}H_{16}$	136	-	10.883	-	0.17	-	4	(1)
50	4,7,7-trimethyl-bicyclo[4,1,0]heptan-3-ol	$C_{10}H_{18}O$	154	10.951	-	0.51	-	5	-	(2)
51	5-methyl-2-(1-methylethenyl)-cyclohexanol	$C_{10}H_{18}O$	154	10.979	10.661	0.09	0.10	4	5	(2)
52	2,6-dimethyl-5,7-octadien-2-ol	$C_{10}H_{18}O$	154	11.143	-	0.12	-	4	-	(2)
53	(2E)-3-pehyl-2,4-pentadien-1-ol	$C_{10}H_{18}O$	154	11.258	-	0.04	-	4	-	(5)
54	2-decyn(e)-1-ol	$C_{10}H_{18}O$	154	11.304	12.189	0.10	0.59	6	6	(5)
55	2,6,6-trimethyl-bicyclo[3,1,1]heptan-3-one	$C_{10}H_{16}O$	152	11.677	-	0.27	-	4	-	(4)
56	*cis*-myrtanol[27,28]	$C_{10}H_{18}O$	154	11.722	-	0.50	-	5	-	(2)
57	2,6,6-trimethyl-2-cyclohexene-1-methanol	$C_{10}H_{18}O$	154	11.733	-	0.43	-	6	-	(2)
58	4-mehthyl-1-(1-methylethyl)-3-cyclohexen-1-ol	$C_{10}H_{18}O$	154	11.850	12.326	0.46	0.38	6	5	(2)
59	2-(3,3-dimethylcyclohexylidene)-ethanol	$C_{10}H_{18}O$	154	11.935	-	0.49	-	4	-	(2)
60	2-hydromethyl-2-methylcyclopentanol	$C_7H_{14}O$	130	-	12.031	-	0.16	-	4	-
61	Myrtenal[24]	$C_{10}H_{14}O$	150	12.206	-	0.07	-	4	-	(3)
62	α,α-4-trimethyl-3-cyclohexene-1-methanol	$C_{10}H_{18}O$	154	12.296	12.724	7.69	4.71	4	4	(2)
63	2,6,6-trimethyl-bicyclo[3,1,1]heptan-3-ol	$C_{10}H_{18}O$	154	12.394	-	0.20	-	5	-	(2)
64	Isothujol	$C_{10}H_{18}O$	154	-	12.411	-	0.32	-	3	(2)
65	Borneol	$C_{10}H_{18}O$	154	12.462	12.924	0.72	0.29	4	6	(2)
66	4-methyl-1-(1-methylethyl)-bicyclo[3,1,0]hexan-3-ol	$C_{10}H_{18}O$	154	12.531	-	0.64	-	6	-	(2)
67	Pinocamphone[24 (*Isopinocamphone*)]	$C_{10}H_{16}O$	152	-	12.534	-	0.19	-	5	(4)
68	3,7,11-trimethyl-2,6,10-dodecatrien-1-ol	$C_{15}H_{26}O$	222	12.783	-	0.28	-	6	-	(5)
69	Rhodinol(or citronellol)[25,26]	$C_{10}H_{20}O$	156	13.018	13.545	2.34	0.89	6	6	(2)
70	Geraniol[24,25,26,27,28]	$C_{10}H_{18}O$	154	13.683	15.785	24.73	24.17	6	6	(2)
71	1-decanol[24]	$C_{10}H_{22}O$	158	13.977	-	2.57	-	5	-	(5)
72	3,7-dimethyl-2,6-octadienal	$C_{10}H_{16}O$	152	14.033	13.849	3.22	0.67	4	5	(3)
73	2,7-dimethyl-2,6-octadien-1-ol	$C_{10}H_{18}O$	154	14.338	-	2.58	-	4	-	(2)

Table 1. Continued

No.	Compound	Chemical formula	Molecular weight	Retention time (min)		Relative area (%)		Appearance (total n=6)		Type
				HD	LPME	HD	LPME	HD	LPME	
74	2-isopropenyl-5-methyl-4-hexenal	$C_{10}H_{16}O$	152	14.660	-	1.13	-	4	-	(4)
75	Dehydroelsholtzia ketone	$C_{10}H_{12}O_2$	164	-	15.555	-	1.01	-	3	(11)
76	Geraniol acetate[24]	$C_{12}H_{20}O_2$	196	16.392	17.870	1.47	0.36	6	6	(8)
77	1-methyl-1-ethenyl-2,4-bis-(1-methylethenyl)-cyclohexane	$C_{15}H_{24}$	204	16.673	18.155	0.20	0.10	4	5	-
78	Caryophyllene[24]	$C_{15}H_{24}$	204	17.328	18.925	0.17	0.57	6	6	-
79	Nerolidyl propionate	$C_{18}H_{30}O_2$	278	-	17.657	-	0.17	-	3	(8)
80	1,1,7-trimethyl-4-methylenedecahydro-1H-cyclopropa[e]azulene	$C_{15}H_{24}$	204	18.118	19.800	0.64	6.96	4	4	-
81	Isoaromadendrene epoxide	$C_{15}H_{24}O$	220	18.590	-	0.15	-	5	-	(11)
82	Isocitronellol	$C_{10}H_{20}O$	156	-	18.691	-	0.15	-	4	(2)
83	Tridecane	$C_{13}H_{28}$	184	18.768	-	0.62	-	5	-	-
84	Pentadecane[28]	$C_{15}H_{32}$	212	18.919	21.092	0.84	0.53	5	4	-
85	α-caryophyllene	$C_{15}H_{24}$	204	19.915	19.526	0.10	2.09	4	5	-
86	(−)-spathulenol	$C_{15}H_{24}O$	220	20.288	-	0.10	-	5	-	-
87	2,3,5,8-tetramethyldecane	$C_{14}H_{30}$	198	-	20.794	-	0.39	-	4	-
88	Ledol	$C_{15}H_{26}O$	222	20.820	-	0.24	-	6	-	-
89	Nerolidol	$C_{15}H_{26}O$	222	21.676	-	0.19	-	6	-	(5)
90	Cubenol	$C_{15}H_{26}O$	222	21.831	-	0.25	-	6	-	-
91	Eudesm-4(14)-en-11-ol	$C_{15}H_{26}O$	222	22.131	-	0.28	-	6	-	-
92	Nonadecane[25,27,28]	$C_{19}H_{40}$	268	22.654	-	0.40	-	6	-	-
93	Octadecane[28]	$C_{18}H_{38}$	254	25.723	-	0.35	-	6	-	-
94	Geraniol propanoate	$C_{13}H_{22}O_2$	210	26.350	-	0.02	-	4	-	-
95	Diisobutyl phthalate	$C_{16}H_{22}O_4$	278	-	26.546	-	1.07	-	5	(9)
96	Levomenol	$C_{15}H_{26}O$	222	26.566	-	0.25	-	5	-	-
97	5-propyldecane	$C_{13}H_{28}$	184	26.800	-	0.21	-	5	-	-
98	Hexadecane	$C_{16}H_{34}$	226	27.010	24.467	0.05	0.23	6	5	-
99	Tridecanoic acid methyl ester	$C_{14}H_{28}O_2$	228	-	27.279	-	0.21	-	4	(8)
100	3-octadecene	$C_{18}H_{36}$	252	27.677	-	0.37	-	5	-	-
101	10-heneicosene[25]	$C_{21}H_{42}$	294	27.882	24.342	0.10	0.05	6	6	-
102	Heneicosane[27,28]	$C_{21}H_{44}$	296	28.179	-	2.57	-	6	-	-
103	Hexadecanal	$C_{16}H_{32}O$	240	28.827	-	0.01	-	6	-	(10)
104	9-eicosyne	$C_{20}H_{38}$	278	-	29.012	-	0.19	-	4	-
105	Heptadecane[28]	$C_{17}H_{36}$	240	29.064	-	0.71	-	6	-	-
106	1,1′-oxybis-decane	$C_{20}H_{42}O$	298	-	29.076	-	0.23	-	4	-
107	Octacosane[25,26]	$C_{28}H_{58}$	394	29.261	24.681	0.17	0.15	6	6	-
108	1-eicosanol	$C_{20}H_{42}O$	298	29.816	-	0.25	-	5	-	(5)
109	3-eicosene[27,28(5-eicosene)]	$C_{20}H_{40}$	280	30.014	-	0.08	-	4	-	-
110	Octadecanal	$C_{18}H_{36}O$	268	31.563	-	0.44	-	6	-	(6)
111	Di-*n*-octyl phthalate	$C_{24}H_{38}O_4$	390	-	32.840	-	1.61	-	5	(9)
112	Octadecyl ester acetic acid	$C_{20}H_{40}O_2$	312	33.128	-	0.14	-	4	-	(8)
113	Squalene	$C_{30}H_{50}$	410	-	34.940	-	6.66	-	5	-

[24,25,26,27,28]: the words indicate these compounds were determined in references from 24 to 28, respectively

Type: related with Table 2

the HD samples on the basis of a mass spectrum database search and retention indices (Table 1), while 53 compounds were detected by peak measurement (91.27% identified). The chromatograms of volatiles from *Rhodiola sachalinensis* by HD and HS-LPME are shown in Fig. 1(a) and (b), respectively. The most abundant compound was geraniol (24.73%), which also was the main peak detected by HD. Geraniol, which was identified as the main compound, has a rose-like odor and is one of the most abundant monoter-

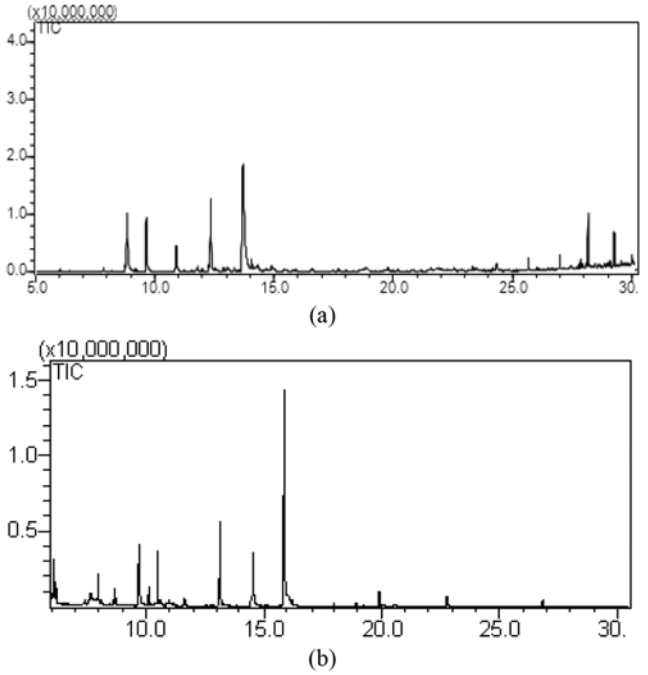

Fig. 1. Chromatograms of the volatiles from *Rhodiola sachalinensis*. (a) HD; (b) HS-LPME.

pene alcohols in the essential oil from *Rosa* sp. [24]. Geraniol was also included in *Rhodiola crenulata* [25,26], *Rhodiola fastigiata* [25], *Rhodiola quadrifida* [27], *Rhodiola sacra* [28] and *Rhodiola himalensis* [28]. Other important constituents were *n*-octanol (15.56%), linalool (14.51%), α,α4-trimethyl-3-cyclohexen-1-methanol (7.69%), and 2,7-dimethyl-2,6-octadienal (3.22%) followed by phenylethyl alcohol (0.11%), borneol (0.72%), ledol (0.24%), and cubenol (0.25%). Rohloff investigated the major chemical composition of the essential oil from rhizomes of *Rhodiola rosea* in Norway and found that it was *n*-decanol (30.38%) [24]. However, other research has not identified *n*-decanol in other *Rhodiola* species [25-28]. In this study, *n*-decanol (2.57%) was identified but was not a major chemical component in *Rhodiola sachalinensis*. To achieve the best possible separation performance for essential oil analysis, these experiments were performed six times.

In contrast to HD, only 68 compounds were identified by using HS-LPME (Table 1). The most important constituent was geraniol (24.17%), which was also the main peak detected by HS-LPME. Geraniol is commonly used in perfumes. Research has shown it to be an effective, plant-based mosquito repellent [http://en.wikipedia.org/wiki/Geraniol]. Other important constituents were *n*-octanol (15.81%), 1,1,7-trimethyl-4-methylenedecahydro-1H-cycloprop(e)azulene (6.96%), squalene (6.66%), and linalool (5.12%). One common downstream product of linalool is vitamin E. Linalool is also used by pest professionals as a flea and cockroach insecticide [http://en.wikipedia.org]. As well as geraniol, geraniol acetate was determined in both the HD (1.47%) and (0.36%) HS-LPME samples. Linalool and linalool oxide (1.89%) were determined in the HS-LPME samples but not in the HD samples.

2. Essential Oils Composition

In the HD and HS-LPME samples, the main chemical classes of volatile compounds were monoterpene alcohols (59.02% and 37.64%) and straight chain aliphatic alcohols (20.761% and 17.63%), which accounted for more than 91% and 79% of the essential oils, respectively (Table 2). *O*-Heterocyclic compounds (8.52%), aromatic compounds (5.92%), and straight chain aliphatic ketones (1.56%) were found more in the HS-LPME samples than in the HD samples.

Table 2. Composition of the essential oil from the HD and HS-LPME samples of *Rhodiola sachalinensis* ordered according to the chemical groups (summarized peak area in percentages)

Numbers	Compounds groups	HD	HS-LPME
(1)	*Monoterpene hydrocarbons*	2.24	4.66
	Oxygenated monoterpenes		
(2)	Alcohols	59.02	37.64
(3)	Aldehydes	3.28	0.67
(4)	Ketones	1.41	0.19
	Straight chain alipathic compounds		
(5)	Alcohols	20.76	17.36
(6)	Aldehydes	1.15	1.15
(7)	Ketones	1.08	1.56
(8)	Acids+esters	1.61	1.80
(9)	*Aromatic compounds*	0.32	5.92
(10)	*Phenols*	0.01	0.00
(11)	*O-heterocyclic compounds*	0.40	8.52
Total		91.27	79.47

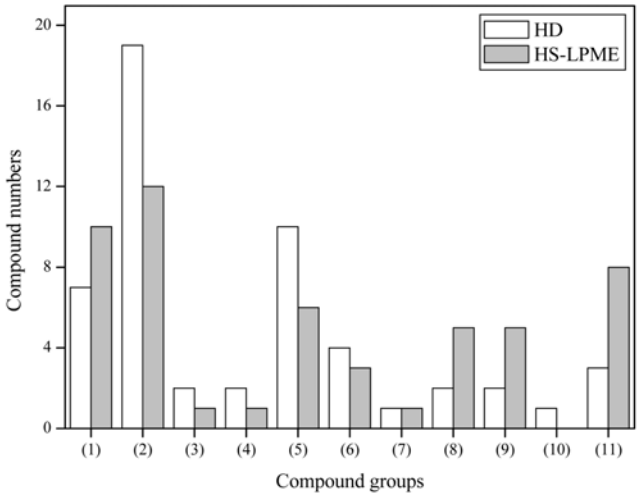

Fig. 2. Numbers of the compounds from the HD and HS-LPME samples of *Rhodiola sachalinensis* ordered according to the compound groups.

The numbers of the compounds from the HD and HS-LPME samples of *Rhodiola sachalinensis* are shown in Fig. 2 ordered according to the compound groups. More monoterpene alcohols and straight chain aliphatic alcohols were determined in the HD samples than in the HS-LPME samples. More *O*-heterocyclic compounds, aromatic compounds, and straight chain aliphatic acids and esters were determined in the HS-LPME samples than in the HD samples. These results suggested that the HD method can hydrolyze some of the thermally unstable constituents, such as linalool oxide, more so than the HD method.

Table 3. Identification of *Rhodiola* species by using the ratio of 3 major components (summarized peak area in percentages)

No.	*Rhodiola* species	*n*-octanol (O)	RSD (%)	Linalool (L)	RSD (%)	Geraniol (G)	RSD (%)	Total (%)	Ratio (O/L/G)
1	*R. sachalinensis*	15.56	3.25	14.51	7.65	24.73	8.55	54.80	1/1/2
2	*R. rosea* L.[24]	2.77	-	2.31	-	12.49	-	17.57	1/1/5
3	*R. crenulata*[25]	13.39	-	2.40	-	53.32	-	69.11	6/1/22
4	*R. fastigiata*[25]	12.29	-	5.13	-	45.33	-	62.75	2/1/9
5	*R. crenulata*[26 (Tibet)]	17.23	22.05	2.47	4.68	51.30	9.95	71.00	7/1/20
6	*R. crenulata*[26 (Yunnan)]	34.70	12.02	2.63	43.36	18.40	31.27	55.73	13/1/7
7	*R. quadrifida*[27]	0.14	-	0.00	-	0.10	-	0.24	1/0/1
8	*R. himalensis*[28]	2.43	-	0.45	-	23.23	-	26.11	5/1/52
9	*R. sacra*[28]	0.00	-	0.18	-	0.13	-	0.31	0/1/1
10	*R. calliantha*[28]	0.00	-	0.00	-	0.00	-	0.00	0/0/0

[24,25,26,27,28]: the words indicate these compounds were determined in references from 24 to 28, respectively

Regarding the different analytical methods for the isolation of the volatile compounds, HD followed by GC/MS revealed a higher number of identified and detected peaks than HS-LPME coupled with GC/MS. The applicability of LPME for essential oil extraction is intimately linked to the parameters of sampling time and temperature conditions. Additionally, the applicability of LPME is influenced by the chosen collecting solvent and the diameter of a single drop. Compared with HD, some other volatile compounds can be extracted by HS-LPME. According to the number of identified compounds from the HD and HS-LPME samples (75 vs. 68), the presented results underscore the excellent suitability of liquid-phase micro-extraction for qualitative analyses.

Floral notes such as linalool and its oxides, nonanal, decanal and geraniol, emphasize the flowery scent of *Rhodiola sachalinensis*, while aliphatic alcohols such as decanol may be responsible for the fat- or wax-like background scent. Regarding the low oil yield and the diverging composition of terpenes and volatiles in *Rhodiola sachalinensis*, the applicability of essential oil or extracts from *Rhodiola sachalinensis* in the cosmetic and perfume industries will be rather restricted to production for the national market.

3. Identification of *Rhodiola* Species

To the best of the authors' knowledge, five papers [24-28] reported that volatiles were determined from nine different *Rhodiola* species (Table 3). We were able to identify *n*-octanol, linalool, and geraniol in all these *Rhodiola* species, except in *Rhodiola calliantha*. On the basis of these results, it was suggested that the identification method for *Rhodiola* species should make use of the ratio of these three compounds. For example, *Rhodiola sachalinensis* could be identified by an *n*-octanol/linalool/geraniol ratio of 1/1/2, and the absence of these three compounds could be used to identify *Rhodiola calliantha*. However, this approach may encounter a few problems. First, the plant must be confirmed as being a member of the *Rhodiola* genus before it is identified. Moreover, the high relative standard deviation (RSD, %) values resulted in inaccuracies in the results. However, using accurate and highly repeatable experimental procedures led to accurate results. Therefore, this method can be used for successfully identifying plant species on the basis of their essential oil content.

CONCLUSIONS

One-hundred-thirteen volatile compounds were identified from *Rhodiola sachalinensis* by HD and HS-LPME. The most abundant compound was geraniol, which also was the main peak detected by HD (24.73%) and HS-LPME (24.17%), respectively. The main chemical classes of volatile compounds were monoterpene alcohols and straight chain aliphatic alcohols, which together accounted for more than 91% of the essential oil. Moreover, on comparing these results with those of other researches, it can be suggested that *Rhodiola* species could be identified by analysis of the three major compounds: *n*-octanol, linalool, and geraniol. These results will form a database for investigating the constituents of natural products and the resources of pharmaceutical, nutrition, and cosmetic products.

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