Chemical Composition of the Essential Oils of Two Rhodiola Species from Tibet

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The essential oils from rhizomes of *Rhodiola crenulata* and *R. fastigiata* in eastern Tibet were analyzed by using GC-MS. The major constituents were geraniol (53.3%), *n*-octanol (13.4%), 2-methyl-3-buten-2-ol (10.8%), citronellol (5.3%), 3-methyl-2-buten-1-ol (4.0%), myteol (3.0%), and linalool (2.4%) for *R. crenulata* and geraniol (45.3%), *n*-octanol (12.3%), 2-methyl-3-buten-2-ol (8.0%), linalool (5.1%), isogeraniol (4.5%), citronellol (4.4%), and *cis*-sabinenehydrate (3.6%) for *R. fastigiata*.

Key words: Rhodiola crenulata, Rhodiola fastigiata, Essential Oil

Introduction

Rhodiola (Crassulaceae) consisting of about 90 species are distributed in the high cold region of the Northern Hemisphere. In China, there are 73 species, mainly growing in the Qinghai-Tibet Platean (Fu and Fu, 1984). Many Rhodiola species such as R. rosea and R. crenulata have been used as traditional medicines for the treatment of longterm illness and weakness due to infection in Tibet and other regions for over 1000 years (Xiong, 1995; Rohloff, 2002). Recent pharmacological studies have showed that the medicinal Rhodiola plants have strong activities of anti-anoxia, antifatigue, anti-toxic, anti-radiation, anti-tumour, anti-aging, and active-oxygen scavenging (Ohsugi et al., 1999) as well as adaptogenic properties (Brekhman and Dardymov, 1969; Kurkin and Zapesochnaya, 1986).

Currently, Rohloff (2002) investigated the volatiles from rhizomes of R. rosea in Norway. The major chemical composition of the essential oil from this species included n-decanol, geraniol, and 1,4-p-menthadien-7-ol, etc. The chemical constituents from rhizomes of R. crenulata in China, including salidroside, tyrosol, pyrogallol, gallic acid, β -sitosterol, crenulatin, kaempferol, and ellagic acid, were reported (Wang et al., 1992; Yu et al., 1993; Du and Xie, 1994). A new flavonoid was obtained

from *R. fastigiata* in southwestern China (Peng *et al.*, 1996). In the present study, the chemical constituents of essential oils from rhizomes of two *Rhodiola* species, *i.e.*, *R. crenulata* and *R. fastigiata*, in eastern Tibet were analyzed using GC-MS.

Materials and Methods

Plant materials

The rhizomes of *R. crenulata* and *R. fastigiata* used in this study were collected from Kongpojiangda (Kongpo Gyamda) County, Linzhi (Nyingchi) district, Tibet in August of 2002. The authenticity of the materials was confirmed by Tibet University, and a voucher specimen for each species was deposited at the MOE Lab for Biodiversity Science and Ecological Engineering, School of Life Sciences, Fudan University. The rhizome samples were cut into small segments, dried and stored at room temperature prior to analysis.

Extraction of essential oils

Each dried sample was ground, weighed (100 g), and steam distilled using a Clevenger-type apparatus for 3 h. The essential oils were collected in a lighter than water oil graduated trap and dried over anhydrous sodium sulfate.

Table I. Chemical constituents of the essential oils from R. crenulata and R. fastigiata grown in Tibet.

2-Methyl-3- buten-2-ol Hexanal Octadiene a-Pinene Carene Octanal Methylpentanol 3-Methyl-2-buten-1-ol 6-Methyl-5-heptene-2-one n-Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol trans-Linaloloxide 6-Methyl-5-heptane-2-ol	4.36 5.03 6.27 7.40 7.68 8.29 8.59 8.72 9.04 9.16 10.58 10.76 10.97	10.8 0.02 0.02 0.02 0.03 0.02 0.01 4.02 0.05 0.28 2.18	8.04 0.03 - - 0.03 - 2.18 - 0.15 1.58
Hexanal Octadiene a-Pinene Carene Octanal Methylpentanol 3-Methyl-2-buten-1-ol 6-Methyl-5-heptene-2-one n-Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol trans-Linaloloxide	6.27 7.40 7.68 8.29 8.59 8.72 9.04 9.16 10.58 10.76 10.97	0.02 0.02 0.03 0.02 0.01 4.02 0.05 0.28 2.18	- - 0.03 - 2.18 - 0.15
a-Pinene Carene Octanal Methylpentanol 3-Methyl-2-buten-1-ol 6-Methyl-5-heptene-2-one n-Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol trans-Linaloloxide	7.40 7.68 8.29 8.59 8.72 9.04 9.16 10.58 10.76 10.97	0.02 0.03 0.02 0.01 4.02 0.05 0.28 2.18	- 0.03 - 2.18 - 0.15
Carene Octanal Methylpentanol 3-Methyl-2-buten-1-ol 6-Methyl-5-heptene-2-one n-Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol trans-Linaloloxide	7.68 8.29 8.59 8.72 9.04 9.16 10.58 10.76 10.97	0.03 0.02 0.01 4.02 0.05 0.28 2.18	- 0.03 - 2.18 - 0.15
Octanal Methylpentanol 3-Methyl-2-buten-1-ol 6-Methyl-5-heptene-2-one n-Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol trans-Linaloloxide	8.29 8.59 8.72 9.04 9.16 10.58 10.76 10.97	0.02 0.01 4.02 0.05 0.28 2.18	2.18 - 0.15
Methylpentanol 3-Methyl-2-buten-1-ol 6-Methyl-5-heptene-2-one n-Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol trans-Linaloloxide	8.59 8.72 9.04 9.16 10.58 10.76 10.97	0.01 4.02 0.05 0.28 2.18	2.18 - 0.15
3-Methyl-2-buten-1-ol 6-Methyl-5-heptene-2-one <i>n</i> -Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol <i>trans</i> -Linaloloxide	8.72 9.04 9.16 10.58 10.76 10.97	4.02 0.05 0.28 2.18	2.18 - 0.15
6-Methyl-5-heptene-2-one <i>n</i> -Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol <i>trans</i> -Linaloloxide	9.04 9.16 10.58 10.76 10.97	0.05 0.28 2.18	_ 0.15
6-Methyl-5-heptene-2-one <i>n</i> -Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol <i>trans</i> -Linaloloxide	9.16 10.58 10.76 10.97	0.28 2.18	0.15
n-Hexanol 1-Octen-3-ol 6-Methyl-5-heptene-2-ol trans-Linaloloxide	10.58 10.76 10.97	2.18	
1-Octen-3-ol 6-Methyl-5-heptene-2-ol <i>trans</i> -Linaloloxide	10.58 10.76 10.97	2.18	
trans-Linaloloxide	10.97		1.50
trans-Linaloloxide	10.97	_	1.18
		_	0.74
	11.37	_	1.56
Linalool	11.92	2.40	5.13
n-Octanol	12.10	13.39	12.29
trans-2-Octenol	12.81	0.76	_
Methyloctene	12.96	0.10	_
Pinocarveol	13.49	_	2.18
Citral	13.78	0.24	0.40
Terpineol	13.90	0.32	0.15
Pentadecanone	13.97	_	1.00
Heptadecene	14.20	_	0.28
Citronellol	14.62	5.25	4.42
Myrtenol	15.05	2.96	_
Isogeraniol	15.16	0.47	4.52
Geraniol	15.69	53.32	45.33
Nonadecane	16.26	=	0.36
Perilla alcohol	17.41	0.37	0.06
cis-Sabinenehydrate	18.30	0.78	3.58
Heneicosene	18.57	-	0.12
Docosane	19.39	_	0.23
Farnesol	19.76	0.10	-
n-Octacosane	20.22	0.19	1.65
p-Allylphenol	20.69	0.31	0.16
Tetracosane	22.14	-	0.16
Acetic acid octadecyl ester	24.26	_	0.14
Stearaldehyde	25.01	_	0.33
Pentadecanal	24.83	0.15	-
Hexadecanoic	26.79	0.13	0.98
Octadecanol	27.03	-	0.54

GC-MS analysis

The GC-MS analysis was performed on a combined GC-MS instrument (Finnigan Voyager, San Jose, CA, USA) using a HP- INNOWax (bondable polyethylene glycol) fused silica capillary column (30 m length, 0.25 mm diameter, 0.25 µm film thickness). A 1 µl aliquot of oil was injected into the column using a 15:1 split injection, which temperature was set up at 250 °C. The GC program was initiated by a column temperature set at 60 °C for 2 min, increased to 250 °C at a rate of 10 °C/min, held for 10 min. Helium was used as the car-

rier gas (1.0 ml/min). The mass spectrometer was operated in the 70 eV EI mode with scanning from 41 to 450 amu at 0.5 s, and mass source was set up 200 °C. The compounds were identified by matching their mass spectral fragmentation patterns with those stored in the spectrometer database using the National Institute of Standards and Technology Mass Spectral database (NIST-MS).

Results and Discussion

The steam distillation of raw materials of R. crenulata and R. fastigiata yielded clear and yel-

Table II. The MS data of the major compounds of the essential oils from R. crenulata and R. fastigiata grown in Tibet.

Compounds	MS data
2-Methyl-3-buten-2-ol	86 (2), 71(100), 59(30), 43(70), 41(25)
3-Methyl-2-buten-1-ol	86(20), 71(100), 68(25), 67(25), 53(30), 43(40), 41(60), 39(25)
Linalool	139(5), 136(10), 121(20), 93(60), 71(100), 69(40), 71(100), 69(40), 55(50), 43(65), 41(65), 39(25)
n-Octanol	112(10), 97(15), 84(60), 83(55), 70(75), 69(70), 57(50), 56(100), 55(80), 43(70), 41(80), 39(50)
Citronellol	156(5), 138(10), 123(20), 109(15), 95(40), 82(45), 81(55), 71(25), 69(85), 67(60), 41(100), 39(20)
Myrtenol	152(2), 121(10), 119(15), 109(10), 108(25), 93(20), 91(45), 79(100), 77(20), 67(15), 55(15), 43(20), 41(30), 39(20)
Isogeraniol	155(2), 154(30), 139(5), 123(20), 121(60), 110(12), 109(80), 95(45), 39(40), 81(80), 69(60), 67(80), 65(10), 55(50), 53(25), 43(45), 41(90), 39(30)
Geraniol	154(2), 139(5), 123(10), 111(10), 93(15), 69(100), 68(20), 55(10), 41(70)
cis-Sabinenehydrate	154(2), 152(40), 121(30), 119(20), 109(70), 105(25), 95(15), 93(25), 81(45), 79(100), 77(40), 67(40), 65(15), 55(10), 53(10), 43(25), 41(20), 39(20)

lowish essential oils (both $0.5\% \pm 0.1\%$ of dry wt.). The analysis of the essential oils from the two species showed differences in chemical compounds (Table I). The MS data of 9 major compounds of Table I are shown in Table II.

In *R. crenulata*, a total of 31 compounds were isolated, in which 28 compounds were identified (about 98.8% of the oil). The constituents identified included geraniol (53.3%), *n*-octanol (13.4%), 2-methyl-3-buten-2-ol (10.8%), citronellol (5.3%), 3-methyl-2-buten-1-ol (4.0%), myrteol (3.0%), and linalool (2.4%) (Table I). In particular, monoterpene alcohols were the most compound group of the oil (65.1%).

In another species, *R. fastigiata*, a total of 36 compounds were isolated and 31 compounds were identified (about 99.5 % of the oil). The major constituents identified were geraniol (45.3%), *n*-octanol (12.3%), 2-methyl-3-buten-2-ol (8.0%), linalool (5.1%), isogeraniol (4.5%), citronellol (4.4%), and *cis*-sabinenehydrate (3.6%) (Table I). In similar to *R. crenulata*, monoterpene alcohols were also the most compound group of the *R. fastigiata* oil (61.8%).

It is notable that geraniol was the most abound individual compound in the essential oils of the two *Rhodiola* species (Table I). Recent studies have indicated that geraniol can sensitize human

colonic cancer cells to 5-fluorouracil treatment (Carnesecchi et al., 2002), inhibit growth and polyamine biosynthesis in human colon cancer cells (Carnesecchi et al., 2001), induce the apoptosis-like cell death (Izumi et al., 1999), and suppress pancreatic tumor growth without significantly affecting blood cholesterol levels (Burke et al., 1997). Our study demonstrates that the Tibetan Rhodiola may be a potential geraniol-rich source for commercial cultivation. Obviously, further investigation of variability in the chemical composition of the essential oils from different Rhodiola plants, especially species growing very special environments such as the Qinghai-Tibet Plateau, is needed.

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