THE VOLATILE CONSTITUENTS OF *Dracocephalum kotschyi* OILS

H. R. Monsef-Esfahani,[1*] F. Karamkhani,[1]
B. Nickavar,[3] K. Abdi,[2] and M. A. Faramarzi[1]

UDC 547.913

The chemical composition of the essential oils of Dracocephalum kotschyi *(Lamiaceae) aerial parts, grown in Iran and obtained from three different methods, were determined by GC and GC/MS. Fifty-seven compounds (93.3%) in the hydrodistillate oil, 55 compounds (94.2%) in the steam distillate oil, and 34 compounds (98.4%) in the hydrolate were identified. The major compounds in the hydrodistillate oil were α-pinene (12.1%), methyl geranate (11.2%), β-ocimene (8.6%), and limonene (7.2%). α-Pinene (15%), methyl geranate (14.5%), limonene (11.2%), and β-ocimene (8.4%) were the most abundant components in the steam distillate oil. The percentages of geraniol (13%), trans-verbenol (11.6%), and terpinen-4-ol (11.2%) were more than other constituents in the hydrolate.*

Key words: *Dracocephalum kotschyi*, essential oil, hydrodistillate, steam distillate, hydrolate.

Dracocephalum kotschyi Boiss., a member of the Lamiaceae family, is an endemic herbaceous wild plant of Iran [1]. It grows spontaneously at an altitude of 2000–3000 m mostly in the north and northeastern parts of the country [2].

There have been few studies conducted on the chemical composition and pharmaceutical effects of *D. kotschyi*. The essential oil composition of the plant was first reported in 1988, in which 42 compounds were identified [3]. The immunomodulatory effect of the hydroalcoholic extract was also investigated [4]. The hydroalcoholic extract and polyphenolic fraction of *D. kotschyi* leaves showed a significant effect in hyperlipidemia [5].

In folk medicine, the distillate of the aerial parts of *D. kotschyi* mixed with some aromatic plants is consumed for gastrointestinal disorders as an antinociceptive [6].

Although the chemical composition of the essential oil of *D. kotschyi* was previously studied, no research has so far been conducted concerning the hydrolate. In the present work regarding the traditional uses of *D. kotschyi*, we compared the composition of the hydrodistillate, steam distillate, and hydrolate of the plant.

In order to compare the chemical compositions of *D. kotschyi* essential oils and the hydrolate by gas chromatography, the volatile constituents of the dried aerial parts of the plant were obtained by means of three methods: hydrodistillation, steam distillation, and hydrodistillation- solvent extraction; they were then analyzed by GC/MS methods. The yields of the oils were 0.5, 0.4 and 0.2%, respectively.

The chemical and class composition of the oils are presented in Tables 1 and 2, respectively. Fifty-seven compounds (representing of 93.3%) in the hydrodistillate oil, 55 compounds (representing of 94.2%) in the steam distillate oil, and 34 compounds (representing of 98.4%) in the hydrolate were identified (Table 1).

The identified compounds and their percentages in both oils and the hydrolate are given in Tables 1 and 2. Regarding the tables, it is evident that the compositions are different qualitatively and quantitatively.

The essential oil obtained by hydrodistillation consisted mainly of hydrocarbon monoterpenes (41.7%), ester monoterpenes (16.2%), and aldehyde monoterpenes (14.1%). The major compounds in the hydrodistilate oil were α-pinene (12.1%), methyl geranate (11.2%), β-ocimene (8.6%), and limonene (7.2%).

1) Department of Pharmacognosy, Fax +98 (21) 66461178, e-mail: monsefes@sina.tums.ac.ir; 2) Medicinal Chemistry Faculty of Pharmacy, Tehran University of Medical Sciences, P. O. Box 14155-6451, Tehran, Iran; 3) Department of Pharmacognosy, School of Pharmacy, Shahid Beheshti University of Medical Sciences, P. O. Box 14155-6153, Tehran, Iran.
Published in Khimiya Prirodnykh Soedinenii, No. 1, pp. 35-37, January-February, 2007. Original article submitted November 24, 2005.

0009-3130/07/4301-0040

TABLE 1. Chemical Composition of *D. kotschyi* Essential Oils and Hydrolate

Compound	RI	HD, %	SD, %	HAF, %	Compound	RI	HD, %	SD, %	HAF, %
α-Pinene	931	12.2	15	-	Myrtenal	1158	0.2	0.2	4.9
Camphene	937	0.2	0.2	-	α-Terpineol	1165	0.1	0.2	2.8
2,4(10)-Thujadiene	940	0.2	0.3	-	Verbenone	1169	0.3	1.2	8.7
6-Methyl-5-hepten-2-one	957	-	-	2.7	*trans*-Carveol	1194	0.5	0.1	3.0
Sabinene	961	3.0	3.6	-	Cumine aldehyde	1201	0.2	0.1	1.0
β-Pinene	964	0.8	0.9	-	Neral	1215	6.6	2.9	6.3
β-Myrcene	980	2.3	2.5	-	Geraniol	1233	0.1	-	13
3-Octanol	978	-	-	0.2	Geranial	1242	5.1	1.3	6.2
ρ-Mentha-1(7),8-diene	990	0.8	0.8	-	Bornyl acetate	1262	0.7	0.8	0.7
α-Terpinene	1004	0.2	-	-	Perilla alcohol	1267	-	0.1	3.7
ρ-Cymene	1007	1.0	0.6	-	ρ-Menth-1-en-9-ol	1271	-	0.2	0.6
Limonene	1018	7.2	11.2	2.3	Methyl geranate	1307	11.2	14.5	3.6
β-Phellandrene	1020	3.9	1.6	1.2	*trans*-Neryl acetate	1340	0.2	0.3	-
(*Z*)-β-Ocimene	1031	8.6	8.4	-	(*Z*)-β-Damascenone	1352	0.2	-	-
(*E*)-β-Ocimene	1037	0.8	0.8	-	Geranyl acetate	1362	4.1	4.7	0.1
γ-Terpinene	1044	0.6	0.2	-	β-Bourbonene	1370	0.5	0.9	-
trans-Sabinene hydrate	1047	0.4	0.4	-	β-Elemene	1377	0.6	0.8	2.5
cis-Linalool oxide	1058	0.2	0.3	0.2	(*E*)-Caryophyllene	1400	0.5	0.7	-
Terpinolene	1073	0.8	0.6	-	α-Humulene	1432	0.1	0.2	-
cis-Sabinene hydrate	1077	0.4	0.4	0.6	*allo*-Aromadendrene	1440	1.1	1.9	-
Linalool	1080	1.0	0.7	2.6	Germacrene D	1464	5.7	7.0	-
1-Octen-3-yl acetate	1094	0.1	0.1	-	Bicyclogermacrene	1474	0.7	0.6	-
6-Camphenol	1097	1.2	0.9	1.1	Germacrene A	1482	0.2	0.1	-
trans-ρ-2-Menthen-1-ol	1099	0.1	0.1	0.5	δ-Cadinene	1501	0.3	0.4	-
cis-ρ-Mentha-2,8-dien-1-ol	1109	0.2	0.3	0.5	Spathulenol	1545	0.7	0.9	0.8
trans-Limonene oxide	1112	0.3	-	1.2	Caryophyllene oxide	1547	0.2	0.2	0.3
neo-allo-Ocimene	1115	1.0	1.0	1.9	Humulene epoxide II	1573	0.2	0.3	-
trans-Verbenol	1121	1.4	0.4	11.6	10-epi-γ-Eudesmol	1598	0.4	0.7	0.7
Pinocarvone	1127	0.2	0.2	0.5	Heptadecane	1697	0.1	0.1	0.7
3-Thujanol	1145	0.8	0.6	0.5	(*E*,*E*)-Farnesol	1726	0.5	0.5	-
Terpinen-4-ol	1154	2.0	0.2	11.2					

RT: Retention time; RI: retention index; HD: Hydrodistillation method; SD: Steam distillation method; HAF: Hydrolate aromatic fraction.

In the steam distillation method, the main constituents were hydrocarbon monoterpenes (49%), ester monoterpenes (20.3%), and hydrocarbon sesquiterpenes (12.2%). α-Pinene (15%), methyl geranate (14.5%), limonene (11.2%), and β-ocimene (8.4%) were the most abundant components in the steam distillate oil.

The hydrolate aromatic fraction consisted mainly of alcohol and aldehyde monoterpenes (51.7% and 18.4%, respectively). The percentages of geraniol (13%), *trans*-verbenol (11.6%), and terpinen-4-ol (11.2%) were higher than other components.

According to Table 2, the percentage of the oxygenated monoterpenoids extracted from the hydrolate (84%) was significantly higher than that using the other methods (39% for the hydrodistillate and 29.8% for the steam distillate). This is in complete agreement with the fact that the oxygenated compounds with high polarity are very soluble in water. As a result, the ratios of alcohol, aldehyde, and ketone monoterpenes are significantly higher than those in the other constituents in the hydrolate. On the contrary, ester monoterpenes in the hydrolate aromatic fraction are less in comparison to the other methods. This is due to the low polarity and solubility of ester monoterpenes compared to the other oxygenated monoterpenes.

TABLE 2. Class Composition of *D. kotschyi* Essential Oils and Hydrolate

Terpenoid class	Content percent, %		
	HD	SD	HAF
Hydrocarbon monoterpenes	41.7	49	6.5
Alcohol monoterpenes	8.2	4.6	51.7
Aldehyde monoterpenes	14.1	3.5	18.4
Ketone monoterpenes	0.5	1.4	9.5
Ester monoterpenes	16.2	20.3	4.4
Total monoterpenes	**80.7**	**78.8**	**90.5**
Hydrocarbon sesquiterpenes	9.4	12.2	2.5
Alcohol sesquiterpenes	1.9	2.5	1.5
Total sesquiterpenes	**11.3**	**14.7**	**4**
Miscellaneous	1.3	0.7	3.9
Total content	**93.3**	**94.2**	**98.4**

HD: Hydrodistillation method; SD: Steam distillation method; HAF: Hydrolate aromatic fraction.

Because of the high molecular weight and low solubility of sesquiterpenes, their percentages were higher in the oils collected by steam distillation (14.7%) and hydrodistillation (11.3%) compared to the hydrolate aromatic fraction (4%). It was also observed that the percentages of sesquiterpenoids in steam distillation methods (14.7%) were somehow higher than the percentage obtained from the hydrodistillation method (11.3%). This finding could be related to the special procedure conditions in the steam distillation method, which resulted in the high-molecular-weight sesquiterpenoids remaining intact [7, 8].

EXPERIMENTAL

Plant Material. The aerial parts of *D. kotschyi* were collected from the Siahbisheh region on the north slope of the Alborz Mountains in Iran at an altitude of 1600–1800 m, during May 2002. Voucher specimens have been deposited in the herbarium of the Faculty of Pharmacy, Tehran University of Medical Sciences, Tehran, Iran.

Isolation Procedures. The air-dried flowering aerial parts (100 g) were crushed and the oil isolation procedure was performed using a Clevenger-type apparatus separately via the hydrodistillation and steam distillation methods for 4 hours. Liquid-liquid extraction for obtaining the aromatic fraction was done on 200 mL of hydrodistilled hydrolate with normal pentane. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure.

Identification of Oil Components. Analytical gas chromatography was carried out using a Thermoquest 2000 GC system with a DB-1 capillary column (30 m × 0.25 mm; 0.25 μm film thickness). The carrier gas was helium with flow 1.5 mL/min; the analysis uses split ratio 1/25 and a flame ionization detector. The column temperature was programmed at 50°C for 1 min, heating to 260°C with a 2.5°C/min rate, and then keeping constant at 260°C for 20 min. GC/MS was performed on a Thermoquest 2000 with a quadropole mass selective detector on capillary column DB-1 (see GC); carrier gas helium; flow rate 1.5 mL/min; oven temperature programmed as described above. The MS operated at 70 eV ionization energy. Mass range was from *m/z* 50–300 amu. Retention indices were calculated by using the retention times of *n*-alkanes that were injected at the same chromatographic conditions. The compounds were identified by comparison of their relative retention indices (RRI, DB-1) with those in the literature [9] and by computer searching followed by matching the mass spectra data with those held in the computer library.

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