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Composition of the Essential Oil of Endemic *Centaurea paphlagonica* (Bornm.) Wagenitz From Turkey

Y. BULENT KOSE*, AYHAN ALTINTAS[†], BETUL DEMIRCI[†], SEZGIN CELIK[‡] and K.H. CAN BASER[‡] Department of Pharmaceutical Botany, Faculty of Pharmacy Anadolu University, 26470 Eskisehir, Turkey Fax: (90)(222)3350750; Tel: (90)(222)3350580-ext. 3704 E-mails: ybkose@anadolu.edu.tr; ybkose@gmail.com

The essential oil obtained by hydrodistillation from endemic *Centaurea paphlagonica* (Asteraceae) in *Plumosipappus* (Czerep.) Wagenitz section from Turkey was analyzed by gas chromatography and gas chromatography/mass spectrometry, simultaneously. Main constituents of the oil were found as hexadecanoic acid (28.9 %), dodecanoic acid (22.8 %) and caryophyllene oxide (9.2 %). Fatty acids were identified as the main constituent groups of the species.

Key Words: *Centaurea paphlagonica*, Asteraceae, Essential oil composition.

INTRODUCTION

Turkey is the main centre of diversity for *Centaurea*¹. Almost 600 species belonging to genus *Centaurea* L. are naturally distributed in Asia, North Africa and America. In Turkey, the genus is represented by 187 species and 118 of them are endemic²⁻¹¹. *Centaurea* species have been widely used for their antidandruff, anti-diarrheic, antirheumatic, antiinflammatory, choleretic, diuretic, digestive, stomachic, astringent, antipyretic, cytotoxic and antibacterial properties in folk medicine^{12,13}.

Volatile constituents studies are available in literature on the following *Centaurea* species: *C. depressa* from Iran¹⁴, *C. eryngioides* and *C. iberica* from Lebanon¹⁵, *C. cineraria* subsp. *umbrosa* from Italy¹⁶, *C. sessilis* and *C. armena*¹⁷, *C. dichroa*¹⁸, *C. mucronifera* and *C. chrysantha*¹⁹, *C. pseudoscabiosa* subsp. *pseudoscabiosa* and *C. hadimensis*²⁰, *C. kotschyi* var. *kotschyi* and *C. kotschyi* var. *decumbens*²¹ and *C. aladaghensis*, *C. antiochia* var. *prealta*, *C. antitauri*, *C. babylonica*, *C. balsamita*, *C. cheirolepidoides*, *C. deflexa*, *C. iconiensis*, *C. lanigera*, *C. ptosimopappoides*²², *C. wagenitzii*, *C. tossiensis* and *C. luschaniana*²³, *C. saligna*²⁴, *C. amaena*²⁵ and *C. tchihatcheffii*²⁶ from Turkey, *C. pelia*, *C. thessala* subsp. *drakiensis*, *C. zuccariniana*, *C. raphanina* subsp. *mixta*, *C. spruneri* from Greece^{27,28}.

[†]Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, 26470 Eskisehir, Turkey. ‡Vocational School, Technical Programs, Kirikkale University, Kirikkale, Turkey.

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The present work reports on the essential oil composition of endemic *Centaurea* species from Turkey *i.e.*, *C. paphlagonica* (Bornm.) Wagenitz. The oil was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) systems.

EXPERIMENTAL

C. paphlagonica was collected in Turkey (Table-1). Voucher specimens are kept at the Herbarium of the Faculty of Pharmacy, Anadolu University in Eskisehir, Turkey (ESSE). The air-dried aerial parts of the plant were hydrodistilled for 3 h using a Clevenger-type apparatus to produce a small amount of essential oil which was trapped in *n*-hexane.

TABLE-1	
INFORMATION ON THE PLANT MATER	IALS

Centaurea spp.	Collection site	Altitude (m)	Collection period	Oil yield* (%)
C. paphlogonica Yo	zgat (B5), Between Çayiralan- çi	1450	July 2004	Trace

*Essential oil yields are given on moisture free basis (v/w); Trace (< 0.1 %).

The GC-MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60 m × 0.25 mm, 0.25 μ m film thickness) was used with helium as carrier gas (0.8 mL/min). GC oven temperature was kept at 60 °C for 10 min and programmed to 220 °C at a rate of 4 °C/min and kept constant at 220 °C for 10 min and then programmed to 240 °C at a rate of 1 °C/min. Split ratio was adjusted at 40:1. The injector temperature was set at 250 °C. Mass spectra were recorded at 70 eV. Mass range was from m/z 35 to 450. The GC analysis was carried out using an Agilent 6890N GC system. FID detector temperature was 300 °C. To obtain the same elution order with GC/MS, simultaneous autoinjection was done on a duplicate of the same column applying the same operational conditions. Relative percentage amounts of the separated compounds were calculated from FID chromatograms. The result of analysis is shown in Table-2.

Identification of components: Identification of the essential oil components were carried out by comparison of their relative retention times with those of authentic samples or by comparison of their relative retention index (RRI) to series of *n*-alkanes. Computer matching against commercial (Wiley GC/MS Library, Adams Library, MassFinder 2.1 Library)^{29,30} and in-house "Baser Library of Essential Oil Constituents" built up by genuine compounds and components of known oils, as well as MS literature data³¹⁻³³ was used for the identification.

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RESULTS AND DISCUSSION

Analyses of the hydrodistilled oil was performed on GC and GC/MS systems. The composition of the oil of Centaurea paphlagonica is given in Table-2. according their relative retention indices (RRI) and with their relative percentages (%). In total 53 compounds were identified, representing 91.2 % of the individual oil.

RRI	Compound	(%)
1093	Hexanal	0.1
1244	2-Pentyl furan	0.1
1360	Hexanol	0.1
1400	Nonanal	0.2
1463	Heptanol	0.1
1496	2-Ethyl hexanol	0.2
1535	Dihydroedulane I*	0.4
1548	(E)-2-Nonenal	0.2
1553	Linalool	0.1
1604	Thymol methyl ether	0.1
1612	β-Caryophyllene	1.1
1687	α-Humulene	0.1
1742	β-Selinene	0.4
1766	Decanol	0.1
1773	δ-Cadinene	0.1
1776	γ-Cadinene	tr
1815	2-Tridecanone	0.1
1827	(E,E)-2,4-Decadienal	0.1
1838	(E) - β -Damascenone	0.2
1864	<i>p</i> -Cymen-8-ol	0.1
1868	(<i>E</i>)-Geranyl acetone	0.1
1932	Isoamylbenzoate	0.1
1941	α-Calacorene	0.1
1945	1,5-Epoxy-salvial(4)14-ene	0.4
1958	(E) - β -Ionone	0.2
2008	Caryophyllene oxide	9.2
2000	Salvial-4(14)-en-1-one (=mintketone)	0.2
2050	(E)-Nerolidol	0.2
2050	Humulene epoxide-II	0.9
2095	Hexyl benzoate	tr
2100	Heneicosane	0.5
2131	Hexahydrofarnesyl acetone	2.8
2144	Spathulenol	1.3
2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	0.9
2192	Nonanoic acid	0.1
2198	Thymol	0.2
2200	Docosane	0.1
2211	Clovenol	0.3
2226	Methyl hexadecanoate	0.1

TABLE-2 COMPOSITION OF THE ESSENTIAL OIL OF Centaurea paphlagonica

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RRI	Compound	(%)
2239	Carvacrol	0.3
2298	Decanoic acid	0.5
2300	Tricosane	1.9
2324	Caryophylla-2(12),6(13)-dien-5α-ol(=Caryophylladienol II)	1.7
2369	Eudesma-4(15),7-dien-1β-ol	0.3
2389	Caryophylla-2(12),6-dien-5α-ol (= <i>Caryophyllenol I</i>)	0.4
2392	Caryophylla-2(12),6-dien-5β-ol (= <i>Caryophyllenol II</i>)	3.3
2500	Pentacosane	0.8
2503	Dodecanoic acid	22.8
2622	Phytol	0.7
2670	Tetradecanoic acid	4.5
2700	Heptacosane	2.8
2822	Pentadecanoic acid	0.5
2931	Hexadecanoic acid	28.9
	Т	'otal 91.2

Hexadecanoic acid (28.9 %), dodecanoic acid (22.8 %) and caryophyllene oxide (9.2 %) were main constituents of the oil of *C. paphlagonica*.

The chemical class distribution of the oil composition of *C. paphlagonica* is reported in Table-3. In the essential oil of *C. paphlagonica*, monoterpenes were scarcely represented (0.9 %). Fatty acids and their esters were main constituents predominated the oil in the ratio of 57.4 %.

TABLE-3 CHEMICAL CLASS DISTRIBUTION OF THE ESSENTIAL OIL COMPONENTS OF *C. paphlagonica*

Chemical class		
Oxygenated Monoterpenes	0.9	
Sesquiterpene Hydrocarbones	1.8	
Oxygenated Sesquiterpenes	18.4	
Diterpenes	0.7	
Fatty acid + esters	57.4	
Others	12.0	

Previously, hexadecanoic acid, dodecanoic acid and caryophyllene oxide were reported from the following Turkish *Centaurea* species *i.e.*, *C. dichroa*¹⁸, *C. saligna*²⁴, *C. wagenitzii*, *C. tossiensis* and *C. luschaniana*²³, *C. amaena*²⁵, *C. tchihatcheffii*²⁶.

Sesquiterpenes like germacrene-D, bicyclogermacrene and β -caryophyllene were found as the main compounds of the oils of *C. pseudoscabiosa* subsp. *pseudoscabiosa*, *C. hadimensis*²⁰, *C. kotschyi* var. *kotschyi*, *C. kotschyi* var. *decumbens*²¹, *C. mucronifera*, *C. chrysantha*¹⁹.

Similarly, Lazari *et al.*^{27,28} has reported caryophyllene oxide, β -elemenene, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, hexacosane and heptacosane as main constituents in the oil of *C. thessela* subsp. *drakiensis*, *C. pelia*, *C. zuccariniana*, *C. raphanina* subsp. *mixta*, *C. spruneri* growing in Greece. Vol. 21, No. 3 (2009) Composition of Essential Oil of Centaurea paphlagonica (Bornm.) Wagenitz 1723

More recently, sesquiterpene and hydrocarbon derivatives were found as principal compounds in the oils of *C. aladaghensis*, *C. antiochia* var. *prealta*, *C. antitauri*, *C. babylonica*, *C. balsamita*, *C. cheirolepidoides*, *C. deflexa*, *C. iconiensis*, *C. lanigera* and *C. ptosimopappoides*²².

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Contact: Claire Shiell Air Pollution 2009, Wessex Institute of Technology Ashurst Lodge, Ashurst, Southampton, SO40 7AA Tel: 44 (0) 238 0293223; Fax: 44 (0) 238 0292853 cshiell@wessex.ac.uk http://www.wessex.ac.uk/09-conferences/air-pollution-2009.html