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Composition of the Essential Oils of *Centaurea sericeae* Wagenitz and *Centaurea ensiformis* P.H. Davis from Turkey

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The essential oil obtained by hydrodistillation from two endemic *Centaurea* L. species (Asteraceae); *Centaurea sericeae* Wagenitz and *Centaurea ensiformis* P.H. Davis from Turkey was analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), simultaneously. Caryophyllene oxide (10.6 %), nonacosane (8.6 %) and hexadecanoic acid (7 %) were the main constituents in the oil of *C. sericeae* and β-eudesmol (29.8 %), hexadecanoic acid (8 %) and caryophyllene oxide (7.6 %) were the main constituents in the oil of *C. ensiformis*.

Key Words: *Centaurea sericeae*, *Centaurea ensiformis*, Asteraceae, Essential oil composition, Turkey.

INTRODUCTION

Almost 600 species belonging to genus *Centaurea* L. are naturally distributed in Asia, North Africa and America¹. In flora of Turkey, *Centaurea* is one of the richest genera². *Centaurea* species have been widely used for their antidandruff, antidiarrheic, antirheumatic, antiinflammatory, choleretic, diuretic, digestive, stomachic, astringent, antipyretic, cytotoxic and antibacterial properties in folk medicine^{3,4}.

EXPERIMENTAL

C. sericeae and *C. ensiformis* were collected in different localities of Turkey: *C. ensiformis* Davis, Mugla: Köycegiz, Yayladag, Sandras Dagi, 1460 m, 37°02. N, 28°46. E, 26 vii 2006, O. Tugay 4254 and Uysal. *C. sericea* Wagenitz Eskisehir: Between Eskisehir-Kütahya, road side, 875 m, 39°43. N, 30°21. E, 15 vii 2005, O. Tugay 3647 and Uysal.

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).

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TABLE-1 COMPOSITION OF THE ESSENTIAL OILS OF Centaurea sp.

RRI	Compound	C. sericea (%)	C. ensiformis (%)
1032	α-Pinene	0.6	0.3
1093	Hexanal	0.4	0.4
1151	δ-4-Carene	_	0.2
1195	Dehydro-1,8-cineole	_	0.1
1203	Limonene	0.2	-
1244	2-Pentyl furan	0.5	0.5
1280	<i>p</i> -Cymene	0.1	0.1
1296	Octanal	0.1	0.1
1348	6-Methyl-5-hepten-2-one	_	0.2
1349	1-Tridecene	0.4	-
1360	1-He xanol	_	0.1
1400	Nonanal	0.4	0.5
1452	1-Octen-3-ol	_	0.1
1452	α, <i>p</i> -Dimethylstyrene	_	tr
1477	4,8-Epoxyterpinolene	_	0.1
1492	Cyclosativene	0.3	-
1497	α-Copaene	_	0.2
1500	Pentadecane	tr	tr
1505	Dihydroedulane II*	0.7	-
1506	Decanal	0.1	0.1
1516	(E)-Theaspirane	0.4	0.3
1532	Camphor	_	0.1
1535	Dihydroedulane I*	0.3	0.1
1541	Benzaldehyde	-	0.2
1553	(Z)-Theaspiran	0.5	0.5
1600	Hexadecane	0.1	-
1602	6-Methyl-3,5-heptadien-2-one	_	0.1
1611	Terpinen-4-ol	_	0.1
1612	β-Caryophyllene	1.6	0.6
1638	β-Cyclocitral	0.2	_
1644	Widdrene (=Thujopsene)	0.1	-
1648	Myrtenal	tr	-
1654	(E,E)-2,5-Epoxy-6,8-megastigmadiene 32.1	0.2	0.1
1668	(Z)-β-Farnesene	tr	-
1687	α-Humulene	0.4	0.2
1688	Selina-4,11-diene (= 4,11-Eudesmadiene)	0.1	-
1700	p-Mentha-1,8-dien-4-ol (=Limonen-4-ol)	_	0.2
1704	γ-Muurolene	0.2	-
1706	α-Terpineol	_	0.1
1718	<i>p</i> -Menth-4-en-3one	_	0.3
1722	Dodecanal	_	-
1726	Germacrene D	_	0.3
1741	β-Bisabolene	1.1	-
1742	β-Selinene	0.9	0.2

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1755	Bicyclogermacrene	tr	0.1
1762	α-Chamigrene	0.4	0.1
1763	Naphthalene	0.2	0.1
1766	1-Dec anol	0.1	tr
1773	δ-Cadinene	0.1	0.1
1776	γ-Cadinene	_	tr
1798	Methyl salicylate	0.2	_
	4,8,12-Trimethyl-1,3(E),7(E),11-		
1823	tridecatetraene	_	0.1
1827	(E,E)-2,4-Decadienal	0.1	0.1
1838	(E)-β-Damascenone	1.5	0.2
1849	Calamenene	0.1	0.2
1864	p-Cymen-8-ol	_	0.1
1868	(E)-Geranyl acetone	1.0	1.1
1882	Aplotaxene	0.5	0.4
1900	Nonadecane	tr	_
1941	α-Calacorene	0.3	0.1
1945	1,5-Epoxy-salvial(4)14-ene	1.4	0.7
1958	(E)-β-Ionone	_	1.0
1973	1-Dodecanol	0.3	_
2001	Isocaryophyllene oxide	0.3	0.4
2008	Caryophyllene oxide	10.6	7.6
2037	Salvial-4(14)-en-1-one (=mintketone)	0.4	0.7
2041	Pentadecanal	0.4	_
2050	(E)-Nerolidol	1.4	1.2
2071	Humulene epoxide-II	2.3	0.9
2092	β-Oplopenone	0.2	0.3
2100	Heneicosane	0.5	_
2103	Guaiol	-	1.0
2131	Hexahydrofamesyl acetone	1.1	3.4
2144	Spathulenol	3.3	2.3
2144	Rosifoliol	-	3.3
2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	1.0	0.6
2198	Thymol	—	1.2
2204	Eremoligenol	0.8	1.2
2239	Carvacrol	1.4	0.7
2257	β-Eudesmol	6.9	29.8
2278	torilenol	0.4	_
2289	Oxo-α-Ylangene	0.6	1.0
2300	Tricosane	2.2	0.3
2316	Caryophylla-2(12),6(13)-dien-5β-ol (=Caryophylladienol I)	0.8	0.3
2369	Eudesma-4(15),7-dien-1β-ol	0.6	0.3
2369	(2E,6E)-Farnesol	0.4	_
2389	Caryophylla-2(12),6-dien-5α-ol (=caryophyllenol I)	0.7	0.6
2392	Caryophylla-2(12),6-dien-5β-ol (=caryophyllenol II)	3.3	2.0

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2400	Tetracosane	0.4	-
2500	Pentacosane	1.4	0.6
2503	Dodecanoic acid	3.2	-
2551	Geranyl linalool	_	0.6
2604	α-Costol	0.5	-
2622	Phytol	1.8	5.1
2670	Tetradecanoic acid	3.7	-
2700	Heptacosane	2.4	1.9
2900	Nonacosane	8.6	4.9
2931	Hexadecanoic acid	7.0	8.0
	Total	84.7	91.0

RRI = Relative retention indices calculated against *n*-alkanes, percentage calculated from FID data tr trace (< 0.1 %), *Correct isomer not identified.

Gas chromatography analysis: 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 the analysis is shown in Table-2.

TABLE-2 CHEMICAL CLASS DISTRIBUTION OF THE ESSENTIAL OIL COMPONENTS OF *Centaurea* sp.

Chemical class	C gaming (0)	C anaifamaia (%)
Chemical class	C. sericea (%)	C. ensiformis (%)
Monoterpene hydrocarbones	0.9	0.6
Oxygenated monoterpenes	2.6	3.6
Sesquiterpene hydrocarbones	5.6	2.1
Oxygenated sesquiterpenes	34.9	53.6
Fatty acid + esters	13.9	8.0
Others	26.8	23.1

Gas chromatography-mass spectrometry analysis: The GC/MS analysis was carried out with an Agilent 5975 GC/MSD system. Innowax FSC column (60 m × 0.25 mm, 0.25 µm 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 35-450.

Identification of components: Identification of the oil components was 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)^{5.6} and in-house "Baser Library of Essential Oil Constituents" built up by genuine compounds and components of known oils, as well as MS literature data^{7.9} was used for the identification.

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RESULTS AND DISCUSSION

Seventy three and 74 compounds representing 84.7 and 91 % of the essential oils were characterized from *C. sericea* and *C. ensiformis*, respectively. Caryophyllene oxide (10.6 %), nonacosane (8.6 %) and hexadecanoic acid (7 %) were the main constituents in the oil of *C. sericeae* and β -eudesmol (29.8 %), hexadecanoic acid (8 %) and caryophyllene oxide (7.6 %) were the main constituents in the oil of *C. ensiformis*.

Essential oils of *C. ensiformis* gathered from different locality of Turkey were previously analyzed only by means of GC/MS¹⁰. Present results are consistent with this report, except for the carvacrol contents. *C. ensiformis* is a Turkish endemic that occurs on serpentine soils and its morphological characters do not allow clear assignment to any of the existing sections². This species have been placed in Cheirolepis-Pseudoseridia complex by Garcia-Jacas *et al.*¹¹. Among the species included in this complex, only *C. cheirolepidoides*¹⁰, *C. kotschyi* var. *decumbens*¹², *C. kotschyi* var. *kotschyi*¹² and *C. deflexa*¹³ have been previously investigated for their essential oil composition and Germacrene D was reported as the main compound ranging from 27.4-44.2 %. *Centaurea ensiformis* showed a very different chemical behaviour from all these species, low producing (0.3 %) of germacrene D.

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