

RESEARCH ARTICLE

Essential Oil Composition of *Centaurea kilaea* Boiss. and *C. cuneifolia* Sm. from Turkey.

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Abstract

Essential oil composition of *Centaurea kilaea* flowers, stems and *C. cuneifolia* flowers were investigated by GC, GC/MS. Flowers and stems of *C. kilaea* afforded very low essential oil yield <0.01% (v/w). Nineteen and twenty compounds were identified in the flower and stem oils which represent 59.5% and 77.6% of the *C. kilaea* oil respectively. The main components of the *C. kilaea* flower oil were hexadecanoic acid 26.2%, tetradecanoic acid 18.1%, β -Eudesmol 3.3% and decanoic acid 3.1%. The stem oil contains hexadecanoic acid 55.5% and β -Eudesmol 3.2%. Flowers of *C. cuneifolia* afforded very low essential oil yield <0.01% (v/w). Twenty five compounds were identified in the flower oil of *C. cuneifolia* which represent 69.92% of the oil. The main components of this oil include hexadecanoic acid 32.9%, tetradecanoic acid 14.4%, heptacosane 6.1% and nonacosane 4.3%. Essential oils obtained from both species have saturated fatty acids and alkanes as the major components, but both oils also contain minor amounts of sesquiterpenes.

Keywords: Asteraceae, *Centaurea*, *C. kilaea*, *C. cuneifolia*, essential oil, hexadecanoic acid.

Introduction

The *Centaurea* L. genus of Asteraceae is represented with more than 205 taxon in Turkey (Davis, 1975; Davis et al., 1988, Guner et al. 2000). In Turkey *Centaurea* species are known with the local names “devedikeni”, “peygamber çiçeđi”, “zerdali dikeni”, “çoban kaldiran” and “Timur dikeni” and have extensive folk medicinal uses (Arif, Kùpeli & Ergun, 2004; Tuzlacı, 2011). The folk medicinal uses of *Centaurea* species include; wound healing, antidiabetic, antidiarrhetic, antirheumatic, anti-inflammatory, colagog, choleric, digestive, stomachic, diuretic, menstrual, astringent, hypotensive, antipyretic, cytotoxic and antibacterial purposes (Arif, Kùpeli & Ergun, 2004; YeŐilada et al., 1999; Demirci et al., 2008a). Phytochemistry studies on various *Centaurea* species reports isolation of flavonoids, sesquiterpene lactones, triterpenes and alkaloid type non-volatile secondary metabolites (Flamini et al., 2002; Flamini et al., 2004; Massiot et al., 1985; Sarker et al., 2001). The essential oils of *Centaurea* species are usually characterized with caryophyllene, eudesmol, germacrene, spathulenol type sesquiterpenes (Dob et al., 2009; Formisano et al., 2010; Senatore et al., 2003); hexadecanoic acid, tetradecanoic acid, dodecanoic acid type fatty acids (Formisano et al., 2008;

Karamenderes, Demirci & Başer, 2008); heptacosane, nonacosane, pentacosane, tricosane type higher alkanes (Demirci et al., 2008a; Formisano et al., 2010; Senatore et al., 2003) and pinene, terpinene, carvacrol type monoterpenes (Karamenderes, Demirci & Başer, 2008; Salmanpour, Khalilzadeh & Sadeghifar, 2009) as the major compounds. Previously there are no reports on the essential oil composition of *C. kilaea* and *C. cuneifolia* from Turkey. There is only one report on the essential oil composition of *C. cuneifolia* from Bulgaria that have β -eudesmol (26.5%) and hexadecanoic acid (17.6%) main components (Roselli et al., 2009). To the best of our knowledge this is the first report on the essential oils of *C. kilaea* and *C. cuneifolia* from Turkey.

Materials and Methods

Plant Materials

Plant materials were collected during the flowering period in July 2009 from İstanbul – Çatalça. Voucher specimens have been deposited in the Herbarium of the Faculty of Pharmacy, Marmara University (Voucher no. MARE 11712 and MARE 14760 for *C. kilaea* and *C. cuneifolia* respectively), Turkey. Plant materials were identified by Dr. Gizem BULUT.

Essential oil isolation

Flowers and stems (100 g each) of the plant sample *C. kilaea* and flowers of *C. cuneifolia* (100 g) were subjected to hydrodistillation for 4 h using a Clevenger- type apparatus to produce the oils. Essential oil yields obtained from flowers, stem of *C. kilaea* and flowers of *C. cuneifolia* were <0.01 (v/w). Oils were trapped in *n*-hexane and kept in amber bottles in -20°C until the analysis.

Gas Chromatography–Mass Spectrometry

The GC-MS analyses were performed with an Agilent 5975C Inert XL EI/CI MSD system operating in EI mode. The GC analyses were done with an Agilent 7890A GC system with same operational conditions employed in GC-MS analysis. Essential oil samples were diluted 1/10 (v/v) with *n*-hexane, simultaneous auto injection was done to obtain the same retention times. Injector and MS transfer line temperatures were set at 250°C. Split ratio was set to 50:1. Innowax FSC column (60 m x 0.25 mm, 0.25 μ m film thickness) and helium as a carrier gas (1 mL/min) was used both in GC and GC-MS analysis. The oven temperature was programmed to 60°C for 10 min. and raised to 220°C, at rate of 4°C/min. The temperature kept constant at 220°C for 10 min. and then raised to 240°C at a rate of 1°C/min. The mass spectra were recorded at 70 eV with the mass range *m/z* 35 to 425. The FID detector temperature was set to 250°C. Relative percentage amounts of the separated compounds were calculated from the integration of the peaks in FID chromatograms. The results of the analysis were given in Table 1. Identification of essential oil components were carried out by comparison of their retention times and mass spectra with authentic samples. Also by comparison of their relative retention indices (RRI) obtained from series of *n*-alkanes to the literature and mass spectra comparison. Mass spectra comparison was done by computer matching with commercial Wiley 8th Ed./NIST 05 Mass Spectra library, Adams Essential Oil Mass Spectral Library, Pallisade 600K Complete Mass Spectra Library and in-house Library built from components of known oils was used for identification.

Table 1. Essential oil composition of *C. kilaea* and *C. cuneifolia* essential oils.

No	RRI ^a	RRI Lit. ^b	Compound	<i>C. kilaea</i> Flower oil	<i>C. kilaea</i> Stem oil	<i>C. cuneifolia</i> Flower oil	Ident. ^c
1	1087	1093	Hexanal	-	-	0.1	RI, MS
2	1212	1213	1,8-Cineole	-	-	0.1	RI, MS
3	1239	1244	2-Pentyl furan	-	-	tr ^d	RI, MS
4	1505	1506	Decanal	-	0.5	0.8	RI, MS
5	1532	1532	Camphor	-	-	tr	Ac, RI, MS
6	1611	1611	Terpinen-4-ol	-	-	0.2	RI, MS
7	1717	1719	Borneol	-	-	0.1	RI, MS
8	1723	1726	Germacrene D	-	-	0.1	RI, MS
9	1734	1742	β -Selinene	-	-	0.2	RI, MS
10	1823	1838	(<i>E</i>)- β -Damascenone	-	0.5	0.1	RI, MS
11	1864	1868	(<i>E</i>)-Geranyl acetone	-	0.3	-	RI, MS
12	1954	1958	(<i>E</i>)- β -Ionone	-	0.3	-	RI, MS
13	2007	2008	Caryophyllene oxide	tr	1.9	0.9	RI, MS
14	2031	2037	Salvial-4(14)-en-1-one	tr	0.7	0.1	RI, MS
15	2036	2135	Hexadecanal	tr	-	-	RI, MS
16	2045	2050	(<i>E</i>)-Nerolidol	-	-	0.5	RI, MS
17	2063	2071	Humulene epoxide II	0.3	0.5	-	RI, MS
18	2100	2100	Heneicosane	-	-	0.4	Ac, RI, MS
19	2101	2104	Viridiflorol	tr	-	-	RI, MS
20	2131	2131	Hexahydrofarnesyl acetone	tr	1.2	1.6	RI, MS
21	2142	2144	Spathulenol	0.4	2.2	1.2	RI, MS
22	2150	2179	Nor-copaanone	-	-	0.2	RI, MS
23	2200	2200	Docosane	tr	-	-	Ac, RI, MS
24	2202	2209	T-Muurolol	1.5	-	-	RI, MS
25	2242		Isospathulenol	1.6	0.4	-	MS
26	2253	2257	β -Eudesmol	3.3	3.2	0.8	RI, MS
27	2282	2298	Decanoic acid	3.1	-	1.0	RI, MS
28	2300	2300	Tricosane	0.8	-	1.8	Ac, RI, MS
29	2381	2384	Farnesyl acetone	-	0.8	-	RI, MS
30	2492	2503	Dodecanoic acid	2.0	1.3	-	RI, MS
31	2500	2500	Pentacosane	0.4	0.8	-	Ac, RI, MS
32	2614	2622	Phytol	-	1.1	-	RI, MS
33	2700	2700	Heptacosane	0.4	0.9	6.1	Ac, RI, MS
34	2704	2670	Tetradecanoic acid	18.1	2.8	14.4	RI, MS
35	2809	2822	Pentadecanoic acid	-	0.4	2.0	RI, MS
36	2900	2900	Nonacosane	1.4	2.3	4.3	Ac, RI, MS
37	2917	2931	Hexadecanoic acid	26.2	55.5	32.9	RI, MS
			TOTAL	59.5	77.6	69.9	

^a Relative Retention Indices on FSC-Innowax Column (60 m x 0.25 mm, 0.25 μ m film thickness) with a custom temperature program and Helium as carrier gas at 1 mL/min flow rate. ^b Relative Retention Indices on FSC-Innowax Column with same temperature program and flow rate reported in the literature (Başer et al., 2011; Demirci & Başer, 2008; Demirci et al., 2008b; Karamenderes, Demirci & Başer, 2008; Köse et al., 2008; Polatoglu et al., 2009; Polatoglu et al., 2011; Tabanca et al., 2006). ^c Identification Method, RI: Relative retention index match with literature. ^f MS: Mass spectra match (match \geq 90%). ^g AC: Retention time and mass spectra match with authentic compound. ^d tr: Trace amount (< 0.1%).

Results and Discussion

Nineteen compounds were identified which represents 59.5% of the essential oil of *C. kilaea* flowers. The oil contained hexadecanoic acid 26.2% and tetradecanoic acid 18.1% main components accompanied by β -eudesmol 3.3%, decanoic acid 3.1% and dodecanoic acid 2.0%. Twenty compounds were identified that represent 77.6% of the *C. kilaea* stem essential oil. The main components of this oil was hexadecanoic acid 55.5% accompanied by β -eudesmol 3.2%, tetradecanoic acid 2.8%, nonacosane 2.3% and spathulenol 2.2%. The essential oils of *C. kilaea* contain very high amounts of fatty acids and minor amounts of sesquiterpene alcohols. Previously essential oils that contain high amounts of fatty acids were reported from *C. aladaghensis*, *C. luschaniana*, *C. saligna* (Altintas et al., 2009; Demirci et al., 2008; Köse et al., 2007).

Twentyfive compounds were identified in the *C. cuneifolia* essential oil which represent 69.9% of the oil. The main components of the oil were hexadecanoic acid 32.9%, tetradecanoic acid 14.4% and heptacosane 6.1%. The oil also contained minor compounds nonacosane 4.3% and pentadecanoic acid 2.0%. This oil contained very low amount of sesquiterpenes or other terpenes. Similar essential oil which comprised of fatty acids and higher alkanes was reported from *C. luschaniana*, *C. saligna* and *C. tossiensis* (Altintaş et al., 2009; Demirci et al., 2008). Investigated essential oils have a chemical composition that is similar to the oils previously reported in the literature. This is the first report on the essential oil composition of *C. kilaea*. Also it is the first report on the essential oil composition of *C. cuneifolia* from Turkey.

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