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Research Article

Essential oil composition of two *Centaurea* L. (Asteraceae) species from Turkey

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ABSTRACT

In this study, aerial parts of *C. cynaus* L. and *C. depressa* Bieb. were analysed by HS-SPME/GC-MS. As a result thirty five and thirty seven components were identified representing 92.3% and 91.1% of the oil, respectively. Germacrene D (14.8%), caryophyllene oxide (19.6%) and butanal (8.7%) were detected the main compounds of *C. cynaus*, however germacrene D (20.6%), caryophyllene oxide (13.3%) and β-eudesmol (12.6%) were detected the major constituents of *C. depressa*.

***Keywords*:** *Centaurea, Essential oil, Germacrene D, Caryophyllene oxide*

İki *Centaurea* L. (Asteraceae) Türünün Uçucu Yağ Kompozisyonu

ÖZET

Bu çalışmada *C. cynaus* L. ve *C. depressa* Bieb. türleri HS-SPME/GC-MS tekniği ile analiz edildi. Sonuçta, sırasıyla toplam yağ miktarları olan %92.3 ve %91.1' lik değerlerden, otuzbeş ve otuzyedi bileşen tespit edildi. Germakren D (%14.8), karyofillenoksit (%19.6) ve butanal (%8.7) *C. cynaus*'un; germakren D (%20.6), karyofillenoksit (%13.3) ve β-eudezmol (%12.6) ise *C. depressa*'nın ana bileşenleri olarak tespit edildi.

Anahtar Kelimeler: *Centaurea, Uçucu yağ, Germakren D, Karyofillen oksit*

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I. INTRODUCTION

CENTAUREA L. belongs to Asteraceae family and distributed in particular in central, southwest and east of the Turkey [1]. With 38 new taxa, *Centaurea* is represented in Turkey with 217 taxa [2-4]; which 111 of are endemic and the rate of endemism genus is 62% [5]. Most of *Centaurea* species are herbaceous perennial herbs grown in mountain slopes and dry lands [6] and these plants are known as peygamber cicegi in Turkey [7]. Chemical studies in the literature shows that the sesquiterpene lactones are the most characteristic constituents of *Centaurea* taxa [8] and were found to be rich in respect to essential oil content [8-10].

The aerial parts of some *Centaurea* species are used in the traditional medicine of many countries like, antiprotozoal, antimicrobial, cytotoxic and antiinflammatory [11,12]. "The genus has been subjected to several phytochemical studies leading to the isolation of sesquiterpene lactones and flavonoids as main secondary metabolites of its species" [13,14]. Athough *Centaurea* is one of the largest members of Compositae family, literatures about the essential oils *Centauera* taxa are limited.

This research deals with the essential oil composition of *C. cynaus* and *C. depressa* species from Turkey that might be helpful qualitative and quantitative essential oil profiles of *Centaurea* taxa.

II. EXPERIMENTAL

A. PLANT MATERIAL

C. cynaus (Kilic 4852) was collected from south of Yelesen village, stony areaes (altitude of 1600-1650 m), Bingol/Turkey, in June 26, 2013. *C. depressa* (Kilic 5075) was collected from west of Dikme village, stony areaes (altitude of 1700-1750 m), Bingol / Turkey, in June 30, 2013. Plant materials were identified with Flora of Turkey (vol. 5) [15] and herbarium samples stored from Department of Garden and Park Plant / Bingol University with 15 and 16 herbarium numbers.

B. HS-SPME PROCEDURE

"Five grams powder of aerial part of studied samples were carried out by a (HS-SPME) head space solid phase microextraction method using a divinyl benzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) fiber, with 50/30 um film thickness; before the analysis the fiber was pre conditioned in the injection port of the gas chromatography (GC) as indicated by the manufacturer. For each sample, 5 g of plant samples, previously homogenized, were weighed in to a 40 ml vial; the vial was equipped with a ''mininert'' valve. The vial was kept at 35°C with continuous internal stirring and the sample was left to equilibratefor 30 min; then, the SPME fiber was exposed for 40 min to the headspace while maintaining the sample at 35°C. After sampling, the SPME fiber was introduced into the GC injector, and was left for 3 min to allow the analyzes thermal desorption. In order to optimize the technique, the effects of various parameters, such as sample volume, sample headspace volume, sample heating temperature and extraction time were studied on the extraction efficiency as previously reported by Verzera *et al.,*" [16].

C. GC-MS ANALYSIS

"A Varian 3800 gas chromatograph directly inter faced with a Varian 2000 ion trap mass spectrometer (VarianSpa, Milan, Italy) was used with injector temperature, 260°C; injection mode, splitless;

column, 60 m, CP-Wax 52 CB 0.25 mm i.d., 0.25 um film thickness. The oven temperature was programmed as follows: 45°C heldfor 5 min, then increased to 80°C at a rate of 10°C/min, and to 240°C at 2°C/min. The carrier gas was helium, used at a constant pressure of 10 psi; the transfer line temperature, 250°C; the ionisation mode, electron impact (EI); acquisit ion range, 40 to 200 m/z; scan rate, 1 us^{-1}. The compounds were identified using the NIST (National Institute of Standardsand Technology) library (NIST/WILEY/EPA/NIH), mass spectral library and verified by the retention indices which were calculated as described by Van den Dool and Kratz" [17]. The relative amounts were calculated on the basis of peak-area ratios. The identified constituents are listed in Table 1.

III. RESULTS & DISCUSSION

In this study, germacrene D (14.8%), caryophyllene oxide (19.6%) and butanal (8.7%) were detected the main compounds of *C. cynaus*, however germacrene D (20.6%), caryophyllene oxide (13.3%) and β-eudesmol (12.6%) were detected the major constituents of *C. depressa*.

C. cynaus and *C. depressa* included high concentrations of germacrene D (14.8% - 20.6%, respectively) and caryophyllene oxide (19.6% - 13.3%, respectively). *C. cynaus* was described by its high content of butanal (8.7%); *C. depressa* showed high amounts of β-eudesmol (12.6%) (Table 1). Among the sesquiterpenes; caryophyllene oxide was found principal constituents of *C. cynaus* (19.6%) and *C. depressa* (13.3%) (Table 1); this compound also major constituents of *C. kurdica* Reichardt (10.5%) and *C. saligna* (K.Koch) Wagenitz (25.2%) [9]. β-eudesmol was found high percentage of *C. saligna* (11.5%) [9] and *C. cuneifolia* (26.5%) [18]. β-caryophyllene was detected the main compound of *C. kurdica* (9.5%) [9], *C. hadimensis* (9.8%) [19] and *C. kotschyi* var. *kotschyi* (12.1%) [20]. β-eudesmol was found high percentage of *C. depressa* (12.6%), but low percentage of *C. cynaus* (1.5%) (Table 1); this compound was also detected at high concentrations from *C. iberica* Trev. ex Spreng. (5.3%), *C. solstitialis* L. subsp. *solstitialis* (15.5%) and *C. virgata* (4.8%) [10]. Sesquiterpenes are the main class of studied *Centaurea* species, among these germacrene D and caryophyllene oxide (Table 1).

"*C. babylonica* L., *C. antitauri* Hayek and *C. lanigera* DC. contained high concentrations of germacrene D (43.0%, 40.2% and 43.1%, respectively) and β-caryophyllene (9.9%, 13.5% and 13.7%, respectively); *C. balsamita* Lam. and *C. antiochia* Boiss. had, similarly to the previous three species, more than 40% of germacrene D, but their content of β-caryophyllene was significantly smaller (1.7% and 4.5%, respectively)" [21]. Also germacrene D (21.2%) and β-caryophyllene (33.9%) were the main constituents of *C. deflexa* Wagenitz; *C. ptosimopappoides* Wagenitz having high amounts of germacrene D (36.9%) and β-caryophyllene (22.5%) [21]. Similarly, in this research germacrene D was the major compounds of *C. cynaus* (14.8%) and *C. depressa* (20.6%); whereas *C. cynaus* and *C. depressa* contained low concentrations of β-caryophyllene (2.6%-3.5%, respectively); it is noteworthy that, β-caryophyllene was not among the major components of studied samples (Table 1). Butanal (8.7%) reported the major component in *C. cynaus*; however this compound determined minor in *C. depressa* (5.4%) (Table 1). Among the sesquiterpenes, caryophyllene oxide was found principal constituents of *C. cynaus* (19.6%) and *C. depressa* (13.3%) (Table 1), this compound also principal constituents of *C. helenioides* Boiss. (18.2%) [22] and C. *behen* L. (15.9%) [23].

Table 1. *Identified components of Centaurea species (%).*

Constituents	***RRI**	***C. cynaus***	***C. depressa***
Methane	755	8.2	7.3
Hexenal	820	-	0.5
Propanal	850	2.7	-
Heptenal	880	-	0.2
1-methoxy, 1-propene	915	1.9	4.9
2-ethylfuran	1018	4.7	3.1
α-pinene	1020	0.3	-
β-pinene	1063	-	0.7
Butanal	1070	8.7	5.4
Nonanal	1076	-	0.3
Limonene	1108	0.8	0.5
2,3-dihydro-1,4-dioxine	1127	1.0	-
Benzene, 1-methyl-2	1174	0.9	0.6
Eucalyptol	1160	1.8	0.9
α-terpineol	1185	-	0.3
Decanal	1203	0.2	0.1
1-undecene	1213	0.6	-
β-sesquiphellandrene	1223	-	0.4
1-penten-3-ol	1255	1.7	-
α-cubebene	1261	0.7	0.2
Benzene, 1-methyl-4	1312	-	0.4
3-methylbutan-1-ol	1340	0.7	-
Ocimene	1385	1.5	0.6
γ-cadinene	1460	-	0.3
Germacrene D	1480	14.8	20.6
γ-muurolene	1490	1.3	-
β-bisabolene	1510	-	2.3
Lauryl alcohol	1548	2.8	-
Bicyclogermacrene	1560	0.6	0.8
Spathulenol	1575	-	1.2
Caryophylleneoxide	1580	19.6	13.3
β-eudesmol	1653	1.5	12.6
Hexadecanoic acid	1691	1.0	1.3
Cyclohexene	1792	0.5	-
1,6-cyclodecadiene	1835	-	2.6
β-caryophyllene	1962	2.6	3.5
Benzaldehyde	1975	-	0.3
Bicyclo (4.4.0) dec-1-ene	1982	0.2	1.2
7-methanoazulene	1992	4.2	1.7
Cyclohexene	2035	0.2	-
α-humulene	2040	1.3	1.1
1,3-hexadiene	2045	-	0.4
α-selinene	2052	0.5	-
β-citronellene	2064	0.5	0.2
Ylangene	2085	0.4	0.1
Bicyclo[4.1.0] hept-2-ene	2149	-	0.5
Cyclohexenol	2175	0.7	-
Tricosane	2235	-	0.4
Trans-anethole	2183	2.4	-
Benzothiazole	2279	0.8	0.3
***RRI:** Relative Retention Index	**Total**	**92.3**	**91.1**

IV. CONCLUSION

In conclusion, *C. cynaus* and *C. depressa* evidenced a similarity, with reference to the presence of the main constituents; germacrene D and caryophyllene oxide was among the principal one in both species. Also the percentages of β-caryophyllene, butanal, methane and β-eudesmol were comparable. This study demonstrates the occurrence of germacrene D / caryophyllene oxide chemotypes of *C. cynaus* and *C. depressa* in Eastern Anatolian region of Turkey.

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