

COMPARISON OF THE ESSENTIAL OILS OF DIFFERENT COLORED *Centaurea tchihatcheffii* FISCH. & MEY. FLOWERS

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Abstract

The potential role of flower color in the yield and composition of essential oil was investigated in the endemic *Centaurea tchihatcheffii* Fisch.&Mey. (Asteraceae). Essential oils obtained by hydrodistillation from different colored flowers of *C. tchihatcheffii* were separately analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC-MS), simultaneously. The main constituent both oils was found as germacrene D (17.6% and 17.4%). The flower color difference was shown not to play a role in essential oil yield and composition.

Key words: Asteraceae, *Centaurea tchihatcheffii*, Essential oil, Germacrene D.

Farklı Renkteki *Centaurea tchihatcheffii* Fisch. & Mey. Çiçek Uçucu Yağların Karşılaştırılması

Bu çalışmada, Asteraceae familyasına ait endemik bir tür olan *Centaurea tchihatcheffii* Fisch. & Mey. türüne ait farklı renkteki çiçek örneklerinin uçucu yağ kimyasal bileşimleri karşılaştırılmıştır. Uçucu yağlar su distilasyonu yöntemi ile elde edilmiştir. Elde edilen uçucu yağlar gaz kromatografisi (GC) ve gaz kromatografisi/kütle spektrometresi (GC-MS) sistemleri ile analiz edilmiştir. Her iki örnekte ana bileşik olarak germakren D (%17.6 ve %17.4) tespit edilmiştir. Renk farklılığının uçucu yağ verim ve bileşiminde rol oynamadığı gözlenmiştir.

Anahtar kelimeler: Asteraceae, *Centaurea tchihatcheffii*, Uçucu yağ, Germakren D.

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INTRODUCTION

In the Flora of Turkey, the genus *Centaurea* is the third richest genus as to the number of species after *Astragalus* and *Verbascum*. In addition to 179 species in the Flora, species number of *Centaurea* raised to about 200 with the latest additions (1-3).

The common local name for cornflower (*Centaurea*) is Peygamberçiçeği in Turkey. *Centaurea* species are distributed almost all over Turkey on very different habitats. It is not a commonly used folk medicine plant but some species like *C. cyanus*, *C. behen* and *C. calcitrapa* are used locally as aperitive, laxative, emanagogue, antipyretic and aphrodisiac (Baytop, 1999). Among the 179 species cited in the Flora of Turkey, 111 are endemic for Turkey and the ratio of endemism is 63%.

Centaurea tchihatcheffii was collected first time by Pierre de Tchihatcheff in 1848. This specimen was published as *C. tchihatcheffii* by Fisher et Meyer in 1854. Synonyms of the species are *Melanoma tchihatcheffii* and *C. purpureiradiata* which were published in the following years by different authors. *C. tchihatcheffii* is a local endemic species and according to the IUCN threat categories it is placed in CR (critically endangered) category. Also, the Bern Convention emphasizes that the plant must be strictly protected. Its flowering period is between April and July. Habitat is fallow fields, roadsides, empty fields, steppe, clayed and basic soils. It is an annual, having a stem 5-50 cm, branched at near base. Leaves are floccose to tomentose or glabrescent. Terminal leaf segments are 2-3 lobed, broadly oblong, lateral leaflets are small, linear whereas the upper leaves are variously or entirely lobed. Capitula are broadly campanulate 12-18 mm long. Leaflets at base of capitula are in 5-8 rows, base appendage brown, 1.5-2 mm, border with white cilia, 9-11 in number. Lateral flowers in capitula pink, light or dark red, purplish, whitish, purple banded at white, black banded at red and dark purple banded at purple flower base, sometimes no band, reverse funnel shaped, crenate at apex, 7-12 in number, 12-22 mm long, arrangement in radial position. Flowers in centre of capitula are tubular, red, pink, hermaphrodite, 25-55 in number. Fruit 2-4 mm long, 7-37 in number per capitula, dark brown, blackish. Hair of fruit pappus like at apex. Pappus in 2 rows, inner ones longer than outer ones, 4 mm long. Stalk of capitula are broadened at base and inside hollow (2).

C. tchihatcheffii grows and is distributed in Ankara, Gölbaşı township, Hacılar village, recreation area in the forest of Süleyman Demirel, area of State Opera and Ballet, Küçük Aşıklar hill, fallowfields near Haymana road. It is classified as "Very local endemic" (2). Sevgiçiçeği (loveflower) yanardöner, gelindüğmesi (bridebutton) are the local names.

Previously, caryophyllene oxide (15.1%), carvacrol (14.7%), acetophenone (6.2%) and spathulenol (5.3%) were reported as main constituents of *C. tchihatcheffii* collected from the same locality (4).

In this present work, the essential oil compositions from different coloured flower samples of *C. tchihatcheffii* are comparatively reported. The hydrodistilled essential oils were subsequently analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), simultaneously.

EXPERIMENTAL

Plant material

Centaurea tchihatcheffii Fisch et Mey. B4 Ankara Gölbaşı township near Mogan Lake, Hacılar Köy, State Opera and Ballet protected area, 8.6.2009, Erik 6711 (red flowering sample); B4: Ankara: Gölbaşı (sample A) B4 Ankara Gölbaşı township, near Mogan Lake, Hacılar Köy, recreation and afforestation area, 8.6.2009, Erik 6710 (pink flowering sample).

Essential oil distillation

Air-dried flowering parts were hydrodistilled for 3 h using a Clevenger-type apparatus to produce small amount of essential oils which was trapped in *n*-hexane.

GC-MS analysis

The GC-MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60 m x 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 to 450.

GC 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 auto-injection 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 analysis results are given in Table 1.

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 3 Library) (5,6) and in-house “Başer Library of Essential Oil Constituents” built up by genuine compounds and components of known oils, as well as MS literature data (7,8) was used for the identification.

RESULTS AND DISCUSSION

Analyses of the essential oils were performed on gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) systems, simultaneously. The detected components of the essential oils of different coloured samples (A and B) of *C. tchihatcheffii* and their relative percentages are given in Table 1 in the order of their relative retention indices (RRI). Forty one and fifty five components were characterized representing 88.4% and 92.0% of the sample A and B, respectively. germacrene D (17.6% and 17.4%), hexadecanoic acid (5.9% and 6.2%), heptacosane (5.8% and 4.4%), β-caryophyllene (4.3% and 5.5%), tricosane (4.1% and 5.0%), caryophyllene oxide (4.0% and 3.7%), bicyclogermacrene (3.8% and 3.1%), found as the main constituents, resp.

According to the results of analyses, colour variations seen in red and pink flowered specimens were shown not to play a role in the yield and composition of essential oils. This is seen as a typical polymorphic situation, which is caused by the genotype of the species, not by environmental factors. It is just an infra-specific variation as there is no other morphological difference than color variation. The other interesting feature of color variation is that it sometimes occurs in different capitula of the same plant.

Table 1. The composition of the essential oils of *Centaurea tchihatcheffii* samples.

RRI	Compounds	A (%)	B (%)
1032	α -Pinene	2.2	2.1
1118	β -Pinene	0.3	0.4
1154	1-Undecene	0.5	0.4
1203	Limonene	-	0.1
1244	2-Pentyl furan	-	0.2
1349	1-Tridecene	3.5	2.1
1400	Nonanal	1.4	2.0
1497	α -Copaene	2.2	1.2
1553	Linalool	0.5	0.5
1549	β -Cubebene	0.8	0.6
1549	1-Tetradecene	0.6	0.4
1600	β -Elemene	0.9	2.1
1612	β -Caryophyllene	4.3	5.5
1671	Acetophenone	1.9	0.9
1668	(Z)- β -Farnesene	2.3	0.9
1687	α -Humulene	2.2	1.0
1726	Germacrene D	17.6	17.4
1742	β -Selinene	-	0.6
1755	Bicyclogermacrene	3.8	3.1
1773	δ -Cadinene	0.4	0.6
1786	Aromadendra-1(10),4(15)-diene	-	0.3
1830	Tridecanal	1.6	1.5
1868	(E)-Geranyl acetone	tr	0.4
1882	Aplotaxene	2.9	2.4
1900	<i>epi</i> -Cubebol	-	tr
1933	Tetradecanal	0.7	0.7
1945	1,5-Epoxy-salvial(4)14-ene	1.0	0.6
1958	(E)- β -Ionone	0.9	-
1957	Cubebol	-	0.7
2001	Isocaryophyllene oxide	0.7	0.6
2008	Caryophyllene oxide	4.0	3.7
2037	Salvial-4(14)-en-1-one	0.8	0.6
2041	Pentadecanal	-	0.5
2069	Germacrene D-4 β -ol	1.7	0.9
2100	Heneicosane	tr	0.5
2144	Spathulenol	3.0	3.5
2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	tr	0.4
2179	Tetradecanol	-	0.5
2226	Methyl hexadecanoate	tr	-
2187	T-Cadinol	-	0.6
2209	T-Muurolol	-	0.6
2247	<i>trans</i> - α -Bergamotol	-	0.5
2255	α -Cadinol	-	0.7
2273	Selin-11-en-4 α -ol	-	1.8
2278	Torilenol	-	0.6
2300	Tricosane	4.1	5.0
2324	Caryophylla-2(12),6(13)-dien-5 α -ol (=Caryophylladienol II)	-	1.4

2392	Caryophylla-2(12),6-dien-5 β -ol (=Caryophyllenol II)	1.0	0.5
2400	Tetracosane	tr	0.6
2456	(Z)-9-Methyl octadecanoate	1.2	
2500	Pentacosane	3.4	3.2
2503	Dodecanoic acid	1.6	-
2509	(Z,Z)-9,12-methyl octadecadienoate	0.8	-
2600	Hexacosane	-	0.5
2622	Phytol	-	1.1
2670	Tetradecanoic acid	-	0.7
2822	Pentadecanoic acid	-	1.7
2700	Heptacosane	5.8	4.4
2900	Nonacosane	1.9	2.0
2931	Hexadecanoic acid	5.9	6.2
Total		88.4	92.0

A: Red flowering sample

B: Pink flowering sample

RRI Relative retention indices calculated against n-alkanes

% calculated from FID data

tr Trace (< 0.1 %)

-: not detected

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