Asian Journal of Chemistry Vol. 22, No. 6 (2010), 4711-4716

Essential Oil Composition of Endemic *Centaurea tchihatcheffii* Fisch. and Mey. from Turkey

AYHAN ALTINTAS*, UFUK KOCA†, BETUL DEMIRCI and K. HUSNU CAN BASER
Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, Eskisehir-26470, Turkey
Fax: (90)(222)3306809; Tel: (90)(222)3350580-Ext: 3710; E-mail: aaltinta@anadolu.edu.tr

The essential oil obtained by hydrodistillation from endemic *Centaurea tchihatcheffii* Fisch. & Mey. (Asteraceae) from Turkey was analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), simultaneously. Main constituents of the oil were found as caryophyllene oxide (15.1 %), carvacrol (14.7 %), acetophenone (6.2 %) and spathulenol (5.3 %).

Key Words: *Centaurea tchihatcheffii*, Asteraceae, Essential oil composition, Caryophyllene oxide, Carvacrol.

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 189 species including 120 endemics, distributed particularly in the Southwest, Central and Eastern parts. The ratio of endemism is quite high (63.5 %)[2-11].

The aerial parts of several species of *Centaurea* have been widely used for their antidandruff, antidiarrheic, antirheumatic, antiinflammatory, choleretic, diuretic, digestive, stomachic, astringent, antipyretic, cytotoxic and antibacterial properties in Anatolian folk medicine[12,13]. Scientific evidence also were provided for their biological activities including antidiabetic, antidiarhetic, antirheumatic, antiinflammatory, antipyretic, analgesic, vasodilatory, cytotoxic and antibacterial[14-19].

Even though *Centaurea* is one of the largest members of Asteraceae, reports on the analysis of the essential oils of this genus are limited. Studies on the volatile constituents are available in literature on the following *Centaurea* species from Turkey: *C. dichroa*[20], *C. mucronifera* and *C. chrysantha*[21], *C. pseudoscabiosa* subsp. *pseudoscabiosa* and *C. hadimensis*[22], *C. kotschyi* var. *kotschyi* and *C. kotschyi* var. *decumbens*[23] and *C. aladaghensis*, *C. antiochia* var. *prealta*, *C. antitauri*, *C. babylonica*, *C. balsamita*, *C. cheirolepidoides*, *C. deflexa*, *C. iconiensis*, *C. lanigera*, *C. ptosimopappoides*[24], *C. wagenitzii*, *C. tossiensis* and *C. luschaniana*[25] and *C. saligna*[26].

Centaurea type specimen was collected by Tchihatcheff from Afyon in 1848 and has been described by Fisch. and Mey. in 1854. The species, endemic to inner

†Department of Pharmacognosy, Faculty of Pharmacy, Gazi University, Ankara-06330, Turkey.

Anatolia, has a very peculiar distribution that grows only at about 20 km south of Ankara, west side of Golbasi district. Although there is a record that a specimen collected from Afyon, there was not any recent collection. Therefore it is an endangered species[27].

In this present work, the essential oil composition of endemic *C. tchihatcheffii* from Turkey is reported. The oil was analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) systems.

EXPERIMENTAL

C. tchihatcheffii was collected from Ankara, 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 MATERIALS

Centaurea spp.	Collection site	Altitude (m)	Collection period	Oil yield* (%)
C. tchihatcheffii	Turkey: Ankara (B4), Golbasi, Mogan Lake	980	May 2006	Trace

*: Essential oil yields are given on moisture free basis (v/w), trace (< 0.1 %).

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.

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 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)[28,29] 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[30-32], was used for the identification.

TABLE-2
CHEMICAL CLASS DISTRIBUTION OF THE ESSENTIAL OIL COMPONENTS OF *C. tchihatcheffii*

Chemical class	(%)
Monoterpene hydrocarbones	0.3
Oxygenated monoterpenes	19.0
Sesquiterpene hydrocarbones	3.9
Oxygenated sesquiterpenes	29.6
Diterpenes	0.6
Others	30.4

RESULTS AND DISCUSSION

Centaurea genus has a great importance in Turkey due to the high percentage of endemism and appealing flowers besides their medicinal usage in Turkish folk medicine. Analyses of the hydrodistilled oil was performed on GC and GC/MS systems. Seventy one compounds representing 83.8 % of the essential oil were characterized as listed in Table-3. Caryophyllene oxide (15.1 %), carvacrol (14.7 %), acetophenone (6.2 %) and spathulenol (5.3 %) were the main constituents in the oil of *C. tchihatcheffii*.

TABLE-3
COMPOSITION OF THE ESSENTIAL OIL OF *C. tchihatcheffii*

RRI	Compound	(%)
1032	α-Pinene	0.3
1093	Hexanal	0.1
1100	Undecane	0.6
1118	β-Pinene	Trace
1244	2-Pentyl furan	0.2
1248	1-Dodecene	0.2
1352	1-Tridecene	2.5
1398	2-Nonanone	0.1
1400	Nonanal	2.7
1496	2-Decanone	0.2
1497	α-Copaene	1.1
1506	Decanal	0.4
1532	Camphor	0.2
1541	Benzaldehyde	0.2
1553	Linalool	1.8
1562	Octanol	0.2
1583	Longifolene (= *Junipene*)	0.2
1591	Bornyl acetate	0.1
1600	β-Elemene	0.2
1604	2-Undecanone	0.1
1612	β-Caryophyllene	0.9
1617	Undecanal	Trace
1638	β-Cyclocitral	0.2
1671	Acetophenone	6.2

1683	*trans*-Verbenol	0.2
1687	α-Humulene	0.2
1688	10-Methyl-2-undecanone	0.1
1706	α-Terpineol	0.2
1719	Borneol	0.2
1725	Verbenone	0.3
1726	Germacrene D	0.2
1741	β-Bisabolene	0.5
1742	β-Selinene	0.4
1751	Carvone	0.6
1763	Naphthalene	0.1
1766	1-Decanol	0.2
1798	Methyl salicylate	0.1
1827	(E,E)-2,4-Decadienal	0.5
1830	Tridecanal	0.8
1841	1-Methyl ethyl dodecanaote	0.1
1857	Geraniol	0.3
1868	(E)-Geranyl acetone	0.6
1882	Aplotaxene	1.7
1933	Tetradecanal	0.3
1945	1,5-Epoxy-salvial(4)14-ene	1.7
1958	(E)-β-Ionone	1.4
1973	1-Dodecanol	0.2
2008	Caryophyllene oxide	15.1
2037	Salvial-4(14)-en-1-one (= mintketone)	1.5
2041	Pentadecanal	0.5
2071	Humulene epoxide-II	1.5
2100	Heneicosane	0.4
2131	Hexahydrofarnesyl acetone	0.9
2135	Hexadecanal	0.1
2144	Spathulenol	5.3
2179	3,4-Dimethyl-5-pentylidene-2(5*H*)-furanone	0.5
2179	Tetradecanol	0.4
2200	3,4-Dimetil-5-pentil-5*H*-furan-2-one	0.5
2239	Carvacrol	14.7
2278	Torilenol	0.4
2289	Oxo-α-ylangene	0.9
2300	Tricosane	1.2
2324	Caryophylla-2(12),6(13)-dien-5α-ol (= *Caryophylladienol* II)	0.5
2369	Eudesma-4(15),7-dien-1β-ol	0.5
2392	Caryophylla-2(12),6-dien-5β-ol (= *Caryophyllenol* II)	2.0
2500	Pentacosane	1.1
2512	Benzophenone	0.2
2622	Phytol	0.6
2700	Heptacosane	1.1
2931	Hexadecanoic acid	4.3
	Total	83.8

RRI relative retention indices calculated against *n*-alkanes; percentage calculated from FID data; trace (< 0.1 %).

The chemical class distribution of the oil composition of *C. tchihatcheffii* is reported in Table-2. In the essential oil of *C. tchihatcheffii*, monoterpene hydrocarbons were scarcely represented (0.3 %). Oxygenated sesquiterpenes were main constituents predominated the oil in the ratio of 29.6 %.

Previously, hexadecanoic acid, dodecanoic acid and caryophyllene oxide were reported from the following Turkish *Centaurea* species: *C. dichroa*[20], *C. wagenitzii*, *C. tossiensis*, *C. luschaniana*[25] and *C. saligna*[26]. Sesquiterpenes like germacrene-D, bicyclogermacrene and β-caryophyllene were found as the main compounds of the oils of *C. mucronifera*, *C. chrysantha*[21], *C. pseudoscabiosa* subsp. *pseudoscabiosa*, *C. hadimensis*[22], *C. kotschyi* var. *kotschyi*, *C. kotschyi* var. *decumbens*[23].

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*[24].

To the best of our knowledge, the oil composition of the *C. tchihatcheffii* has not been reported and therefore the results obtained in this study can be evaluated as the first report on the oil composition of this species.

ACKNOWLEDGEMENT

The authors would like to thank Assist. Prof. Dr. Hatice Colgecen (Department of Biology, Faculty of Science, Zonguldak Karaelmas University) for her help for collection and identification of the plant material.

REFERENCES

1. G. Wagenitz, *Centaurea* L. in South-West Asia: Patterns of Distribution and Diversity, Proc. Royal Soc., Edinburgh, UK, Vol. 89B, pp. 11-21 (1986).
2. P.H. Davis, Flora of Turkey and East Aegean Islands; Univ. Press: Edinburgh, Vol. 5, pp. 465-585 (1975).
3. Y.B. Kose, A. Altintas, B. Demirci, S. Celik and K.H.C. Baser, *Asian J. Chem*., **21**, 1719 (2009).
4. P.H. Davis, R.R. Mill and K. Tan, Flora of Turkey and East Aegean Islands; Univ. Press: Edinburgh, Vol. 10 (1988).
5. A. Duran and H. Duman, *Ann. Bot. Fennici*, **39**, 43 (2001).
6. I. Turkoglu, H. Akan and S. Civelek, *Bot. J. Linn. Soc*., **143**, 207 (2003).
7. M.E. Uzunhisarcikli, M. Teksen and E. Dogan, *Ann. Bot. Fennici*, **42**, 309 (2005).
8. Z. Aytac and H. Duman, *Pak. J. Bot*., **37**, 563 (2005).
9. M. Vural, H. Duman, Z. Aytac and N. Adiguzel, *Belg. J. Bot*., **139**, 252 (2006).
10. G. Wagenitz, F.H. Hellwig, G. Parolly and L. Martins, *Willdenowia*, **36S**, 423 (2006).
11. Z. Kaya and M. Vural, *Novon: J. Botanical Nomenclature*, **17**, 198 (2007).
12. R. Arif, E. Kupeli and F. Ergun, *Gazi Universitesi Fen Bilimleri Dergisi*, **17**, 149 (2004).
13. T. Baytop, Therapy with Medicinal Plants in Turkey, Past and Present, Nobel Tip Basimevi, Istanbul, Turkey, edn. 2 (1999).
14. M. Kaij-A-Kamb, M. Amoros and L. Girre, *Pharm. Acta Helv.*, **67**, 178 (1992).
15. U. Koca, G. Toker and E. Kupeli Akkol, *Tropical J. Pharm. Res.*, **8**, 193 (2009).
16. U. Koca and B. Ozcelik, *Turk. J. Pharm. Sci*., **6**, 125 (2009).
17. U. Koca, I. Pesin-Süntar, H. Keles, E. Yesilada and E. Kupeli-Akkol, *J. Ethnopharmacol*., **126**, 551 (2009).
18. F. Orallo, M. Lamela, M. Camina, E. Uriatre and M. Calleja, *Planta Med*., **64**, 116 (1998).

19. A.F. Barrero, J.E. Oltra, I. Rodriguez, A. Barragan, D.G. Gravalos and P. Ruiz, *Fitoterapia*, **66**, 227 (1995).
20. A. Altintas, Y.B. Kose, E. Yucel, B. Demirci and K.H.C. Baser, *Khim. Prir. Soedin*., **40**, 604 (2004).
21. H. Dural, Y. Bagci, K. Ertugrul, H. Demirelma, G. Flamini, P.L. Cioni and I. Morelli, *Biochem. Syst. Ecol*., **31**, 1417 (2003).
22. G. Flamini, K. Ertugrul, P.L. Cioni, I. Morelli, H. Dural and Y. Bagci, *Biochem. Syst. Ecol*., **30**, 953 (2002).
23. K. Ertugrul, H. Dural, O. Tugay, G. Flamini, P.L. Cioni and I. Morelli, *Flav. Fragr. J*., **18**, 95 (2003).
24. G. Flamini, M. Tebano, P.L. Cioni, Y. Bagci, H. Dural, K. Ertugrul, T. Uysal and A. Savran, *Plant Syst. Evol*., **261**, 217 (2006).
25. Y.B. Kose, B. Demirci, E. Yucel and K.H.C. Baser, *J. Essen. Oil Res*., **20**, 335 (2008).
26. A. Altintas, Y.B. Kose, A. Kandemir, B. Demirci and K.H.C. Baser, *Chem. Nat. Comp*., **45**, 276 (2009).
27. T. Ekim, *Karaca Arboretum Magazine*, **2**, 137 (1994).
28. F.W. McLafferty and D.B. Stauffer, The Wiley/NBS Registry of Mass Spectral Data, J Wiley and Sons, New York (1989).
29. D. Joulain, W.A. Konig and D.H. Hochmuth, Terpenoids and Related Constituents of Essential Oils, Library of MassFinder 2.1, Hamburg, Germany (2001).
30. D. Joulain and W.A. Konig, The Atlas of Spectra Data of Sesquiterpene Hydrocarbons, EB-Verlag, Hamburg, Germany (1998).
31. ESO 2000, The Complete Database of Essential Oils, Boelens Aroma Chemical Information Service, The Netherlands (1999).
32. W.G. Jennings and T. Shibamoto, Quantitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary GC, Academic Pres, New York (1980).

(*Received*: 10 October 2009; *Accepted*: 20 February 2010) AJC-8466