Composition of the Volatile Oils of *Anthemis coelopoda* var. *coelopoda* from Turkey

Türkiye'den *Anthemis coelopoda* var. *coelopoda*'nın Uçucu Yağ Bileşimi

Research Article

Gülden Doğan*, Azize Demirpolat and Eyüp Bağcı
Firat University, Science Faculty, Biology Department, Elazıg, Turkey.

ABSTRACT

In this study, hydro distilled essential oils derived from the aerial parts of *Anthemis coelopoda* var. *coelopoda* (Asteraceae) grown in Turkey were analysed by GC and GC-MS system. Fifty seven components were identified representing 90.7% of the oils. It was determined that *Anthemis coelopoda* var. *coelopoda* essential oil contained β-caryophyllene (21.8%), nerolidol (10.8%), azulene (9.5%), borneol (5.5%), linalool (4.3%) and cyclopentadecane (4.2%) as major compounds. Essential oil analysis of the *Anthemis coelopoda* var. *coelopoda* has shown that it has β-caryophyllene/nerolidol and azulene chemotype.

Key Words
Anthemis, essential oil, β-Caryophyllene, nerolidol, azulene.

ÖZET

Bu çalışmada Türkiye'de yetişen *Anthemis coelopoda* var. *coelopoda* türünün su damıtma yöntemi ile toprak üstü kısımlarından elde edilen uçucu yağları GC ve GC-MS'de analiz edilmiştir. Toplam yağın %90.7'sinde 57 bileşen belirlenmiştir. *Anthemis coelopoda* var. *coelopoda*'nın uçucu yağının içerdiği bu bileşenlerden β-karyofillen (%21.8), nerolidol (10.8 %), azulen (%9.5), borneol (%5.5), linalool (%4.3) ve siklopentadekan (%4.2) büyük bileşenlerdir. Uçucu yağ çalışmaları *Anthemis coelopoda* var. *coelopoda* için β-karyofillen/nerolidol ve azulen kemotip olduğunu göstermiştir.

Anahtar Kelimeler
Anthemis, uçucu yağ, β-karyofillen, nerolidol, azulen.

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Correspondence to: G. Doğan, Firat University, Science Faculty, Biology Department, Elazig, Turkey.

Tel: +90 424 237 0000/3611 Fax: +90 424 233 0062 E-Mail: gdogan@firat.edu.tr

INTRODUCTION

Anthemis L. is the second largest genus in Compositae, tribe Anthemideae. With its more than 210 species [1] it is outnumbered only by Artemisia L. which contains more than 500 species when *Seriphidium* (Besser) Fourr. is included [2,3]. The total geographical range of *Anthemis* encompasses most of western Eurasia, the Mediterranean region, and a small part of eastern Africa. While central Europe is inhabited by a few archaeophytic species, the main centre of diversity is found in southwestern Asia where 150 of 210 species occur, including all of the presently accepted subgenera and sections. The position of the genus within the tribe Anthemideae is still unresolved and infrageneric taxonomy of *Anthemis*, mainly based on life form, achene morphology, and achene anatomy, is in need of revision. According to some authors, the subgenus *Cota* should be treated as an independent genus [4].

Genus *Anthemis* (family Asteraceae, tribe Anthemideae) comprises of 62 species in Europe, which are divided into three subgenera according to the botanical classification [5]. Subgenus *Anthemis* includes four sections Hiorthia, *Anthemis*, *Maruta* and Chia [6]. The genus *Anthemis* L. is divided into three subgenera (*Anthemis*, *Maruta*, and *Cota*) according to the Flora of Turkey. In Turkey 81 taxa belonging to 51 species, 29 of which are endemic (54%). These plants prefer dry, open sites on wood-steppe hillsides and grow especially on calcareous soils [7].

All of these *Anthemis* species are called as "Papatya" in Turkey, and this plants extensively used in Turkish folk medicine for the treatment of gastrointestinal disorders, hemorrhoid, stomach ache and kidney stones [8-13]. Papatya is a common name given to plants whose flowers resemble those of Roman and German chamomile. Many *Anthemis* spp. are used as herbal tea and for food flavoring, as well as cosmetics and in the pharmaceutical industry [14].

The species of the *Anthemis* genus are widely used in the pharmaceutics, cosmetics and food industry. The flowers of the genus have well-documented use as antiseptic and healing herbs, the main components being natural flavonoids and essential oils [15]. In Europe extracts, tinctures, tisanes (teas), and salves are widely used as anti-inflammatory, antibacterial, antispasmodic, and sedative agents. Extracts are used to allay pain and irritation, clean wounds and ulcers, and aid prevention as well as therapy of irradiated skin injuries, treatment of cystitis and dental afflic- tions [16]. The antimicrobial activity of the essential oils and different extracts from several *Anthemis* species has been reported before [17-19]. The occurrence of sesquiterpene lactones, flavonoids, and essential oils in various *Anthemis* species has been reported in previous works [14]. Sesquiterpene lactones have received considerable attention because of their chemo-ecological functions [20,21], biological activities, and taxonomic significance [22,23]. They represent one of the major classes of secondary metabolites in the genus *Anthemis*. Three skeletal types of sesquiterpene lactones-guaianolides, germacranolides, and eudesmanolides have been detected in *Anthemis* species [24].

Anthemis coelopoda Boiss. is erect, sparsely pubescent and annual. Stems much branched, 20-25 cm. This species flowering at 5th and 7th months. *Anthemis coelopoda* has three varieties in Turkey (var. *coelopoda*, var. *longiloba* and var. *bourgaei*) [7].

The aim of the present study was to perform a detailed chemical composition of the essential oil hydrodistilled from the aerial parts of *Anthemis coelopoda* var. *coelopoda* from the eastern Anatolian region in Turkey. The obteined results could be use in the clarification of infrageneric taxonomy of the genus *Anthemis*.

MATERIALS AND METHODS

Plant Source

Anthemis coelopoda var. *coelopoda* specimen was collected from natural localities (Bingol/Karlıova) in Turkey. The plant materials were collected with scissors, placed in plastic bags and transported to the laboratory. Voucher specimen was deposited in the Herbarium of the Fırat University of Elazıg (FUH) under registration number 7652.

Extraction of the essential oil

The essential oil was extracted by hydrodistillation using a modified Clevenger apparatus coupled to a 2 L round-bottom flask. A total of 100 g of fresh plant material (aerial parts) and 1 L of water were used for the extraction. The extraction was performed over 3 hour period. Subsequently, the hydrolate was collected and centrifuged at 10.000 rpm for 10 minutes. The organic phase was removed with the aid of a Pasteur pipette, and subsequently transferred to an black coloured vials, wrapped in parafilm and aluminum foil and 4°C under refrigeration until analysis. The yields of oils were calculated on the basis of the dry mass.

Gas chromatography (GC) analysis

The essential oil was analysed using HP 6890 GC equipped with FID detector and HP-5 MS (30 m x 0.25 mm *i.d.*, film thickness 0.25 μm) capillary column was used. The column and analysis conditions were the same as in GC-MS expressed as below. The percentage composition of the essential oils was computed from GC-FID peak areas without correction factors.

Gas chromatography/Mass spectrometry (GC-MS) analysis

GC-MS analyses of the oils were performed on a Hewlett Packard Gas Chromatography HP 6890 interfaced with Hewlett Packard 5973 mass spectrometer system equipped with a HP 5-MS capillary column (30 m x 0.25 mm id, film thickness 0.25 μm). The oven temperature was programmed from 70-240°C at the rate of 5°C/min. The ion source was set at 240°C and electron ionization at 70 eV. Helium was used as the carrier gas at a flow rate of 1 mL/min. Scanning range was 35 to 425 amu. Diluted oil in n-hexane (1.0 μL) was injected into the GC-MS.

The identification of constituents was performed on the basis of retention indices (RI) determined by co-injection with reference to a homologous series of n-alkanes, under identical experimental conditions. Further identification was performed by comparison of their mass spectra with those from NIST 98 Libraries (on ChemStation HP) and Wiley 7th Version. The relative amounts of individual components were calculated based on the GC (HP-5MS column) peak area (FID response) without using correction factors. The identified constituents of the essential oils are listed in Table 1.

RESULTS AND DISCUSSION

In this study, the chemical composition of the essential oils of dried aerial parts of *Anthemis coelopoda* var. *coelopoda* was analysed by GC and GC-MS. Fifty seven components representing 90.7% of the oils were characterized. The yields of essential oils from the sample was 0.4 (v/w). According to our results, the main compounds of *A. coelopoda* var. *coelopoda* were β-caryophyllene (21.8%), nerolidol (10.8%), azulene (9.5%), borneol (5.5%), linalool (4.3%) and cyclopentadecane (4.2%). The compositions of the essential oils are in Table 1.

β-caryophyllene was found as the major compound in the essential oil of *A. coelopoda* var. *coelopoda*. Furthermore β-caryophyllene has been detected as the main compound in the essential oil of aerial parts of *A.* cretica subsp. pontica from Turkey (20.26%) [26], *A. dipsacea* from Turkey (5.6%) [14], flower and leaves of *Anthemis altissima* from Iran (25.3% and 17.2% respectively) [25]. On the other hand, β-caryophyllene has not been reported for the essential oils of *A. pseudocotula* from Turkey [26], *A. tinctoria* from Slovak Republic (Holla et al., 2000), *Anthemis* melampodina from Lübnan [18], *A. xylopoda* from Turkey [19], *A. coelopoda* var. *bourgaei* and *A. aciphylla* var. *aciphylla* from Turkey [13].

Azulene was reported the major compound in chemical constituents of the oils of *A.* cretica subsp. pontica from Turkey (14.98%) [26] and in our study with *A. coelopoda* var. *coelopoda* (9.5%) (Table 1), but it was not determined in the essential oils of *A. pseudocotula* [26], *A. tinctoria* [17], *A. altissima* [27], *A. hyalina* [28], *A. xylopoda* [19], *A. coelopoda* var. *bourgaei* and *A. aciphylla* var. *aciphylla* [13], *A. dipsacea*, *A. pectinata* var. pectinata and *A. pseudocotula* samples are noteworthy [14].

According to Bagher et al. (2008), *cis*-chrysanthenyl acetate (27.3%), hexyl butanoate

Table 1. The Composition of the Essential Oils of *Anthemis coelopoda* var. *coelopoda*.

No	Compounds	RI	*A. coelopoda* **var.** *coelopoda*
1.	α-Pinene	1021	0.4
2.	Sabinene	1052	0.1
3.	β-Pinene	1056	0.1
4.	β-Myrcene	1064	0.1
5.	Octanol	1067	0.1
6.	Artemisia triene	1069	0.1
7.	dl-Limonene	1095	0.3
8.	Eucalyptol	1098	0.9
9.	1,3,6-Octatriene	1100	0.7
10.	1,5-Heptadien-4-one	1117	0.1
11.	Linalool	1148	4.3
12.	2H-Pyran-3(4H)-one	1151	0.5
13.	Chrysanthenone	1164	0.1
14.	Camphor	1183	3.7
15.	Borneol	1200	5.5
16.	3-Cyclohexen-1-ol	1206	0.4
17.	Camphene	1215	1.2
18.	Benzocyloheptatriene	1306	0.1
19.	2,4-Decadienal	1313	0.1
20.	Decanoic acid	1354	0.2
21.	α-Copaene	1360	0.1
22.	β-Bourbonene	1366	0.3
23.	β-Elemene	1370	0.7
24.	β-Caryophyllene	1394	21.8
25.	β-Cubebene	1400	0.1
26.	5,9-Undecadien-2-one	1412	0.1
27.	*Trans*-β-Farnesene	1415	1.5
28.	α-Humulene	1418	2.3
29.	Aromadendrene	1421	0.1
30.	*Trans*-β-Ianone	1433	0.1
31.	Germacren D	1435	2.7
32.	Eudesma-4(14),11-diene	1441	0.6
33.	Germacren B	1445	0.9
34.	Germacren A	1452	0.1
35.	α-Amorphene	1456	0.3

Table 1. The Composition of the Essential Oils of *Anthemis coelopoda* var. *coelopoda*. (continue)

36.	δ-Cadinene	1458	0.3
37.	Napfthalene	1479	0.3
38.	1,4-dimethyl-azulene	1481	1.3
39.	Sabinene	1483	0.3
40.	Nerolidol	1499	10.8
41.	1H-Cycloprop(e)azulene	1504	1.0
42.	3-Cyclohexen-1-carboxaldehyde	1514	0.8
43.	Fonenol	1521	0.7
44.	α-Calacorene	1526	0.7
45.	Bicyclo (4.4.0) dec-1-ene	1532	2.0
46.	β-Guaiene	1539	1.5
47.	α-Selinene	1540	1.0
48.	p-Mentha-1,(7), 8(10)-dien-9-ol	1547	0.6
49.	*Trans*-Caryophyllene	1566	0.5
50.	Azulene	1578	9.5
51.	Cyclopentadecane	1602	4.2
52.	2-Pentadecanone	1631	0.1
53.	1,2-Benzenedicarboxylic acid	1640	0.2
54.	Hexadecanoic acid	1693	3.6
55.	Cembrene	1747	0.2
56.	Neophytadiene	1793	0.1
57.	Nonadecane	1903	0.3
	Total		90.7

RI: Retention Indice.

(16%), and myrcene (7%), while the leaf oil contained isobornyl formate (30.6%), *trans*-ethyl chrysanthemumate (15%) and p-mentha-1,5-diene-8-ol (13.7%) showed the highest percentage in the *A. coelopoda* Boiss. flower oil from Gilan province in Rodbar [28]. This compounds (*cis*-chrysanthenyl acetate, hexyl butanoate, isobornyl formate, *trans*-ethyl chrysanthemumate) was not determined in the essential oils of *A. coelopoda* var. *coelopoda* in our study. Whereas p-mentha-1,5-diene-8-ol was not detected but low amounts p-mentha-1,(7), 8(10)-dien-9-ol (0.6%) in our study with *A. coelopoda* var. *coelopoda*.

The studies undertaken on *A. tinctoria* [17] showed that the main components of the oils were 1,8-cineole (7.9%), β-pinene (7.3%), decanoic acide (5.4%) and β-pinene (4.4%). Santolinatriene (27.33%), β-pinene (6.44%) and sabinene (6.09%) have been reported major components in *A. melampodina* Delile [18]. Hexadecanoic acid has been detected as the main compound in the essential oil of aerial parts of *A. dipsacea*, *A. pectinata* var. pectinata and *A. pseudocotula* from Turkey (13.5%-9.5%-2.7%, respectively) [14]. In our study; 1,8-cineole, decanoic acide, santolinatriene and sabinene were not determeined as major constituents, whereas β-pinene and β-pinene were determeined in very low amounts in *A. coelopoda* var. *coelopoda* (0.4%-0.1%, respectively). Furthermore hexadecanoic acid (or palmitic acid) (3.6%) one of the major compounds in our sample.

Javidnia et al. (2004), studied essential oils of the flowers, leaves and stems of *Anthemis altissima* growing wild in Iran were separately obtained by hydrodistillation and analysed by GC–MS. A total of 123 components were identified in the essential oils of the investigated organs. The main components of the flower and leaf essential oils were β-caryophyllene (25.3% and 17.2%), caryophyllene-oxide (6.5% and 9.6%) and spathulenol (5.4% and 17.4%), respectively. Non-terpenic compounds were the main components of the stem oil. Palmitic acid (39.6%) and linoleic acid (36.2%) constituted the main compounds of the stem oil [25].

Kilic et al. reported that (2011), the essential oils of water-distilled aerial parts of *Anthemis pseudocotula* and *Anthemis* cretica subsp. pontica were analysed by GC-MS. As a result thirty-five and forty compounds were identified representing 93.1% and 89.0% of the oils, respectively. The main compounds of *A. pseudocotula* were 1,8-cineole (39.40%), camphor (9.36%), artemisiaketone (5.68%), filifolene (5.15%), and α-terpineol (4.69%), whereas β-caryophyllene (20.26%), azulene (14.98%), spathulenol (6.03%), and germacrene D (5.82%) were the major constituents of *A. cretica* subsp. pontica [26]. This indicates compliance with our work. But their study demonstrates the occurrence of the 1,8-cineole chemotype of *A. pseudocotula* whereas β-caryophyllene/nerolidol and azulene chemotype of the *A. coelopoda* var. *coelopoda* in our study.

In another study, *A. aciphylla* var. *aciphylla* were characterized by a high percentage of irregular monoterpenes [santolinatriene (44.2%)], followed by [methyl chavicol (4.1%) and terpineol (3.2%)]. Monoterpene hydrocarbons [β-pinene (45.2%)] and irregular monoterpenes [santolinatriene (14.8%)] were found to be the main components in the essential oil from the overground parts of *A. coelopoda* var. *bourgaei* [13].

According to Uzel et al. (2004) [19], borneol (31.8% – 30.15%) was among the main compounds of the flowers and leaves of *A. xylopoda*, respectively; according to Albay et al. (2009) [29], borneol (10.6%) also was among the main components of *A. cretica* subsp. argaea from Turkey. Whereas borneol (5.5%) was detected as the major constituent in our study with *A. coelopoda* var. *coelopoda*, this compound was not determined in the essential oils of *A. hyalina* [30] and *A. triumfetti* [31].

Saroglou et al. (2006), reported that the volatile composition of eight *Anthemis* species. The main constituents of the investigated populations of each taxon have been revealed as follows: *A. altissima*: linalool, *trans*-caryophyllene, *cis*-chrysanthenyl acetate; *A.* auriculata: spathulenol, *trans*-caryophyllene, β-eudesmol; *A. chia*: *cis*-chrysanthenyl acetate, *trans*-caryophyllene, germacrene-D; *A. cotula*: germacrene-D, spathulenol; *A. tinctoria*: spathulenol, caryophyllene oxide, t-cadinol; *A.* melanolepis: p-cymene, chrysanthenone, *trans*-verbenol, caryophyllene oxide; *A. tomentosa*: linalool, 1,8-cineole; *A. werneri* subsp. werneri: nopol, terpineol-4, *trans*-caryophyllene. Sesquiterpene hydrocarbons were shown to be the main group of constituents of all taxa [32]. In our study determeined as high percantage of sesquiterpene hydrocarbons of *A. coelopoda* var. *coelopodA*.

This study demonstrates the occurrence of β-caryophyllene/nerolidol and azulene chemotype of the *Anthemis coelopoda* var. *coelopoda* in the eastern Anatolian region of Turkey.

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