Composition of the volatile oils of two *Anthemis* L. taxa from Turkey

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Abstract

The essential oils of water-distilled aerial parts of *Anthemis pseudocotula* and *Anthemis cretica* subsp. *pontica* (Asteraceae) were analysed by GC-MS. As a result thirty-five and forty components were identified representing 93.1% and 89.0% of the oils, respectively. The main compounds of *A. pseudocotula* were 1,8-cineole (39.4%), camphor (9.36%), artemisiaketone (5.68%), filifolene (5.15%), and α-terpineol (4.69%) whereas, caryophyllene (20.26%), azulene (14.98%), spathulenol (6.03%), and germacrene D (5.82%) were the major constituents of *A. cretica* subsp. *pontica.*

Key words: Anthemis, 1,8-Cineole, Caryophyllene.

Introduction

The genus *Anthemis* L. (family Asteraceae, tribe Anthemideae) is divided into three sections (Anthemis, Maruta, and Cota) according to the Flora of Turkey (Davis, 1975). In Turkey only 50 species have been recorded of which about 54% are endemic. These plants prefer dry, open sites on wood-steppe hillsides and grow especially on calcareous soils

(Davis, 1975). Furthermore, the genus *Anthemis* (tribe Anthemideae Cass.) consists of more than 210 species. The total geographical distribution of *Anthemis* encompasses most of western Eurasia, the Mediterranean, and a small part of eastern Africa. While the central European region is inhabited by only a few archaeophytic species, the main centre of diversity is located in southwestern Asia with 150-210 species, including all of the presently accepted subgenera and sections. Some species inhabit northern America and the southern hemisphere as well (Oberprieler, 2001). 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 (Oberprieler, 2001).

The species of the genus *Anthemis* are widely used in the pharmaceutics, cosmetics, and food industry. The flowers of the genus have a well-documented use as antiseptic and healing herbs, the main components being flavonoids and essential oils (Vaverkova *et al*., 2001). In Europe extracts, tinctures, tisanes (teas), and salves are widely used as anti-inflammatory, antibacterial, antispasmodic, and sedative agents, respectively. The activity of the essential oils and different extracts from several *Anthemis* species has been reported previously (Holla *et al*., 2000; Grace, 2002). Sesquiterpene lactones have received considerable attention because of their chemo-ecological functions (Cis *et al*., 2006; Nawrot *et al*., 1983), biological activities, and taxonomic significance (Picman, 1986; Zhang *et al*., 2005). 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 (Seaman, 1982).

A. cretica is a highly polymorphic species in which a number of different taxa are recognizable and have been variously treated at specific or infraspecific levels by some authors (Davis, 1975). Having all of the above-mentioned in mind, the aim of this study was set to perform a detailed chemical composition of the essential oil hydrodistilled from the above-ground parts of *A. pseudocotula* and *A. cretica* subsp. *pontica* from the eastern Anatolian region in Turkey. The obtained results could be of use in the clarification of infrageneric taxonomy of the genus *Anthemis*.

Material and Methods

Plant material

The aerial part of samples were collected from their natural habitats. *A. pseudocotula* Boiss. was collected from Elazig-Keban, Asagi Cakmak village, in May 2010 at an altitude of 1300 m. *A. cretica* subsp. *pontica* (Willd.) Grierson was also collected from Elazig-Keban, Guneytepe village, in June 2010, at an altitude of 1350 m. The voucher specimens have been deposited at the Herbarium of department of Biology, Firat University.

Isolation of the essential oils

Air-dried aerial parts of the plant materials were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h.

Gas chromatography-mass spectrometry (GC-MS) analysis

The oils were analysed by GC-FID-MS, using a Hewlett Packard system. HP-Agilent 5973 N GC-MS system (Elazig-Turkey) with 6890 GC in the Plant Products and Biotechnology Research Laboratory (BUBAL) in Firat University. A HP-5 MS column (30 m × 0.25 mm i.d., film tickness (0.25 µm) was used with helium as the carrier gas. Injector temperature was 250 ºC, split flow was 1 ml/min. The GC oven temperature was kept at 70 ºC for 2 min, raised to 150 ºC at a rate of 10 ºC/min then kept constant at 150 ºC for 15 min, and finally raised to 240 ºC at a rate of 5 ºC/min, Alkanes were used as reference points in the calculation of relative retention indices (RRI). Mass spectra were taken at 70 eV and a mass range of 35 - 425. Component identification was carried out using spectrometric electronic libraries (WILEY, NIST). Cluster analysis (Wang et al., 2009) was applied to classify of compounds of *A. pseudocotula* and *A. cretica* subsp. *pontica* in Fig. 1-2.

Statistical analysis

The statistical software Cropstat (IRRI 2005) was used to perform the ANOVA and pattern analysis. Standard analyses of variance (anova) were used to analyze the data obtained.

Results and Discussion

The chemical composition of the essential oil of dried aerial parts of *A. pseudocotula* and *A. cretica* subsp. *pontica* were analysed by GC-MS. Thirty-five and forty compounds were identified in *A. pseudocotula* and *A. cretica* subsp. *pontica*, respectively, accounting for 93.1% and 89.0% of the of the respective total essential oils. The yields of essential oils from the two samples were 0.3 and 0.4 ml, respectively. The main compounds of *A. pseudocotula* were 1,8-cineole (39.4%), 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.* The compositions of the essential oils are listed in Table I.

Classification results are shown in dendrograms for essential oils in *A. pseudocotula* (Fig. 1) and *A. cretica* subsp. *pontica* (Fig. 2). *A. pseudocotula* and *A. cretica* subsp. *pontica* were both classified into three main groups. In *A. pseudocotula* 1,8-cineole first group, camphor second group and other constituents were determined as third group (Fig. 1), whereas in *A. cretica* subsp. *pontica* β-caryophyllene first group, germacrene D second group and other constituents were determined third group (Fig. 2).

1,8-Cineole (eucalyptol) was found as the major compound in the essential oil of *A. pseudocotula* (39.40%) in Table I and Fig. 1. Furthermore 1,8-cineole (8.49%) has been detected as the main compound in the essential oil of aerial parts of *A. wiedemanniana* Fisch. & Mey. from Turkey (Kivcak *et al*., 2007), *A. tinctoria* L. from Slovak Republic (7.9%) (Holla *et al*., 2000), *A. segetalis* Ten. from Montenegro (6.1%) (Radulovic *et al*., 2009), flower and leaf *A. xylopoda* O. Schwarz from Turkey (5.45%-16.74%) (Uzel *et al*., 2004), and *A. triumfetti* (L.) DC. (5.8%) from Montenegro (Pavlovic *et al*., 2006). On the other hand, 1,8-cineole has not been reported for the essential oils of *A. marschalliana* Willd. subsp. *pectinata* (Boiss.) from Turkey (Albay *et al*., 2009), *A. cretica* L. subsp. *argaea* Boiss. & Bal. (Albay *et al*., 2009), from Turkey, *A. hyalina* DC. (Sajjadi and Mehregan, 2006) from Iran, and also *A. altissima* L. from Iran (Rezaee *et al*., 2006) samples.

Camphor was also detected as a the major compound in the essential oil of *A. pseudocotula* (9.36%, Table I and Fig. 1), whereas camphor was not detected in the essential oils of *A. marschalliana* subsp. *pectinata* (Albay *et al*., 2009), *A. cretica* subsp. *argaea* (Albay *et al*., 2009), *A. wiedemanniana* (Kivcak *et al*., 2007), *A. segetalis* (Radulovic *et al*., 2009), *A. tinctoria* (Holla *et al*., 2000), and *A altissima* (Rezaee *et al*., 2006) samples. Moreover camphor has been reported as one of the major compound in the volatile constituents of flowers (11.6%), and leaves (1.7%) of *A. hyalina* (Sajjadi and Mehregan, 2006), in the essential oil of *A. triumfetti* (15.0%) (Pavlovic *et al*., 2006), and in our study with *A. pseudocotula* (9.36%) and *A. cretica* subsp. *pontica* (4.39%) (Table I).

Azulene was detected as one of the major compounds in the essential oil of *A. cretica* subsp. *pontica* (4.39%) (Table I). However the absence of this compound from the essential oils of *A. pseudocotula* (Table I), *A. marschalliana* subsp. *pectinata*, *A. cretica* subsp. *argaea* (Albay *et al*., 2009), *A. wiedemanniana* (Kivcak *et al*., 2007), *A. segetalis* (Radulovic *et al*., 2009), *A. tinctoria* (Holla *et al*., 2000), *A. altissima* (Rezaee *et al*., 2006), *A. hyalina* (Sajjadi and Mehregan, 2006), *A. xylopoda* (Uzel *et al*., 2004), and *A. triumfetti* (15.0%) samples are noteworthy (Pavlovic *et al*., 2006).

The studies undertaken on *A. tinctoria* (Holla *et al*., 2000) showed that the main components of the oils were 1,8-cineole (7.9%), β-pinene (7.3%), decanoic acid (5.4%), and α-pinene (4.4%). Santolinatriene (27.33%), α-pinene (6.44%), and sabinene (6.09%) have been reported major components in *A. melampodina* Delile (Grace, 2002).

Spathulenol was reported the major compound in chemical constituents of the leaf (18.2%) and flower (18.7%) oils of *A. altissima* (Rezaee *et al*., 2006), also in *A. marschalliana* subsp. *pectinata* (21.7%) (Albay *et al*., 2009) and in our study with *A. cretica* subsp. *pontica* (6.03%) (Table I), but it was not determined in the essential oils of *A. xylopoda* (Radulovic *et al*., 2009) and in *A. pseudocotula* (Table I) which is noteworthy. While germacrene D (12.6%) was among the main components of *A. segetalis* (Radulovic *et al*., 2009), and in our study with *A. cretica* subsp. *pontica* (5.82%) (Table I), the cited component is not a major component of the *A. wiedemanniana* (Kivcak *et al*., 2007), *A. tinctoria* (Holla *et al*., 2000), and *A. triumfetti* (Pavlovic *et al*., 2006) essential oils, respectively, whereas germacrene D (0.37%) was determined in very low amounts in *A. pseudocotula* (Table I).

According to Uzel *et al.* (2004), borneol (31.8 % - 30.15%) were among the main components in the flowers and leaves of *A. xylopoda*, respectively; according to Albay *et al*. (2009) borneol (10.6%) also was among the main components of *A. cretica* subsp. *argaea* from Turkey. Whereas borneol was detected in low amounts (3.72% and 3.26%) in our study with *A. pseudocotula* and *A. cretica* subsp. *pontica*, respectively (Table I), this compound was not determined in the essential oils of *A. hyalina* (Sajjadi and Mehregan, 2006) and *A. triumfetti* (Pavlovic *et al*., 2006).

Linalool (12.75%), the major compound in *A. wiedemanniana* (Kivcak *et al*., 2007), was not determined in *A. xylopoda* (Uzel *et al*., 2004) and in *A. pseudocotula* (Table I). Sabinene (19.5%) was determined the main component in *A. segetalis* (Radulovic *et al*., 2009), but in our study this compound was not determined as a major constituent both *A. pseudocotula* (2.52%) and *A. cretica* subsp. *pontica* (0.12%) (Table I).

α-Pinene (14.3%) was analyzed as the major constituent in *A. cretica* subsp. *argaea* (Albay *et al*., 2009) and 14.4% in *A. triumfetti* (Pavlovic *et al*., 2006), but this constituent (1.33%) was not among the main components in leaf oil of *A. xylopoda* (Uzel *et al*., 2004) and *A. pseudocotula* (2.45%) (Table I). Also β-pinene was determined one of the main components in *A. cretica* subsp. *argaea* (14.6%) (Albay *et al*., 2009), in *A. triumfetti* (16.9%) (Pavlovic *et al*., 2006), and in *A. tinctoria* (7.3%) (Holla *et al*., 2000), but this compound was not determined in the essential oil of *A. xylopoda* (Uzel *et al*., 2004) and in *A. cretica* subsp. *pontica* in this study (Table I).

Conclusions

This study demonstrates the occurrence of the 1,8-cineole chemotype of *A. pseudocotula* and β-caryophyllene chemotype of *A. cretica* subsp. *pontica* in eastern Anatolian region of Turkey (Table I and Fig. 1-2). Other *Anthemis* species have different types of essential oils, like the α/β-pinene chemotype in *A. cretica* subsp. *argaea* (Albay *et al*., 2009) and the sabinene/germacrene D chemotype in *A. segetalis* (Radulovic *et al*., 2009).

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Table I. Composition of the essential oils of *A. pseudocotula* and *A. cretica* subsp. *pontica*

Compound	RRI*	*A. pseudocotula* (%)	*A. cretica* subsp. *pontica* (%)
Santolina triene	997	0.98	-
Tricyclene	1014	0.08	-
Bicyclo[3.1.0]hex-2-ene	1016	0.18	-
α-Pinene	1022	2.45	0.55
Camphene	1034	1.70	0.06
Sabinene	1052	2.52	0.12
β-Pinene	1056	1.50	-
6-Methyl-5-hepten-2-one	1060	-	0.18
β-Mrycene	1064	-	0.23
1,3,6-Heptatriene	1066	0.50	-
Mrycene	1069	-	0.64
β-Phellandrene	1224	0.28	-
α-Terpinene	1086	0.98	-
p-Cymene	1092	1.26	-
Limonene	1095	0.36	0.35
1,8-Cineole	1098	39.40	0.65
Cis-Ocimene	1100	-	0.90
1,3,6-Octatriene	1108	-	0.17
Artemisiaketone	1117	5.68	-
γ-Terpinene	1120	3.07	0.77
1.3.6-Heptatriene	1133	0.65	-
α-Terpinolene	1137	0.22	-
Bicyclo[3.2.0]hept-2-ene	1148	1.31	-
Linalool	1151	-	2.88
2*H*-Pyran-3(4*H*)-one	1161	-	0.44
Filifolene	1164	5.15	-
1,4-Cyclohexadiene	1166	0.35	-
Camphor	1186	9.36	4.39
Borneol	1205	3.72	3.26
Naphthalene	1215	-	0.12
α-Terpineol	1216	4.69	-
β-Fenchyl alcohol	1231	-	0.55
Propanal	1249	0.17	-

δ-3-Carene	1253	0.50	-
3-Cyclohexen-1-one	1258	2.92	-
m-Menthadien-6-ol	1276	-	0.36
*Iso*bornyl acetate	1283	0.48	-
Eugenol	1340	0.12	-
3-Carene	1361	0.20	-
β-Bourbenene	1370	-	0.21
3,5-Heptadienal	1373	0.71	-
Benzene	1378	0.80	-
β-Elemene	1394	-	1.64
β-Caryophyllene	1400	0.13	20.26
Aromadendrene	1406	-	0.28
Bicyclo[3.1.1]hept-2-ene	1415	-	0.80
1,6,10-Dodecatriene	1416	-	1.16
3-Dodecan-1-al	1424	0.44	-
α-Humulene	1425	-	1.77
β-Selinene	1430	-	0.47
β-Lonone	1433	-	0.10
Germacrene D	1435	0.37	5.82
Eudesmol	1440	-	1.17
Bicyclogermacrene	1445	-	1.20
Germacrene A	1452	-	0.37
Spathuneol	1495	-	6.03
α-Gurjunene	1505	-	0.20
α-Selinene	1541	-	5.30
6-Isopropenyl	1576	-	0.46
Azulene	1579	-	14.98
Phenol	1586	-	0.40
Cyclopentadecane	1602	0.03	-
2-Pentadecanone	1634	-	4.64
n-Hexadecanoic acid	1692	-	0.35
Nonadecane	1903	-	0.43
	Total	93.1	89.0

*RRI relative retention indices
- : not detected

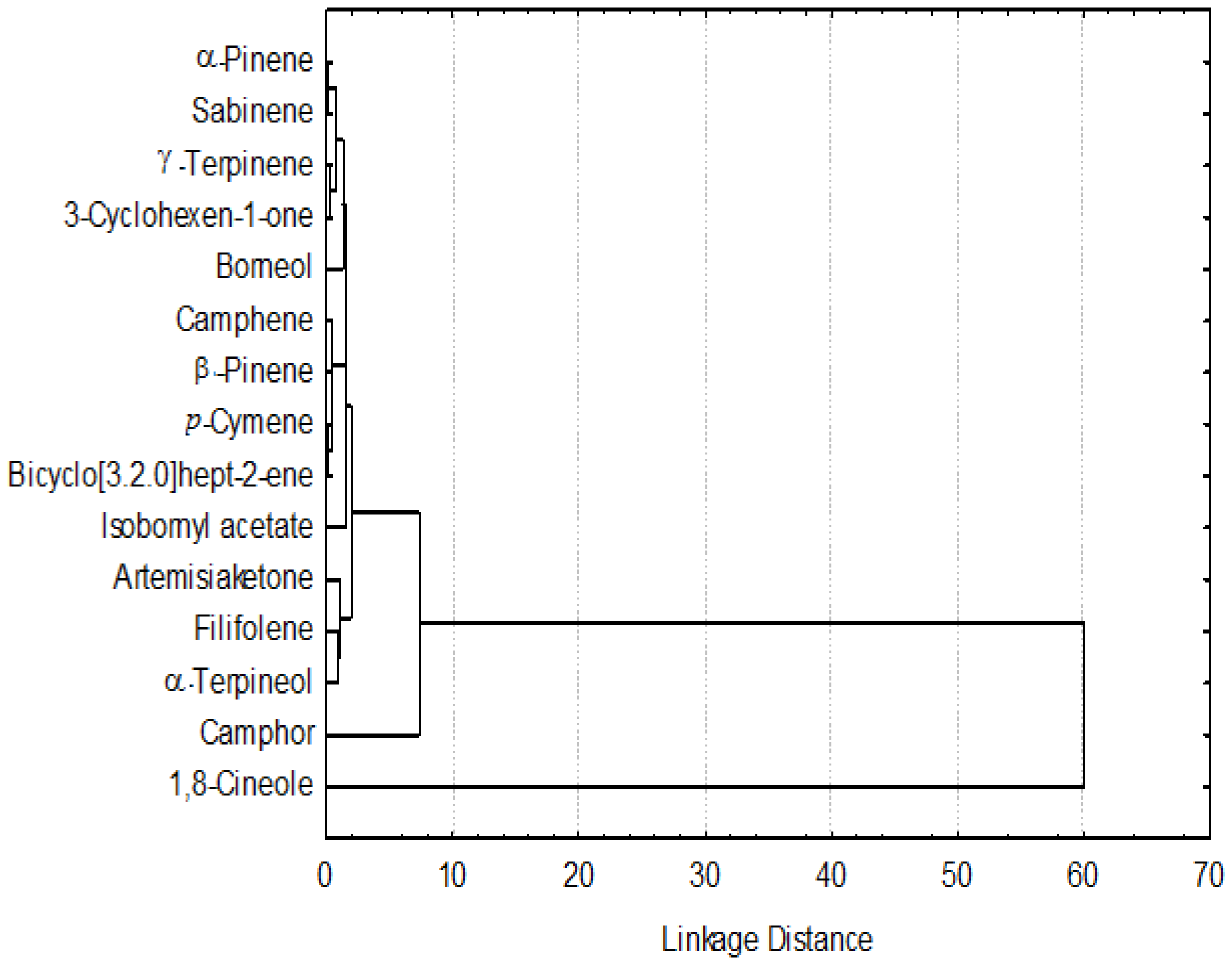

Fig. 1 Dendrogram presenting hierarchical clustering of major compounds of essentail oils of *A. pseudocotula*

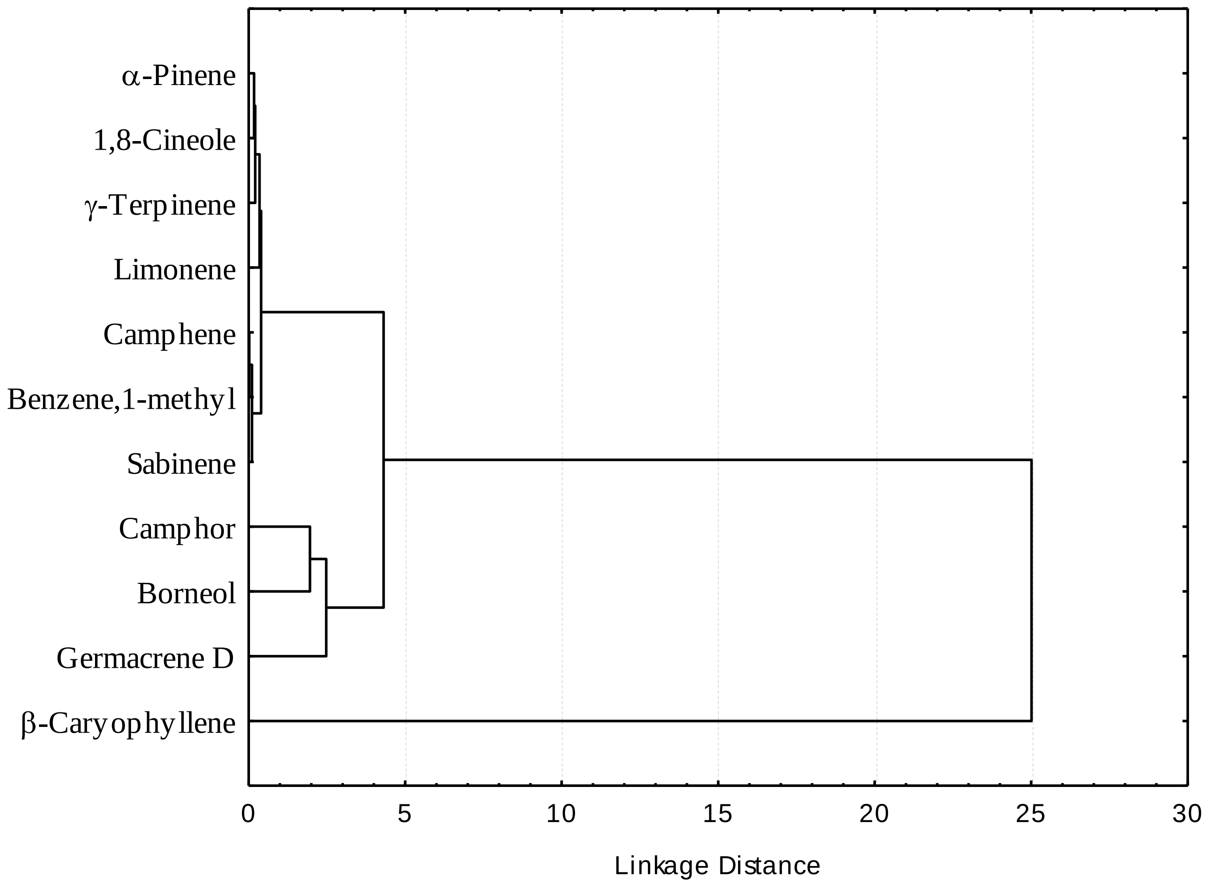

Fig. 2 Dendrogram presenting hierarchical clustering of major compounds of essentail oils of *A. cretica* subsp. *pontica*.