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RESEARCH ARTICLE

Determination of the volatile compounds of *Anthemis cretica* subsp. *anatolica* (Boiss.) Grierson

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Abstract
Chemical composition of the essential oils obtained by hydrodistillation from the aerial parts of *Anthemis cretica* subsp. *anatolica* was analyzed by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS) systems. The essential oil of *A. cretica* subsp. *anatolica* was characterized by the presence of a high percentage of oxygenated sesquiterpenes (57.9%). Twenty-seven compounds were identified representing 96.6 % of the essential oil of *A. cretica* subsp. *anatolica*. The main components of the oil were spathulenol (27.0%) and hexadecanoic acid (14.3%).

Keywords: *Anthemis cretica* subsp. *anatolica*; essential oil; GC-FID and GC-MS

Introduction

Genus *Anthemis* L. (Asteraceae) is represented by 51 species, 81 taxa (Grierson & Yavin, 1975) and *Anthemis cretica* L. by twelve subspecies in Turkey (Ozbek, 2012).

Anthemis species have several biological activities and are widely used in folk medicine for treatment of gastrointestinal disorders, haemorrhoids, cough, stomach aches and liver failure (Baytop, 1999; Kultur, 2007; Ugurlu & Secmen, 2008; Gonenc et al., 2011; Korkmaz & Karakus, 2015). In addition, they are able to soothe pains and irritations and to clean wounds (Pavlovic et al., 2006) and utilized as herb teas, in cosmetics, and in the pharmaceutical industry (Kivcak et al., 2007). Several *Anthemis* spp. have been studied for their essential oils (Javidnia et al., 2004; Uzel et al., 2004; Kurtulmus et al., 2009; Yusufoglu et al., Tawaha et al., 2015; 2018; Orlando et al., 2019), secondary metabolites, terpenoids, sesquiterpene lactones, flavonoids and coumarins (Hofer & Greger, 1985; Bruno et al., 1997; Vajs et al., 1999; Gonenc et al., 2011; Venditti et al., 2016; Alessandro et al., 2016; Guragaç Dereli et al., 2018). Neuroprotective effects (Orlando et al., 2019), cytotoxic (Tawaha et al., 2015), antioxidant and antimicrobial (Uzel et al., 2004; Kivcak et al., 2007; Albayrak & Aksoy, 2013; Stojkovic et al., 2014) activities of *Anthemis* species have been reported. In the current study essential oil of the aerial parts of *Anthemis cretica* L. subsp. *anatolica* (Boiss.) Grierson was analysed by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS) systems.

Materials and Methods

Plant Material

The aerial parts of *A. cretica* subsp. *anatolica* was collected while flowering in the vicinity of Nevşehir, 14.06.2014 and determined by M. Ufuk Ozbek. Voucher specimen has been deposited at the Herbarium of the Istanbul University, Faculty of Pharmacy, Istanbul, Turkey (Voucher specimens no: ISTE 115055).

Isolation of the essential oil

The air-dried plant material was hydrodistilled for 3 hours using a Clevenger-type apparatus. The essential oil of *A. cretica* subsp. *anatolica* was dried over anhydrous sodium sulphate and stored at 4°C in the dark until analysed. The oil yield was calculated as 0.22%, v/w on dry weight basis.

GC and GC/MS Conditions

The oil was analysed by capillary GC and GC/MS using an Agilent GC-MSD system.

GC/MS analysis

The GC/MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60m x 0.25mm, 0.25μm 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 40:1. The injector temperature was at 250°C. MS were taken 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. In order to obtain the same elution order with GC/MS, simultaneous injection was performed using the same column and appropriate operational conditions. FID temperature was 300°C.

Identification of compounds

Identification of the essential oil components was 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 (Curvers et al., 1985). Computer matching against commercial (Wiley GC/MS Library, MassFinder Library) (McLafferty & Stauffer, 1989; Hochmuth, 2008) 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 (Joulain and Koenig, 1998; ESO 2000, 1999) was used for the identification. Relative percentage amounts of the separated compounds were calculated from FID chromatograms.

Results and Discussion

The essential oil of *A. cretica* subsp. *anatolica* was characterized by the presence of a high percentage of oxygenated sesquiterpenes (57.9%). Twenty-seven compounds were identified representing 96.6 % of the essential oil of *A. cretica* subsp. *anatolica* (Table 1). The main components of the oil were spathulenol (27.0%) and hexadecanoic acid (14.3%). Hitherto the essential oil composition of *A. cretica* subsp. *anatolica* has not been investigated.

According to literature the essential oils of aerial parts of *Anthemis cretica* L. subsp. *messanensis* (Brullo) Giardina & Raimondo contained (*E*)-chrysanthenyl acetate (28.8 and 24.2%), 14-hydroxy-*α*-humulene (8.1 and 5.3%), santolina triene (8.0 and 5.8%) and *α*-pinene (6.7 and 5.4%) resp. 1,8-cineole (13.3 and 12.2% resp.) was the main component of both flower and leaf oils of *Anthemis cretica* L. subsp. *columnae* (Ten.) Frezen together with *δ*-cadinene (9.0 and 8.2% resp.) and (*E*)-caryophyllene (8.3 and 5.6% resp.) (Riccobono et al., 2017).

The essential oil composition of *A. cretica* L. ssp. *carpatica* (Willd.) Grierson was analyzed by GC and GC/MS. The main constituents have been identified as *cis*-thujone (39.0%), *trans*-thujone (13.5%), and yomogi alcohol (7.1%) (Pavlovic et al., 2010).

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Table 1. Composition of the essential oil of *Anthemis cretica* subsp. *anatolica*

RI[a]	RI[b]	Compounds	%	IM
1213	1213[c]	1,8-Cineole	1.3	t_R, MS
1466	1460[d]	α-Cubebene	tr	MS
1497	1488[c]	α-Copaene	0.4	MS
1532	1515[d]	Camphor	0.5	t_R, MS
1550	1559[d]	*cis*-α-Bergamotene	0.3	MS
1590	1579[d]	Bornyl acetate	0.4	t_R, MS
1612	1598[d]	β-Caryophyllene	0.6	t_R, MS
1658	1658[e]	Sabinyl acetate	0.4	MS
1718	1686[h]	γ-Guaiene	0.6	MS
1726	1708[c]	Germacrene D	1.1	MS
1751	1735[d]	Bicyclogermacrene	2.2	MS
1755	1737[d]	β-Curcumene	0.5	MS
1772	1756[d]	δ-Cadinene	1.2	t_R, MS
1776	1763[d]	γ-Cadinene	0.8	MS
1786	1774[d]	*ar*-Curcumene	0.6	MS
2000	2005[f]	*trans*-Sesquisabinene hydrate	1.1	MS
2008	2008[f]	Caryophyllene oxide	2.7	t_R, MS
2041	2036[d]	(*E*)-Nerolidol	1.1	t_R, MS
2069	2057[d]	Germacrene D-4-ol	1.9	MS
2096	2085[e]	*cis*-Sesquisabinene hydrate	7.7	MS
2144	2126[c]	Spathulenol	27.0	t_R, MS
2191	2187[c]	T-Cadinol	7.9	MS
2255	2238[d]	β-Eudesmol	8.5	MS
2300	2300[e]	Tricosane	5.4	t_R, MS
2400	2400[g]	Tetracosane	3.2	t_R, MS
2600	2600[g]	Hexacosane	4.9	MS
2931	2913[d]	Hexadecanoic acid	14.3	MS
		Grouped compounds (%)		
		Oxygenated monoterpenes	1.8	
		Sesquiterpenes hydrocarbones	8.3	
		Oxygenated sesquiterpenes	57.9	
		Others	28.6	

RI[a]: Retention indices experimentally calculated against *n*-alkanes; RI[b]: reported literature retention indices on RRI from literature, [c] (Kaya et al., 2017); [d] (Babushok et al., 2011); [e] (Ozek et al., 2014); [f] (Hulley et al., 2018); [g] (Kendir et al., 2019); [h] (Ozturk et al., 2014) for polar column values %: calculated from FID data; IM: Identification Method: t_R, Identification based on comparison with co-injected with standards on a HP Innowax column; MS, identified on the basis of computer matching of the mass spectra.

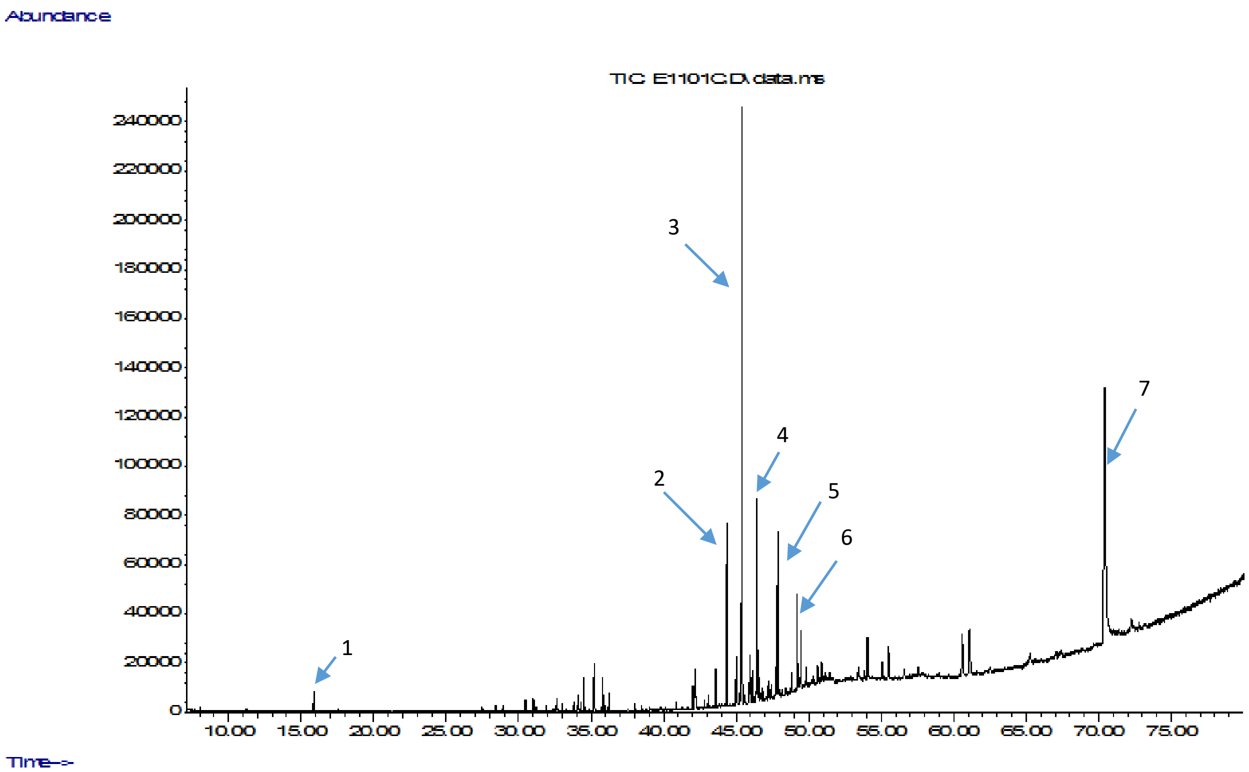

Figure 1. GC chromatogram of essential oil of *Anthemis cretica* subsp. *anatolica.* Number corresponds to (1) 1,8-cineole, (2) *cis*-sesquisabinene hydrate, (3) spathulenol, (4) T-cadinol, (5) β-eudesmol, (6) tricosane, (7) hexadecanoic acid.

The essential oil of water-distilled aerial parts of *A. cretica* subsp. *pontica* was analyzed by GC-MS. β-caryophyllene (20.26%), azulene (14.98%), spathulenol (6.03%) and germacrene D (5.82%) were the major constituents of *A. cretica* subsp. *pontica* (Kilic et al., 2011).

The essential oil obtained from all the parts of *Anthemis cretica* subsp. *argaea* by hydrodistillation was analysed by GC-FID and GC-MS. Forty-four components representing 89.6% of the total oil was characterized and the main components of the plant was found to be β-pinene (14.6%), *a*-pinene (14.3%), borneol (10.6%) and β-acorenol (6.5%) from *A. cretica* ssp. *argaea* (Albay et al., 2009).

The major components (camphor 80.6%, camphene 10.6% and p-cymene 2.8%) were identified for essential oil of *Anthemis cretica* subsp. *albida* (Boiss.) Grierson (Dolarslan & Gurkok, 2018).

In our present study, we examined chemical composition of essential oil obtained from the aerial parts of *A. cretica* subsp. *anatolica* collected in the vicinity of Nevşehir. Yield of essential oil obtained by hydrodistillation was found to be 0.22%. Essential oil components are seen at Table 1. Major components of the essential oil of *A. cretica* subsp. *anatolica* have been identified as spathulenol and hexadecanoic acid. Based on the previously published essential oil data (Albay et al., 2009; Pavlovic et al., 2010; Kilic et al., 2011; Riccobono et al., 2017; major components of *A. cretica* subsp. *anatolica* were quite distinct than those of *A. cretica* subsp. *carpatica*, subsp. *columnae*, subsp. *messanensis* as well as *A. cretica* subsp. *pontica* supporting the taxonomical separation of this subspecies from the aforementioned subspecies.

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