Acta Pharm. Sci. Vol 56 No: 2. 2018
DOI: 10.23893/1307-2080.APS.05611

The Essential Oils of Two Achillea L. species from Turkey

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ABSTRACT

Chemical composition of the essential oils obtained by hydrodistillation from the aerial parts of *Achillea biebersteinii* Afan. and *A. wilhelmsii* C. Koch were analyzed by GC-FID and GC-MS. The essential oils of *A. biebersteinii* and *A. wilhelmsii* were characterized by the presence of a high percentage of oxygenated monoterpenes 72.9% and 49%, respectively. Sixty-four compounds were identified in the essential oil of aerial parts of *A. biebersteinii* representing 95.9 % of the essential oil. The main components of *A. biebersteinii* essential oil were 1,8-cineole (34.6%) and camphor (12.9%). Fourty-two compounds were identified in the essential oil of aerial parts of *A. wilhelmsii* representing 88.2 % of the essential oil. Main component of the essential oil of A. wilhelmsii was determined as camphor (32.0%).

Keywords: *Achillea biebersteinii, Achillea wilhelmsii,* essential oil, GC-FID and GC-MS.

INTRODUCTION

Genus *Achillea* L. (Asteraceae) is represented by more than 140 species in all around the world. The genus is widespread in Europe, Asia, North America and Middle East[1]. There are 59 taxa of *Achillea* found in Turkey which are divided into 6 sections *Ptarmica* (DC.) W. Koch, *Arthrolepis* Boiss., *Babounya* Boiss., *Santalinoidea* DC., *Millefolium* (DC.) W. Koch, and *Filipendulinae* (DC.) Boiss. Among them, 31 taxa are endemic to Turkey (%53)[2-4]. The essential oil composition of several *Achillea* spp. growing in Turkey have been studied[5]. Antioxidant, insecticidal and herbicidal activities of *A. biebersteinii* oils were reported[6-13]. The antimicrobial activity of *A. wilhelmsii* subsp. *wilhelmsii* essential oil was tested against several microorganisms and strong inhibitory activity was observed against *Enterobacter aerogenes, Proteus vulgaris* and *Alternaria brassicola*[14] species.

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(Received 14 March 2018, accepted 19 March 2018)

Biological activities of various *Achillea* species include angiogenic[7], antifungal[8,15], antibacterial[16], antimicrobial[14,17], hepatoptotective[18], herbicidal[8], insecticidal[11,19], antioxidant[16,18] antiradical[17] and protective effects against oxidative stress[6,20].

In the present work, chemical composition of the *Achillea biebersteinii* and *A. wilhelmsii* essential oils were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) systems.

MATERIALS AND METHODS

Plant Materials

The aerial parts of *Achillea biebersteinii* Afan. and *A. wilhelmsii* C. Koch were collected while flowering in the vicinity of Adana and Kayseri, respectively. The plant species were identified by Prof. Mecit Vural and voucher specimens have been deposited at the Herbarium of the Istanbul University, Faculty of Pharmacy, Istanbul, Turkey. (Voucher specimens no: ISTE 115056 and ISTE 115058 resp.)

Isolation of the Essential Oils

The air-dried plant materials were hydrodistilled for 3 hours using a Clevenger-type apparatus. *A. biebersteinii* and *A. wilhelmsii* oils were dried over anhydrous sodium sulphate and stored at 4 °C in the dark until analysed. The yield of essential oils were calculated as 0.98 % and 0.18 %, v/w on dry weight basis, resp.

GC and GC/MS Conditions:

The oils were analyzed 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 done by 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[21]. Computer matching against commercial (Wiley GC/MS Library, MassFinder 3 Library)[22,23] 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[24,25] was used for the identification. Relative percentage amounts of the separated compounds were calculated from FID chromatograms. The results of analysis are shown in Table 1.

Table 1. Composition of the essential oils of *Achillea biebersteinii* and *A. wilhelmsii*

RRI	Compounds	A %	B %	IM
1014	Tricyclene	tr	-	MS
1032	α-Pinene	2.6	-	t_R, MS
1035	α -Thujene	tr	-	MS
1076	Camphene	-	0.4	t_R, MS
1118	β-Pinene	1.1	-	t_R, MS
1132	Sabinene	1.1	0.4	t_R, MS
1138	Thuja-2,4 (10)-dien	tr	-	MS
1188	α-Terpinene	2.5	-	t_R, MS
1195	Dehydro-1,8-cineole	tr	-	t_R, MS
1203	Limonene	0.2	0.2	t_R, MS
1213	**1,8-Cineole**	**34.6**	3.3	t_R, MS
1255	γ-Terpinene	0.5	-	t_R, MS
1280	p-Cymene	3.4	0.6	t_R, MS
1290	Terpinolene	0.1	-	t_R, MS
1409	Rosefuran	tr	-	MS
1437	α-Thujone	0.2	-	MS
1445	Filifolone	0.3	-	MS
1451	β-Thujone	0.1	-	MS
1452	1-Octen-3-ol	tr	-	t_R, MS
1474	trans-Sabinene hydrate	0.6	0.6	t_R, MS
1483	Isonerol oxide	-	0.8	MS
1499	α-Campholene aldehyde	0.2	-	MS
1522	Chrysanthenone	2.4	-	MS
1532	**Camphor**	**12.9**	**32.0**	t_R, MS
1538	trans-Chrysanthenyl acetate	2.3	-	MS
1544	Dihydroachillene	0.5	0.5	MS

1553	Linalool	0.2	0.7	t_R, MS
1556	cis-Sabinene hydrate	0.8	tr	t_R, MS
1571	trans-p-Menth-2-en-1-ol	0.5	-	MS
1582	cis-Chrysanthenyl acetate	0.1	-	MS
1586	Pinocarvone	0.7	0.5	MS
1591	Bornyl acetate	0.4	0.5	t_R, MS
1600	Chrysanthenyl propionate	tr	-	MS
1611	Terpinen-4-ol	1.7	tr	t_R, MS
1612	β-Caryophyllene	tr	0.8	t_R, MS
1617	Lavandulyl acetate	-	2.0	MS
1638	cis-p-Menth-2-en-1-ol	0.4	-	MS
1648	Myrtenal	0.3	-	MS
1651	Sabina ketone	0.2	-	MS
1670	trans-Pinocarveol	0.6	-	t_R, MS
1663	cis-Verbenol	0.6	-	MS
1683	trans-Verbenol	4.0	0.6	MS
1687	Lavandulol	-	4.1	t_R, MS
1706	α-Terpineol	3.6	1.2	t_R, MS
1719	Borneol	2.0	2.6	t_R, MS
1725	Verbenone	0.1	-	t_R, MS
1726	Germacrene D	0.1	2.3	MS
1742	β-Selinene	-	0.4	MS
1747	p-Mentha-1,5-dien-8-ol	0.3	-	MS
1748	Piperitone	0.8	-	t_R, MS
1751	Bicyclogermacrene	-	1.5	MS
1755	Terpinyl acetate	6.0	-	t_R, MS
1758	cis-Piperitol	tr	-	MS
1764	cis-Chrysanthenol	0.7	-	MS
1776	γ-Cadinene	-	0.6	MS
1804	Myrtenol	0.2	-	MS
1845	(E)-Anethole	-	tr	MS
1864	p-Cymen-8-ol	0.1	-	t_R, MS
1882	1-Isobutyl 4-isopropyl-2,2-dimethyl succinate	-	tr	MS
1889	Ascaridole	3.1	-	MS
1900	Isoshyobunone	-	tr	MS
1916	Shyobunone	-	1.5	MS
1969	cis-Jasmone	0.4	-	MS

2008	Caryophyllene oxide	0.3	3.5	t_R, MS
2057	13-Tetradecanolide	-	1.9	MS
2065	p-Mentha-1,4-dien-7-ol	0.2	-	MS
2113	Cumin alcohol	0.3	-	t_R, MS
2131	Hexahydrofarnesyl acetone	-	0.2	t_R, MS
2144	Spathulenol	0.1	3.7	t_R, MS
2273	(2E,6E)-Farnesyl acetate	-	0.9	MS
2191	T-Cadinol	-	2.2	MS
2192	Eugenol	0.4	-	t_R, MS
2198	Thymol	0.1	2.6	t_R, MS
2239	Carvacrol	0.2	-	t_R, MS
2257	β-Eudesmol	0.1	2.6	MS
2260	15-Hexadecanolide	0.2	1.0	MS
2300	Tricosane	tr	-	t_R, MS
2316	Caryophylladienol I	-	1.2	MS
2324	Caryophylladienol II	0.2	4.1	MS
2353	Caryophyllenol I	-	2.2	MS
2392	Caryophyllenol II	-	1.7	MS
2600	Hexacosane	0.1	-	MS
2607	Octadecanol	-	2.3	MS
2931	Hexadecanoic acid	0.2	-	MS
	Grouped compounds (%)			
	Monoterpene hydrocarbones	12.0	2.1	
	Oxygenated monoterpenes	72.9	49.0	
	Sesquiterpenes hydrocarbones	0.1	5.6	
	Oxygenated sesquiterpenes	0.7	22.7	
	Others	10.2	8.8	

RRI: Relative retention indices experimentally calculated against n-alkanes; %: calculated from FID data; IM: Identification Method: tR, 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 with those of the in-house Baser Library of Essential Oil Constituents, Adams, MassFinder and Wiley libraries. A: Achillea biebersteinii Afan., B: A. wilhelmsii C. Koch.

RESULTS AND DISCUSSION

A. biebersteinii oils contained camphor and 1,8-cineole as main constituents[6]. In a sample of Ankara origin α-terpinyl acetate (7%) was also encountered in this oil[9]. A sample from Sivas contained 1,8-cineole (31%), camphor (14%) α-thujone (13%), p-cymene (5%), β-thujone (3%), borneol (3%) as other significant constituents[6,10].

Camphor (40%), artemisia alcohol (18%), yomogi alcohol (16%), and 1,8-cineole (7%) were reported as main constituents in *A. wilhelmsii* oil[14]. Camphor (41%) was also the main constituent in another study together with caryophylladienol II (6%), borneol (6%), camphene (6%)[6,26].

Previously, 1,8-cineole and camphor rich oils were reported by several authors from *Achillea* species growing outside Turkey[6].

According to another study which reported the compositions of essential oils of several *Achillea* species, *A. biebersteinii* has been found to be rich in oxygenated monoterpenes. Piperitone, p-cymene, and camphor were found as main components in the oil of this plant sample, collected from a different locality.[1]

In our present study, we examined chemical composition of essential oils obtained from the aerial parts of *A. biebersteinii* and *A. wilhelmsii* collected in the vicinity of Adana and Kayseri. Yield of essential oils obtained by hydrodistillation for *A. biebersteinii* and *A. wilhelmsii* were found to be 0.98% and 0.18%, respectively. Essential oil components of two *Achillea* species are seen at Table 1. *A. bibersteinii* and *A. wilhelmsii* oils were characterized by the presence of a high percentage of oxygenated monoterpenes (72.9% and 49%). Sixty-four compounds were identified in oil of the aerial parts representing 95.9 % of the *A. biebersteinii* oil. The main components of the *A. biebersteinii* oil were 1,8-cineole (34.6%) and camphor (12.9%). Fourty-two compounds were identified in oil of the aerial parts representing 88.2 % of the *A. wilhelmsii* oil. Main component determined for *A. wilhelmsii* is camphor (32.0%). These compounds have also been previously reported in *Achillea* essential oils[6].

ACKNOWLEDGMENT

We thank Prof. Mecit Vural for identification of the plant materials.

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