



Full Length Article

Chemical Composition of the Essential Oils of some *Achillea* Species Growing Wild in Turkey

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ABSTRACT

Native *Achillea* plants (*A. biebersteinii*, *A. aleppica*, *A. tenuifolia*, *A. magnifica*, *A. cucullata*) were collected from nine localities of Southeastern and Eastern of Turkey during the flowering period. The essential oils of five *Achillea* species were obtained by hydrodistillation and analysed by GC-MS. Generally the principal constituents of the oils were 1,8 cineol+ascaridol, camphor, isoscaridol, 1,8 cineol and camphor as *A. biebersteinii*, *A. aleppica*, *A. tenuifolia*, *A. magnifica*, *A. cucullata*, respectively. Chemical composition of essential oils of *Achillea* species are highly variable, which may be due to the differences in their chemical polymorphic structure and environmental conditions. © 2010 Friends Science Publishers

Key Words: *Achillea* sp.; Essential oil composition; Chemical polymorphism; Turkey

INTRODUCTION

The genus *Achillea* is represented by about 85 species throughout the world and the flora of Turkey includes 42 of total, 23 of *Achillea* species are endemics in Turkey (Duman, 2000). Genus *Achillea* is known locally as "saricivanpercemi". Indigenous uses of *Achillea* species are diuretic, emmenagog agents, wound healing, for curing stomachache, diarrhea and antispasmodic (Yesilada *et al.*, 1993; Baytop, 1999; Konyalioglu & Karamenderes, 2005). Magiatis *et al.* (2002) reported that *Achillea* plants are antiseptic and infection preventing properties. Also the plants have been used in medicinal and cosmetic preparations. Aburjai and Hudaib (2006) reported that *Achillea* species had constituents such as flavonoids (aglycones & glycosides), sesquiterpene lactones and essential oils. Some researchers have reported the major constituent of several *Achillea* species as 1,8-cineole, camphor, piperitone and ascaridole in Turkey (Kusmenoglu *et al.*, 1995; Ozen *et al.*, 2003; Toker *et al.*, 2003; Baris *et al.*, 2006; Kordali *et al.*, 2009).

The *Achillea* genus has a wide distributional range, from deserts and sea coasts to nival pioneer biota and from rock fissure and talus to ruderal habitats (Celik & Akpulat, 2008). The morphologic and chemical composition of *Achillea* species was affected by environmental conditions, because of a chemically polymorphic and perennial (Bezir *et al.*, 2003). The aim of this study was to determine the essential oil contents and their compositions in *Achillea* species, *A. biebersteinii*, *A. aleppica*, *A. tenuifolia* and

endemic ones *A. magnifica*, *A. cucullata*, collected from different locations of Eastern and Southeastern in Turkey.

MATERIALS AND METHODS

Plant description and sample collection: Plant material of *Achillea* species were collected from nine different places in Eastern and Southeastern of Turkey during the flowering period, in June at 2007. The locations, the plant species, altitudes and oil yield are listed in Table I. The GPRS results of collection area are also given Fig. 1. The collection area has the characteristics of terrestrial climate. The climate is characterized by warm to hot, dry summers and cold, snowy winters. The plants of *Achillea biebersteinii*, *A. aleppica*, *A. magnifica*, *A. tenuifolia* and *A. cucullata*, were got and voucher specimens kept in the herbarium. Aerial parts of *Achillea* samples were dried at room temperature. Flowers and leaves were separated after drying. All samples were hydro-distilled for essential oil by grossly pulverized powdered plant (25 g) using a Clevenger type apparatus for 3 h.

GC-MS analysis: GC-MS analysis was conducted in the Plant Physiology Laboratory in Biology Department of Kahramanmaraş Sutcu Imam University. Qualification of the oil was made using a Agilent 5975C Mass Spectrometer coupled with a Agilent GC-6890II series (Agilent Technologies, USA). The GC was equipped with HP-88 capillary column (100 m × 250 μm × 0.20 μm film thickness) and helium (He) was used as carrier gas with flow rate of 1.0 mL/min. The GC oven temperature was

programmed as follows: 70°C for 1 min, up to 230°C at 10°C/min and then kept at 230°C at 20 min. The injector temperature was 250°C. The mass spectrometer was operating in EI mode at 70 eV. Split ratio was 20:1. Mass range 35-400 m/z ; scan speed (amu/s): 1000. A 10 μ L of the oil was mixed with 0.5 mL diethyl ether and 1 μ L of the concentrations injected into the column. The components of the oil were identified by comparing their retention indices and mass spectra with those of pure authentic samples and NIST98, Willey7n.1 and Flavor2 libraries reference compounds. Each analysis was repeated three times.

Statistical analysis: Mean percentage content values (\pm standard deviation, SD) of the individual components of the analysed samples in each location were calculated by Excel programme.

RESULTS

The essential oil rates of *Achillea* species ranged from 0.2% to 0.9% for locations (Table I). The oil composition of *Achillea* samples collected from nine growing sites were determined and 33 compounds were identified by a GC/MS (Table II). According to maximum constituent, four chemotypes were identified; 1,8 cineole, ascaridol, isoascaridol and camphor.

Two different chemotypes were obtained from *A. biebersteinii*. The 1,8 cineole chemotype of *A. biebersteinii* is widespread in Genc/Bingöl and Midyat/Mardin, except Kurtalan/Siirt. The oil of *A. biebersteinii* from Genc/Bingöl was constituted 1,8 cineol (15.04%), camphor (14.55%) and d-piperitone (12.53%). The *A. biebersteinii* collected from Midyat/Mardin had 1,8 cineol (31.76%), camphor (27.46%) and d-piperitone (11.97%), while its oil at Kurtalan/Siirt was dominated by ascaridol (61.95%), followed by p-cymene (15.61%) and 1,8 cineol (5.05%). Main compounds of *A. biebersteinii* collected from Komurhan/Elazig were 1,8 cineol (42.17%), camphor (15.92%) and p-cymene (5.67%).

All samples of *A. aleppica* was camphor chemotype. *A. aleppica* existing at Hazar/Elazig had camphor (34.02%), 1,8-cineol (20.02%) and p-cymene (14.16%) as major components. The major constituents oil of Keban/Elazig were camphor (32.95%), 1,8-cineol (26.11%) and α -pinene (3.89%). *A. tenuifolia* was of isoascaridol (24.34%), 1,8-cineole (15.45%) and p-cymene (14.16%) as major components in Soguksu/Batman. The main components identified in the oil of *A. magnifica* collected from Erzurum provinces were 1,8-cineol (30.43%), camphor (23.21%) and α -pinene (5.28%). The main compounds in the oil of *A. cucullata* occurring at Malatya province were camphor (32.65%), 1,8-cineol (29.20%) and isoborneol (3.51%).

DISCUSSION

Four chemotypes were identified in *Achillea* species were as 1,8 cineole, ascaridol, isoascaridol and camphor.

Table I: The altitudes of collection localities and essential oil yields of investigated *Achillea* species

Species	Collected area	Altitudes (m)	Oil Rate (%)
<i>A. biebersteinii</i>	Bingol/Genc	1305	0.6
<i>A. biebersteinii</i>	Mardin/Midyat	995	0.2
<i>A. aleppica</i>	Elazig/Hazar	1256	0.4
<i>A. tenuifolia</i>	Batman/Soguksu	553	0.6
<i>A. biebersteini</i>	Siirt/Kurtalan	693	0.9
<i>A. aleppica</i>	Elazig/Keban	1072	0.6
<i>A. biebersteinii</i>	Elazig/Komurhan	951	0.5
<i>A. magnifica</i>	Erzurum/Center	1755	0.5
<i>A. cucullata</i>	Malatya/Center	1379	0.4

Fig. 1: The map of collection area

Δ 1: Bingol/Genc (*A. biebersteinii*), Δ 2: Mardin/Midyat (*A. biebersteinii*), Δ 3: Siirt/Kurtalan (*A. biebersteinii*), Δ 4: Elazig/Komurhan (*A. biebersteinii*) Δ 5: Elazig/Hazar (*A. aleppica*), Δ 6: Elazig/Keban (*A. aleppica*), Δ 7: Batman/Soguksu (*A. tenuifolia*), Δ 8: Erzurum/Center (*A. magnifica*), Δ 9: Malatya/Center (*A. cucullata*)



The other *Achillea* (*A. pseudoalleppica*, *A. coarctata* & *A. oligocephala*) species major constituents of these species were camphor (29.1%) for *A. pseudoalleppica* (Ozen *et al.*, 2003), 1,8 cineole (20.1%) for *A. coarctata* and 1,8 cineole (18.6%) *A. oligocephala* (Toker *et al.*, 2003). We were obtained two different chemotypes from *A. biebersteinii*, 1,8 cineole and ascaridol. Many investigations on oils of *A. biebersteinii* showed that they are 1,8 cineole (Chialva *et al.*, 1993; Kusmenoglu *et al.*, 1995; Morteza-Semnani *et al.*, 2005; Ghani *et al.*, 2008), camphor (Kordali *et al.*, 2009), piperitone (Baris *et al.*, 2006) and the ascaridol chemotype (Rustaiyan *et al.*, 1998; Bader *et al.*, 2003).

Our study revealed that *A. aleppica* had camphor chemotype. The other *Achillea* species showed the camphor chemotype in *A. crithmifolia*, *A. tenuifolia*, *A. kellalensis*, *A. vermicularis* and *A. gonioccephala* (Kundakovic *et al.*, 2007). *A. tenuifolia* collected from Southeastern of Turkey indicated isoascaridol, 1,8-cineole and p-cymene. The previous studies reported that the major constituents of *A. tenuifolia* were γ -muurolene (Jaimand & Rezaee, 2001) and camphor (Rustaiyan *et al.*, 1999; Aghjani *et al.*, 2000).

A. magnifica collected from Erzurum provinces was of 1,8-cineol as major component. There are very little information about chemical composition of test species. Ulubelen *et al.* (1989) isolated a new triterpene magnificol

Table II: Essential oil composition of some *Achillea* species growing wild in East of Turkey

Component	RT (min)	1*	2	3	4	5	6	7	8	9
α -Pinene	10.89	0.17±0.12**	0.51±0.01	0.06±0	4.47±0.02	2.18±0.01	3.89±0.08	0.21±0.01	5.28±0.10	1.31±0.02
Camphene	11.35	0.22±0.02	1.32±0.01	-	2.86±0.02	3.98±0.01	0.73±0.08	0.33±0.01	3.97±0.10	1.33±0.01
β -Pinene	11.66	0.16±0.01	0.42±0.01	-	3.84±0.03	1.28±0.01	0.55±0.05	0.18±0.01	2.81±0.09	0.81±0.01
Sabinene	11.76	0.08±0.01	-	-	-	-	-	-	3.02±0.07	-
α -phellandrene	12.00	0.05±0.01	0.39±0	0.06±0	0.08±0	-	-	0.08±0.02	-	-
α -terpinene	12.15	0.63±0.03	0.22±0	-	1.11±0.01	0.40±0.01	-	-	1.01±0.5	-
1, 8- Cineole	13.07	15.04±0.41	31.76±0.34	5.05±0.28	42.17±0.31	29.02±0.25	26.11±1.95	15.45±0.98	30.43±0.96	29.20±0.49
p-Cymene	13.37	7.54±0.31	2.86±0.06	15.61±0.72	5.67±0.04	3.11±0.02	3.57±0.21	14.16±0.92	3.65±0.09	3.22±0.05
Linalool	15.89	0.68±0.01	0.29±0.03	0.09±0.05	0.13±0	1.06±0	0.31±0.01	0.36±0.16	0.59±0.03	3.77±0.06
Thujone	16.54	0.48±0.08	-	-	0.93±0.05	0.71±0.01	4.07±0.27	0.35±0	2.45±0.24	2.41±0.05
Terpineol	16.65	1.82±0.07	3.96±0.03	0.85±0.01	0.81±0.01	0.88±0.01	-	1.04±0.03	-	-
Borneol	17.19	3.31±0.15	0.68±0.01	0.59±0.15	2.95±0.03	1.73±0.01	1.72±0.08	0.34±0.01	2.73±0.06	2.13±0.03
Menthol	17.30	1.84±0.07	3.00±0.04	0.60±0.02	1.37±0.02	1.13±0.01	0.77±0.12	0.96±0.05	1.03±0.02	0.96±0.02
2-cyclohexan-3-ol	17.57	0.60±0.03	1.40±0.04	0.41±0.01	0.34±0.01	0.43±0.01	0.40±0.04	0.64±0.28	0.50±0.12	0.32±0.01
Isoterpinolene	17.71	0.62±0.07	0.69±0	0.18±0.00	0.85±0.10	1.06±0.01	1.08±0.09	0.59±0.13	0.82±0.02	0.78±0.02
Camphor	17.93	14.55±0.41	27.46±0.09	3.17±0.08	15.92±0.13	34.02±0.20	32.95±0.30	3.81±0.10	23.21±0.31	32.65±0.06
Isoborneol	18.36	5.78±0.14	2.79±0.54	-	1.31±0.03	3.45±0.02	2.18±0.31	0.77±0.08	2.31±0.06	3.51±0.20
α -thujenal	18.59	0.27±0.01	-	-	0.34±0	0.29±0.01	0.25±0	0.34±0.15	-	-
Myrtenal	18.79	0.38±0.01	0.68±0.01	-	1.01±0.01	1.01±0	0.89±0.08	0.78±0.15	0.99±	0.85±.02
Myrtenol	18.96	0.63±0.09	0.77±0.01	-	0.74±0	0.97±0.01	0.62±0.03	0.79±0.22	0.69±0.01	0.78±0.02
Carvone	19.69	1.27±0.34	0.69±0.38	-	1.07±0.01	0.96±0.01	0.81±0.02	1.45±0.58	0.58±0.01	1.15±0.03
d-piperitone	20.08	12.53±0.29	11.97±.38	-	0.64±0.01	0.72±0.05	1.24±0.14	-	0.75±0.33	3.49±0.07
Piperitone oxide	20.21	0.68±0.09	0.42±0.01	-	0.19±0	0.29±0.02	0.29±0.03	1.03±0.05	0.18±0	0.24±0.01
p-menthe-1,4-dien-7-ol	21.29	3.10±0.48	0.25±0.03	-	0.61±0.01	0.50±0	0.79±0.09	9.41±1.44	0.77±0	0.38±0.08
ascaridol	21.37	-	-	61.95±1.05	-	-	-	-	-	-
Caryophyllene oxide	21.45	2.28±0.48	0.23±0.03	-	0.24±0	0.16±0.01	0.30±0.04	5.27±2.05	0.60±0.12	0.16±0.01
Thymol	22.21	0.87±0.01	-	-	-	-	-	-	-	-
Spathulenol	22.30	1.94±0.48	0.88±0.02	-	1.48±0.03	1.54±0	1.31±0.15	2.23±0.18	1.75±0.02	0.87±0
Carvacrol	22.75	3.89±0.42	0.310.01	1.50±0.06	0.67±0.21	0.35±0.02	0.42±0.07	0.56±0.16	0.58±0.06	0.22±0.01
Isoascaridol	22.99	9.36±0.02	0.31±0.07	-	-	0.34±0	1.51±0.23	24.34±1.77	0.34±0.11	0.86±0.01
Isoeugenol	23.26	0.59±0.20	0.12±0	-	-	0.30±0.02	0.33±0	0.17±0	0.55±0	-
Heptacosene	23.52	0.17±0.01	0.07±0	-	0.08±0.01	0.09±0.01	0.17±0.06	0.44±0.03	0.17±0	-
β -eudesmol	23.68	0.40±0.01	0.14±0.01	0.22±0.01	0.17±0	0.29±0.01	0.29±0.04	0.44±0.04	0.91±0.01	0.13±0.01
Total		91.93	94.08	90.34	92.05	92.25	87.55	86.09	92.67	91.53

*1: Bingol/Genc (*A. biebersteinii*), 2: Mardin/Midyat (*A. biebersteinii*), 3: Siirt/Kurtalan (*A. biebersteinii*), 4: Elazığ/Kömürhan (*A. biebersteinii*), 5: Elazığ/Hazar (*A. aleppica*), 6: Elazığ/Keban (*A. aleppica*), 7: Batman/Soguksu (*A. tenuifolia*), 8: Erzurum/Center (*A. magnifica*), 9: Malatya/Center (*A. cucullata*)

**± SD

together with four acetylenic compounds from *Achillea magnifica*, which were not previously obtained from *Achillea* species. Two *Achillea* species, *A. magnifica* and *A. cucullata*, are endemic to the Anatolian Diagonal and Irano-Turanian (Ir.-Tur.) regions (Davis, 1982; Sahin *et al.*, 2006).

About different chemotypes, Rahimmalek *et al.* (2009) reported that there are high level of chemical polymorphism within and among *Achillea* species due to genetic, environment and their interaction. The authors stated that essential oil yield and their components is related to genetic and climatic factors, growth phase (vegetative or flowering stage), development of organs and plant part. We found a great chemical polymorphism in our study in the species. Bezic *et al.* (2003) also reported that *Achillea* species adapts to new environments and morphologic and chemical composition can be affected by environment. On the other hand, Bader *et al.* (2003) stated that there was no association between the geographic origin of the plant and essential oil composition.

In conclusion, essential oil content changed according to the region therewith medicinal characters of the plants are also changed. Thus to obtained uniform chemical contents, we recommended that the plants should be grown in cultural conditions as the next step.

Acknowledgment: Authors wish to thank Dr. Hulya Hosgoren, University of Dicle, Faculty of Art and Sciences, Diyarbakir, Turkey for her help in identification of the plant material.

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(Received 05 February 2010; Accepted 03 April 2010)