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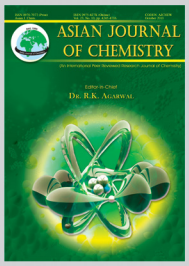

Composition of the Essential Oils of *Anthemis hyalina* DC., *Achillea nobilis* L. and *Cichorium intybus* L. Three Asteraceae Herbs Growing Wild in Iran

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Water-distilled essential oils from the aerial parts of *Anthemis hyalina* DC. (syn. *A. crassipes* Boiss.), *Achillea nobilis* L. and *Cichorium intybus* L. were analyzed by GC and GC-MS. Twenty-four components of the oil of *Anthemis hyalina* were characterized, representing 98.1 % of the total components detected. The major constituents were identified as carvacrol (38.4 %) and α-pinene (30.9 %). The oil of *Achillea nobilis* was characterized by higher amount of artemisia ketone (46.7 %), among the 30 components comprising 95.4 % of the total oil detected. Hexadecanoic acid (32.9 %), nonadecane (26.1 %) and *trans*-α-bergamotene (14.0 %) were the main components among the 14 constituents characterized in the oil of *Cichorium intybus* representing 100 % of the total components detected.

Key Words: *Anthemis hyalina*, *Achillea nobilis*, *Cichorium intybus*, Asteraceae, Essential oil, Carvacrol, α-Pinene, Artemisia ketone, Hexadecanoic acid, Nonadecane, *Trans*-α-bergamotene.

INTRODUCTION

The genus *Anthemis*, which comprises *ca.*130 species, is a floral element of the Mediterranean, but some species are also found in Southwest Asia and South Africa. There are 39 species growing wild in Iran, among which 15 are endemic[1,2]. Several *Anthemis* species are used in Iranian folk medicine as medicinal plants[3]. The essential oil of *A. nobilis* possesses interesting antiinflammatory and sedative properties in rat[4]. There are also reports on antimicrobial and larvicidal activities of the essential oils of *A. xylopoda* and *A. melampodina*, respectively[5,6]. The phytochemical studies of several *Anthemis* species have led to the isolation of sesquiterpene lactones and flavonoids[7-10].

The chemical composition of the essential oils from the flowers and leaves of *Anthemis hyalina*, collected from Ghazvin Province, were analyzed by GC and GC/MS. *cis*-Chrysanthenyl acetate (14.9 and 17.8 %), camphor (11.6 and 1.7 %) and myrcene (3.6 and 16.9 %) were found to be the major constituents of the oils of flower and leaves, respectively[11].

The genus *Achillea* comprises more than 200 species, most indigenous to Europe and the Middle East. Ninteen species of the genus *Achillea* are found in Iran, among which seven are endemic[1,2]. The genus *Achillea* is used in folk medicine in the treatment of boils, internal injuries and intestinal colic[12]. Pharmacological studies have shown that these species have antimicrobial, antiinflammatory and antiallergic activities[13-15]. *A. millefolium* (Yarrow) has been used to reduce sweating and to stop bleeding[16]. The aqueous and methanolic extracts of *A. ageratum* has exhibited analgesic and antiinflammatory activity[17]. *A. fragrantissima* is used in folk medicine for the treatment of gastro-intestinal disturbances and various infections, among them infection of the eye[18]. Chemical studies on several *Achillea* species have resulted in the isolation of sesquiterpene lactones, phenolic and acetylenic compounds[18-20]. The oils of some *Achillea* species have been reported[21-23].

Three species of the genus *Cichorium* are found in Iran *i.e.*, *C. endivia* L., *C. intybus* L. and *C. pumilum* Jacq[1,2]. *Cichorium intybus* L.(Chicory) a typical Mediterranean plant indigenous to Europe, Western Asia, Egypt and North America, varies in perianth colour from white, red to blue and the flowering period is from June to September[24]. *C. intybus* is a medicinal plant used to promote apetite and digestion, contains bitter-tasting sesquiterpene lactones. Roots of the plant elaborate eudesmanolides, germacranolides and guaianolides, accumulated mainly as glycosides[25-33].

Some of the guaianolides isolated from *C. intybus* play a role in chemical defence of chicory plant as antifeedants, phytoalexins and possess cytotoxic activity towards cultured

cancer cells[28,29,34-36]. Pharmacological studies of the root extracts from *C. intybus* have shown their antiinflammatory and hepatoprotective activities[37,38].

From a leaf extract, some sesquiterpene lactones, several coumarin and cinnamic acid derivatives have been found[39,40]. The flower extract of the plant afforded anthocyanins[41].

In this work, we report on the analysis of the essential oils of aerial parts of *Anthemis hyalina*, *Achillea nobilis* and *Cichorium intybus* grown wild in Iran.

EXPERIMENTAL

The aerial parts of *A. hyalina* and *A. nobilis* both were collected from Sanandaj, Province of Kordestan, Iran, in June 2007 and The aerial part of *C. intybus* was collected from Qhom, Province of Markazi, Iran, in July 2006 during the flowering stage. Voucher specimens have been deposited at the Herbarium of the Research Institute of Forests and Rangelands (TARI), Tehran, Iran.

Isolation of the essential oils: Air-dried aerial parts of *Anthemis hyalina* (120 g), *Achillea nobilis* (135 g) and *Cichorium intybus* (110 g) was separately subjected to hydrodistillation using a Clevenger-type apparatus for 3 h. After decanting and drying of the oils over anhydrous sodium sulfate, the corresponding yellowish coloured oils were recovered (in the yield of 0.12, 0.20 and 0.18 % (w/w)], respectively).

Gas chromatography: GC analysis was performed on a Schimadzu 15A gas chromatography equipped with a split/splitless injector (250 ºC) and a flame ionization detector (250 ºC). Nitrogen was used as carrier gas (1 mL/min) and the capillary column used was DB-5 (50 m × 0.2 mm, film thickness 0.32 µm). The column temperature was kept at 60 ºC for 3 min and then heated to 220 ºC with a 5 ºC/min rate and kept constant at 220 ºC for 5 min. Relative percentage amounts were calculated from peak area using a Schimadzu C-R4A chromatopac without the use of correction factors.

Gas chromatography-mass spectroscopy: GC-MS analysis was performed using a Hewlett-Packard 5973 with a HP-5MS column (30 m × 0.25 mm, film thickness 0.25 µm). The column temperature was kept at 60 ºC for 3 min and programmed to 220 ºC at a rate of 5 ºC/min and kept constant at 220 ºC/min for 5 min. The flow rate of Helium as carrier gas (1 mL/min). MS were taken at 70 eV. The retention indices for all the components were determined according to the Van Den Dool method, using *n*-alkanes as standards. The compounds were identified by (RRI, DB5) with those reported in the literature and by comparison of their mass spectra with the Wiley library or with the published mass spectra[42].

RESULTS AND DISCUSSION

The composition of the essential oils of *Anthemis hyalina*, *Achillea nobilis* and *Cichorium intybus* are listed in Tables 1-3, respectively, in which the percentage and relative indices of components are given. As it is shown, the oil of *A. hyalina* consists of five monoterpene hydrocarbons (36.4 %), six oxygenated monoterpenes (43.6 %), one sesquiterpene hydrocarbon (1.0 %), six oxygenated sesquiterpenes (9.5 %) and six aliphatic compounds (7.6 %). Carvacrol (38.4 %) and

TABLE-1
COMPOSITION OF THE ESSENTIAL OIL OF *Anthemis hyaline*

Compound	*RRI	Percentage
Nonane	899	1.2
α-Pinene	939	30.9
β-Pinene	980	3.4
Myrcene	991	0.7
Limonene	1031	0.7
1,8-Cineole	1033	1.8
(E)-α-Ocimene	1050	0.7
Camphor	1143	0.8
Borneol	1165	0.8
α-Terpineol	1189	0.4
Thymol	1290	1.4
Carvacrol	1298	38.4
Decanoic acid	1498	1.4
δ-Cadinene	1524	1.0
Dodecanoic acid	1568	0.9
Spathulenol	1576	2.0
Caryophyllene oxide	1581	0.7
Guaiol	1595	1.5
10-Epi-γ-Eudesmol	1619	1.5
Hinesol	1638	1.8
β-Eudesmol	1649	2.0
Apiole	1680	3.4
Tetradecanoic acid	1771	0.1
6,4,10-Trimethyl-2-pentadecanone	1872	0.6
Monoterpene hydrocarbons	–	36.4
Oxygenated monoterpenes	–	43.6
Sesquiterpene hydrocarbons	–	1.0
Oxygenated sesquiterpenes	–	9.5
Others	–	7.6
Total	–	98.1

*RRI: Relative retention indices were calculated against *n*-alkanes.

α-pinene (30.9 %) were the major compounds in this oil. In the oil of *A. hyalina* monoterpenes (80.0 %) predominated over sesquiterpenes (10.5 %) and other compounds (7.6 %).

As mentioned before, the composition of the flower and leaf oils of the plant[11] show differentially to the aerial parts oil for the concentration of main components.

Only a few reports on the analysis of essential oils of *Anthemis* species have been published. The composition of the essential oils of leaves and flowers of *A. altissima* L. var. *altissima* and *A. talyshensis* A. Fedor., have been the subject of our previous studies. β-Thujone (33.7 and 19.7 %, respectively) was found to be the major constituent in the leaf and flower oils of *A. altissima* and α-eudesmol (18.2 %), borneol (13.3 %) and hexadecanoic acid (9.5 %) were the predominant constituents of the oil of *A. talyshensis*[43,44].

The oil of *A. carpatica* was reported to contain α-thujone (40.2 %), β-thujone (13.3 %) and yomogi alcohol (18.5 %)[45] and in the oil of *A. montana*, α-thujone (46.9 %), β-thujone (16.0 %) and *trans*-chrysanthenyl acetate (11.3 %) were abundant[46].

The oil from the flower heads of *A. tinctoria* were reported to contain 1,8-cineole (7.9%), β-pinene (7.3 %) and decanoic acid (5.4 %) as major components[47].

The oil of *Achillea nobilis* consist of two monoterpene hydrocarbons (0.5 %), 14 oxygenated monoterpenes (69.7 %), six sesquiterpene hydrocarbons (1.8 %), six oxygenated sesquiterpenes (21.6 %) and two aliphatic compounds (1.8 %). Artemisia ketone (46.7 %) was the major compounds in this

TABLE-2
COMPOSITION OF THE ESSENTIAL OIL OF *Achillea nobilis*

Compound	*RRI	Percentage
Camphene	953	0.2
Yomogi alcohol	998	4.5
ρ-Cymene	1026	0.3
1,8-Cineole	1033	7.0
Artemisia ketone	1062	46.7
Artemisia alcohol	1083	1.5
α-Campholenal	1125	0.1
Lavandulol	1166	2.0
Terpinen-4-ol	1177	0.2
α-Terpineol	1189	0.2
trans-Carveol	1217	0.4
Lavandulyl acetate	1289	0.2
Neryl acetate	1365	0.9
Geranyl acetate	1383	0.6
β-Caryophyllene	1418	0.4
β-Selinene	1485	0.3
α-Selinene	1494	0.1
(E,E)-α-Farnesene	1508	0.4
Geranyl isobutyrate	1514	4.8
δ-Cadinene	1524	0.3
α-Calacorene	1542	0.3
Bornyl angelate	1563	0.6
Spathulenol	1576	4.3
Dillapiol	1622	0.7
Epi-α-Cadinol	1640	8.4
β-Eudesmol	1649	4.8
Selin-11-en-4-α-ol	1652	3.4
Khusinol	1674	0.2
Aristolone	1756	0.5
Hexadecanoic acid	1973	1.1
Monoterpene hydrocarbons	–	0.5
Oxygenated monoterpenes	–	69.7
Sesquiterpene hydrocarbons	–	1.8
Oxygenated sesquiterpenes	–	21.6
Others	–	1.8
Total	–	95.4

*RRI: Relative retention indices were calculated against *n*-alkanes.

TABLE-3
COMPOSITION OF THE ESSENTIAL OIL OF *Cichorium intybus*

Compound	*RRI	Percentage
β-Caryophyllene	1418	1.5
trans-α-Bergamotene	1436	14.0
Germacrene D	1480	1.6
Pentadecane	1500	0.7
Spathulenol	1576	2.9
Caryophyllene oxide	1581	1.9
Tetradecanol	1676	4.5
Heptadecane	1700	3.9
Octadecane	1800	1.0
6,4,10-trimethyl-2-pentadecanone	1872	6.2
Hexadecanol	1879	0.9
Nonadecane	1900	26.1
Hexadecanoic acid	1973	32.9
Eicosane	2000	1.9
Monoterpene hydrocarbons	–	–
Oxygenated monoterpenes	–	–
Sesquiterpene hydrocarbons	–	17.1
Oxygenated sesquiterpenes	–	4.8
Others	–	28.1
Total	–	100

*RRI: Relative retention indices were calculated against *n*-alkanes.

oil, followed by epi-α-cadinol (8.4 %), 1,8-cineole (7.0 %), geranyl isobutyrate (4.8 %), β-eudesmol (4.8 %), yomogi alcohol (4.5 %) and spathulenol (4.3 %).

As can be seen from the above information, in the oil of *A. nobilis* monoterpenes (70.2 %) predominated over sesquiterpenes (23.4 %) and other compounds (1.8 %).

The composition of the essential oil of *A. nobilis*, from Italy, were reported to contain germacrene D (46.0 %) as the main component[48].

Camphor (17.0 %), 1,8-cineole (15.8 %), terpinen-4-ol (10.0 %), borneol (7.2 %) and β-eudesmol (7.1 %) were reported as the main constituents in the oil of *A. nobilis*, from Kazakhstan[49].

In the essential oil of *A. nobilis* grown in Yugoslavia the prevailing components were α-thujone (25.7 %), artemisia ketone (14.8 %), borneol (9.9 %) and camphor (8.2 %)[50].

The chemical composition of the essential oils of *A. nobilis* subsp. *sipylea* and *A. nobilis* subsp. *neilreichii* collected from Turkey and their antimicrobial activities were investigated. Fragranol (19.3 %), chrysanthenone (17.1 %), linalool (16.4 %) and dihydro-eudesmol (13.2 %) were the major constituents in the former oil and piperitone (16.3 %), linalool (14.1 %), α-bisabolol (12.8 %) and 1,8-cineole (12.6 %) in the later. The essential oils of *A. nobilis* subspecies showed a board spectrum of antimicrobial activity[51].

The water-distilled essential oils from aerial parts of *A. pachycephala*, *A. oxyodonta* and stems, leaves and flowers of *A. biebersteinii*, were analyzed by GC and GC/MS. The oil of *A. pachycephala* was found to contain 1,8-cineole (27.7 %) and camphor (27.4 %) as the major constituents. The oil of *A. oxyodonta* was characterized by higher amounts of 1,8-cineole (38.5 %) and artemisia ketone (23.0 %).

The oils obtained from stems and leaves of *A. biebersteinii* were rich in camphor (38.1 and 33.7 %, respectively) and borneol (22.6 and 20.8 %, respectively).

The other main component of the stem oil was 1,8-cineole (13.5 %). In the flower oil of the plant, camphor (36.3 %) and 1,8-cineole (22.3 %) were the predominant compounds[23]. Hexadecanoic acid (32.9 %), nonadecane (26.1 %) and *trans*-α-bergamotene (14.0 %) were the main constituents among the 14 characterized, comprising 100 % of the total components detected in the oil of *C. intybus*. Thus the oil consists of three sesquiterpene hydrocarbons (17.1 %), two oxygenated sesquiterpenes (4.8 %) and nine aliphatic compounds (78.1 %).

Seeds from *C. intybus* harvested in Argentina were extracted with petroleum ether and raw oil was obtained. Gas chromatography analysis of the oil revealed high levels of linoleic acid (59.8 %) representing nearly (21.0 %) of saturated fatty acids[52].

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