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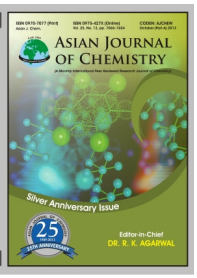

Chemical Composition of Endemic *Inula macrocephala* Boiss. and Kotschy ex Boiss. from Turkey

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The essential oil components of aerial parts of *Inula macrocephala* Boiss. and Kotschy ex Boiss. was investigated by GC and GC-MS. The yield of oil is *ca.* 0.13 mL/100 g. Thirty five components were identified representing 90.7 % oil. Borneol (26.4 %), β-caryophyllene (15.3 %), *p*-cymene (10.2 %) and bornyl acetate (8.9 %) were identified major components of plant. The results were discussed in terms of natural products, renewable resources and chemotaxonomy.

Key Words: *Inula*, Essential oil, Borneol, β-Caryophyllene.

INTRODUCTION

Plants have always been part of the daily life of man, since it is used for food, medicine and sometimes in religious rites. Numerous members of tribe Anthemideae (Asteraceae) are important ornamental crops, as well as medicinal and aromatic plants. Many of these plants produce essential oils used in folk and modern medicine as well as in the cosmetic and pharmaceutical industries[1]. Asteraceae is one of the largest plant family and many genera and species have worldwide distribution comprising many useful plants, so it has been the subject of chemotaxonomical studies[2]. The genus *Inula* L., mostly perennial herbs or shrubs distributed in Turkey, comprises 31 taxa of the Asteraceae (Compositae) family, belonging to the tribe Inuleae. *Inula macrocephala* Boiss. and Kotschy ex Boiss. is an endemic and glandular perennial plant, has usually solitary capitulum and the smaller proportions of stem and leaves at once distinguish this species from its closest relative, *I. helenium* L.[3,4].

Several species in *Inula* L. genus are used as traditional herbal medicines throughout the world. The roots of *Inula hupehensis* have been used to treat many diseases, including bronchitis, diabetes and intestinal ulcers[5]. The characteristic compounds of the *Inula* are sesquiterpenes and monoterpenes[5]. The absence of sesquiterpene lactones situates *I. ensifolia* L. closer to some representatives of the postulated *Inula decurrens* group, *i.e. Inula bifrons* L. and *Inula conyza* DC. Moreover, *I. germanica* L. is rich in exudate flavonoids, derivatives of luteolin, scutellarein and quercetagenin, whereas only one derivative of luteolin was found in *I. salicina* L. exudate and no flavonoids in an exudate of *I. ensifolia* were found[6]. It seems that, neither exudate flavonoids nor esterified thymol derivatives are helpful chemotaxonomical markers within *Inula*. The flavonoids due to limited data available and the thymol derivatives due to their common occurrence in members of Inuleae and in plants of Helenieae and Eupatorieae tribes. Further phytochemical studies of *Inula* sp. are needed to support classification efforts, which nowadays are based mainly on morphological traits. In some *Inula* species, such as *I. britannica* L., *I. salicina* L., *I. bifrons* L., *I. conyza* DC. and *I. spiraeifolia* L. thymol derivatives, rather than sesquiterpenoids, are the major root constituents[7,8]. Recently, much attention has been paid to thymol derivatives, due to their diverse biological activities. Thymol derivatives, isolated from many species of *Inula*, have shown antibacterial activities[9,10]. The usefulness of thymol derivatives as insecticides and transdermal drug delivery enhancers has also been reported[11,12].

The species lacks detailed phytochemical investigation. Several studies on the chemical composition of the essential oil of *Inula* L. taxa have been reported; *Inula viscosa* (L.) Aiton. from Turkey[13], *Inula viscosa* (L.) Greuter from Spanish[14], *Inula viscosa* from *Italian*[15,16] and *Inula graveolens* (L.) Desf. from French[17]. However, almost all of these published essential oil compositions were different from each other. Therefore, the aim of this present study is to examine the chemical composition of the essential oils isolated from aerial parts of *I. macrocephala* by GC-MS; and to evaluate the chemical data that might be helpful in potential usefulness and chemotaxonomy of this plant.

EXPERIMENTAL

I. macrocephala was collected from east part of Pinarlar village (altitude of 1350-1400 m), Elazig/Turkey, in June 2010. A voucher specimen number kept at the Firat University Herbarium (FUH-9750)

Isolation of the essential oil: Air-dried aerial parts of the plant material (100 g) were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h.

Gas chromatographic analysis: The essential oil was analyzed using HP 6890 GC equipped with and FID detector and an HP-5 MS column (30 m × 0.25 mm i.d., film tickness 0.25 μm) capillary column was used. The column and analysis conditions were the same as in GC-MS. The percentage composition of the essential oils was computed from GC-FID peak areas without correction factors.

Gas chromatography/mass spectrometry: The oils were analyzed by GC-MS, using a Hewlett Packard system. HP-Agilent 5973 N GC-MS system with 6890 GC in Plant Products and Biotechnology Research Laboratory (BUBAL) in Firat University. 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 and programmed to 150 ºC at a rate of 10 ºC/min and then kept constant at 150 ºC for 15 min to 240 ºC at a rate of 5 ºC/min. Alkanes were used as reference points in the calculation of relative retention indices. MS were taken at 70 eV and a mass range of 35-425. Component identification was carried out using spectrometric electronic libraries (WILEY, NIST). The identified constituents of the essential oils are listed in Table-1.

RESULTS AND DISCUSSION

The essential oil components of aerial parts of *Inula macrocephala* was investigated by GC and GC-MS. The yield of oil is *ca.* 0.30 mL/100 g. Thirty five component were identified representing 90.7 % oil. The oils were complex mixtures of non-terpenes, monoterpenes and sesquiterpenes. Abundant group of essential oil of *I. macrocephala* were monoterpenes, on the other hand sesquiterpenes were the minor group of the oil. Borneol (26.4 %), β-caryophyllene (15.3 %), *p*-cymene (10.2 %) and bornyl acetate (8.9 %) were identified as major components of *Inula macrocephala*. Borneol (26.4 %) and *p*-cymene (10.2 %) were the main monoterpenes, from the sesquiterpenes β-caryophyllene (15.3 %) was the main compound of the oil (Table-1).

The essential oil of *Inula graveolens* (L.) Desf. from Corsica was investigated and the main constituents were bornyl acetate (56.8 %), borneol (7.6 %) and τ-cadinol (7.8 %). In the second part, six samples of *I. graveolens* essential oil, obtained at different stages of development of the plant, were investigated. Bornyl acetate and borneol were always the two major compounds[18]. Then, in order to determine the chemical variability of *I. graveolens*, 22 samples were analyzed, obtained from several plants collected in a restricted area in different localities during the flowering stage. Bornyl acetate (43.1-73.1 %) and borneol (3.7-32.2 %) were the main compounds for 20 samples. Sample 21 exhibited borneol (41.9 %) and bornyl acetate (16.6 %) as the major components, while the composition of sample 22 was a typical (borneol 41.9 % and τ-cadinol 23.8 %)[18]. Like these results bornyl acetate (8.9 %) and borneol (26.4 %) were the main compounds for our study (Table-1). Borneol (3.26-3.72 %) was also among the main components of *Anthemis pseudocotula* and *A. cretica* subsp. *pontica* (Asteraceae) from Turkey[19]. In the analysis of the essential oil of *Inula graveolens*[18]; bornyl acetate (56.8 %), borneol (7.6 %) and τ-cadinol (7.8 %) were found as the major oil components. Present analysis results were not similar with this study findings, because of the absence of the τ-cadinol (except bornyl acetate and borneol) in present samples.

TABLE-1
CHEMICAL PROFILES OF *Inula macrocephala*

No	Compounds	RRI	Percentage (%)
1	2 Hexenal	965	0.3
2	Mrycene	995	0.1
3	α-Thujene	1015	0.3
4	α-Pinene	1021	4.1
5	Camphene	1034	0.6
6	β-Pinene	1056	0.4
7	Benzene, 1-methyl-2	1070	0.1
8	*p*-Cymene	1093	10.2
9	1,8-Cineole	1095	2.5
10	*trans*-Sabinene hydrate	1126	0.1
11	*trans*-Pinocarveole	1178	0.8
12	Camphor	1181	0.3
13	Borneol	1200	26.4
14	2-Cyclohexan-1-ol	1207	0.1
15	Bicyclo (3,3,1) hept-2-ene	1220	1.4
16	Bornylacetate	1280	8.9
17	Thymol	1289	2.6
18	β-Elemene	1350	0.5
19	α-Copaene	1360	0.3
20	*trans*-Caryophyllene	1393	0.4
21	Aromadendrene	1421	0.1
22	Germacrene D	1435	0.2
23	α-Selinene	1442	1.5
24	Naphthalene	1456	0.4
25	Spathulenol	1495	1.7
26	δ-Cadinene	1458	0.2
27	α-Selinene	1485	0.3
28	β-Caryophyllene	1498	15.3
29	Muurolene	1523	1.6
30	α-Cadinol	1539	3.4
31	Ledol	1600	1.6
32	2-Pentadecanone	1631	0.4
33	Hexadecanoic acid	1690	0.8
34	Pentacosane	1900	2.1
35	Tricosane	1903	0.6
	Total		90.7

RRI, relative retention index

The chemical composition of the essential oil obtained from the aerial parts of *Inula crithmoides* L. from central Italy was analyzed by GC and GC/MS and 22 components were identified, the major ones being *p*-cymene (30.1 %), 1-methylethyl-trimethylbenzene (18.7 %), scopoletin (15.3 %) and α-pinene (13.1 %)[20]. Like this study, *p*-cymene (7.3-10.2 %) was detected one of the major component of *Inula macrocephala* (Table-1) and *Gundelia tournefortii* var. *tournefortii* (Asteraceae) from Turkey, respectively[21]. On the

other hand, α-pinene (4.1%) was identified in low amounts in the present study (Table-1). Among the sesquiterpenes, β-caryophyllene (15.3 %) was determined as one of the major constituents in our study (Table-1). It is noteworthy that, this compound was not reported as major component in the essential oil of *Inula crithmoides* L. from Italy[20], *Inula graveolens* from *Corsica*[18] and in *Inula oculus-christi* L. from Iran[22]. On the other hand, β-caryophyllene (3.2 %) was detected as one of the minor compound of *Tripleurospermum parviflorum* (Willd.) Pobed essential oil from Turkey[23], which was in the Asteraceae family like *Inula*. Mathela *et al.*[24] reported that thymyl isobutyrate, thymol, thymyl isovalerate, 8 α-hydroxy presilphiperfolene and intermedeol have been isolated from steam volatile extract of *I. cuspidata* and identified from their spectral data, synthesis and chemical modification of major constitutents. Whereas it is noteworthy that, thymol (2.6 %) was identified only small amounts in this study (Table-1). Pentacosane (13.7 %) was determined main constituent of the volatile oil of *Inula oculus-christi* L. from Iran[22], whereas pentacosane (2.1 %) was determined the minor compound of *I. macrocephala* from Turkey (Table-1). Differences were found in some studied oils from Turkey[13] (25.2 % borneol, 22.5 % isobornyl acetate and 19.5 % bornyl acetate), from Spain[14] (38.8 % fokienol and 7.71 % nerolidol), from France[17] (21.1 % fokienol, 8.6 % nerolidol and 6.2 % eudesm-6-en-4a-ol) and from Italy[16] (62.37 % 12-carboxyeudesma-3,11 (13) diene).

It is surprising that large qualitative and quantitative differences were found between *Inula* species in view of main compounds. As seen above, an opposite correlation was noticed for mono and sesquiterpenes hydrocarbons and oxygenated sesquiterpenes between *Inula* species. Inter and intraspecific variations in the essential oils composition of many genera patterns like *Senecio L.*[25] and *Nepeta L.*[26] were previously reported, depending on genetic, environmental factors, ontogeny, season, plant part analyzed and analytical methods. The findings showed that the genus *Inula* had a considerable variation in essential oil composition and this study demonstrates the occurrence of the borneol/β-caryophyllene chemotype in the eastern Anatolian region of Turkey. Moreover this result is significant to chemotaxonomic evaluation of the genus and family patterns.

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