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Constituents of the Essential Oils of *Helichrysum graveolens* (Bieb.) Sweet from Turkey

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In this study, the essential oils of *Helichrysum graveolens* species from Turkey were investigated and 72 components were identified by GC, GC-MS. Essential oil was hydrodistilled by using Clevenger apparatus from the aerial parts of plants collected from the natural habitats. The essential oils yield is very low and 0.1 (v/w). Seventy two constituents were comprised the 82.97 % of the total essential oil extracted from the *Helichrysum graveolens*. The predominant compounds of *Helichrysum graveolens* were as α-cubebene (10.5 %), β-caryophyllene (9.4 %), azulene-octahydro (7.5 %), caryophyllene oxide (8.2 %). The results were discussed in view of chemotaxonomy and natural products.

Key Words: *Helichrysum graveolens*, Asteraceae, Essential oil.

INTRODUCTION

Helichrysum is a typical aromatic plant of the Asteraceae family[1]. The Helichrysum species are xerophytes growing at a wide range of altitudes from the sea level up to 1700 m. preferably on sandy or loamy soils, which are distributed from the lower-meso-Mediterranean to the lower-sub-humid bioclimatic environment[2]. The name of the plant, from the Greek "helios", sun and "chryos", gold, relates to the typical bright yellow coloured inflorescences which represent the drug[2,3]. *Helichrysum* species are generally known under the names "olmez cicek or altinotu" in Turkish and are widely used as herbal tea in Turkey[4,5].

The inflorescence of *Helichrysum* species have long been known in herbal medicine in World for its choleretic, diuretic, antiinflammatory and detoxifying activities. These effects of *Helichrysum* species are due to the flavonoids that they contain[6].

The genus is an important source of secondary metabolites[7-10] and most of the species have been studied for their content of essential oils[11-15] which are produced in glandular trichomes located on the flower petals, sepals and bracts and also on the stem leaves[16]. Although biological activities of many *Helichrysum* species have been investigated in different countries, there are only a few reports of the *Helichrysum* species belonging to Turkish flora[17,18].

The information concerning the essential oil composition of *H. graveolens* has not been reported before. Only the composition of the essential oil of *H. chasmolycicum* has been studied previously[19]. The current study presents the results of GC-MS analysis of the essential oils of *H. graveolens* for the first time from Turkey.

EXPERIMENTAL

Helichrysum graveolens specimens were collected from natural habitats in Bursa, 2009 (Elkiran 1041).

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

Gas chromatographic (GC) analysis: The essential oil was analyzed using HP 6890 GC equipped with a FID detector and an HP-5 MS column (30 m × 0.25 mm i.d., film thickness 0.25 mm) 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 (GC-MS) analysis: The oils were analyzed by GC-MS, using a Hewlett Packard system. HP-Agilent 5973N GC-MS system with 6890 GC in Plant Products and Biotechnology Res. Lab. (BUBAL) in Firat University. HP-5 MS column (30 m × 0.25 mm i.d., film thickness 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 (RRI). 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.

TABLE-1
CONSTITUENTS OF THE ESSENTIAL OILS
FROM *Helichrysum graveolens* (Bieb.) SWEET

No.	Compounds	RRI	Percentage (%)
1	Bicyclo [2,2,1] hept-2-ene	1000	0.03
2	α-Pinene	1021	0.48
3	α-Fenchene	1033	0.40
4	β-Pinene	1055	0.04
5	4-Hexen-3-one	1078	0.02
6	Benzene, 1-methyl-4	1091	0.06
7	dl-Limonene	1094	0.10
8	L-Linalool	1147	0.02
9	3-Cyclohexen-1-ol	1205	0.01
10	α-Terpineol	1215	0.05
11	Carvacrol	1295	0.14
12	Ethanone	1316	0.03
13	Isoterpinolene	1322	0.03
14	α-Ylangene	1355	1.03
15	α-Copaene	1360	0.24
16	β-Bourbonene	1365	1.73
17	β-Elemene	1370	1.31
18	1,4-methano-1*H*-indene	1372	0.07
19	Tetradecane	1378	0.03
20	Isoledene	1381	0.11
21	β-Caryophyllene	1393	9.44
22	B-Germacrene	1399	0.06
23	Himachala-2,4-diene	1402	0.33
24	α-Amorphene	1408	1.90
25	β-Farnesene	1415	0.50
26	α-Humulene	1419	1.30
27	*cis*-Calamenene	1424	0.13
28	2-Isopropenyl-4a,8-dimethyl	1430	0.20
29	α-Cubebene	1433	10.50
30	α-Cedrene	1437	2.98
31	Δ-Selinene	1439	0.99
32	Butanoic acid	1441	2.80
33	γ-Amorphene	1442	0.33
34	α-Selinene	1445	0.66
35	α-Muurolene	1447	0.17
36	α-Gurjunene	1450	0.18
37	Tricyclo[5.4.0.02,8]undec-9-ne,2,6,6,9-tetramethyl-	1455	0.50
38	Δ-Cadinene	1458	0.74
39	*cis*-Calamenene	1460	0.61
40	Epizonarene	1470	1.00
41	Selina-3,7 (11)-diene	1473	0.90
42	Naphthalene,1,2,3,4-tetrahydro	1476	0.13
43	4,4-Dimethyl-3-3(3-methylbut-3-enylidene)	1484	0.60
44	Spathulenol	1495	0.92
45	Caryophyllene oxide	1498	8.22
46	Aromadendrene	1503	0.22
47	Veridiflorol	1506	0.73
48	Cyclohexene, 6-ethenyl-6-methyl-1	1512	1.00
49	Humulene epoxide II	1514	0.51
50	Azulene-octahydro	1524	7.50
51	2-Naphthalenemethanol	1526	0.76
52	1,10-di-epi-Cubenol	1528	1.56
53	Naphthalene,1,2,3,4,4a,5,6,8a	1531	0.66
54	α-Cadinol	1537	1.30
55	β-Eudesmol	1539	3.98
56	Neo-Intermedeol	1541	0.32
57	α-Calacorene	1544	0.49
58	Limonene oxide	1547	0.60
59	1,6-Dimethyl-4-naphthalene	1548	0.70
60	*cis*-β-Guaiene	1562	0.33
61	6-Ethyl-1,3-dimethylindan 5-carbaldehyde	1564	0.62
62	Aromadendrene, dehydro	1574	2.28
63	Ledene oxide-(II)	1584	1.00
64	7H-2,4a-Methanonaphthalen-7-one	1604	1.03
65	Caryophyllene-(i1)	1607	0.26
66	Dodeca-1,6-dien-12-ol,	1644	0.24
67	2-Heptadecanone	1660	0.20
68	*n*-Hexadecanoic acid	1692	0.08
69	Heneicosane	1789	0.04
70	9-Tricosane	1888	0.04
71	Tricosane	1902	0.47
72	Tetracosane	1949	0.06
Total			82.97

RRI = Relative retention index

RESULTS AND DISCUSSION

The essential oil yields of *H. graveolens* was (0.1 %) (v/w). The results of the GC and GC/MS analyses are given in Table-1, where the compounds are listed according to their order of elution. Total 72 components are identified in essential oil of *H. graveolens*.

Seventy two constituents, representing 72.97 % of the total components in the essential oil extracted from the *H. graveolens*. α-Cubebene (10.50 %), β-caryophyllene (9.44 %), azulene-octahydro (7.5 %), caryophyllene oxide (8.22 %) are the major compounds determmined in the *H. graveolens* essential oil (Table-1). α-Cubebene (10.5 %) was detected as one of the major components in the essential oil of *H. graveolens* (Table-1), it was not detected in *H. noeanum*[20].

Caryophyllene oxide (8.22 %) was determined as major constituent in the essential oil of *H. graveolens*. This compound was also reported as a major component in the essential oil of *H. aucheri* (23.00 %)[21], *H. leucocephalum* (10.1 %) and *H. artemisioides* (10.6 %)[22].

The composition of indigenous South African three species (*Helichrysum dasyanthum*, *H. excisum* and *H. petiolare*) were dominated by the presence of monoterpenes such as 1,8-cineole (20-34 %), α-pinene (3-17 %) and *p*-cymene (6-10 %)[23,24]. For all three species, 1,8-cineole was the major constituent with viridiflorol (18.2 %) (sesquiterpene) also present in high concentration in *Helichrysum excisum*.

The essential oil profile of *Helichrysum felinum* was reported totally different from that of any of the other species (*Helichrysum dasyanthum*, *H. excisum*, *H. petiolare*), with the monoterpenes largely absent. Its profile consisted of a variety of sesquiterpenes in low concentrations with β-caryophyllene (27.6 %) dominating together with α-humulene (9.4 %), alloaromadendrene (7.3 %) and caryophyllene oxide (6.9 %) as main constituents. This correlates with data obtained for Greek species where sesquiterpenes also dominated[12,24]. It will be said that *H. noeanum* species from Turkey also has sesquiterpene dominated essential oil.

It is reported that 1,8-cineole possess antiinflammatory activity[25] and terpenes such as α-pinene and sesquiterpenes such as β-caryophyllene exhibited activity *in vitro* 5- lipoxygenase assay[12,24]. The chemical constituents of the essential oil of *H. cymosum* indicated that two major compounds are α-pinene (12.4 %) and 1,8-cineole (20.4 %). 1,8-Cineole has known antimicrobial properties and may possibly contribute to the antimicrobial effect of the *H. cymosum* oil[26,27].

1,8-Cineole (27.70 %), β-pinene (11.60 %), α-humulene (α-caryophyllene) (10.80 %), β-caryophyllene (10.39 %) are the major compounds of *Helichrysum bracteiferum*[28].

The essential oils of *Helichrysum stoechas* isolated from the flowers and from the leaves collected during the flowering period were obtained in a yield of 0.3 % (v/w) and 0.8 % (v/w), respectively. The GC and GC-MS analyses revealed that the monoterpene hydrocarbon fraction were dominant in both oils, attaining 93 and 98 % of the total oils from the flowers and leaves, respectively. α-Pinene was the major component in both oils, amounting to 69 % in the flower oil and 78 % in that of leaf[29].

Helichrysum odoratissimum is one of the most commonly used medicinal plants in South Africa. The essential oil from the herb was extracted and characterized for the first time using different drying methods. The oils isolated from fresh, air-dried, sun-dried and oven-dried aerial parts of the plant yielded 0.28, 0.46, 0.33 and 0.36 %, respectively. The fresh leaf oil was characterized by a high content of oxygenated monoterpenes with the main constituents as *p*-menthone (35.4 %), pulegone (34.2 %) and 1,8-cineole (13.0 %). The dried plant oils had limonene (31.6-22.6 %), μ-caryophyllene (13.0-12.0 %) and α-pinene (10.0-7.7 %) as their major constituents[30]. Chemical studies of various species of *Helichrysum* have shown that they synthesize a large array of metabolites[7-10].

The findings showed that the genus *Helichrysum* had a considerable variation in essential oil composition and this study demonstrates the occurrence of α-cubebene chemotype of *Helichrysum graveolens* in central Anatolian region of Turkey. The essential oils composition of the *Helichrysum graveolens* from Turkey show that they have contributed to the medicinal usage of this plant as a crop and their oils in the pharmaceutical, cosmetic and industrial purposes.

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