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Composition of the Essential oil of Endemic *Haplophyllum megalanthum* Bornm. from Turkey

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Abstract: The composition of the essential oil produced from the flowering aerial parts of *Haplophyllum megalanthum* Bornm. (Rutaceae), endemic to Turkey, was analyzed by GC and GC-MS. Among the fifty-eight compounds constituting about 91.7 % of the essential oil, the main components were characterized as palmito-γ-lactone (45.8 %), octadecatrienoic acid (10.7 %), linoleic acid (6.5 %), octadecatetraenoic acid (6.3 %) and nonacosane (4.8 %).

Keywords: *Haplophyllum megalanthum*; essential oil composition; palmito-γ-lactone; octadecatrienoic acid; linoleic acid; octadecatetraenoic acid; nonacosane.

1. Plant Source

Haplophyllum A. Juss. (Rutaceae) is a genus, comprising of about 70 species distributed from the Mediterranean to eastern Siberia [1]. It is represented by 14 species in the Flora of Turkey [2].

The aerial parts of *H. megalanthum* Bornm. were collected during the flowering period from Manisa. The plant was identified by one of the authors (M.A.O.) and a voucher specimen (No: 1350) is deposited in the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Ege University.

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2. Previous Studies

Haplophyllum species have been shown to possess alkaloids [3-7], lignans [5-7], coumarins [5], flavonoids [7] and volatile constituents [8-11] with important biological activities [3,4,6,11].

To the best of our knowledge, there is no report found in the literature on the chemical and biological properties of *H. megalanthum*, an endemic species of Turkey. In the present study, the chemical composition of the essential oil of this plant is reported for the first time.

3. Present Study

Aerial parts (100 g) were subjected to hydrodistillation for 3 hours using a Clevenger-type apparatus to provide the essential oil. Yellow colored oil was obtained in 0.1 % (v/w) yield.

The GC-MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60 m x 0.25 mm, 0.25 μm 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 at 40:1. The injector temperature was set at 250°C. Mass spectra were recorded at 70 eV. Mass range was from *m/z* 35 to 450.

The GC analysis was carried out using an Agilent 6890N GC system. FID detector temperature was 300°C. To obtain the same elution order with GC/MS, simultaneous autoinjection was done on a duplicate of the same column applying the same operational conditions. Relative percentage amounts of the separated compounds were calculated from FID chromatograms. The result of analysis is shown in Table 1.

Identification of the essential oil components were carried out by comparison of their relative retention times with those of authentic samples or by comparison of their relative retention indices (RRI) to series of *n*-alkanes. Computer matching against commercial (Wiley GC-MS Library, Adams Library, MassFinder 3 Library) [12,13] and in-house "Başer Library of Essential Oil Constituents" built up by genuine compounds and components of known oils, as well as MS literature data [14,15] were used for the identification.

Fifty eight compounds were characterized representing 91.7 % of the oil (Table 1). Fatty acids and their derivatives were found in large quantities. Palmito-γ-lactone was detected as the major component constituting 45.8 % of the essential oil. Other significant compounds were octadecatrienoic acid (10.7 %), linoleic acid (6.5 %), octadecatetraenoic acid (6.3 %) and nonacosane (4.8 %) followed by dodecanoic acid (2.5 %) and hexadecanoic acid (2.3 %).

Previous studies on the chemical compositions of the oils obtained from *Haplophyllum* species growing in different countries showed that members of this genus possess essential oils with different compositions. For example, essential oils of *H. glabrrimum* Bge. ex Boiss. [16], *H. robustum* Bge. [17], *H. tuberculatum* (Forssk.) A. Juss. [11], *H. linifolium* (L.) G. Don. fil. [18] contained monoterpenes as the main constituents. Elemol and β-eudesmol were reported as the major components of *H. furfuraceum* Bge. ex Boiss. essential oil whereas *H. virgatum* Spach. essential oil was found to be rich in aliphatic ketones namely, 2-nonanone and 2-undecanone [19]. Major constituents of *H. lissonotum* C. Town. essential oil were detected as caryophyllene oxide, β-caryophyllene, humulene oxide II, α-humulene and caryophylla-4(14),8(15)-dien-5β-ol while the essential oil of *H. buxbaumii* (Poir.) G. Don. subsp. *mesopotamicum* (Boiss.) C. Town. was found to possess hexadecanoic acid, ethyl linolenate, phytol and caryophyllene oxide as the main compounds [10].

Table 1. Composition of the essential oil of *H. megalanthum*

RI	Compound	(%)	RI	Compound	(%)
1032	α-Pinene	0.5	1773	δ-Cadinene	0.2
1093	Hexanal	t	1760	isodihydrocarveol	0.3
1174	Myrcene	0.1	1827	(*E,E*)-2,4-Decadienal	0.2
1203	Limonene	t	1857	Geraniol	0.2
1218	β-Phellandrene	0.1	1868	(*E*)-Geranyl acetone	0.3
1220	*cis*-Anhydrolinalool oxide	0.1	1900	*epi*-Cubebol	t
1225	(*Z*)-3-Hexenal	0.3	1957	Cubebol	0.1
1244	2-Pentyl furan	t	1958	(*E*)-β-Ionone	0.1
1246	(*Z*)-β-Ocimene	0.1	2037	Salvial-4(14)-en-1-one	0.2
1253	*trans*-Anhydrolinalool oxide	0.1	2050	(*E*)-Nerolidol	0.4
1266	(*E*)-β-Ocimene	0.1	2100	Heneicosane	0.1
1400	Nonanal	0.2	2131	Hexahydrofarnesyl acetone	0.1
1460	2,6-Dimethyl-1,3(*E*),5(*E*),7-octatetraene	t	2144	Spathulenol	0.3
1505	Dihydroedulane II	0.1	2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	0.2
1535	β-Bourbonene	0.4	2209	T-Muurolol	0.4
1553	Linalool	0.4	2210	Copaborneol	0.4
1589	β-Ylangene	0.1	2278	torilenol	0.2
1591	Bornyl acetate	0.1	2300	Tricosane	1.5
1597	β-Copaene	0.1	2369	Eudesma-4(15),7-dien-1β-ol	0.3
1612	β-Caryophyllene	t	2500	Pentacosane	0.4
1638	β-Cyclocitral	t	2503	Dodecanoic acid	2.5
1655	(*E*)-2-Decenal	t	2622	Phytol	1.3
1661	Alloaromadendrene	0.4	2857	Palmito-γ-lactone (=4-Hexadecanolide)	45.8
1694	Neral	0.1	2900	Nonacosane	4.8
1704	γ-Muurolene	0.1	2931	Hexadecanoic acid	2.3
1726	Germacrene D	1.1	3061	Stearolactone (=4-Octadecanolide)*	0.9
1740	α-Muurolene	t	3290	Linoleic acid (=(*Z,Z*)-9,12-octadecadienoic acid)	6.5
1742	Geranial	0.2	3157	Octadecatrienoic acid*	10.7
1755	Bicyclogermacrene	t	3274	Octadecatetraenoic acid*	6.3
				Total	**91.7**

RI: Relative retention indices calculated against n-alkanes; %: calculated from FID data; t: trace (< 0.1 %);
*Tentatively identified :
Stearolactone: EIMS, 70 eV, $C_{18}H_{34}O_2$, *m/z* (rel.int.): 282[M]$^+$, 264(9), 246(7), 220(11), 195(3), 166(5), 151(6), 137(5), 123(9), 111(14), 97(30), 85(100), 69(28), 55 (36), 41(29).
Octadecatrienoic acid: EIMS, 70 eV, $C_{18}H_{30}O_2$, *m/z* (rel.int.): 278[M]$^+$ (3), 235(2), 218(4), 205(5), 193(5), 149(10), 136(33), 121(29), 107(28), 93(52), 79(89), 67(100), 55(49), 41(49).
Octadecatetraenoic acid: EIMS, 70 eV, $C_{18}H_{28}O_2$, *m/z* (rel.int.): 276[M]$^+$ (2), 220(1), 189(3), 175(2), 161(5), 147(19), 133(11), 119(16), 105(22), 93(51), 79(100), 67(58), 55(25), 41(33).

Considering the Turkish *Haplophyllum* species, only *Haplophyllum myrtifolium* Boiss., an endemic species to Turkey, has been investigated for its essential oil composition [8]. Moreover, in another study, volatile fractions of the petroleum ether and alkaloid extracts of the same species were analyzed by GC-MS [9]. Linalool (12.8 %), β-caryophyllene (10.3 %) and methyleugenol (5.9 %) were identifed as the major components of the essential oil of *H. myrtifolium* [8]. However, in our study, the amount of linalool was found to be 0.4 % in the oil of *H. megalanthum*, whereas β-caryophyllene was detected in trace amount. Methyleugenol was not detected in the oil of *H. megalanthum*.

In conclusion, the composition of *H. megalanthum* oil, with a very high content of fatty acids and their derivatives, differ significantly from the compositions of other oils of *Haplophyllum* species.

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