

## COMPOSITION OF THE ESSENTIAL OIL OF *Haplophyllum myrtifolium*\*

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*The chemical composition of the essential oil of Haplophyllum myrtifolium Boiss., endemic to Turkey, was examined by GC/MS. Ninety-seven compounds were characterized with linalool (12.8%),  $\beta$ -caryophyllene (10.3%), and methyleugenol (5.9%) as the main constituents.*

**Key words:** *Haplophyllum myrtifolium*, Rutaceae, essential oil composition, linalool,  $\beta$ -caryophyllene, methyleugenol, hydrodistillation, GC/MS analysis.

The genus *Haplophyllum* (Rutaceae) is represented by about seventy species distributed in an area stretching from the Mediterranean to Eastern Siberia [1], and has been shown to contain lignans, quinoline alkaloids, coumarins, and flavonoids [2–12]. The limited number of reports on the occurrence of volatile compounds in the representatives of this genus [13, 14] have prompted us to analyze the essential oil of *Haplophyllum myrtifolium* Boiss., a perennial herb endemic to Turkey [15]. Previous studies on this species have shown the presence of quinoline alkaloids [16] and lignans [11]. In the present study, we report the chemical composition of the essential oil of *H. myrtifolium* for the first time.

Relative retention indices (RRI) and relative percentage amounts of the ninety-seven volatile compounds characterized making up 85.3% of the essential oil are presented in Table I. The major components were linalool (12.8%),  $\beta$ -caryophyllene (10.3%), and methyleugenol (5.9%).

### EXPERIMENTAL

**Plant Material and Distillation.** The aerial parts of *H. myrtifolium* were collected during the flowering period from Honaz, Denizli, in June 2000. A voucher specimen, No 1250, is deposited in the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Ege University. A 1.85 kg portion of fresh plant material was subjected to hydrodistillation using a Clevenger type apparatus defined in the USP [17].

**GC/MS Analysis.** The chemical composition of the essential oil of *H. myrtifolium* was examined by GC/MS, using a Hewlett-Packard GCD system. An HP-Innowax FSC column (60  $\times$  0.25 mm  $\phi$ , with 0.25 mm film thickness) was used with helium as carrier gas (1 mL/min). The GC oven temperature was kept at 60°C for 10 min, programmed to increase to 220°C at a rate of 4°C/min, kept constant at 220°C for 10 min, and then programmed to increase to 240°C at a rate of 1°C/min. Alkanes were used as reference points in the calculation of relative indices (RRI). The split ratio was adjusted at 50:1. The injection temperature was at 250°C. MS were taken at 70 eV. Mass range was from  $m/z$  35 to 425. A library search was carried out using the Wiley GC/MS Library and the TBAM Library of Essential Oil Constituents.

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TABLE 1. Composition of the Essential Oil of *Haplophyllum myrtifolium*

RRI	Compound	%	RRI	Compound	RRI
1032	$\alpha$ -Pinene	0.1	1700	<i>p</i> -Mentha-1,8-dien-4-ol (=Limonen-4-ol)	0.4
1118	$\beta$ -Pinene	Tr.	1706	$\alpha$ -Terpineol	0.5
1176	$\alpha$ -Phellandrene	0.8	1726	Germacrene D	0.6
1203	Limonene	0.5	1742	Geranial	1.0
1218	$\beta$ -Phellandrene	1.9	1755	Bicyclogermacrene	0.2
1220	<i>cis</i> -Anhydrolinalool oxide	0.5	1766	Decanol	0.2
1225	( <i>Z</i> )-3-Hexenal	0.3	1773	$\delta$ -Cadiene	0.2
1244	Amylfuran (=2 Pentylfuran)	Tr.	1798	Methylsalicylate	0.2
1246	( <i>Z</i> )- $\beta$ -Ocimene	0.4	1808	Nerol	Tr.
1253	<i>trans</i> -Anhydrolinalool oxide	0.3	1815	2,6-Dimethyl-3( <i>E</i> ), 5( <i>Z</i> ), 7-octatriene-2-ol	0.3
1255	$\gamma$ -Terpinene	0.2	1830	2,6-Dimethyl-3( <i>E</i> ), 5( <i>E</i> ), 7-octatriene-2-ol	1.2
1266	( <i>E</i> )- $\beta$ -Ocimene	0.9	1838	$\beta$ -Damascenone	0.2
1280	<i>p</i> -Cymene	0.3	1854	Germacrene B	1.0
1285	Isoamyl-isovalerate	0.4	1857	Geraniol	3.7
1286	2-Methylbutyl-2-methylbutyrate	1.0	1864	<i>p</i> -Cymen-8-ol	0.1
1290	Terpinolene	0.1	1880	Benzyl 2-methylbutyrate	0.7
1327	( <i>Z</i> )-3-Hexenylacetate	0.2	1896	Phenylethyl-isobutyrate	0.1
1348	6-Methyl-5-hepten-2-one	0.2	1900	Nonadecane	0.1
1360	Hexanol	0.2	1937	Phenethyl alcohol	0.1
1391	( <i>Z</i> )-3-Hexenol	0.3	1988	2-Phenylethyl 2-phenylbutyrate	1.8
1400	Nonanal	1.1	2008	Caryophyllene oxide	1.4
1438	Hexyl-2-methylbutyrate	0.1	2030	Methyleugenol	5.9
1450	<i>trans</i> -Linalool oxide (Furanoid)	1.7	2050	( <i>E</i> )-Nerolidol	0.5
1460	2,6-Dimethyl-1,3( <i>E</i> ),5( <i>E</i> ),7-octatetraene	0.5	2100	Heneicosane	0.6
1474	<i>trans</i> -Sabinene hydrate	0.1	2131	Hexahydrofarnesylacetone	0.3
1477	4,8-Epoxyterpinolene	0.1	2148	( <i>Z</i> )-3-Hexen-1-yl-benzoate	1.6
1478	<i>cis</i> -Linalool oxide (Furanoid)	1.2	2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	0.2
1482	( <i>Z</i> )-3-Hexenyl-2-methylbutyrate	0.3	2186	Mintsulphide	0.1
1497	$\alpha$ -Copaene	0.1	2186	Eugenol (=2-Methoxy-4-(2-propenyl)phenol)	1.5
1500	Pentadecane	0.3	2192	Nonanoic acid	0.2
1500	<i>cis</i> -Tagetone	0.1	2200	<i>trans</i> -Methyl-isoeugenol	0.2
1503	2-Methoxy-3- <i>sec</i> -butylpyrazine	0.1	2200	Docosane	0.6
1507	( <i>E,E</i> )-2,4-Heptadienal	0.3	2217	Chavibetol (=2-Methoxy-5-(2-propenyl)phenol)	1.4
1522	<i>trans</i> -Tagetone	0.1	2218	4-Vinylguaiaicol	0.2
1535	$\beta$ -Bourbonene	0.1	2239	Carvacrol	0.1
1553	Linalool	12.8	2300	Tricosane	0.7
1562	Octanol	0.2	2400	Tetracosane	0.3
1571	<i>trans-p</i> -menth-2-en-1-ol	0.2	2431	Methyloctadecanoate (=Methylstearate)	0.2
1588	Bornylformate	0.7	2456	( <i>Z</i> )-9-Methyloctadecenoate (=Methylolate)	0.4
1597	Bornylacetate	2.9	2500	Pentacosane	1.9
1600	Hexadecane	0.2	2503	Dodecanoic acid	0.3
1600	$\beta$ -Elemene	0.3	2600	Hexacosane	0.4
1612	$\beta$ -Caryophyllene	10.3	2622	Phytol	0.8
1616	Hotrienol	0.2	2655	Benzylbenzoate	0.1
1650	$\gamma$ -Elemene	0.4	2670	Myristic acid	0.2
1687	$\alpha$ -Humulene	0.9	2700	Heptacosane	0.4
1690	Cryptone	0.2	2931	Hexadecanoic acid	3.9
1694	Neral	0.6	3067	Squalene	3.5
1700	Heptadecane	0.1		<b>Total</b>	<b>85.3</b>

RRI: Relative Retention Indices.

Tr. Trace (&lt; 0.1 %).

## REFERENCES

1. J. C. Willis, *A Dictionary of Flowering Plants and Ferns*, 8th ed, revised by Airy H. K. Shaw, 1980, p. 532., Cambridge University Press, Cambridge.
2. I. Kostova, A. Ivanova, B. Mikhova, and A. Vitkova, *Monatsh. Chem.*, 131 (2), 191 (2000).
3. B. Gozler, R. Daniel, T. Gozler, N. Unver, and M. Hesse, *Phytochemistry*, **42**, 695 (1996).
4. B. Gozler, T. Gozler, H. Saglam, and M. Hesse, *Phytochemistry*, **42**, 689 (1996).
5. T. Gozler, B. Gozler, A. Linden, and M. Hesse, *Phytochemistry*, **43**, 1425 (1996).
6. J. M. Prieto, M. C. Recio, R. M. Giner, S. Manez, A. Massmanian, P. G. Waterman, and M. C. Rios, *Z. Naturforsch.*, **51**, 618 (1996).
7. R. Filippini, A. Piovan, G. Innocenti, R. Caniato, and E. M. Cappelletti, *Phytochemistry*, **49**, 2337 (1998).
8. I. A. Bessonova, *Chem. Nat. Compd.*, **35**, 589 (1999); *Chem. Abstr.*, 133, 147517 (2000).
9. V. I. Akhmedzhanova, *Chem. Nat. Compd.*, 35, 552 (1999); *Chem. Abstr.*, 133, 147512 (2000).
10. A. J. Al-Rheaily, A. T. Al-Howiriny, S. M. Ahmad, and A. M. Al-Yahya, *Phytochemistry*, **57**, 597 (2001).
11. U. Evcim, B. Gozler, A. J. Freyer, and M. Shamma, *Phytochemistry*, **25**, 1949 (1986).
12. A. Ulubelen, S. Oksuz, B. Halfon, Y. Aynehchi, T. J. Mabry, and S. A. Matlin, *Phytochemistry*, **23**, 2941 (1984).
13. M. Yari, S. Masoudi, and A. Rustaiyan, *J. Essent. Oil. Res.*, **12**, 69 (2000).
14. E. J. Brunke, F. J. Hammerschmidt, M. A. Abd El-Kawy, and E. A. El-Kashoury, *Herba Hung.*, **30**, 34 (1991) (The Ovidtest Database).
15. P. H. Davis, *Flora of Turkey and the East Aegean Islands*, **2**, University Press, Edinburgh, 1967.
16. B. Sener, A. Mutlugil, N. Noyanalpan, and J. R. Lewis, *J. Fac. Pharm. Gazi*, **7**, 17 (1990).
17. *The United States Pharmacopeia*, 16th Ed, p. 1214, 1985, United States Pharmacopeial Convention, Inc.