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Composition of Essential Oils of *Calamintha nepeta* (L.) Savi Subsp. *nepeta* and *Calamintha nepeta* (L.) Savi Subsp. *glandulosa* (Req.) P.W. Ball

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The oils were extracted from aerial parts of the two subspecies of *Calamintha*: subsp. *nepeta* (A, B, C) and subsp. *glandulosa* (D, E) using an Eppendorf Microdistiller®. Oils were analyzed by GC/MS. *Trans*-piperitone oxide (44.4 %), piperitenone oxide (11.7 %) and limonene (7.1 %) were detected as main constituents in sample A; pulegone (11.9 %), menthone (11.9 %), carvacrol (10.0 %) and limonene (7.5 %) were found as main constituents in sample B; *trans*-piperitone oxide (30.9 %), caryophyllene oxide (7.8 %) were detected as main constituents in sample C of *C. nepeta* subsp. nepeta oils and pulegone (19.5 %), menthone (9.7 %), caryophyllene oxide (7.9 %), *trans*-piperitone oxide (5.7 %) and menthol (5.0 %) were detected as main constituents in sample D; *trans*-piperitone oxide (34.2 %), limonene (17.3 %) and piperitenone oxide (10.8 %) were found as main constituents in sample E.

Key Words: *Calamintha nepeta*, Labiatae, Essential oil composition.

INTRODUCTION

The genus *Calamintha* Miller (Lamiaceae) is distributed in Europe, Eastern Mediterranean region, Central Asia, North Africa and America[1,2]. In Turkey it is represented by 9 species and 12 taxa, five being endemic to Turkey. The ratio of endemism is over 45 %[3-5]. Recently, a new taxon, *Calamintha pamphylica* Boiss. and Heldr. subsp. *alanyense* S. Alan and A. Ocak has been reported[6].

Calamintha is known as Güzel Nane, Dag Nanesi, Miskotu, Tibbi Miskotu, Yabani Ogulotu and used as folk medicine in Turkey. It also has horticultural uses[1,7]. *Calamintha* species are used as stimulant, antispasmodic, emmenagogue, digestive, antiseptic, diaphoretic, expectorant and for strengthening central nervous system[1,2,8]. They are also used for stomach and throat ache, kidney disorders and as a spice [9,10]. The essential oil compositions of several subspecies of *Calamintha nepeta* have been reported as shown in Table-1[11-21].

EXPERIMENTAL

Aerial parts of the *Calamintha nepeta* (L.) Savi subsp. *nepeta* were collected from following regions of the Içel: Tarsus (A), Içel: Silifke (B), Bartin (C) province and *Calamintha nepeta* (L.) Savi subsp. *glandulosa* (Req.) P.W. Ball was collected from the following regions of the Zonguldak (D) and Manisa (E) province.

TABLE-1
ESSENTIAL OIL COMPOSITIONS OF SEVERAL *Calamintha nepeta*

Calamintha ssp.	Main components	Ref.
C. nepeta	Piperitone oxide, piperitenone oxide	11
C. nepeta	Pulegone (49.6 %), menthone (9.4 %)	12
C. nepeta	Pulegone (37.5-79.1 %), menthone (2.1-37.4 %), limonene (4.9-10.7 %)	13
C. nepeta	Pulegone (21.4 %), menthone (19.8 %), piperitenone (16.4 %), isopulegone (14.1 %)	14
C. nepeta ssp. *nepeta*	Menthone (52.7 %), pulegone (9.1 %), piperitone (7.8 %), neomenthol (7.6 %), menthol (4.3 %), limonene (4.0 %)	15
C. nepeta ssp. *glandulosa*	Pulegone (40.5 %), menthone (23.6 %)	16
C. nepeta ssp. *glandulosa*	Pulegone (37.5 %), menthone (17.6%), piperitenone (15.0 %), piperitone (10.2 %)	17
C. nepeta ssp. *glandulosa*	Pulegone (41.0 %), menthone (32.0 %), piperitone (7.3 %), piperitenone (7.0 %)	18
C. nepeta ssp. *glandulosa*	Piperitenone oxide (43.8 %), *trans*-piperitone oxide (25.2 %), limonene (13.0 %)	19
C. nepeta ssp. *glandulosa*	Piperitone oxide (30.7-74.2 %), piperitenone oxide (4.7-52.0 %)	20
C. nepeta ssp. *glandulosa*	Pulegone (42.0 %), piperitone (40.4 %)	21

TABLE-2
COMPOSITION OF THE ESSENTIAL OILS OF *Calamintha nepeta* subsp. *nepeta* AND *Calamintha nepeta* subsp. *glandulosa*

RI	Compounds	A (%)	B (%)	C (%)	D (%)	E (%)
1018	Methyl 2-methyl butyrate	–	–	–	–	tr
1032	α-Pinene	1.0	0.5	–	–	1.3
1035	α-Thujene	–	0.2	–	–	0.1
1051	2,5-Diethyl tetrahydrofuran	tr	–	–	–	tr
1063	Ethyl 2-methylbutyrate	–	–	–	–	tr
1076	Camphene	0.1	0.1	–	–	0.2
1093	Hexanal	–	–	–	–	0.1
1118	β-Pinene	1.8	0.7	–	–	1.6
1132	Sabinene	0.6	0.3	–	–	0.7
1151	Propyl 2-methyl butyrate	–	–	–	–	tr
1174	Myrcene	1.0	1.5	–	0.1	1.1
1183	Pseudo-limonene	0.5	–	–	–	0.1
1185	Isobutyl 2-methylbutyrate	–	-	–	–	tr
1188	α-Terpinene	–	1.1	–	–	tr
1192	2-Heptanone	–	–	–	–	tr
1203	**Limonene**	**7.1**	**7.5**	0.1	0.3	**17.3**
1213	1,8-Cineole	–	0.6	–	0.7	0.3
1218	β-Phellandrene	0.1	–	–	–	–
1220	3-Octanone	–	–	–	–	tr
1223	3-Methyl cyclopentanone	–	–	–	0.3	–
1224	*o*-Mentha-1(7),5,8-triene	–	–	–	–	tr
1225	(Z)-3-Hexenal	tr	0.1	–	–	–
1232	(E)-2-Hexenal	–	–	–	–	tr
1244	2-Pentyl furan	tr	–	–	–	tr
1246	(Z)-β-Ocimene	–	0.3	–	–	tr
1247	6-Methyl-2-heptanone	–	–	–	–	tr
1255	γ-Terpinene	–	7.0	–	0.1	0.1
1266	(E)-β-Ocimene	–	0.2	–	–	–
1267	5-Methyl-3-heptanone	tr	0.1	–	–	tr
1280	*p*-Cymene	0.1	3.3	–	–	0.4
1285	Isoamyl isovalerate	–	–	0.1	–	tr
1286	2-Methylbutyl 2-methyl butyrate	–	–	–	–	0.2
1290	Terpinolene	–	0.2	–	–	tr
1296	Octanal	–	–	–	–	tr
1299	2-Methylbutyl isovalerate	–	–	0.1	–	–
1303	Amyl isovalerate	–	–	–	–	tr
1327	(Z)-3-Hexenyl acetate	–	–	–	–	tr
1345	3-Octyl acetate	–	–	–	–	tr
1348	6-Methyl-5-heptene-2-one	–	–	–	–	tr
1393	3-Octanol	1.0	1.0	0.4	1.2	1.7
1400	Nonanal	–	–	0.6	–	0.1
1450	*trans*-Linalool oxide (Fur.)	–	–	–	0.2	–
1451	α-*p*-Dimethylstyrene (=*p*-Cymenene)	0.1	–	–	–	0.1
1452	1-Octen-3-ol	0.5	0.4	–	0.1	–
1458	*cis*-1,2-Limonene epoxide	–	–	0.1	–	–
1468	*trans*-1,2-Limonene epoxide	0.1	–	–	–	–
1473	Acetic acid	–	–	–	0.1	–
1474	*trans*-Sabinene hydrate		2.2	1.8	2.3	1.2
1475	**Menthone**	3.0	**11.9**	1.0	**9.7**	0.2
1482	(Z)-3-hexenyl-2-methyl butyrate	–	–	0.3	–	0.2
1496	3-Nonanol	–	–	0.2	–	0.1
1497	Menthofuran	–	-	–	0.2	–
1497	α-Copane	0.1	–	0.2	–	–
1503	Isomenthone	0.1	5.3	0.1	3.0	–
1506	Decanal	–	–	0.1	–	–
1507	(E,E)-2,4-heptadienal	0.1	–	–	–	–
1532	Camphor	–	–	–-	0.7	–
1535	β-Bourbonene	0.5	0.3	0.2	–	0.8
1541	Neomenthylacetate	–	–	–	0.1	–
1549	β-Cubebene	–	–	0.1	–	–
1553	Linalool	0.3	0.2	0.6	0.5	1.3
1556	*cis*-Sabinene hydrate	–	0.3	0.2	0.3	0.2
1562	Isopinocamphone	–	–	–	–	0.1
1565	8,9-Limonene epoxide-I	0.1	–	tr	–	0.2
1568	1-Methyl-4-acetyl-cyclohexene	–	–	–	–	tr
1571	8,9-Limonene epoxide-II	0.1	–	–	–	0.2
1574	Menthylacetate	–	–	–	0.2	–
1575	*trans*-*p*-Menth-2-en-1-ol	–	0.2	0.1	0.2	–
1586	Pinocarvone	0.1	–	–	–	–
1588	*cis*-Isopulegone	0.1	0.3	–	0.8	–
1590	Bornyl acetate	0.2	–	0.1	–	0.5
1598	*trans*-Isopulegone	–	0.1	–	0.8	–
1600	β-Elemene	–	–	0.2	–	–
1600	Hexadecane	–	–	–	0.2	–
1602	β-Copaene	0.1	–	–	–	–
1604	Neomenthol	–	–	–	0.2	–
1611	Terpinen-4-ol	–	–	–	1.2	1.2
1612	β-Caryophyllene	4.2	4.5	4.6	–	–
1614	Carvacrol methyl ether	–	1.3	–	–	–
1624	*trans*-Dihydrocarvone	–	–	–	0.1	0.2
1628	Aromadendrene	–	0.1	–	–	–
1638	*trans*-*p*-Menth-2,8-dien-1-ol	0.2	0.1	–	0.2	0.2
1639	Menthol	–	0.1	–	5.0	–
1651	Bornyl isobutyrate	–	–	0.2	–-	–
1655	(E)-2-Decenal	–	–	0.2	–	–
1658	Dihydrocarvyl acetate	–	–	–	1.4	–
1662	**Pulegone**	0.8	**12.0**	1.2	**19.5**	0.1
1664	Nonanol	–	–	0.2	–	–
1668	(Z)-β-Farnesen	–	–	0.1	–	–
1670	*trans*-Pinocarveol	–	–	–	–	0.1
1675	Isomenthol	–	0.3	–	–	–
1678	*cis*-*p*-Menth-2,8-dien-1-ol	0.1	–	–	–	0.3
1686	γ-Humulene	0.2	–	–	–	–
1687	α-Humulene	1.0	0.3	0.3	–	–
1700	Heptadecane	–	–	tr	–	–
1683	*trans*-Verbenol	–	0.1	–	–	–
1704	γ-Muurolene	–	0.1	–	–	–
1706	α-Terpineol	0.4	0.7	tr	0.4	1.2
1719	Borneol	0.5	0.4	0.2	0.5	1.0
1726	Germacrene D	–	1.8	1.3	–	–
1729	α-Methyl cinnamaldehyde	–	–	0.3	–	0.1

1738	*cis*-Piperitone oxide	0.6	1.5	–	1.7	2.2
1741	β-Bisabolene	–	0.7	–	–	–
1748	Piperitone	–	–	–	2.0	–
1751	***trans*-Piperitone oxide**	**44.36**	5.3	**30.9**	5.7	**34.2**
1755	Bicyclogermacrene	–	0.4	–	–	–
1757	Carvone	–	–	–	0.3	–
1764	(E)-2-undecenal	–	–	0.2	0.2	–
1773	δ-Cadinene	–	0.2	0.1	–	–
1776	2-Oxo-1,4-cineole	–	–	–	0.2	–
1776	γ-Cadinene	–	0.1	–	–	–
1784	(E)-α-Bisabolenene	–	0.2	–	–	–
1786	8-Hydroxy menthone	–	–	–	0.1	–
1797	Benzyl isobutyrate	–	–	0.2	–	–
1800	Octadecane	–	–	–	0.1	–
1808	Nerol	0.1	–	–	–	–
1811	*trans-p*-Mentha-1(7),8-dien-2-ol	–	0.1	–	–	0.2
1827	(E,E)-2,4-Decadienal	–	–	0.1	–	–
1833	2-Hydroxy piperitone (=Diosphenol)	–	tr	–	–	–
1849	Pulegone epoxide	–	–	–	0.9	–
1850	*trans*-Carveol	–	0.1	–	0.1	–
1864	*p*-Cymen-8-ol	0.2	–	0.1	0.3	–
1865	Isopiperitenone	0.3	0.1	0.1	–	1.8
1868	(E)-Geranyl acetone	–	–	0.4	0.4	–
1880	Benzyl 2-methyl butyrate	–	–	0.3	–	–
1902	Benzyl isovalerate	–	–	–	–	0.2
1906	Ascaridole	–	0.1	–	–	–
1931	8-Methylthio menthone (=*trans-p*-mentha-8-methylthio-3-one)	–	–	–	1.9	–
1946	*cis-p*-Mentha-8-methylthio-3-one	–	–	–-	1.2	–
1946	4-Hydroxy piperitone	0.3	–	0.1	–	0.2
1949	Piperitenone	0.5	5.1	0.4		2.4
1958	E-β-ionone	–	–	0.4	–	–
1966	2-Ethyl-hexanoic acid	–	–	–	–	0.1
1983	**Piperitenone oxide**	**11.69**	1.4	**6.9**	2.6	**10.79**
2001	Isocaryophyllene oxide	0.7	0.1	1.6	0.4	0.2
2003	8,9-Dehydrothymol	–	0.3	0.2	–	0.3
2008	**Caryophyllene oxide**	3.8	0.8	**7.8**	**7.9**	2.0
2037	Salvial-4(14)-en-1-one	–	–	0.3	–	0.1
2045	Humulene epoxide-I	0.1	–	–	–	–
2069	Octanoic acid	–	–	–	–	0.2
2071	Humulene epoxide-II	1.0	0.1	0.4	0.4	0.1
2080	Cubenol	–	–	0.2	–	–
2100	Heneicosane	–	–	0.1	0.2	–
2131	Hexahydro farnesyl acetone	–	–	4.2	1.1	0.2
2144	Spathulenol	1.7	0.5	0.2	0.2	0.2
2179	Tetradecanol	–	–	0.5	–	–
2181	Isothymol	–	0.1	–	–	–
2186	Eugenol	–	–	0.1	–	–
2192	Nonanoic acid	–	–	–	–	0.4
2198	Thymol	1.0	4.2	1.3		1.3
2220	(2E,6Z)-Farnesal	–	–	0.3	–	–
2221	Isocarvacrol	–	tr	–	–	–
2239	**Carvacrol**	–	**10.0**	1.2	0.4	–
2257	Methylethyl hexadecanoic acid	–	–	0.2	–	–
2282	Ethyl hexadecanoate	–	–	0.2	0.7	–
2297	Isophytol	–	–	0.3	–	–
2300	Tricosane	–	–	0.1	0.1	–
2316	Caryophylladienol I	0.1		0.4		0.1
2324	Caryophylla-2(12),6(13)-dien-5α-ol (=Caryophylladienol II)	0.2	0.1	–	0.3	–
2332	Menthofurolactone	–	–	–	0.4	–
2364	Caryophylla-2(12),6-dien-5α-ol (=Caryophyllenol I)	0.2	–	–	0.2	–
2369	Eudesma-4(15),7-dien-1β-ol	–	0.1	1.0	0.6	0.3
2384	Hexadecanol	–	–	2.0	–	–
2396	Farnesyl acetone	–	0.1	–	–	0.3
2405	Caryophylla-2(12),6-dien-5β-ol (=Caryophyllenol II)	–	0.1	1.1	0.9	–
2419	2-Decenoic acid	–	–	–	0.2	–
2472	1-Heptadecanol	–	–	0.1	–	–
2497	Phytyl acetate	–	–	0.5	–	–
2500	Pentacosane	–	–	tr	–	–
2607	Octadecanol	–	–	3.3	–	–
2622	Phytol	–	–	4.7	–	–
2700	Heptacosane	–	–	1.9	–	–
2705	Tetradecanoic acid	–	–	–	–	0.1
2931	Hexadecanoic acid	–	0.3	1.1	1.9	1.0

A: Içel: Silifke, Uzuncaburç on July 11, 2003 (ESSE 14393).
B: Içel: Tarsus, on July 12, 2003 (ESSE 14398).
C: Bartin: Kurucasile, on August 28, 2003 (ESSE 14402).
D: Zonguldak: Kozlu, on August 26, 2003 (ESSE 14400).
E: Manisa: Turgutlu, on July 29, 2001 (ESSE 14381).

Essential oil production: Aerial parts were subjected to water distillation for 3 h using a Clevenger-type apparatus to yield oils in the following percentages: 0.2 %, 1.5 %, trace, 0.1% and 0.5 % for **A**, **B**, **C**, **D** and **E**, respectively.

GC/MS conditions: The GC/MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60 m × 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 ºC for 10 min and programmed to 220 ºC at a rate of 4 ºC/min and kept constant at 220 ºC for 10 min and then programmed to 240 ºC at a rate of 1 ºC/min. Split ratio was adjusted 40:1. The injector temperature was at 250 ºC. MS were taken at 70 eV. Mass range was from m/z 35-450. Library search was carried out using Wiley GC/MS Library and BASER Library of essential oil constituents. The compounds characterized in the oils are listed in Table-2.

RESULTS AND DISCUSSION

During the present study, 54, 68 and 75 components were characterized representing 93.0, 99.8 and 90.7 % of the oils of *Calamintha nepeta* (L.) Savi subsp. *nepeta* (A, B, C). *Trans*-piperitone oxide (44.4 %), piperitenone oxide (11.7 %) and limonene (7.1 %) were detected as main constituents in sample **A**. Pulegone (11.9 %), menthone (11.9 %), carvacrol (10.0 %) and limonene (7.5 %) were found as main constituents in sample **B**. *Trans*-piperitone oxide (30.9 %), caryophyllene oxide (7.8 %) were detected as main constituents in sample **C**.

62 and 82 components were characterized representing 84.2, 93.5 % of the oils of *Calamintha nepeta* (L.) Savi subsp. *glandulosa* (Req.) P.W. Ball (D, E). Pulegone (19.5 %), menthone (9.7 %), caryophyllene oxide (7.9 %), *trans*-piperitone oxide (5.7 %) and menthol (5.0 %) were detected as main constituents in sample **D**. *Trans*-piperitone oxide (34.2 %), limonene (17.3 %) and piperitenone oxide (10.8 %) were found as main constituents in sample **E**.

The previous and present studies have indicated that *Calamintha nepeta* oils are rich in 3-oxo compounds. Their 1,2-epoxy derivatives may predominate in some oils[22,23].

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