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Essential Oil Composition of *Mentha longifolia* (L.) Hudson from the Middle Region of Turkey

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The essential oil of *Mentha longifolia* (L.) Hudson originating from the middle region of Turkey (Kirikkale) was obtained by steam distillation and clevenger-type method with a overall yield of 0.65 and 0.39 %, respectivelly. These essential oils were analyzed by capillary GC-MS using DB-5 and Carbowax-20M columns. Besides, the plant was examined by head-space method *via* PE-Wax. The essential oils are rich in linalool.

Key Words: *Mentha longifolia* (L.) Hudson, Essential oil composition, Capillary GC-MS, Head space.

INTRODUCTION

Mentha is a genus of aromatic perennial herbs belonging to the family of Lamiaceae found over a wide area of the world[1]. The essential oils of several mentha species can be used as natural additives in many foods, medicine, mouthwash, toothwash, chewing gum and confectionary[2] because of their pesticidal, fungicidal, antiinflammatory and antimicrobial properties[3,4].

It is known that geographic origin influences the chemical composition and the yield of the essential oil. Israel's[5] are rich of piperitonone, the samples of mentha from Italy, England, Turkey[5] and Sudan[6] are rich in carvone. Germany[7], France, Poland, Egypt, Africa, India[5] and Lithuania's samples are rich in piperitenone oxide. *Cis*-Carveol was found in high amounts in essential oil of *Mentha longifolia* grown in Iran[9].

The plant of *Mentha longifolia* (L.) Hudson are very common in the middle, south, east and marmara regions of Turkey. In a study[10], the essential oil of *M. longifolia* (L.) Hudson collected from Çatalca was mainly rich in menthyl acetate, Karaburun in menthone, Abant and Armutlu in hydrocarbons. In another study[11], the essential oils of mentha species from northern Turkey were discussed chemotypically on the results of soil, essential oil analysis and chromosome counts. However, the essential oils of these mentha species were investigated only according to their main components and the other chemical components were not given.

The aim of this study is to investigate and clarify the chemical composition of the essential oil of *Mentha longifolia* (L.) Huds. growing wild at Kirikkale in the middle region of Turkey and using by the regions people in food and dying.

The plant collected from Kirikkale was analyzed qualitatively and quantitatively *via* GC and GC-MS on two different columns, on a polar column Carbowax-20M (Table-1) and on a apolar column DB-5 (Table-2).The plant was examined by head space *via* PE-Wax column (Table-3). IR, refractive indices and the yield of the essential oils were analyzed as well. (Table-4).

EXPERIMENTAL

Mentha longifolia (L.) Hudson used in this study was collected from Kirikkale/Turkey (Herbarium number is ISTF-3731). The essential oil was obtained by steam distillation for *ca.* 1 h with a yield of 0.65 % and by a clevenger-type method for *ca.* 2 h with a yield of 0.39 %.

The chemical composition of the essential oils were analyzed using a Carlo Erba 8000 GC-Instrument (FID) combined with a Fisans. Inc. MD 800 MS System. Two capillary colums, Carbowax 20M (polyethylene glycol, 60 m, 0.25 mm I.D.) and DB-5 (5 % phenyl methylsiloxane, 60 m, 0.25 mm I.D.), were used. The operating conditions were as follows: injection temperature 260°C, Helium carier gas flow: 20 psi. Split ratio: 1/100. E.I:70 eV. Temperature programming: 40°C (5 min) - 240°C at 5°C/min, hold 15 min.

The result of head space analysis was obtained by using Perkin Elmer HS 40XL headspace Sampler, Perkin Elmer Auto System XL GC and Perkin Elmer Turbo MS spectrometer. The column was PE-Wax (60 m × 0.25 mm I:D, ft: 0.25 μm), Injector temperature 150°C, helium carrier gas flow 1 mL/min, temperature programming: 60°C hold 5 min.

The IR spectra were recorded using a Jasco FT/IR-5300 instrument. The refractive index was measured with a Carl-Zeiss instrument model 15884.

RESULTS AND DISCUSSION

The essential oil, obtained by steam distillation was marked as **A** and by clevenger-type method as **B**.

The chemical composition of **A** and **B** are listed in Tables 1 and 2. The linear retention indices (RI) for all the compounds were determined by co-injection of the sample with a solution containing the homologous series of *n*-alkanes. The individual constituents were identified by their linear retention indices and also by comparing their mass spectra with the Wiley and Nist mass spectral database and with the literature data.

TABLE-1
PERCENTAGE COMPOSITION OF ESSENTIAL OILS OF
M. longifolia ON CARBOWAX-20M

RT (min)	Compounds	**A** Area (%)	**B** Area (%)	RI
17.40	β-Citronellene	6.95	6.37	950
17.56	α-Thujene	1.30	1.25	1038
18.09	α-Terpinene	3.06	2.97	1184
18.76	Limonene	10.20	9.45	1194
19.18	β-Phellandrene	1.35	1.19	1204
19.41	1,8-Cineole	3.18	2.14	1212
19.89	*cis*-Ocimene	4.07	3.73	1250
20.40	γ-Terpinene	3.48	2.14	1255
20.51	δ-3-Carene	6.12	5.91	1289
21.40	*p*-Cymene	0.79	0.64	1294
21.68	δ-2-Carene	3.11	2.97	1388
23.33	3-Octanyl acetate	0.84	0.77	1422
24.59	α-Pyronene	0.54	0.27	1435
25.17	3-Octanol	0.36	0.33	1441
27.41	Acetic acid	1.69	1.32	1459
29.74	Linalool	25.74	28.35	1539
30.04	Linalyl acetate	3.52	3.52	1548
31.55	*trans*-Caryophyllene	1.69	1.29	1595
32.46	α-Thujone	4.30	5.59	1685
33.01	2,7-Dimethyl-1,6-octadiene	0.89	1.08	1705
33.29	2,6-Dimethyl-6-hepten-3-one	0.28	0.38	1713
34.19	Terpinyl acetate	4.06	4.02	1725
34.61	Neryl acetate	0.78	1.10	1732
34.86	*trans*-Isolimonene	0.29	0.36	1800
35.20	3-Decen-2-one	0.71	0.79	1822
35.37	Lavanduyl acetate	1.65	1.27	1825
35.73	2,3,4,5-Tetramethyl-3-hexene	2.56	3.08	1833
35.86	2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-one	–	1.66	1838
37.50	2-Hydroxy-3-methyl-6-(1-methyl-ethyl)-2-cyclohexen-1-one	0.39	0.43	1856
37.63	*trans*-Geraniol	0.68	0.77	1870
38.67	Thymol acetate	0.35	0.40	1896
45.15	Thymol	1.37	1.85	2121
45.92	Carvacrol	1.07	1.43	2148

The result of head space analysis of the mentha plant is given in Table-3.

The IR spectras, refractive indices and yields are given in Table-4.

TABLE-2
PERCENTAGE COMPOSITION OF ESSENTIAL OILS OF *M. longifolia* ON DB-5

RT (min)	Compounds	**A** Area (%)	**B** Area (%)	RI
24.95	α-Thujene	0.16	–	931
25.44	α-Pinene	0.14	–	939
26.85	β-Citronellene	0.10	0.20	947
27.04	γ-Campholenaldehyde	0.35	–	960
27.33	β-Myrcene	4.38	8.15	991
28.29	α-Phellandrene	0.77	1.53	1005
28.75	α-Terpinene	4.86	8.33	1018
29.25	Limonene	6.25	11.37	1031
29.40	β-Phellandrene	0.73	1.31	1031
29.49	1,8-Cineole	6.87	9.54	1033
30.30	γ-Terpinene	3.00	3.22	1062
31.58	Linalool	41.34	27.59	1098
32.09	3-Octanol acetate	0.69	0.77	1124
32.60	α-Pyronene	0.12	0.24	1146
33.14	β-Pyronene	0.11	0.25	1149
34.10	*p*-Menthone	0.28	0.34	1154
34.53	Isomenthone	0.24	0.38	1165
35.08	3-Decen-2-one	0.30	0.74	1188
35.36	α-Terpineol	0.67	1.18	1191
35.61	6-Nonen-1-ol	3.60	5.49	1213
35.76	2,6-Dimethyl-6-hepten-3-one	0.39	–	1218
35.96	1-Undecyne	0.67	–	1220
36.13	*cis*-3-Hexenyl-2-methyl butanoate	0.11	–	1225
36.83	Linalyl acetate	8.12	2.40	1239
37.21	Carvone	2.18	2.30	1242
37.53	3,7-Dimethyl-1,6-octadien-3-ol-4-one	3.54	4.18	1260
38.17	Thymol	0.70	1.13	1290
38.60	Carvacrol	0.48	0.93	1298
39.11	Diosphenol	0.11	0.48	1310
40.19	Terpinyl acetate	0.43	–	1345
40.31	Neryl acetate	3.61	2.42	1360
40.55	2,5,6,6-Tetramethyl-2,4-cyclohexadiene-1-one	0.24	0.20	1373
40.71	Geranyl acetate	1.06	1.72	1383
41.14	4-Ethenyl-1,4-dimethyl cyclohexene	0.12	–	1390
43.12	β-Elemene	0.06	–	1391
43.34	*cis*-Caryophyllene	1.82	1.12	1404
44.33	6,6-Dimethyl-2-methylene-bicyclo[3.1.1] heptane	0.15	–	1447
45.03	γ-Cadinene	0.11	–	1506
45.79	δ-Cadinene	0.16	0.25	1515
46.81	3-Oxo-α-Ionone	0.76	0.37	1524

TABLE-3
RESULT OF HEAD SPACE ANALYSIS ON PE-WAX

RT (min)	Compound	Area (%)	RI
12.63	Limonene	10.28	1194
13.03	1,8-Cineole	15.42	1212
15.82	3-Octanol acetate	7.97	1422
18.65	*p*-Menthone	4.48	1525
19.65	Linalool	26.21	1539
19.86	Linalyl acetate	8.08	1548
22.04	Terpinyl acetate	14.85	1725
22.74	2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-one	12.72	1838

TABLE-4
IR SPECTRA, REFRACTIVE INDICES AND YIELDS OF THE ESSENTIAL OILS

Essential oil	IR spectra (cm^{-1})	$n_D^{25°C}$	Yield (%)
A	3449, 3084, 2925, 1716, 1455, 1374, 1259, 1112, 997	1.4629	0.65
B	3446, 3084, 2926, 1736, 1451, 1374, 1255, 1116, 997	1.4621	0.39

The major components of the two oils (**A** and **B**) were linalool (25.74, 28.35 %), limonene (10.20, 9.45 %), β-citronellene (6.95, 6.37 %), Δ-3-carene (6.12, 5.91 %), respectively on carbowax-20 M. Linalool (41.34 %), linalyl acetate (8.12 %), 1,8-cineole(6.87 %), limonene (6.25 %) were detected as major components of **A** on DB-5. On the same column, the main components of **B** were linalool (27.59 %), limonene (11.37 %), 1,8-cineole (9.54 %), α-terpinene (8.33 %). The head space analysis of the mentha plant on PE-WAX was characterized by a high contribution of the following compound *i.e.*, linalool (26.21 %), 1,8-cineole (15.42 %), terpinyl acetate (14.85 %).

The common components of investigated mentha in this study are linalool, limonene, 1,8-cineole, terpinyl acetate and linalyl acetate. Linalool is a naturally-occuring terpene alcohol with many commercial applications, such as a scent in domestic products such as soap, detergent, shampoo and lotion and also as a chemical intermediate. One common product of linalool is the well-known vitamin E.

Limonene is a hydrocarbon, classed as a terpene. It is a clear, colourless liquid at room temperatures with an extremely strong smell of oranges. D-limonene is used in food manufacturing as a flavouring agent and added to cleaning products such as hand cleansers to give a lemon-orange fragrance. Limonene is increasingly used as an enviromentally friendly

alternative to mineral oils as a solvent for cleaning purposes, such as the removal of oil from machine parts, being more easily biodegrable than the mineral oils and produced from a renewable source.

1,8-Cineole is a repellent agent and the *Mentha longifolia* Hudson in this study can be appreciated with this property.

Terpinyl acetate and linalyl acetate are valuable fragrance compounds which were found in the *Mentha longifolia* Hudson in this study by head space analysis higher amounts than the others, **A** and **B**. The essential oils **A** and **B** being enriched in linalyl acetate by converting their linalool component to linalyl acetate, can be more utilized in cosmetic and flavour industries.

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