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Essential Oil Compositions of Four Mushrooms: *Scleroderma verrucosum*, *Cortinarius infractus*, *Hypholama capnoides* and *Hypholama fasciculare* from Turkey

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The chemical composition of the essential oils obtained from four varieties of Mushrooms, *ie. Scleroderma verrucosum*, *Cortinarius infractus*, *Hypholama capnoides* and *Hypholama fasciculare* were analyzed by GC-MS. 13, 36, 8 and 10 components, respectively were identified in the essential oils and the main components were found to be 3-octanone from *S. verrucosum*, musk ambrette from *C. infractus*, 1-octen-3-ol from *H. capnoides* and *H. fasciculare* in the ratios of 49.1, 62.3, 21.7 and 18.2 %, respectively. The isolated essential oils of the fruiting bodies of mushrooms were also tested for antimicrobial activity against the bacteria *E. coli*, *K. pneumoniae*, *P. aeruginosa*, *E. faecalis*, *S. aureus*, *B. cereus* and the fungus *C. tropicalis*, at maximum essential oil concentrations in hexane of 500, 200, 50 and 250 µg/mL, respectively. No biological activity was observed against all the test microorganisms.

Key Words: *Scleroderma verrucosum*, *Cortinarius infractus*, *Hypholama capnoides*, *Hypholama fasciculare*, *Essential oil*, Antimicrobial activity, GC-MS.

INTRODUCTION

Scleroderma verrucosum (Bull.) Pers. (Sclerodermataceae), *Cortinarius infractus* Berk. (Cortinariaceae), *Hypholoma capnoides* (Fr.) P. Kumm. (Strophariaceae) and *Hypholoma fasciculare* (Huds.) P. Kumm. (Strophariaceae) grow in Turkey[1-3]. One of the mushrooms *H. capnoides* is an edible, two of them *S. verrucosum* and *H. fasciculare* are not edible and the last one *C. infractus* is not known as a food source mushrooms.

Previous phytochemical studies in the mushrooms of *H. capnoides* and *H. fasciculare* have shown the presence of different natural compounds

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including triterpene compounds[4], aryl alcohols[5], fatty acids[6] and chlorinated aromatics[7]. Antioxidant activity of *H. fasciculare* is previously reported in literature[8]. To our knowledge, there is no published report on the chemical composition and antimicrobial activity of the essential oils of *S. verrucosum*, *C. infractus*, *H. capnoides* and *H. fasciculare*. As part of this systematic research, the essential oil constituents of the mushrooms were obtained by the widely used hydrodistillation method in a Clevenger-type apparatus. The obtained crude essential oils were then investigated by GC-MS technique. Identification of the compounds was made by a typical library search (NIST, WILLEY) and literature comparison[9-12].

EXPERIMENTAL

Plant material: *S. verrucosum*, *C. infractus*, *H. capnoides* and *H. fasciculare* were harvested from the Liser High Plateau-Maçka (Trabzon-Turkey) in October-November 2005. Voucher specimens have been deposited in the Fungarium of Fatih Faculty of Education at Karadeniz Technical University, Trabzon-Turkey (*S. verrucosum*; SES 2439-2005, *C. infractus*; 2440-2005, *H. capnoides*; SES 2441-2005 and *H. fasciculare*; SES 2442-2005). The mushrooms were identified immediately after collection[1-3].

Isolation of the essential oil: Crude essential oils of *S. verrucosum*, *C. infractus*, *H. capnoides* and *H. fasciculare* were obtained from the fruiting bodies of mushrooms (*ca.* 40 g, each) by hydrodistillation in a Clevenger-type apparatus with cooling bath (-15ºC) system (3 h) (yields: 0.15, 0.10, 0.10 and 0.12 % (v/w), respectively). The chemical constituents of the oils were determined by GC-MS analysis (Agilent-6890N/5973 Network System)[9-12].

Gas chromatography: GC-MS analyses were performed using an Agilent-5973 Network System. A mass spectrometer with an ion trap detector in full scan mode under electron impact ionization (70 eV) was used. The chromatographic column used for the analysis was HP-5 capillary column (30 m × 0.32 mm i.d., film thickness 0.25 μm). Helium was used as carrier gas at a flow rate of 1 mL/min. The injections were performed in splitless mode at 230°C. 1 μL essential oil solution in hexane (HPLC grade) was injected and analyzed with the column held initially at 60°C for 2 min and then increased to 260°C with a 5°C/min heating ramp and subsequently kept at 260°C for 13 min. The relative percentage amounts of the separated compounds were calculated from total ion chromatograms by a computerized integrator.

Antimicrobial activity assessment: All test microorganisms were obtained from the Refik Saydam Hifzissihha Institute (Ankara, Turkey) and were as follows: *Escherichia coli* ATCC 25922, *Yersinia*

TABLE-1
IDENTIFIED COMPONENTS IN THE ESSENTIAL OILS OF THE MUSHROOMS: *Scleroderma verrucosum*, *Cortinarius infractus, Hypolama capnoides* and *Hypolama fasciculare*[a,b]

No.	Compd.	A		B		C		D		Exp. RI	Lit. RI
		Area (%)	Q (%)	Area (%)	Q (%)	Area (%)	Q (%)	Area (%)	Q (%)		
1	Santene	-	-	0.2	81	-	-	-	-	886	889
2	Anisole	0.3	93	-	-	-	-	-	-	922	920
3	Tricyclene	-	-	0.5	95	-	-	-	-	930	927
4	α-Pinene	1.6	94	3.2	94	8.7	94	7.2	94	940	939
5	Camphene	2.0	97	3.7	95	8.5	95	8.9	95	956	954
6	Benzaldehyde	0.3	80	-	-	-	-	-	-	961	960
7	β-Pinene	-	-	2.4	95	-	-	-	-	980	979
8	1-Octen-3-ol	-	-	1.9	90	21.7	90	18.2	90	982	979
9	3-Octanone	49.1	87	0.7	91	8.0	91	5.3	91	986	984
10	Myrcane	0.7	86	-	-	-	-	-	-	993	991
11	3-Octanol	26.8	80	0.3	80	14.3	80	11.1	80	994	991
12	α-Terpinene	-	-	0.4	93	-	-	-	-	1017	1017
13	*o*-Cymene	-	-	0.1	94	-	-	-	-	1029	1026
14	*dl*-Limonene	2.6	96	5.5	96	10.8	96	14.2	96	1032	1029
15	Benzene acetaldehyde	0.5	91	0.3	91	-	-	-	-	1043	1042
16	Cumene	-	-	-	-	1.6	80	-	-	1064	1065
17	*n*-Octanol	5.1	90	-	-	-	-	-	-	1067	1068
18	Terpinolene	0.2	96	-	-	-	-	-	-	1086	1089
19	E-Pinocarveol	-	-	0.5	87	-	-	-	-	1136	1139
20	Camphor	-	-	0.6	95	-	-	-	-	1143	1146
21	Pinocarvone	-	-	0.4	86	-	-	-	-	1161	1165
22	Borneol	0.2	90	0.5	90	-	-	-	-	1165	1169
23	Terpinen-4-ol	-	-	0.2	94	-	-	-	-	1174	1177
24	α-Terpineol	-	-	0.2	80	-	-	-	-	1187	1189
25	Myrtenol	-	-	0.5	80	-	-	-	-	1193	1196
26	(2E,4E)-Nonadienal	-	-	0.3	80	-	-	-	-	1213	1212
27	Bornyl acetate	3.2	96	6.9	96	8.4	98	13.8	96	1286	1289
28	E-Sabinyl acetate	-	-	0.2	80	-	-	-	-	1294	1291
39	(2E,4E)-Decadienal	-	-	0.2	87	-	-	-	-	1316	1317
30	α-Copaene	-	-	0.2	98	-	-	-	-	1377	1377
31	E-Caryophyllene	-	-	0.3	98	-	-	1.3	80	1420	1419
32	α-Humulene	-	-	0.2	98	-	-	-	-	1455	1455
33	Germacrene-D	-	-	0.2	93	-	-	-	-	1481	1485
34	δ-Cadinene	-	-	0.1	97	-	-	-	-	1525	1523
35	E-Nerolidol	-	-	0.3	87	-	-	1.5	87	1565	1563
36	Caryophyllene oxide	-	-	0.4	80	-	-	-	-	1585	1583
37	Hexadecane	-	-	0.4	94	-	-	-	-	1600	1600
38	α-Cadinol	-	-	0.3	87	-	-	1.5	91	1657	1654
39	Musk ambrette	-	-	62.3	80	-	-	-	-	1926	1930
40	Manool	-	-	0.4	80	-	-	-	-	2058	2057
41	Dehydroabietal	-	-	0.2	99	-	-	-	-	2271	2275
42	4-Epi-Abietal	-	-	0.3	86	-	-	-	-	2303	2299
Total identified isolate		92.6		95.3		82.0		83.0			

Unknown	RI	m/z (%)	A	B	C	D
Un-1	915	103(4), 85(84), 75(40), 56(28), 55(100), 53(8).	-	-	-	3.4
Un-2	916	103(4), 85(68), 75(28), 59(100), 56(12).	-	-	3.3	-
Un-3	934	89(56), 85(99), 73(98), 69(20), 57(100), 53(8).	-	-	-	3.8
Un-4	935	93(4), 89(44), 85(72), 73(88), 57(100), 53(8).	-	-	4.0	-
Un-5	981	100(4), 83(100), 71(36), 67(8), 58(20), 55(56).	-	-	2.4	4.5
Un-6	982	126(4), 105(12), 83(100), 71(44), 55(72), 51(4).	0.5	-	-	-
Un-7	1005	138(16), 93(28), 81(100), 69(20), 57(28), 50(2).	0.7	-	-	-
Un-8	1064	120(16), 105(36), 81(32), 68(28), 57(100), 51(12).	-	-	1.8	-
Un-9	1153	137(8), 120(100), 91(60), 65(80), 51(12).	-	-	2.3	-
Un-10	1555	218(8), 160(52), 145(100), 105(36), 91(24), 55(8).	-	-	-	1.7
Un-11	1715	208(4), 182(8), 109(24), 96(56), 69(60), 57(100).	-	0.6	-	-
Total Unknown			1.2	0.6	13.8	13.4
Total identified isolate			92.6	95.3	82.0	83.0
Total			93.8	96.6	95.8	96.4

[a]RI, retention index; LRI, literature retention index; Q: Quality; **A**: *Scleroderma verrucosum;* **B**: *Cortinarius infractus;* **C**: *Hypolama capnoides ;* **D**: *Hypolama fasciculare*; [b]Compounds are listed in order of elution. RI (retention index) values are calculated from retention times relative to that of *n*-alkanes (C_6-C_{32}) on the non-polar HP-5 column.

pseudotuberculosis ATCC 911, *Klebsiella pneumoniae* ATCC 13883, *Enterococcus faecalis* ATCC 29212, *Pseudomonas auroginosa* ATCC 10145, *Staphylococcus aureus* ATCC 25923, *Bacillus cereus* 709 ROMA, *Candida albicans* ATCC 60193, *Candida tropicalis* ATCC 13803.

Agar well diffusion method: The antimicrobial activities of the essential oils of *S. verrucosum*, *C. infractus*, *H. capnoides* and *H. fasciculare* were tested by the agar dilution method against 7 bacteria and 2 yeast like fungi[13,14].

RESULTS AND DISCUSSION

The composition of essential oils of *S. verrucosum*, *C. infractus*, *H. capnoides* and *H. fasciculare* were analyzed by GC-MS with HP-5 column. A total of 13, 36, 8 and 10 components were characterized on the basis of a typical library search with selecting only the components showing matches exceeding 80 %, which represented about 92.6, 95.3, 82.0 and

83.0 % of total composition of the essential oils in *S. verrucosum*, *C. infractus*, *H. capnoides* and *H. fasciculare*, respectively[9-12]. The general chemical profile of the essential oils, the percentage content and retention indices of the constituents are summarized in Table-1.

The main constituents of the investigated essential oils of mushrooms are the following: 3-octanone (49.1 %) and 3-octanol (26.8 %) in *S. verrucosum*; musk ambrette (62.3 %) and *dl*-limonene (5.5 %) in *C. infractus*; 1-octen-3-ol (21.7 %) and 3-octanol (14.3 %) in *H. capnoides*; and 1-octen-3-ol (18.2 %) and *dl*-limonene (14.2) in *H. fasciculare*. As shown in the Table-1, the essential oil compositions of *H. capnoides* and *H. fasciculare* are similar.

The antimicrobial activity of the essential oils from *S. verrucosum*, *C. infractus*, *H. capnoides* and *H. fasciculare* were tested against the bacteria *E. coli*, *K. pneumoniae*, *P. aeruginosa*, *E. faecalis*, *S. aureus*, *B. cereus* and the fungus *C. tropicalis* at maximum essential oil concentrations in hexane of 500, 200, 50 and 250 µg/mL, respectively, by using ampicillin and fluconazole as standard antibacterial and antifungal agents. However, no antimicrobial activity was observed against all the test microorganisms[13,14].

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