Asian Journal of Chemistry Vol. 21, No. 7 (2009), 5505-5509

Essential Oils in Mosses (*Brachythecium salebrosum, Eurhynchium pulchellum* and *Plagiomnium undulatum*) Grown in Turkey

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The essential oils of *Brachythecium salebrosum, Eurhynchium pulchellum* and *Plagiomnium undulatum* were investigated by GC-FID and GC-MS. A total of 39 compounds were identified, constituting over 85.2, 80.9 and 88.8 % of total oil composition of *B. salebrosum, E. pulchellum* and *P. undulatum* and the main components of them were *n*-nonanal (66.3 and 36.2 %) and γ-elemene (24.1 %), respectively. Sesquiterpene hydrocarbons (51.7 %) were shown to be the main group of *P. undulatum*. Aliphatic aldehydes were the major constituents of *B. salebrosum* and *E. pulchellum* with the ratio of 73.3 and 57.9 %, respectively.

Key Words: *Brachythecium salebrosum, Eurhynchium pulchellum, Plagiomnium undulatum*, Essential oils, GC-FID, GC-MS.

INTRODUCTION

The chemistry of mosses has been subject to investigations over the last 30 years mainly because of the abundance of aliphatic/aromatic aldehydes and terpenoids[1-4]. The mosses are represented by *ca.* 25000 taxa worldwide and differ by the lack of oil bodies[5-7]. Most of the review articles on the chemistry of mosses mentioned the absence or only scattered occurrence of terpenoid compounds particularly sesquiterpene hydrocarbons. But, later investigations showed the occurrences of a great variety of mono-, sesqi- and diterpenes and in addition, many aliphatic and aromatic compounds[1-4]. Some mosses generate a pleasant, sometimes distinct odour in the fresh state.

In Turkey, the genera *Brachythecium, Eurhynchium* and *Plagiomnium* are represented by 23, 8 and 15 taxa, respectively[5-7]. Previous study on the essential oil of *Plagiomnium undulatum* (Hedw.) T. J. Kop. (Mniaceae) which was collected from Germany and Austria, has shown the presence of *n*-heptanal, α-pinene, camphene, 3-octanone, β-pinene, 2-pentylfuran, Δ-3-carene, limonene, E-2-octenal, 1-octen-3-ol, 1-octanol, *n*-nonanal, pinocarvone, borneol, β-cyclocitral, bornylacetate,

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2E,4E-decadienal, α-terpiylacetate, geosmin, β-cedrene, amphora-4,11-diene, β-ionone, β-bisabolene, β-sesquiphellandrene, 1-epi-cubenol, α-cadinol, 3-methoxy-bibenzyl, abietatriene and manool. To our best of knowledge, there is no previous report on the composition of the essential oil analysis of *Brachythecium salebrosum* (F. Weber & D. Mohr) Schimp, (Brachytheciaceae) and *Eurhynchium pulchellum* (Hedw.) Jenn. (Brachytheciaceae). The volatile constituents of the fresh mosses were obtained by hydrodistillation method in a Clevenger-type apparatus. The obtained crude essential oils were then investigated by GC and GC-MS technique[8-17].

EXPERIMENTAL

Brachythecium salebrosum (F. Weber & D. Mohr) Schimp was collected on the stony place in *Corylus* sp. communities from Akçaabat-Yidizli Village, Trabzon, Turkey (at a height of *ca.* 450 m) in April 2008. *Eurhynchium pulchellum* (Hedw.) Jenn. was collected in and edge of the forest under the *Carpinus batulus, Alnus glutinosa* and *Rhodendron ponticum* from Akçaabat-Yidizli Village, Trabzon, Turkey (at a height of *ca.* 500 m) in April 2008. *Plagiomnium undulatum* (Hedw.) T. J. Kop. was collected on the soil of the forest under the *Carpinus batulus* and *Alnus glutinosa* from Akçaabat-Yidizli Village, Trabzon-Turkey (at a height of *ca.* 550 m) in April 2008. The mosses were authenticated immediately after collection[5-7]. Voucher specimens were deposited in the Herbarium of the Department of Biology, (Özdemir-1110, 1112 and 1111, respectively), Karadeniz Technical University, Turkey.

Isolation of the essential oils: The fresh plant materials were separated and cut into small pieces. Crude essential oils of *B. salebrosum*, *E. pulchellum* and *P. undulatum* were obtained from the fresh mosses (*ca.* 50 g, each) by hydrodistillation in a Clevenger-type apparatus with cooling bath (-12 ºC) system (4 h) (yields: 0.14, 0.05 and 0.18 % (v/w), respectively). The obtained oils were dissolved in HPLC grade *n*-hexane (0.5 mL) and dried over anhydrous sodium sulphate and stored at 4-6 ºC in a sealed brown vial. One mL of the essential oils was directly injected separately into GC and GC-MS instrument.

Gas chromatography and Gas chromatography-mass spectrometry (GC-MS) analysis: GC-FID and GC-MS analyses were done as described previously[8].

Identification of components: Retention indices of all the components were determined by Kovats method using *n*-alkanes (C_6-C_{32}) as standards. The constituents of the oil were identified by comparison of their mass spectra with those of mass spectral libraries (NIST and Wiley), authentic compounds (β-pinene, decane and pentacosane) and with data published in the literature[8-17].

RESULTS AND DISCUSSION

Collected mosses were carefully inspected for the contaminations and the other plant materials and the soil were completely removed. The essential oils of the mosses were obtained by the widely used hydrodistillation method in a Clevenger-type apparatus. The obtained crude essential oils were then investigated by GC-FID

and GC-MS technique[8-17]. Chemical composition of the essential oils of *B. salebrosum, E. pulchellum* and *P. undulatum* are listed in Table-1. The GC-MS analysis of the essential oils of *B. salebrosum, E. pulchellum* and *P. undulatum* allowed the identification of 19, 7 and 25 components, respectively. Altogether, 39 essential components were identified by GC and GC-MS with HP-5 column. The number of volatile compounds present in the oil of *P. undulatum* is greater than in *B. salebrosum* and *E. pulchellum*.

TABLE-1
IDENTIFIED COMPONENTS IN THE ESSENTIAL OILS OF *B. salebrosum, E. pulchellum* AND *P. undulatum*

Lit. RI[8-17]	Exp. RI	Compound	A[a,b]	B[a,b]	C[a,b]
			% Area	% Area	% Area
902	904	*n*-Heptanal	2.7	-	-
979	977	β-Pinene[c]	1.4	-	-
984	984	3-Octanone	1.0		-
990	990	2-Pentyl furan	0.5	-	-
999	999	*n*-Octanal	1.7	-	-
1000	1000	Decane[c]	0.3	8.1	-
1068	1070	*n*-Octanol	3.1	-	-
1101	1103	*n*-Nonanal	66.3	36.2	6.1
1202	1204	*n*-Decanal	1.1	4.6	1.3
1264	1266	(2*E*)-Decenal	0.4	-	-
1307	1309	*n*-Undecanal	0.5	5.1	1.3
1317	1320	(2E,4E)-Decadienal	0.3	-	-
1391	1393	β-Elemene	-	-	1.1
1408	1409	Tetrahydrogeranyl acetone	0.7	-	-
1419	1420	(E)-Caryophyllene	-	-	1.1
1437	1435	γ-Elemene	-	-	24.1
1460	1462	Allo-aromadendrene	-	-	1.2
1462	1465	Farnesan	0.3	-	-
1471	1469	β-Acoradiene	-	-	1.1
1480	1479	γ-Muurolene	-	-	1.7
1497	1497	Viridiflorene	-	-	2.3
1500	1502	α-Muurolene	-	4.9	2.1
1507	1510	(Z)-α-Bisabolene	-	-	1.5
1514	1516	γ-Cadinene	-	-	2.1
1523	1525	δ-Cadinene	-	-	11.7
1531	1534	(E)-γ-Bisabolene	-	-	0.6
1539	1541	α-Cadinene	-	-	0.7
1576	1578	Germacrene D-4-ol	-	-	0.9
MS-1	1586	Chiloscyphone	-	-	2.7
1613	1616	*n*-Tetradecanal	0.3	-	0.7
MS-2	1632	Di-epi-α-Cedrene	-	-	0.4

Lit. RI[8-17]	Exp. RI	Compound	A[a,b]	B[a,b]	C[a,b]
			% Area	% Area	% Area
1642	1645	Tau-Muurolol	-	-	7.3
1654	1653	α-Cadinol	-	-	9.5
1717	1720	*n*-Pentadecanal	-	12.0	2.9
1790	1791	1-Octadecene	0.9	-	-
1855	1853	Hexahydrofarnesyl acetone	3.1	10.0	2.6
1876	1878	*n*-Hexadecanol	0.3	-	-
1943	1941	(*E*)-Phytol	0.3	-	-
2500	2501	Pentacosane[c]	-	-	1.8
		Total isolate	85.2	80.9	88.8
MS-1	m/z (%):	218(12), 175(36), 147(98), 107(100), 91(80), 69(75), 55(48).			
MS-2	m/z (%):	204(48), 161(72), 147(24), 119(100), 105(64), 93(52), 55(68).			

A = *Brachythecium salebrosum*, B = *Eurhynchium pulchellum*, C = *Plagiomnium undulatum*. [a]RI calculated from retention times relative to that of *n*-alkanes (C_6-C_{32}) on the non-polar HP-5 column. [b]Percentages obtained by FID peak-area normalization. [c]Identified by authentic samples.

TABLE-2
CHEMICAL CLASS DISTRIBUTION IN THE ESSENTIAL OILS OF *B. salebrosum, E. pulchellum* AND *P. undulatum*

Compound class	A		B		C		
	% Area	N[a]	% Area	N[a]	% Area	N[a]	
						Exp.	Lit.[4]
Terpenoids							
Monoterpene hydrocarbons	1.4	1	-	-	-	-	5
Oxygenated monoterpenes	-	-	-	-	-		3
Sesquiterpene hydrocarbons	0.3	1	4.9	1	51.7	14	3
Oxygenated sesquiterpenes	-	-	-	-	20.4	4	2
Oxygenated diterpenes	0.3	1	-	-	-	-	2
Terpene related compounds	3.8	2	10.0	1	2.6	1	4
Aldehydes	73.3	8	57.9	4	12.3	5	4
Hydrocarbons	1.2	2	8.1	1	1.8	1	-
Others	4.9	4	-	-	-	-	6

[a]N = Number of compounds; A = *Brachythecium salebrosum*, B = *Eurhynchium pulchellum*, C = *Plagiomnium undulatum*

The main constituents of *B. salebrosum* were *n*-nonanal (66.3 %), *n*-octanol (3.1 %), hexahydrofarnesyl acetone (3.1 %), *n*-heptanal (2.7 %) and *n*-octanal (1.7 %). The major components of *E. pulchellum* were *n*-nonanal (36.2 %), *n*-pentadecanal (12.0 %), hexahydrofarnesyl acetone (10.0 %), *n*-decane (8.1 %) and *n*-undecanal (5.1 %). The main components of *P. undulatum* was γ-elemene (24.1 %), δ-cadinene (11.7 %), α-cadinol (9.5%), τ-muurolol (7.3 %) and *n*-nonanal (6.1 %). *n*-Nonanal (66.3, 36. and 6.1 %), *n*-undecanal (0.5, 5.1 and 1.3 %) and hexahydrofarnesyl acetone (3.1, 10.0 and 2.6 %) were present in all three plants of mosses, respectively.

The qualitative and quantitative determination of essential oil of *B. salebrosum* and *E. pulchellum* showed that major constituents were aliphatic aldehydes with

the ratio of 73.3 and 57.9 %, respectively. Sesquiterpene hydrocarbons were shown to be the main group of constituents of *P. undulatum* with the ratio of 51.7 %. Oxygenated sesquiterpenes can be seen only in the essential oil of *P. undulatum* (Table-2).

In comparison with the previously reported composition of the essential oil of *P. undulatum*[4], showed quite differences and only *n*-nonanal and α-cadinol were the same. Monoterpene hydrocarbons, oxygenated monoterpenes and sesquiterpene hydrocarbons were present in the oil of *P. undulatum* collected from Germany and the monoterpene hydrocarbons are major constituent of the oil[4]. But, we only observed sesquiterpene hydrocarbons which is a main component in the essential oil of *P. undulatum*. The general chemical profile of the essential oils of mosses showed big differences in present case, which can be explained by the environmentally, locality and the subspecies of the plant used.

ACKNOWLEDGEMENTS

This study was supported by grants from Karadeniz Technical University Research Fund and State Planning Agency (DPT) of Turkey.

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(*Received*: 29 October 2008; *Accepted*: 30 April 2009) AJC-7499