Asian Journal of Chemistry Vol. 22, No. 9 (2010), 7285-7290

Volatile Constituents in Mosses (*Brachythecium albicans* (Hedw.) Schimp., *Bryum pallescens* Schleich. ex Schwagr and *Syntrichia intermedia* Brid.) Grown in Turkey

TURAN OZDEMIR†, OSMAN UCUNCU, TAYYIBE BEYZA CANSU, NURAN KAHRIMAN and NURETTIN YAYLI*
Department of Chemistry, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey
Fax: (90)(462)3253196; Tel: (90)(462)3772486
E-mail: yayli@ktu.edu.tr

The essential oils of mosses [*Brachythecium albicans* (Hedw.) Schimp., *Bryum pallescens* Schleich. ex Schwagr and *Syntrichia intermedia* Brid.] have been investigated by GC and GC/MS. The main compounds found in the oils of *B. albican*, were nonanal (41.0 %) and 4,4-dimethyl-E-2-pentene (6.6 %). The major components identified in the oils of *B. pallescens*, were nonanal (29.3 %) and Z-phytol (8.9 %). E-2-tetradecen-1-ol (9.9 %) and nonanal (8.3 %) were the main compounds found in the oil of *S. intermedia*. The essential oils of *B. albican*, *B. pallescens* and *S. intermedia* were rich in aldehydes (51.3, 41.7 and 18.0 %), hydrocarbons (13.5, 7.9 and 24.1 %) and alcohols (4.3, 9.2 and 13.5 %), respectively. The amounts of terpenoids present in the investigated mosses are generally less than non-terpenoid compounds.

Key Words: *Brachythecium albicans*, *Bryum pallescens*, *Syntrichia intermedia*, Essential oils, GC-FID, GC-MS.

INTRODUCTION

Mosses are used as traditional medicine for the treatment of broken bones, eye diseases, eczema, cuts, bites and burns in China and India[1]. The mosses are represented by approximately 25.000 taxa in the world[2-4]. Mosses generate distinct, sometimes a pleasant odour in the fresh state. The essential oil composition of the mosses has been investigated to identify aliphatic/aromatic aldehydes and terpenoids[5-11]. Most of the articles on the chemistry of mosses mentioned the absence or trace amount of terpenoid compounds but, latest investigations showed the occurrences of a great variety of terpenes[6-10].

In Turkey, the genus Brachythecium, Bryum and Syntrichia are represented by 26, 45 and 23 taxa (19, 30 and 15 species and 7, 15 and 8 varieties)[4-6], respectively. To our best of knowledge, there are no previous report on the composition of the

†Department of Biology, Faculty of arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey.

essential oil analysis of *B. albican*, *B. pallescens* and *S. intermedia*. 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-FID and GC-MS technique[12-22].

EXPERIMENTAL

Brachythecium albicans (Hedw.) Schimp. was collected in water from Sebinkarahisar, Kinik, Gümüshane, Turkey (at a height of *ca.* 1370 m) in April 2009. *Bryum pallescens* Schleich. ex Schwagr was collected in water from Sebinkarahisar, Temeltepe, Gümüshane, Turkey (at a height of *ca.* 1243 m) in March 2009. *Syntrichia intermedia* Brid. was collected on soil from Sebinkarahisar, Ekecek, Gümüshane, Turkey (at a height of *ca.* 1360 m) in March 2009. The mosses were authenticated immediately after collection[2-4]. Voucher specimens were deposited in the Herbarium of the Department of Biology, (ÖZ-1158, ÖZ-1160 and 1154, 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. albican*, *B. pallescens* and *S. intermedia* 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: 0.18, 0.12 and 0.11 % (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 µL of the essential oils was directly injected separately into GC and GC-MS instrument.

Gas chromatography (GC) and Gas chromatography-mass spectrometry (GC-MS) analysis: GC-FID and GC-MS analyses were done as described previously[13,15].

Identification of components: Retention indices of all the components were determined by Kovats method using *n*-alkanes (C_6-C_{32}) as standards. Identification of individual components was made by comparison of their retention times with those of available analytical standards (*n*-decane, *n*-tetradecane, *n*-pentadecane, *n*-hexadecane, *n*-heptadecane, *n*-octadecane, *n*-nonadecane, *n*-eicosane, *n*-heneicosane, *n*-docosane, *n*-tricosane, *n*-tetracosane and *n*-pentacosane) and by computer search, matching mass spectral data with those held in Nist and Wiley library of mass spectra and literature comparison[12-22]. Component relative concentrations were obtained directly from GC peak areas obtained with GC-FID.

RESULTS AND DISCUSSION

The plant material was collected at different locations in Giresun,Turkey[2-4]. Before hydrodistillation the plant material was carefully inspected for contaminations. Conifer needles, other plant material and soil were completely removed. The essential oils of mosses (*B. albican*, *B. pallescens* and *S. intermedia*) were obtained by hydrodistillation method in a Clevenger-type apparatus. The obtained crude essential

TABLE-1
IDENTIFIED COMPONENTS IN THE ESSENTIAL
OILS OF *B. albican*, *B. pallescens* and *S. intermedia*

Exp. RI**	Lit. RI	Compounds	*B. albican*	*B. pallescens*	*S. intermedia*
			Area (%)*	Area (%)*	Area (%)*
		Monoterpenes			
1013	1013	3-Δ-Carene	0.4	–	–
1031	1029	Limonene	0.7	–	–
		Sesquiterpenes			
1506	1506	E,E-α-Farnesene	–	1.3	–
1515	1514	γ-Cadinene	–	1.2	–
1463	1458	E-β-Farnesene	–	–	0.6
		Sesquiterpenoids			
1577	1573	Z-dihydro apofarnesol	–	–	1.2
1596	1595	Carotol	5.8	–	–
1686	1686	Cyclonellyl tiglate	–	–	3.3
1693	1693	Acorenone	1.1	–	–
		Diterpenes			
2034	2034	Kaur-16-ene	–	0.9	–
2218	2218	Neophytadiene	–	–	0.7
		Diterpenoid			
2117	2117	Z-Phytol	1.2	8.9	2.0
		Terpene rel. compounds			
1455	1455	Geranyl acetone	–	–	0.5
1488	1489	E-β-Ionene	0.8	–	–
1848	1847	Hexahydrofarnesyl acetone	2.5	5.7	6.3
1917	1915	Farnesyl acetone	–	1.1	–
		Aldehydes			
1002	999	Octanal	1.1	–	0.6
1058	1055	2-Octenal	0.9	–	–
1102	1101	Nonanal	41.0	29.3	8.3
1165	1162	2E-Nonenal	2.3	1.6	–
1204	1202	Decanal	1.2	3.8	1.4
1268	1264	2E-Decenal	0.9	–	0.7
1295	1293	2E,4Z-Decadienal	–	1.8	–
1306	1307	Undecanal	1.3	–	1.6
1318	1317	2E,4E-Decadienal	1.7	4.1	0.4
1410	1409	Dodecanal	–	–	0.6
1512	1510	Tridecanal	0.4	1.1	1.3
1574	1570	E-2-Tridecenal	–	–	0.8
1615	1613	Tetradecanal	0.5	–	2.3
		Alcohols			
977	978	1-Octen-3-ol	0.5	–	–
1674	1673	Tetradecanol	–	5.1	2.1
1715	1713	E-2-Tetradecen-1-ol	0.8	2.0	9.9
1773	1774	Pentadecanol	0.9	2.1	1.1
1877	1876	Hexadecanol	1.1	–	–

2080	2078	Octadecanol	0.5	–	0.4
2285	2284	Eicosanol	0.5	–	–
		Hydrocarbons			
970	972	4,4-Dimethyl-E-2-pentene	6.6	–	–
1001	1000	Decane	0.8	–	0.3
1401	1400	Tetradecane	–	–	0.5
1500	1500	Pentadecane	0.4	–	–
1592	1590	Hexadecene	–	–	0.6
1600	1600	Hexadecane	–	–	1.3
1700	1700	Heptadecane	–	2.5	0.5
1791	1790	Octadecene	–	0.8	1.0
1800	1800	Octadecane	–	–	0.8
1893	1891	Nonadecene	1.2	1.9	4.1
1899	1900	Nonadecane	–	–	4.9
1987	1988	Eicosene	–	1.0	0.6
1999	2000	Eicosane	–	–	0.5
2100	2100	Heneicosane	0.7	–	0.6
2189	2189	Docosene	–	1.7	0.3
2198	2200	Docosane	–	–	0.4
2299	2300	Tricosane	1.3	–	0.8
2400	2400	Tetracosane	0.3	–	0.8
2500	2500	Pentacosane	2.2	–	1.6
		Others			
967	969	1-Octen-3-one	–	–	0.2
984	984	3-Octanone	1.4	–	1.7
991	991	2-Pentyl furan	0.9	3.1	1.1
1295	1294	2-Undecanone	2.0	–	0.6
1403	1401	2-Dodecanone	–	1.4	–
1497	1496	2-Tridecanone	–		3.1
1676	1676	β-Asarone	1.0	–	–
1921	1922	Methyl hexadecanoate	0.6	–	–
2005	2005	Hexadecyl acetate	–	–	0.7
2146	2143	Oleic acid	–	1.8	–

[a] % Area obtained by FID peak-area normalization. [b]RI calculated from retention times relative to that of n-alkanes (C_6-C_{32}) on the non-polar HP-5 column.

oils were then investigated by GC-FID and GC-MS technique[12-22]. Retention indices, percentages and chemical composition, of the essential oils of *B. albican*, *B. pallescens* and *S. intermedia* are listed in Table-1. Thirty-six components were identified from the oil of *B. albican*, representing 87.5 % of the total oil and the major compounds were nonanal (41.0 %), 4,4-dimethyl-E-2-pentene (6.6 %), carotol (5.8 %), hexahydrofarnesyl acetone (2.5 %) and 2E-nonenal (2.3 %). In the essential oil of *B. pallescens*, 23 components were identified, representing 84.2 % of the total oil and nonanal (29.3 %), Z-phytol (8.9 %), hexahydrofarnesyl acetone (5.7 %), tetradecanol (5.1 %) and decanal (3.8 %) were the main constituents. Forty-five compounds were identified from the oil of *S. intermedia*, representing 77.6 % of the total oil and E-2-tetradecen-1-ol (9.9 %), nonanal (8.3 %), hexahydrofarnesyl

acetone (6.3 %), eicosene (4.9) and nonadecene (4.1 %) were the major components of the oil.

The volatiles of most mosses were abundant in aliphatic and aromatic aldehydes (*n*-heptanal, *n*-nonanal, E,E-2,4-decadienal, benzaldehyde, phenyl acetaldehyde), aliphatic alcohols (*n*-octanol, 1-octen-3-ol, *etc*.) and hydrocarbons (C_{12}-C_{18}, saturated, mono- and di-unsaturated)[6-11]. We also observed the similar aliphatic-aldehydes and hydrocarbons in the oils of mosses. Chemical class distributions for the mosses are listed in Table-2.

TABLE-2
CHEMICAL CLASS DISTRIBUTION IN THE ESSENTIAL OILS OF *B. albican*, *B. pallescens* and *S. intermedia*

Constituents	A		B		C	
	Area (%)	NC*	Area (%)	NC*	Area (%)	NC*
Terpenoids						
Monoterpene hydrocarbons	1.1	2	–	–	–	–
Sesquiterpene hydrocarbons	–	–	2.5	2	0.6	1
Oxygenated sesquiterpenes	6.9	2	–	–	4.5	2
Diterpene hydrocarbons	–	–	0.9	1	0.7	1
Oxygenated diterpene	1.2	1	8.9	1	2.0	1
Terpene related compounds	3.3	2	6.8	2	6.8	2
Aldehydes	51.3	10	41.7	6	18.0	10
Alcohols	4.3	6	9.2	3	13.5	4
Hydrocarbons	13.5	8	7.9	5	24.1	18
Others	5.9	5	6.3	3	7.4	6
Total	87.5	36	84.2	23	77.6	45

A: *Brachythecium albicans*; B: *Bryum pallescens*; C: *Syntrichia intermedia*. *NC: Number of compounds.

In addition, a few terpenoid compounds from the oils of *B. albican*, *B. pallescens* and *S. intermedia* were detected. Some of them could be readily identified by their characteristic mass spectra in mosses[12-22]. In present samples, 3-Δ-carene, limonene, E,E-α-farnesene, γ-cadinene, E-β-farnesene, Z-dihydroapofarnesol, carotol, cyclonellyl tiglate, acorenone, kaur-16-ene, neophytadiene and Z-phytol were identified with the total ratio of 9.2, 11.8 and 7.8 %, respectively.

The qualitative and quantitative determination of essential oil of *B. albican*, *B. pallescens* and *S. intermedia* showed that major constituents were aliphatic aldehydes (51.3, 41.7 and 18.0 %) and hydrocarbones (13.5, 7.9 and 24.1 %), respectively. Generally, the number of volatile compounds present in the oil of *S. intermedia*, is more than in *B. albican*, *B. pallescens*. The chemical composition differences of the samples might be caused by the ecological niches, climatic conditions and other biotic factors.

ACKNOWLEDGEMENTS

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

REFERENCES

1. B. Dulger, Ö. Tonguc Yayintas and A. Gonuz, *Fitoterapia*, **76**, 730 (2005).
2. A.J.E. Smith, The Moss Flora of Britain and Ireland, Second Edition, Cambridge University Press (2004).
3. G. Uyar and B. Çetin, *J. Biol*., **26**, 203 (2004).
4. H. Kürschner and A. Erdag, *Turk. J. Bot*., **29**, 95 (2005).
5. M.G.B. Zoghbia, E.H.A. Andrade, R.C.L. Lobato, A.C.C. Tavares, A.P.S. Souza, C.C.C. Conceiçao and E.F. Guimaraesc, *Biochem. System. Ecol*., **33**, 269 (2005).
6. C. Suire, G. Bourgeois and T. Koponen, *J. Hattori Bot. Lab.*, **89**, 233 (2000).
7. R. Mues, Chemical Constituents and Biochemistry, In eds.: A.J. Shaw and B. Goffinet, Bryophyte Biology, Cambridge University Press, Cambridge, p. 150 (2000).
8. Y. Asakawa, Chemical Constituents of the Bryophytes, In eds.: W. Herz, G.W. Kirby, R.E. Moore, W. Steglich and C. Tamm, Progress in the chemistry of Organic Natural Compounds, Vol. 65, Springer Verlag, Vienna, New York (1995).
9. Y. Saritas, M.M. Sonwa, H. Iznaguen, W.A König, H. Muhle and R. Mues, *Phytochemistry*, **57**, 443 (2001).
10. L. Li and J. Zhao, *Molecules*, **14**, 2195 (2009).
11. T. Özdemir, N. Yayli, T.B. Cansu, C. Volga and N. Yayli, *Asian J. Chem*., **21**, 5505 (2009).
12. R.P. Adams, Identification of Essential Oil Components by Gas Chromatography-Mass Spectroscopy, Allured, Carol Stream, IL, USA (2004).
13. N. Yilmaz Iskender, N. Yayli, N. Yildirim, T.B. Cansu and S. Terzioglu, *J. Oleo Sci*., **58**, 117 (2009).
14. H.D. Skaltsa, C. Demetzos, D. Lazari and M. Sokovic, *Phytochemistry*, **64**, 743 (2003).
15. O. Üçüncü, N. Yayli, C. Volga, N. Yayli and S. Terzioglu, *Asian J. Chem*., **21**, 6569 (2009).
16. N. Yayli, A. Yasar, C. Güleç, A. Usta, S. Kolayli, K. Coskunçelebi and S. Karaoglu, *Phytochemistry*, **66**, 1741 (2005).
17. D.M. Lazari, H.D. Skaltsa and T. Constantinidis, *Flav. Frag. J*., **14**, 415 (1999).
18. N. Yilmaz Iskender, N. Yayli, A. Yasar, K. Coskunçelebi and N. Yayli, *Asian J. Chem*., **21**, 6290 (2009).
19. K. Akpinar, N. Yildirim, O. Üçüncü, S. Terzioglu and N. Yayli, *Asian J. Chem*., **21**, 1225 (2009).
20. N. Yayli, A. Yasar, N. Yayli, C. Albay, Y. Asamaz, K. Coskunçelebi and S. Karaoglu, *Pharm. Biol.*, **47**, 7 (2009).
21. O. Üçüncü, N. Yayli, A. Yasar, S. Terzioglu and N. Yayli, *Nat. Prod. Comp*., **3**, 925 (2008).
22. P. Torres, J. Ayala, C. Grande, J. Anaya and M. Grande, *Phytochemistry*, **52**, 1507 (1999).

(*Received*: 11 February 2010; *Accepted*: 24 June 2010) AJC-8830