Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7321-7326

Essential Oil Composition from The Flower, Leaf and Stem of *Polygonum alpinum* from Turkey

OSMAN ÜÇÜNCÜ†, NURAN YAYLI, AHMET YASAR, CANAN ALBAY, NURETTIN YAYLI* and SALIH TERZIOGLU‡
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 volatile oil of *Polygonum alpinum* L. (Polygonaceae) was prepared by hydrodistillation of flower, leaf and stem and characterized by GC and GC-MS. A total of 44, 41 and 38 compounds were identified, constituting over 94.4, 96.3 and 97.2 % of oil composition of the flower, leaf and stem of *P. alpinum*, respectively. Esters were shown to be the main group of constituents (flower: 46.2 %, leaf: 59.1 %, stem: 82.5 %). The major components of the oils of *P. alpinum* were ethyl hexadecanoate (flower: 11.7 %, leaf: 15.0 %, stem: 21.1%), methyl linoleate (flower: 30.7 %, leaf: 11.7 %, stem: 36.7 %) and ethyl linoleate (leaf: 25.8 %, stem: 14.7 %). Terpenoids were the minor constituents in all parts (flower: 5.6 %, leaf: 11.0 %, stem: 6.4 %) of the *P. alpinum*.

Key Words: Polygonaceae, *Polygonum alpinum*, Essential oil, GC-FID, GC-MS.

INTRODUCTION

The genus *Polygonum* L. (Polygonaceae) represented 38 species in Turkey[1-3]. It is annual, perennial or suffrutescent herbs or climbers. Nine species of them are endemics to Turkey[1-3]. Aerial parts of some of the species have been used in folk medicine and/or dyeing the yarn into yellow in Turkey[4]. *Polygonum alpinum* All. is the only member of Sect. *Aconogonon* Meissn. in Turkey and clearly differs from the other Turkish species with its flowers in diffuse panicles. This alpine species is distributed in slopes and screes, 1900-3000 m above sea level[1].

Phytochemical studies on the *P. alpinum* has shown the isolation and identification of a number of flavonoids[5]. Previous works on the essential oils from *Polygonum* L. genus included *P. odoratum* Lour, *P. hydropiper* Opiz and *P. cuspidatum*[6-11]. The major components in the essential oil of *P. odoratum* were

†Department of Chemistry, Faculty of Arts and Sciences, Kafkas University, 36000 Kars, Turkey.
‡Department of Forest Botany, Faculty of Forestry, Karadeniz Technical University, 61080 Trabzon, Turkey.

decanal (27.73 %), dodecanal (44.05 %) and decanol (10.88 %)[6]. Four diffrent studies reveled the main constituents of *P. hydropiper* were (Z)-3-hexenal, (Z)-3-hexenol, decanal, undecanal, dodecanal, 3-sulfanyl-hexanal, 3-sulfanyl-hexan-1-ol[7]; (E)-β-farnesene (35.68 %), (E)-caryophyllene (9.21 %), (E)-nerolidol (6.86 %) and α-humulene (5.95 %)[8]; (E)-β-farnesene (44.1 %), phytol (10.8 %), (E)-caryophyllene (9.3 %) and (E)-nerolidol (6.9 %)[9]; dodecanal (3-40 %), (E)-2-hexenal (20-35 %), decanal (4-22 %), (Z)-3-hexen-1-ol (4-31 %), hexanal (1.7-5.1 %) and β-caryophyllene (1.7-2.3 %)[10]. The main components in the oil of *P. cuspidatum* were thiophenes (38.09 %), phenanthrenes (4.78 %), fluorenes (3.81 %), biphenyls (3.47 %), anthracenes (2.92 %) and naphthalenes (2.27 %)[11]. The literature survey did not reveal any reports on the essential oil composition from the flower, leaf and stem parts of the *P. alpinum*. The crude volatiles were investigated by GC-FID and GC-MS technique[12-23]. The identification of the substances was performed by comparison of retention indexes on HB-5 column (determined relatively to the retention times of a series of *n*-alkanes), authentic compounds and mass spectra with literature (Nist and Wiley)[12-23]. The present study was undertaken to verify the composition of the volatile compounds present in the flower, leaf and stem parts of the *P. alpinum*.

EXPERIMENTAL

Polygonum alpinum L. was collected in Uzungöl-Demirkapi village, Trabzon, Turkey (at heights of *ca.* 2900 m) in the northeastern part of Turkey on July 18, 2008. The plant was authenticated by Prof. S. Terzioglu[1-3]. Voucher specimen was deposited in the Herbarium of the Faculty of Forestry, KATO (KATO: 11833), Karadeniz Technical University, Turkey.

Isolation of the essential oils: The fresh plant materials were separated into flower, leaf and stem parts and they were freezed with liquid nitrogen and then grounded into small pieces. The essential oils from fresh aerial parts (*ca.* 60 g, each) of *P. alpinum* were isolated by hydrodistillation in a Clevenger-type apparatus[12,13] with cooling bath (-15 ºC) system (4 h) (yields: 0.10, 0.08 and 0.06 % (v/w), respectively). The obtained oils were extracted with HPLC grade *n*-hexane (0.5 mL) and dried over anhydrous sodium sulphate and stored at 4-6 ºC in a sealed brown vial.

Gas chromatography (GC): The capillary GC-FID analysis was performed using an Agilent-5973 Network System, equipped with a FID (supplied with air and hydrogen of high purity) and a split inlet. 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. One 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 240 °C with a 3 °C/min heating ramp. The identity of each compound was supported by comparing their retention indices (RI) with published data[12-22]. The sample was analyzed twice and the percentage composition of oil was computed from the GC peak areas without using correction factors.

Gas chromatography-mass spectrometry (GC/MS): GC-MS analysis was 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. One 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 240 °C with a 3 °C/min heating ramp.

Identification of constituents: Retention indices of all the components were determined by Kovats method using *n*-alkanes (C_6-C_{32}) as standards. The constituents of the oils were identified by comparison of their mass spectra with those of mass spectral libraries (NIST and Wiley), authentic compounds (α-pinene, γ-terpinene, linalool, decane, heptadecane, nonadecane, heneicosane, tricosane, tetracosane and pentacosane) and with the published data in the literature[12-23].

RESULTS AND DISCUSSION

The chemical composition of the essential oils from the flower, leaf and stem of *P. alpinum* are presented in Table-1. In all, 63 essential compounds were identified by GC-FID and GC-MS with HP-5 column[12-23]. The flower oil was revealed the presence of 42 components, representing 94.4 % of the total oil. The major constituents of the flower oil were methyl linoleate (30.7 %), heneicosane (12.7 %), ethyl hexadecanoate (11.7 %), tricosane (8.2 %) and tetracosane (6.5 %). Forty one compounds were identified in the leaf, representing 96.3 % of the total oil. The main components of the leaf oil were ethyl linoleate (25.8 %), ethyl hexadecanoate (15.0 %), methyl linoleate (11.7 %), pentacosane (9.8 %) and neophytadiene (3.9 %). On the other hands, 38 components accounting for 97.2 % of constituents of the stem oil were identified and the major compounds were methyl linoleate (36.7 %), ethyl hexadecanoate (21.1 %), ethyl linoleate (14.7 %), isopropyl linoleate (5.8 %) and isopropyl hexadecanoate (3.1 %). Terpenoids (flower: 5.6 %, leaf: 11.0 %, stem: 6.4 %) were the minor constituents in the oils.

The chemical class distributions of the volatile constituents are summarized in Table-2. The compounds were separated into six classes, which were terpenoids (monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpene, diterpene hydrocarbon and terpene related compounds), aldehydes, carboxylic acids, esters, hydrocarbons and others (Table-2). The major constituents were esters (flower: 46.2 %, leaf: 59.1 %, stem: 82.5 %) and hydrocarbons (flower: 35.9 %, leaf: 12.9 %, stem: 1.0 %) in the oils of *P. alpinum*. The numbers of the identified terpenoids in the flower, leaf and stem of *P. alpinum* were 14, 15 and 15 compounds, respectively. Twenty-three components were common to all tree part of the plant with the total ratio of 62.0, 52.3 and 67.5 %, respectively. It could be concluded that the compositions of the volatile oils extracted from the

TABLE-1
IDENTIFIED COMPONENTS IN THE ESSENTIAL OILS OF *P. alpinum* [a,b]

Compounds	Flower (% area)	Leaf (% area)	Stem (% area)	Ex. RI	Lit. RI
Monoterpene hydrocarbons					
α-Pinene	0.6	0.9	0.6	939	939
o-Cymene	0.4	0.3	0.4	1025	1026
γ-Terpinene	0.2	-	-	1058	1060
α-Terpinolen	0.3	-	0.2	1191	1189
Oxygenated monoterpenes					
Linalool	-	-	0.5	1095	1096
trans-Thujone	1.3	0.9	1.6	1110	1114
Iso-3-Thujanol	0.2	-	0.4	1136	1138
Safranal	-	0.3	-	1199	1197
Pulegone	-	0.2	-	1234	1237
Sesquiterpene hydrocarbons					
Cyclosativene	-	0.4	0.1	1373	1371
E-Caryophyllene	0.3	0.4	0.4	1421	1419
Germacrene D	0.7	-	-	1484	1485
(Z)-α-Bisabolone	-	0.3	-	1504	1504
δ-Amorphene	0.3	0.2	0.2	1525	1523
Oxygenated sesquiterpenes					
E-Nerolidol	0.2	0.3	0.2	1563	1363
Caryophyllene oxide	-	-	0.1	1585	1583
α-Cadinol	0.3	0.4	0.2	1656	1654
Drimenol	-	-	0.8	1770	1767
Diterpene hydrocarbon					
Neophytadiene	-	3.9	-	2220	2222
Terpene related compounds					
(E)-α-Damascone	0.3	-	-	1392	1393
Ethyl geranate	0.2	0.7	-	1397	1395
Geranyl acetone	0.3	0.6	0.3	1458	1455
(E)-β-Ionone	-	0.6	0.1	1487	1485
Hexahydro farnecylacetone	-	1.0	-	1847	1845
Phytol acetate	-	1.6	-	2219	2218
Others					
Decane	0.9	0.8	0.4	1001	1000
Benzene acetaldehyde	-	0.3	0.2	1042	1042
Nonanal	2.5	0.4	-	1097	1101
2E-Nonen-1-al	0.4	0.4	0.3	1163	1162
Ethyl benzoate	0.5	0.3	0.4	1175	1173
Naphthalene	-	-	0.2	1182	1181
2-Phenyl ethyl acetate	-	0.2	-	1260	1258
Undecanal	0.3	-	-	1309	1307
2E,4E-Decadienal	0.2	-	-	1319	1317
Eugenol	0.2	-	-	1362	1359
Tridecanal	0.2	-	-	1513	1510

Methyl dodecanoate	-	0.3	-	1529	1526
1-Hexadecene	0.8	2.0	0.5	1591	1590
Ethyl dodecanoate	0.4	1.7	0.2	1598	1595
Benzophenone	0.7	0.7	0.2	1630	1628
Heptadecanal	0.4	-	-	1684	1682
Heptadecane	0.3	-	-	1702	1700
Pentadecanal	0.2	-	-	1714	1713
Tetradecanoic acid	0.5	1.1	0.6	1770	1768
Ethyl tetradecanoate	0.5	1.6	0.3	1797	1796
Pentadecanoic acid	-	0.6	0.8	1868	1866
Isobutyl phthalate	0.5	0.5	0.5	1874	MS
Nonadecane	0.9	-	-	1901	1900
Methyl hexadecanoate	0.9	1.2	1.2	1924	1922
Cyclohexadecanolide	-	-	1.2	1936	1935
Ethyl hexadecanoate	11.7	15.0	21.1	1995	1993
Palmitic acid	-	3.8	3.1	1984	1984
Isopropyl hexadecanoate	1.0	0.8	1.6	2027	2025
Methyl linoleate	30.7	11.7	36.7	2097	2096
Heneicosane	12.7	-	-	2100	2100
Linolenic acid	0.3	-	0.5	2152	2150
Ethyl linoleate	-	25.8	14.7	2175	2172
Docosane	5.0	-	-	2199	2200
Isopropyl linoleate	-	-	5.8	2201	MS
9,12,15-Octadecatrien-1-ol	-	2.0	-	2203	MS
Tricosane	8.2	0.7	0.4	2301	2300
Tetracosane	6.5	1.6	-	2402	2400
Pentacosane	1.4	9.8	0.2	2601	2600

[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 *P. alpinum*

Constituents	Flower		Leaf		Stem	
	% Area	NC[a]	% Area	NC[a]	% Area	NC[a]
Terpenoids						
Monoterpene hydrocarbons	1.5	4	1.2	2	1.2	3
Oxygenated monoterpenes	1.5	2	1.4	3	2.5	3
Sesquiterpene hydrocarbons	1.3	3	1.3	4	0.7	3
Oxygenated sesquiterpenes	0.5	2	0.7	2	1.3	4
Diterpene hydrocarbons	-	-	3.9	1	-	-
Terpene related compounds	0.8	3	4.5	5	0.4	2
Aldehydes	4.2	7	1.1	3	0.5	2
Carboxylic acids	0.8	2	5.5	3	5.0	4
Esters	46.2	8	59.1	11	82.5	10
Hydrocarbons	35.9	8	12.9	4	1.0	3
Others	1.7	3	4.7	3	2.1	4
Total	94.4	42	96.3	41	97.2	38

[a]NC: Number of compounds

flower, leaf and stem were different as expected. All parts of the oils were rich in non-terpenoid components mostly esters and hydrocarbons in the total ratio of 82.1 % in flower, 72.0 % in leaf and 83.5 % in stem.

ACKNOWLEDGEMENTS

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

REFERENCES

1. M.J.E. Coode and J. Cullen, in ed.: P.H. Davis, *Polygonum* L. Flora of Turkey and the East Aegean Islands. Edinburgh University Press, Vol. 2, p. 269 (1967).
2. P.H. Davis, *Polygonum* L. Flora of Turkey and the East Aegean Islands. Edinburgh University Press, Vol. 10, p. 84 (1988).
3. A. Güner, N. Özhatay, T. Ekim and K.H.C. Baser, *Polygonum* L. Flora of Turkey and the East Aegean Islands. Edinburgh University Press, Vol. 11, p. 54 (2000).
4. T. Baytop, Therapy with Medicinal Plants, Istanbul University Publications (1984).
5. L.O. Demirezer, A. Kuruüzüm, Z. Güvenalp and H. Süleyman, *Pharm. Biol.*, **44**, 462 (2006).
6. M.V. Hunter, J.J. Brophy, B.J. Ralph and F.E. Bienvenu, *J. Essent. Oil Res.*, **9**, 603 (1997).
7. C. Starkenmann, L. Luca, Y. Niclass, E. Praz and D. Roguet, *J. Agric. Food Chem.*, **54**, 3067 (2006).
8. T. Naotaka and M. Mitsuo, *Koryo, Terupen, oyobi Seiyu Kagaku ni kansuru Toronkai Koen Yoshishu*, **48**, 34 (2004) (In Japanese).
9. M. Mitsuo and T. Naotaka, *Flav. Fragr. J.*, **22**, 188 (2007).
10. J. Jiang, *Flav. Fragr. J.*, **20**, 455 (2005).
11. J. Suan, X. Chen, X. Jiang and J. Yu, *J. Chin. Mass Spec.*, **7**, 242 (2006).
12. N.Y. Iskender, N. Yayli, N. Yildirim, T.B. Cansu and S. Terzioglu, *J. Oleo Sci.*, **58**, 117 (2009).
13. K. Akpinar, N. Yildirim, O. Üçüncü, N. Yayli, S. Terzioglu and N. Yayli, *Asian J. Chem.*, **21**, 1225 (2009).
14. R.P. Adams, Identification of essential oil components by Gas Chromatography/Quadrupole Mass Spectroscopy, Allured, Carol Stream, IL, USA (2004).
15. N. Yayli, A. Yasar, C. Güleç, A. Usta, S. Kolayli, K. Coskunçelebi and S. Karaoglu, *Phytochemistry*, **66**, 1741 (2005).
16. H.A. Priestap, C.M. Van Baren, P. Di Leo Lira, J.D. Coussio and A.L. Bandoni, *Phytochemistry*, **63**, 221 (2003).
17. H.D. Skaltsa, C. Demetzos, D. Lazari and M. Sokovic, *Phytochemistry*, **64**, 743 (2003).
18. S. Terzioglu, A. Yasar, N. Yayli, N. Yilmaz, S. Karaoglu and N. Yayli, *Asian J. Chem.*, **20**, 3277 (2008).
19. K. Javidnia, R. Miri, M. Kamalinejad, H. Sarkarzadeh and A. Jamalian, *Flav. Fragr. J.*, **19**, 213 (2004).
20. O. Üçüncü, N. Yayli, A. Yasar, S. Terzioglu and N. Yayli, *Nat. Prod. Com.*, **3**, 925 (2008).
21. N. Yayli, A. Yasar, N. Yayli, M. Albay and K. Coskunçelebi, *Nat. Prod. Com.*, **3**, 941 (2008).
22. J.L. Berdague, C. Denoyer, J.L. Le Quéré and E. Semon, *J. Agric. Food Chem.*, **39**, 1257 (1991).
23. J.C. Leffingwell and E.D. Alford, *J. Environ. Agric. Food Chem.*, **4**, 899 (2005).

(*Received*: 28 March 2009; *Accepted*: 24 August 2009) AJC-7770