

Difference in Volatile Composition of *Chenopodium murale* from Two Different Locations of Cyprus

Kaan Polatođlu^{*1}, Betül Demirci², İhsan Çalış³ and Kemal Hüsnu Can Başer⁴

¹Department of Analytical Chemistry, Faculty of Pharmacy, Istanbul Kemerburgaz University, 34217, Istanbul, Türkiye

²Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, 26470, Eskişehir, Türkiye

³Department of Pharmacognosy, Faculty of Pharmacy, Near East University, Nicosia, Turkish Republic of Northern Cyprus

⁴Department of Botany and Microbiology, Faculty of Science, King Saud University, 11451 Riyadh, Saudi Arabia

(Received August 25, 2015; Revised March 24, 2016; Accepted April 08, 2016)

Abstract: Volatile composition of *Chenopodium murale* from Deđirmenlik and Salamis locations of Cyprus were trapped with headspace solid-phase microextraction (HS-SPME) technique and analyzed by GC-MS. Twenty-one compounds were identified comprising of 80.5% of the volatile sample from the Deđirmenlik and twenty-six compounds were identified comprising of 82.2% of the volatile from the Salamis sample. Volatiles of *C. murale* from Deđirmenlik contained 18.7% benzaldehyde, 8.6% yomogi alcohol 6.8% 1-hexanol and 6.5% dihydromyrcenol as the main components whereas volatiles of the sample from Salamis contained 20.5% yomogi alcohol, 14.5% camphor, 8.1% 1-hexanol and 6.6% 2-ethyl-hexanol. The volatiles of *C. murale* from both locations contained unexpected irregular monoterpene yomogi alcohol which is previously known to be restricted to Asteraceae genus. Both locations showed variations in their compositions which suggests the chemotype variation could be observed from this species.

Keywords: Chenopodiastrium; *Chenopodium murale*; yomogi alcohol; benzaldehyde; camphorvolatiles. © 2016 ACG publications. All rights reserved.

1. Plant Source

Chenopodium murale L. (Syn: *Chenopodiastrium murale* (L.) S. Fuentes, Uotila & Borsch) from genus Chenopodiastrium is a natural growing weed that finds an edible use in Cyprus. The leaves of this plant is collected during its flowering period and it is consumed as pickles. In our phtochemical survey of edible wild plants of Cyprus we report the volatile composition of *C. murale*. The plant material was collected from two different locations of Cyprus during the flowering period in January and February 2012 from Salamis and Deđirmenlik villages, respectively. Herbarium specimens were deposited to the herbarium of Near East University, Institute of Environmental Sciences with voucher specimen numbers 6791 and 6794 respectively. The plant materials were identified by Dr. Kaan Polatođlu.

2. Previous Studies

The phytochemical studies on the genus *Chenopodium* was previously given in a comprehensive review [1]. Previous phytochemical studies on *C. murale* reports isolation of kaempferol-3-O- α -L-

* Corresponding author: E-mail: kaanpolatoglu@gmail.com

Rhamnopyranoside-7-O- β -D-xylopyranosyl(1 \rightarrow 2)-O- α -L-rhamnopyranoside, kaempferol-7-rhamnoside, kaempferol-3,7-dirhamnoside, kaempferol-3-rhamnoside-7-glucoside, herbacetin, quercetin, scopoletin [2]; kaempferol-3-O-[(4- β -D-apiofuranosyl)- α -L-rhamnopyranoside]-7-O- α -L-rhamnopyranoside, kaempferol-3-O-[(4- β -D-xylopyranosyl)- α -L-rhamnopyranoside]-7-O- α -L-rhamnopyranoside [3]; 3,7-dihydroxy-3'-(4-hydroxy-3-methylbutyl)-5,6,4'-trimethoxyflavone, 5,7-dihydroxy-3'-(2-hydroxy-3-methyl-3-butenyl-3,6,4'-trimethoxyflavone, β -sitosterol-3-O- β -D-glucoside, stigmaterol-3-O- β -D-glucoside [4] from the aerial parts of the plant. The essential oil composition of *C. murale* originating from Israel was reported to contain *cis*-ascaridole (27.5%), limonene (9.4%), α -terpinylacetate (8.9%) and *cis*-isoascaridole (6.4%) as the main constituents [5]. The other species of this genus were reported to contain high amounts of ascaridole derivatives [5-8] and the other compounds namely: limonene, α -terpinene [5], *p*-cymene [9], carvacrol [10]. Essential oils of *Chenopodium* species were reported to have antimicrobial [11, 12], antifungal [13, 14], leishmanicidal [15] and antioxidant [13] activities.

3. Present Study

The volatiles of *Chenopodium murale* from two different locations in Cyprus were investigated with HS-SPME/GC-MS. Volatiles were isolated from fresh aerial parts of the plant material (0.5 g). The plant material were placed in a 10 mL vial and sealed with parafilm. Headspace solid phase microextraction was used for the isolation of the volatiles. A manual SPME injector (Supelco, Ballafonte, PA, USA) that have a fibre coated with a layer of polydimethylsiloxane/divinylbenzene (65 μ m - PDMS/DVB-blue) was used for the adsorption of the volatiles. Prior to the analysis of adsorbed volatiles on the fiber a blank run was initiated with the fiber to make sure it does not contain any contamination. After the blank run the fiber was inserted into the vial through the parafilm and exposed to the plant volatiles for 15 min at 50°C. The SPME injector was then immediately manually inserted to the injection port for desorption of the plant volatiles for GC-MS analysis. The volatiles were analyzed by GC-MS using a Hewlett Packard GCD system. An HP-Innowax FSC column (60 m \times 0.25 mm, 0.25 μ m film thickness) and helium as carrier gas (0.8 mL/min). The oven temperature was programmed to 60 °C for 10 min and raised to 220 °C at a rate of 4 °C/min. The temperature was kept constant at 220 °C for 10 min and then raised to 240 °C at a rate of 1 °C/min. The injector temperature was set at 250 °C. Splitless injection mode was employed. Mass spectra were recorded at 70 eV with the mass range *m/z* 35 to 450. The relative percentage of the components of the volatiles were calculated from the integration of the peaks obtained from GC-MS analysis. The results of the analysis are given in Table 1.

Twenty-one compounds were identified comprising of 80.5% of the volatile sample from the Değirmenlik and twenty-six compounds were identified comprising of 82.2% of the volatile from the Salamis sample. Volatiles of *C. murale* from Değirmenlik contained 18.7% benzaldehyde, 8.6% yomogi alcohol 6.8% 1-hexanol and 6.5% dihydromyrcenol as the main components whereas volatiles of the sample from Salamis contained 20.5% yomogi alcohol, 14.5% camphor, 8.1% 1-hexanol and 6.6% 2-ethyl-hexanol. The major components of the both samples differed from each other. Salamis sample contained minor amounts of benzaldehyde (3.2%) and dihydromyrcenol in lower amount (4.3%). The Değirmenlik sample contained yomogi alcohol and camphor in minor amounts (8.6% and 5.1% respectively). The existence of these differences suggest that the chemotype variation of this species could exist. However further studies are required in order to point out exact chemotypes of *C. murale*. The occurrence of yomogi alcohol is interesting because it is an irregular monoterpene which was reported to be restricted to the genus Asteraceae [16]. However previously irregular monoterpenes were also reported from other sources including species of Lamiaceae and Convolvulaceae [17, 18] and from *Eryngium burgei* of Apiaceae [19]. The volatiles obtained from *C. murale* also contained dihydromyrcenol, 2-butoxyethanol and lilial. Dihydromyrcenol, 2-butoxyethanol and lilial compounds were first obtained by synthesis. However these substances later were also reported from many plant sources [20-25]. This is the first report on the volatile compounds of edible *C. murale*.

Table 1. Volatile composition of *Chenopodium murale* from two different locations of Cyprus.

RRI L.	RRI	Compound	Relative Percentage		Identification Method	Ref.
			Değirmenlik	Salamis		
1348	1348	6-Methyl-5-hepten-2-one	3.0	2.3	RRI, MS	[26]
1360	1360	1-Hexanol	6.8	8.1	RRI, MS	[27]
1391	1391	(Z)-3-Hexen-1-ol	1.5	1.7	RRI, MS	[28]
1395	1395	2-Butoxy ethanol	1.0	5.1	RRI, MS	[27]
1403	1403	Yomogi alcohol	8.6	20.5	RRI, MS	[27]
1473	1473	Dihydromyrcenol	6.5	4.3	RRI, MS	[27]
1496	1496	2-Ethyl hexanol	2.7	6.6	RRI, MS	[27]
1532	1532	Camphor	5.1	14.5	RRI, MS	[28]
1541	1541	Benzaldehyde	18.7	3.2	RRI, MS	[26]
1553	1553	Linalool	4.1	2.6	RRI, MS	[26]
1562	1562	Octanol	1.0	1.7	RRI, MS	[28]
1591	1591	Bornyl acetate	tr	1.5	RRI, MS	[29]
1600	1600	α -Isophorone	tr	1.1	RRI, MS	[27]
	1663	Phenyl acetaldehyde	4.3	0.2	MS	
1664	1664	Nonanol	-	0.2	RRI, MS	[28]
1703	1681	6-Oxoisophorone	-	0.9	MS	[27]
1719	1719	Borneol	0.1	1.0	RRI, MS	[28]
	1718	<i>p</i> -Menth-4-en-3-one	-	1.0	MS	
1751	1751	Carvone	5.2	-	RRI, MS	[26]
1856	1856	Geraniol	-	0.6	RRI, MS	[29]
1868	1868	(<i>E</i>)-Geranyl acetone	0.1	0.6	RRI, MS	[29]
1896	1896	Benzyl alcohol	2.6	2.5	RRI, MS	[27]
1957	1958	(<i>E</i>)- β -Ionone	1.3	0.9	RRI, MS	[29]
1973	1973	1-Dodecanol	-	0.6	RRI, MS	[29]
2009	2009	<i>trans</i> - β -ionone-5,6-epoxide	0.9	0.5	RRI, MS	[27]
2072	2072	Lilial	-	tr	RRI, MS	[27]
2239	2239	Carvacrol	5.5	tr	RRI, MS	[28]
Total			80.5	82.2		

RRI L.: Relative retention indice of the compound in the literature. RRI: Relative retention indices calculated against *n*-alkanes. Relative percentages of individual compounds were calculated from the MS data. tr: trace (<0.1%). Identification method based on the relative retention indices (RRI) of authentic compounds on the HP Innowax column; MS, identified on the basis of computer matching of the mass spectra with those of the Wiley and MassFinder libraries and comparison with literature data. Ref.: Reference related to RRI of the compound.

Acknowledgments

This research was financially supported by The Scientific and Technological Research Council of Turkey (TUBITAK- TOVAG 1110138).

References

- [1] Z. Kokanova-Nedialkova, P. T. Nedialkov and S. D. Nikolov (2009). The genus *Chenopodium*: phytochemistry, ethnopharmacology and pharmacology, *Pharmacogn. Rev.* **3**, 280.
- [2] N. H. El-Sayed, A. S. Awaad, M. S. Hifnawy and T. J. Mabry (1999). A Flavonol triglycoside from *Chenopodium murale*, *Phytochemistry* **51**, 591-593.
- [3] A. A. Gohar, G. T. Maatooq and M. Niwa (2000). Two Flavonoid glycosides from *Chenopodium murale*, *Phytochemistry* **53**, 299-303.
- [4] B. Ahmad, Q. Jan, S. Bashir, M. I. Choudhary and M. Nisar (2003). Phytochemical evaluation of *Chenopodium murale* Linn., *Asian J. Plant Sci.* **2**, 1072-1078.
- [5] V. Dembitsky, I. Shkrob and L. O. Hanus (2008). V. Ascaridole and related peroxides from the genus *Chenopodium*, *Biomed. Pap. Fac. Univ. Palacky Olomouc Czech Repub.* **152**, 209-215.
- [6] C. Q. Bai, Z. L. Liu and Q. Z. Liu (2011). Nematicidal constituents from the Essential Oil of *Chenopodium ambrosioides* aerial parts, *E-J. Chem.* **9**, 143-148.
- [7] A. D. Bossou, S. Mangelinckx, H. Yedomonhan, P. M. Boko, M. C. Akogbeto, N. D. Kimpe, F. Avlessi and D. C. K. Shounhloue (2013). Chemical composition and insecticidal activity of plant essential oils from Benin against *Anopheles gambiae* (Giles), *Parasite. Vector.* **6**, 337.
- [8] R. Omidbaigi, F. Sefidkon and F. B. Nasrabadi (2005). Essential oil content and composition of *Chenopodium ambrosioides* L., *J. Essent. Oil Bear. Pl.* **8**, 154-158.

- [9] L. A. Usman, A. A. Hamid, N. O. Muhammad, N. O. Olawore, T. I. Edewor and B. K. Saliu (2010). Chemical constituents and anti-inflammatory activity of leaf essential oil of Nigerian grown *Chenopodium album*, L., *Excli J.* **9**, 181-186.
- [10] L. Monzote, J. Pastor, R. Scull and L. Gille (2014). Antileishmanial activity of essential oil from *Chenopodium ambrosioides* and its main components against experimental cutaneous leishmaniasis in BALB/c mice, *Phytomedicine* **21**, 1048-1052.
- [11] O. Tzakou, A. Pizzimenti, F. C. Pizzimenti, V. Sdrafkakis and E. M. Galati. (2006). Composition and antimicrobial activity of *Chenopodium botrys* L. Essential oil from Greece, *J. Essent. Oil Res.* **19**, 292-294.
- [12] Y. Zhang, W. Chen and Y. Chen. (2002). Chinese drug composition for treatment of peptic ulcer and preparation thereof, US. Pat. **6**, 344, 219.
- [13] R. Kumar, A. K. Mishra, N. K. Dubey and Y. B. Tripathi (2007). Evaluation of *Chenopodium ambrosioides* oil as a potential source of antifungal, antiaflatoxigenic and antioxidant activity, *Int. J. Food Microbiol.* **115**, 159-164.
- [14] C. M. Jardim, G. N. Jham, O. D. Dhingra and M. M. Freire (2008). Composition and antifungal activity of the essential oil of the Brazilian *Chenopodium ambrosioides* L., *J. Chem. Ecol.* **34**, 1213-1218.
- [15] L. Monzote, A. M. Montalvo, S. Almanonni, R. Scull, M. Miranda and J. Abreu. (2006) Activity of the essential oil from *Chenopodium ambrosioides* grown in Cuba against *Leishmania amazonensis*, *Chemotherapy* **52**, 130-136.
- [16] P. M. Dewick (2001). Medicinal Natural Products, A biosynthetic approach. 2nd. edition John Wiley and Sons. West Sussex, England.
- [17] Y. Kashima and M. Miyazawa (2014). Chemical Composition and Aroma Evaluation of Essential Oils from *Evolvulus alsinoides* L., *Chem. Biodivers.* **11**, 396-407.
- [18] M. C. M. I. Garcia-Vallejo, J. Sanz, M. Bernabe and A. Velasco-Negueruela (1994). Necrodane (1, 2, 2, 3, 4-pentamethylcyclopentane) derivatives in *Lavandula luisieri*, new compounds to the plant kingdom, *Phytochemistry* **36**, 43-45.
- [19] M. Mohammadhosseini, B. Mahdavi and H. Akhlaghi (2013). Characterization and Chemical Composition of the Volatile Oils from Aerial Parts of *Eryngium bungei* Bioss. (Apiaceae) by Using Traditional Hydrodistillation, Microwave Assisted Hydrodistillation and Head Space Solid Phase Microextraction Methods Prior to GC and GC/MS Analyses: A Comparative Approach, *J. Essent. Oil Bear. Pl.* **16**, 613-623.
- [20] L. Jirovetz, C. Puschmann, A. Stojanova, S. Metodiev and G. Buchbauer (2000). Analysis of the essential oil volatiles of Douglas fir (*Pseudotsuga menziesii*) from Bulgaria, *Flav. Fragr. J.* **15**, 434-437.
- [21] N. Radulović, P. Blagojević and R. Palić (2010). Comparative Study of the Leaf Volatiles of *Arctostaphylos uva-ursi* (L.) Spreng. and *Vaccinium vitis-idaea* L. (Ericaceae), *Molecules* **15**, 6168-6185.
- [22] J. Rohloff and A. M. Bones (2005). Volatile profiling of *Arabidopsis thaliana* - Putative olfactory compounds in plant communication, *Phytochemistry* **66**, 1941-1955.
- [23] L. R. Scrivanti, G. Bernardello and A. M. Anton (2008). The foveola of *Bothriochloa alta* (Poaceae: Andropogoneae): Extrafloral nectary or secretory gland of essential oils, *Flora* **203**, 55-59.
- [24] A. S. C. Sing, J. Smadja, H. Brevard, L. Maignial, A. Chaintreau and J. P. Marion (1992). Volatile constituents of faham (*Jumellea fragrans* (Thou.) Schltr.), *J. Agric. Food Chem.* **40**, 642-646.
- [25] G. Vernin, E. Vernin, C. Vernin, J. Metzger and A. Soliman (1991). Extraction and gc-ms-specma data bank analysis of the aroma of *Psidium guajava* L. fruit from Egypt, *Flav. Fragr. J.* **6**, 143-148.
- [26] K. H. C. Başer, T. Özek, B. Demirci and H. Duman (2000). Composition of the essential oil of *Glaucosciadium cordifolium* (Boiss.) Burt et Davis from Turkey, *Flav. Fragr. J.* **15**, 45-46.
- [27] K. Polatoğlu, S. Aرسال, B. Demirci and K. H. C. Başer (2016). Unexpected Irregular Monoterpene “Yomogi Alcohol” in the Volatiles of the *Lathyrus* L. species (Leguminosae) of Cyprus, *J. Oleo Sci.* **65**, 241-249.
- [28] K. H. C. Başer, B. Demirci, N. Tabanca, T. Özek and N. Gören (2001). Composition of the essential oils of *Tanacetum armenum* (DC.) Schultz Bip., *T. balsamita* L., *T. chiliophyllum* (Fisch. & Mey.) Schultz Bip. var. *chiliophyllum* and *T. haradjani* (Rech. fil.) Grierson and the enantiomeric distribution of camphor and carvone, *Flav. Fragr. J.* **16**, 195-200.
- [29] N. Kirimer, N. Tabanca, T. Özek, G. Tümen and K. H. C. Baser (2000). Essential oils of annual *Sideritis* species growing in Turkey, *Pharm. Biol.* **38**, 106-111.