Nat. Vol. & Essent. Oils, 2014; 1(1): 60-65

NVEO
Natural Volatiles & Essential Oils

RESEARCH ARTICLE

Comparison of GC Profiles of *Achillea crithmifolia* and *Origanum heracleoticum* Essential Oils and Headspace Volatiles

Gordana Stojanović*, Olga Jovanović, Goran Petrović, Violeta Mitić and Vesna Stankov Jovanović

Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia

* *Corresponding author. E-mail: stgocaus@yahoo.com*,

Abstract

The GC-FID and GC-MS analysis of hydrodistilled essential oils (EO) and head space volatiles (HSV) of the dried above-ground parts at the flowering stage of *Achillea crithmifolia* Waldst. & Kit. and *Origanum heracleoticum* L. were done. The qualitative monoterpene's composition of EO and corresponding HSV was similar for studied samples, which could not be claimed for their quantitative composition. For some compounds difference in the prevalence was manifold, for instance: carvacrol (*O. heracleoticum,* EO 80.1%, HSV 6.3%) and β-pinene (*A. crithmifolia,* EO 2.7%, HSV 18.4%). As a conclusion, HS volatiles can provide a quick insight into the qualitative composition of plant monoterpenes but could not replace the analysis of essential oils. HSV analysis could be important in the case of lack of material for obtaining the essential oil as well as in the case when the objective is to analyze one single specimen of plant species.

Keywords: *Achillea crithmifolia*, *Origanum heracleoticum*, essential oil composition, head space volatiles

Introduction

In the analysis of the secondary metabolites of plants it would be preferable if the applied method is fast and the generation of artifacts is minimal. Obtaining essential oils (EO) by hydrodistillation or steam distillation is time-consuming (the duration of the distillation is usually two to three hours) and possibility of the formation of artifacts is more probable due relatively high temperature in aqueous solution. Also, the most volatile components could be lost during distillation, essential oil extraction and storage. Traditional head space (HS) method enables the analysis of volatile compounds obtained after the establishment of vapor-liquid equilibrium within a closed container. Time of analysis is much shorter (10-20 minutes) than for hydrodistillation, one can work at lower temperatures with or without solvent, and without loss of highly volatile components. Further, an advantage of HS technique is in the fact that it requires less of the plant material (masses lower than one gram in head space in comparison to usually more than 100 g for obtaining essential oil). Although head space GC is widely used (Buchbauer et al. 1993, Vuorela et al. 1989, Rouseff & Cadwallader, 2001, Zhu et al. 2005, Serban et al. 2012) limited number of articles is focused on analysis of the head space volatile components obtained directly from the plant material under static conditions (Abu-Lafi et al. 2007, Simonović et al. 2014). Continuing a previous examination (Simonović et al. 2014) we considered that it is of interest to compare EO and HSV composition for more samples in order to determine their compatibility. For this purpose, the analysis of essential oils and head space volatiles of *Achillea crithmifolia* Waldst. & Kit. and *Origanum heracleoticum* L. were done.

Materials and Methods

Plant material

Data on plant material as well as oil yield are given in the Table 1.

Isolation of volatiles

The essential oils and HSV was obtained applying previously described procedure (Simonović et al., 2014).

Gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analyses

The GC-FID and GC-MS analysis (three repetitions) was performed using an Agilent Technologies 7890B GC equipped with a fused silica capillary column (HP-5MS, 250 µm x 25 m, film thickness 0.25 µm, Agilent Technologies, USA) and coupled with a 7890A FID and 5977A MS detector of the same company, recording at 70 eV. Full scan spectra were acquired over the range 35-500 amu (scan time 5 scans/sec). GC was operated under the following conditions- injector temperature: 250°C; interface temperature: 300 °C; oven temperature: programmed from 50-290°C at 4 °C/min, then isothermal for 10 min; carrier gas: He, 1.0 mL/min, constant flow mode, vacuum outlet (37 cm/sec linear velocity); injected volume: 1 µL of 1/100 diluted solution of oil in diethyl ether, split ratio 40:1, and 500 µL of HS volatiles were injected, split ratio 10:1. Constituents were identified by comparison of their linear retention indices relative to the retention times of C_8-C_{40} *n*-alkanes on the HP-5MS column (Van Den Dool & Kratz, 1963) with those reported in the literature (Adams, 2007), by comparison of their mass spectra with from Wiley 6, NIST02, and MassFinder 2.3, by the application of the AMDIS software (Automated Mass Spectral Deconvolution and Identification System, Ver. 2.1, DTRA/NIST, 2002). The percentage composition of the oil was computed from the GC peak areas without the use of any correction factors. GC and GC-MS analysis results are given in Table 2.

Results and Discussion

GC-FID and GC-MS analysis resulted in the identification of 49 components in the A. *crithmifolia* EO and 22 components in the A. *crithmifolia* HSV (Table 2). Except 1-octene and *trans*-salvene (total 0.3%), all other HSV components were ingredients of EO also. It is evident that more volatile components such as α- and β-pinene (oil: α-pinene 1.5%, β-pinene 2.7%; HSV: α-pinene 7.9%, β-pinene 18.4%) were more abundant in HSV while the main component *cis*-thujone (51.8% in the oil and 48.5% in the HSV) and its isomer *trans*-thujone (4.7% in the oil and 3.8% in the HSV) were represented approximately equally in the EO and HSV.

The number of identified components in the *O. heracleoticum* essential oil and HSV (17 in EO and 18 in HSV) was less than in *A. crithmifolia* EO and HSV. Thymol and borneol were identified only in EO while sabinene, δ-3-carene, and *p*-mentha-2,4(8)-diene were identified only in HSV. The most abundant compound of EO was carvacrol (80.1 %) while in the HSV it was p-cymene (44.5%). As well as for *A. crithmifolia* sample, more volatile components (all which elute before linalool) were more abundant in HSV. There was a noticeable inverse ratio of overall content of γ-terpinene and *p*-cymene (both are biochemical precursors of carvacrol) and carvacrol in the *O. heracleoticum* oil and HS volatiles (EO ratio 0.17; HSV ratio 9.72). This could be consequence of chemical transformations during hydrodistillation and/or different components' volatility.

It is apparent that the composition of the examined essential oils and corresponding HS volatiles are significantly different in quantitative terms for moust monoterpenes while for the sesquiterpenes,

additionally exists the difference in qualitative terms. As a conclusion, HS volatiles can provide a quick insight into the qualitative composition of plant monoterpenes but could not replace the analysis of essential oils. HSV analysis could be important in the case of lack of material for obtaining the essential oil as well as in the case when the objective is to analyze one single specimen of plant species.

Table 1. Data on plant material and oil yield

No.	Species	Location	Harvesting date	Voucher code[a]	Plant material for the preparation of samples	Oil yield (w/w), %
1	*Achillea crithmifolia* Waldst. & Kit.	Pirin, Bulgaria	26.7.2013	7297	Finely chopped dried above-ground part of the plant in bloom	0.32
2	*Origanum heracleoticum* L.	Pirot, Serbia	11.09.2103.	7299	Finely chopped dried above-ground part of the plant in bloom	3.16

[a] in the"Herbarium Moesiacum Niš" (HMN), Department of Biology and Ecology, Faculty of Science and Mathematics, University of Niš

Table 2. Chemical composition (%) of *A. crithmifolia* Waldst. & Kit. and *O. heracleoticum* L. essential oils (EO) and head space volatiles (HSV)

				A. crithmifolia		***O. heracleoticum***	
	RI	**AI**	**Compound**	**EO**	**HSV**	**EO**	**HSV**
1	794	788	1-Octene	-	0.1	-	-
2	850	847	*cis*- Salvene	0.1	2.2	-	-
3	861	858	*trans*- Salvene	-	0.2	-	-
4	923	921	Tricyclene	tr	0.1	-	-
5	928	924	α-Thujene	0.1	0.1	**1.3**	**9.0**
6	934	932	α-Pinene	**1.5**	**7.9**	0.6	3.6
7	951	946	Camphene	0.6	2.0	0.1	1.1
8	975	969	Sabinene	0.8	1.0	-	0.1
9	980	974	β-Pinene	**2.7**	**18.4**	0.2	1.5
10	992	988	Myrcene	0.1	0.8	**0.8**	**5.8**
11	1007	1002	α-Phellandrene	tr	-	0.1	0.7
12	1013	1008	δ-3-Carene	-	-	-	0.3
13	1020	1014	α-Terpinene	1.2	tr	0.8	4.1
14	1027	1020	*p*-Cymene	3.8	4.8	**8.5**	**44.5**
15	1031	1024	Limonene	0.2	0.5	0.2	1.4
16	1034	1026	1,8-Cineole	**7.2**	**7.5**	-	-
17	1060	1054	γ-Terpinene	0.5	0.1	**4.9**	**16.8**
18	1068	1065	*cis*-Sabinene hydrate	0.3	-	0.3	0.5
19	1090	1085	*p*-Mentha-2,4(8)-diene	0.1	-	-	0.1

NVEO
Natural Volatiles & Essential Oils

				A. crithmifolia		*O. heracleoticum*	
	RI	**AI**	**Compound**	**EO**	**HSV**	**EO**	**HSV**
20	1099	1095	Linalool	-	-	0.8	2.4
21	1101	1098	*trans*-Sabinene hydrate	0.3	-	-	-
22	1110	1101	*cis*-Thujone	**51.8**	**48.5**	-	-
23	1119	1112	*trans*-Thujone	4.7	3.4	-	-
24	1123	1118	*cis*-*p*-Menth-2-en-1-ol	0.5	-	-	-
25	1127	1124	Chrysanthenone	1.5	0.3	-	-
26	1142	1135	*trans*-Pinocarveol	0.6	-	-	-
27	1148	1141	Camphor	4.7	0.7	-	-
28	1160	1154	Sabina ketone	0.5	-	-	-
29	1164	1160	*cis*-Chrysanthenol	0.2	-	-	-
30	1166	1160	Pinocarvone	0.1	-	-	-
31	1169	1165	Borneol	1.8	0.5	0.1	-
32	1180	1174	Terpinen-4-ol	1.5	-	-	-
33	1187	1181	Thuj-3-en-10-al	0.2	-	-	-
34	1193	1186	α-Terpineol	0.5	-	-	-
35	1195	1194	Myrtenol	0.1	-	-	-
36	1199	1195	Myrtenal	0.2	-	-	-
37	1209	1207	*trans*-Piperitol	0.1	-	-	-
38	1238	1235	*trans*-Chrysanthenyl acetate	3.0	0.6	-	-
39	1243	1234	Ascaridole	1.9	-	-	-
40	1245	1241	Carvacrol, methyl ether	-	-	0.1	0.1
41	1257	1249	Piperitone	0.1	-	-	-
42	1263	1261	*cis*-Chrysanthenyl acetate	0.1	-	-	-
43	1290	1287	Bornyl acetate	0.3	-	-	-
44	1291	1289	Thymol	-	-	0.1	-
45	1292	1289	*p*-Cymen-7-ol	0.1	-	-	-
46	1304	1298	Carvacrol	-	-	**80.1**	**6.3**
47	1309	1295	Iso-Ascaridol	0.6	-	-	-
48	1352	1350	α-Terpinyl acetate	1.6	-	-	-
49	1402	1392	*Z*-Jasmone	0.5	-	-	-
50	1405	1403	Methyl eugenol	0.1	-	-	-
51	1427	1417	(*E*)-Caryophyllene	0.6	0.2	0.7	0.2

NVEO
Natural Volatiles & Essential Oils

				A. crithmifolia		*O. heracleoticum*	
	RI	**AI**	**Compound**	**EO**	**HSV**	**EO**	**HSV**
52	1461	1452	α-Humulene	0.1	-	-	-
53	1488	1484	Germacrene D	0.3	-	-	-
54	1592	1582	Caryophyllene oxide	0.3	-	-	-
55	1682	1674	Valeranone	0.2	-	-	-
56	1691	1684	α-Bisabolone oxide A	0.2	-	-	-
57	1739	1730	Chamazulene	0.6	-	-	-
				Total	**Total**	**Total**	**Total**
				99.1	99.7	99.7	98.5
				Monoterpenoids 96.2	Monoterpenoids 97.0	Monoterpenoids 99.0	Monoterpenoids 98.3
				Sesquiterpenoids 1.7	Sesquiterpenoids 0.2	Sesquiterpenoids 0.7	Sesquiterpenoids 0.2
				Others 1.2	Others 2.5	Others 0	Others 0

RI: experimentally determined indices by co-injection of a homologous series of *n*-alkanes C_8–C_{40} on HP-5MS column (Van Den Dool & Kratz 1963); **AI**: Adams retention indices (Adams, 2007); **tr**, trace <0.1%); **-**: not detected. Components represented by more than 5% at least in one of the samples are in bold.

Acknowledgment: Financial support of the Ministry of Education, Science and Technological Development of Serbia (Grant No. 172047) is gratefully acknowledged.

REFERENCES

Abu-Lafi, S., Odeh, I., Dewik, H., Qabajah, M., Imam, A., Dembitsky, V. M., Hanus, L.O. (2007). Natural compounds of Palestine flora. Comparison analysis by static headspace and steam distillation GC-MS of semivolatile secondary metabolites from leaves of cultivated Palestinian Majorana syriaca, *Biomedical papers of the Medical Faculty of the University Palacký, Olomouc, Czechoslovakia*, *151***,** 21-29.

Adams, R. P. (2007). *Identification of essential oil components by gas chromatography/mass spectroscopy*. Allured Publishing Corporation: Illinois.

Buchbauer, G., Jirovetz, L., Wasicky, M., Nikiforov, A. (1993). Headspace and essential oil analysis of apple flowers, *Journal of Agricultural and Food Chemistry, 41*, 116–118.

National Institute of Standards and Technology, NIST Chemistry WebBook, Nist Standard Reference database Website. 2005. [http://webbook.nist.gov/chemistry/]; accesed December 2013.

Rouseff, R. L. & Cadwallader, K. (2001). Headspace Techniques for Food Aroma Volatiles: An Overview. In R. L. Rouseff. & Cadwallader K (Eds.), *Headspace Analysis of Foods and Flavours: Theory and Practice, Vol. 488* (pp. 1-8). Kluwer Academic/Plenum Publishers, New York.

Serban, E., Socaci, S., Tofana, M., Maier, S., Bojita, M. (2012). Advantages of "*headspace*" technique for GC/MS analisys of essential oils. *Farmacia, 60*, 249-256.

Simonović, S., Stankov-Jovanović, V., Mitić, V., Ilić, M., Petrović, G., Stojanović, G. 82014). Chemical Composition of *Angelica pancicii* Essential Oil Determined by Liquid and Headspace GC-MS Techniques. *Nat ural Product Communication, 9*, 271-272.

Stein, S. E. National Institute of Standards and Technology (NIST) Mass Spectral Database and Software, Version 3.02. 1990.

Van Den Dool, H., & Kratz, P. D. (1963). A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. *Journal of Chromatography A, 11,* 463–471.

Vuorela, H., Pohjola, J., Krause, C., Hiltunen, R. (1989). Application of headspace gas chromatography in essential oil analysis. Part IX. Selective loss of terpene compounds during hydrodistillation. *Flavour and Fragrance Journal, 4*,117–120.

Zhu, J. Y. & Chai, X. S. (2005). Some Recent Developments in Headspace Gas Chromatography. *Current Analytical Chemistry, 1*, 79-83.