Asian Journal of Chemistry Vol. 20, No. 2 (2008), 1290-1294

Effects of Diurnal and Ontogenetic Variability on Essential Oil Composition of Oregano (*Origanum vulgare* var. hirtum)

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This study was carried out to determine the effects of diurnal and stage of harvesting on the essential oil components of oregano (*Origanum vulgare* var. hirtum). The samples were collected at three different stages of flowering (before and after flowering) and six different times (06:00, 09:00, 12:00, 15:00, 18:00 and 21:00 h) with drying under shade or sunshine. Essential oil was obtained by hydrodistillation method and analyzed with GC-MS. Results showed that the main compound of *O. vulgare* var. hirtum was thymol. The harvest stage affected the compounds of essential oil such that *p*-cymene increased at full flowering while γ-terpinene decreased. Drying methods and harvesting time showed a minor effect on volatile compounds. The highest variation in composition of essential oil in relation to harvest stage was determined in *p*-cymene and γ-terpinene. It was concluded that the harvest stage along with drying under shade should be firstly considered.

Key Words: Oregano, *Origanum vulgare* var. hirtum, Essential oil composition, Harvest stage, Harvest time, Drying method.

INTRODUCTION

Oregano (*Origanum vulgare* var. hirtum) is an annual aromatic plant, belonging to the *Lamiaceae* family, which grows in several parts of the world. A total of 38 *Origanum* species are spread in the Mediterranean, Euro-Siberian and Iran-Siberian regions[1]. Most of Origanum species, over 75 %, are concentrated in the East Mediterranean sub region. Of them, 16 species are endemic in the flora of Turkey[2]. *Origanum* is traditionally used for the treatment of asthma, indigestion, headaches, stomach disorders and rheumatism. Besides use in perfume and soap industry, *Origanum* species are also used as powerful disinfectants. Its oil is also used in seasoning of Italian, Spanish and Turkish cuisine[3,4].

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The essential oil content of *Origanum* varies within the species and subspecies. Carvacrol and thymol are the dominant compounds of the essential oil, the concentration of which varies depending on climatic, seasonal conditions and geographical distribution or harvesting season, drying techniques[5,6] and the time of day. Several researchers[7-9], recorded alternations in the volatile compounds of oregano as affected by harvest stage or harvesting season. Limited literature is available about the drying techniques of *Origanum* spp. Jerkovic *et al.*[7] recorded that some compounds evaporate or completely disappear during drying while others are retained.

The study reports effects of harvest stage, harvest time and drying techniques on the essential oil components of *O. vulgare* var. hirtum.

EXPERIMENTAL

This study was carried out during 2003-04 at the fields and laboratories of the Department of Field Crops, Faculty of Agriculture, University of Ankara. *O. vulgare* var. hirtum was grown under the field conditions with two irrigations. The fresh herb samples were taken at three stages *i.e.* before and after flowering during summer season, at six different times (06:00, 09:00, 12:00, 15:00, 18:00, 21:00 h) during day and were dried under shade or sunshine.

Essential oil obtained by hydrodistillation method of herb samples was stored at 4 ºC before using and analyzed by GC-MS. The analysis was performed using a Hewlett Packard 6890 N GC equipped with HP-5 MS capillary column (30 m × 0.25 μm) and HP 5973 mass selective detector. For GC-MS detection an electron ionization system with ionization energy of 70 eV was used. Helium was carrier gas at a flow rate of 1 mL/min. Injector and MS transfer line temperatures were set at 220 and 290 ºC, respectively. Column temperature was initially kept at 50 ºC for 3 min then gradually increased to 150 ºC at a 3 ºC/min rate, held for 10 min and finally raised to 250 ºC at 10 ºC/min. Diluted samples (1/100 in acetone, v/v) of 1.0 μL were injected automatically and in the splitless mode[5]. Individual components were identified by spectrometric analyses using computer library.

RESULTS AND DISCUSSION

The results (Table-1) show that the essential oil composition of *O. vulgare* var. hirtum affected by different harvest stages, times and drying methods. GC/MS analysis of the oil resulted in 17 main compounds representing about 96-98 % of the oil. The major compound of the *O. vulgare* var. hirtum was thymol (52 %), followed by γ-terpinene (15-17%), *p*-cymene (12-13 %), α-terpinene (2 %) and β-caryophyllene (2 %). However, this sequence changed with harvest stage except for thymol which remained the highest irrespective of harvest stage. Thymol was followed

TABLE-1
THE VARIATIONS IN ESSENTIAL OIL COMPOSITIONS OF *Origanum vulgare* var. hirtum AS AFFECTED BY STAGE AND TIME OF HARVESTING ALONG WITH DRYING METHODS

Compounds	RT	Drying status	Before flowering							Full flowering							After flowering							Gen. Avg.
			6:00	9:00	12:00	15:00	18:00	21:00	Avg.	6:00	9:00	12:00	15:00	18:00	21:00	Avg.	6:00	9:00	12:00	15:00	18:00	21:00	Avg.	
α-Pinene	8.62	Shade	0.80	0.69	0.77	0.74	0.62	0.72	0.72	0.67	0.46	0.60	0.71	0.73	0.60	0.63	0.52	0.52	0.48	0.62	0.56	0.56	0.54	0.63
		Sun	0.97	0.80	0.70	0.62	0.62	0.62	0.72	0.63	0.47	0.56	0.65	0.68	0.68	0.61	0.62	0.54	0.54	0.42	0.54	0.49	0.53	0.62
Camphene	9.18	Shade	0.16	0.14	0.15	0.16	0.14	0.16	0.15	0.13	0.11	0.12	0.16	0.16	0.13	0.14	0.12	0.10	0.10	0.13	0.13	0.11	0.12	0.13
		Sun	0.20	0.15	0.16	0.15	0.15	0.16	0.16	0.12	0.11	0.11	0.13	0.15	0.15	0.13	0.13	0.12	0.10	0.10	0.13	0.11	0.12	0.14
1-Octen-3-ol	10.53	Shade	0.22	0.20	0.20	0.20	0.18	0.20	0.20	0.27	0.23	0.24	0.22	0.22	0.26	0.24	0.19	0.24	0.27	0.26	0.26	0.27	0.25	0.23
		Sun	0.23	0.22	0.23	0.22	0.23	0.20	0.22	0.33	0.26	0.23	0.21	0.21	0.22	0.24	0.33	0.22	0.27	0.26	0.20	0.26	0.26	0.24
Myrcene	11.07	Shade	1.78	1.73	1.71	1.82	1.59	1.72	1.72	1.38	1.22	1.47	1.44	1.40	1.47	1.40	1.26	1.23	1.13	1.32	1.19	1.28	1.24	1.45
		Sun	1.85	1.19	1.67	1.62	1.59	1.51	1.57	1.27	1.06	1.24	1.35	1.49	1.33	1.29	1.41	1.14	1.13	1.02	1.42	1.04	1.19	1.35
α-Phellandrene	11.57	Shade	1.23	1.18	1.21	1.25	1.11	1.25	1.21	1.11	0.90	1.01	1.13	1.00	0.99	1.02	0.97	0.88	0.85	1.06	0.97	0.98	0.95	1.06
		Sun	1.43	1.32	1.20	1.14	1.10	1.11	1.22	0.99	0.78	0.93	1.01	0.98	0.97	0.94	0.93	0.87	0.91	0.70	0.83	0.79	0.84	1.00
α-Terpinene	12.14	Shade	2.73	3.10	2.79	3.08	2.62	2.70	2.84	2.26	2.15	2.17	2.11	1.46	1.94	2.02	2.19	2.02	2.01	2.27	2.16	2.25	2.15	2.33
		Sun	2.92	3.00	2.70	2.61	2.62	2.42	2.71	1.95	1.63	1.91	1.85	1.48	1.51	1.72	1.94	1.67	2.00	1.61	1.60	1.74	1.76	2.07
p-Cymene	12.53	Shade	7.97	6.35	7.62	7.05	6.65	8.12	7.29	15.32	11.51	16.18	18.83	23.29	19.55	17.45	12.82	12.45	11.55	13.01	11.95	12.87	12.44	12.39
		Sun	8.04	6.86	8.25	6.85	7.33	7.60	7.49	15.03	13.89	14.43	17.51	22.98	20.76	17.43	14.91	14.16	11.13	12.78	21.71	11.57	14.38	13.10
γ-Terpinene	14.22	Shade	22.19	22.23	20.87	23.06	22.65	22.80	22.3	15.20	16.01	14.74	14.56	10.56	13.78	14.14	15.89	13.91	14.26	15.92	15.26	15.61	15.14	17.20
		Sun	22.34	22.14	21.86	22.73	22.60	21.96	22.3	13.44	12.05	12.90	13.44	11.11	10.73	12.28	12.95	12.12	14.15	12.38	11.51	12.57	12.61	15.72
Isoborneol	19.00	Shade	0.35	0.26	0.33	0.29	0.37	0.38	0.33	0.34	0.28	0.36	0.33	0.36	0.35	0.34	0.34	0.39	0.29	0.29	0.26	0.29	0.31	0.33
		Sun	0.35	0.33	0.39	0.41	0.44	0.41	0.39	0.39	0.35	0.39	0.32	0.55	0.36	0.39	0.45	0.31	0.28	0.43	0.33	0.32	0.35	0.38
4-Carvomenthenol	19.59	Shade	0.53	0.50	0.53	0.60	0.45	0.45	0.51	0.69	0.65	0.74	0.65	0.66	0.69	0.68	0.67	0.84	0.77	0.72	0.70	0.71	0.74	0.64
		Sun	0.52	0.60	0.56	0.59	0.56	0.53	0.56	0.78	0.82	0.76	0.70	0.69	0.74	0.75	0.89	0.79	0.78	0.78	0.66	0.80	0.78	0.70
Carcacrol methylether	22.73	Shade	3.91	3.63	3.56	3.67	3.55	3.59	3.65	4.46	4.08	4.83	4.49	4.88	4.93	4.61	3.59	4.29	3.79	3.52	3.59	3.74	3.75	4.01
		Sun	3.87	3.82	3.69	3.65	3.87	3.80	3.78	4.53	4.44	4.55	4.69	4.97	4.79	4.66	4.70	3.98	3.59	3.83	4.97	3.81	4.15	4.20
Thymol	25.27	Shade	47.72	50.55	47.04	49.46	51.62	48.72	49.19	52.64	57.75	51.19	48.80	46.90	47.41	50.78	55.37	55.81	58.08	55.26	57.25	55.14	56.15	52.04
		Sun	47.23	49.30	48.78	50.17	49.12	50.61	49.20	54.06	58.14	55.40	51.38	46.06	49.92	52.49	50.47	56.51	58.58	58.91	47.87	59.68	55.34	52.34
Carvacrol	25.45	Shade	0.95	1.05	4.49	1.06	0.95	0.95	1.58	1.11	1.07	1.18	1.74	2.09	1.93	1.52	2.04	1.76	1.64	1.51	1.50	1.56	1.67	1.59
		Sun	0.93	1.23	1.40	0.97	0.96	0.89	1.06	1.20	1.20	1.28	1.81	2.02	2.02	1.59	2.95	2.15	1.65	1.61	2.07	1.71	2.02	1.56
β-Caryophyllene	30.33	Shade	2.88	2.59	2.73	2.35	2.53	2.61	2.62	1.76	1.82	1.93	1.75	1.90	1.93	1.85	2.04	2.37	2.26	1.88	2.10	2.17	2.14	2.20
		Sun	2.83	2.63	2.54	2.59	2.80	2.76	2.69	1.73	1.63	1.92	1.71	1.86	1.79	1.77	2.32	1.89	1.95	1.99	1.94	1.99	2.01	2.16
α-Humulene	31.70	Shade	0.34	0.29	0.32	0.27	0.29	0.30	0.30	0.22	0.22	0.24	0.21	0.23	0.24	0.23	0.24	0.30	0.28	0.23	0.25	0.26	0.26	0.26
		Sun	0.33	0.30	0.29	0.30	0.32	0.31	0.31	0.22	0.21	0.24	0.21	0.23	0.22	0.22	0.29	0.23	0.24	0.25	0.24	0.25	0.25	0.26
β-Bisabolene	34.03	Shade	1.90	1.55	1.79	1.38	1.62	1.59	1.64	0.71	0.64	0.80	0.87	1.36	1.08	0.91	0.77	0.86	0.81	0.76	0.77	0.81	0.80	1.12
		Sun	1.76	1.66	1.71	1.65	1.76	1.73	1.71	0.78	0.73	0.78	0.81	1.39	1.09	0.93	1.20	0.92	0.78	0.94	1.21	0.83	0.98	1.21
Caryophyllene oxide	36.86	Shade	0.51	0.20	0.34	0.30	0.34	0.44	0.36	0.99	0.84	1.12	1.15	1.31	1.23	1.11	0.65	0.89	0.74	0.72	0.66	0.75	0.74	0.73
		Sun	0.37	0.38	0.40	0.46	0.44	0.36	0.40	1.33	1.36	1.30	1.19	1.38	1.39	1.33	1.35	1.13	1.05	1.13	1.31	1.10	1.18	0.97
Total		Shade	96.17	96.24	96.45	96.74	97.28	96.70	96.62	99.26	99.94	98.92	99.15	98.51	98.51	99.07	99.67	98.86	99.31	99.48	99.56	99.36	99.39	98.34
		Sun	96.17	95.93	96.53	96.73	96.51	96.98	96.46	98.78	99.13	98.93	98.97	98.23	98.67	98.77	97.84	98.75	99.13	99.14	98.54	99.06	98.75	98.02

by γ-terpinene, *p*-cymene and β-caryophyllene; *p*-cymene, γ-terpinene and α-terpinene and γ-terpinene, *p*-cymene and carvacrolmethyl ether at before and after flowering, respectively. Carvacrol percentage increased when the harvest was delayed. Jerkovic *et al.*[7] found increase in carvacrol content of fresh and dried samples when the harvest was delayed. Kokkini *et al.*[10] indicated that the essential oil compound was chanced by location and harvest season while oil yield in summer season remained higher than that of autumn.

The highest α-pinene, myrcene, α-phellandrene, α-terpinene, β-caryophyllene and β-bisabolene were determined in plants harvested before flowering. The highest thymol was obtained after flowering while *p*-cymene was higher at full flowering at other harvest stages. The most affected compound by harvest stage was *p*-cymene which increased from 7.29 % before flowering to 17.45 % at full flowering. β-Caryophyllene had the highest value (2.62-2.69 %) before flowering, which decreased to the lowest at full flowering. The essential oil before flowering had higher γ-terpinene than at the later harvests. Johnson *et al.*[11] found that *p*-cymene was higher in early March than the later sampling. In general, thymol content increased as the harvest stage was delayed.

Drying methods slightly influenced some compounds of the oil. Before flowering, carvacrol decreased when the plants were dried under sun. However, thymol at full flowering increased with drying under sun. γ-Terpinene percentage both at full and after flowering was reduced by sun drying. Cesare *et al.*[6] recorded that air-dried oregano plant materials at 35ºC had the higher contents of thymol and carvacrol than that dried at room temperature. Marzi[12] observed that high temperatures during drying process had negative effects on the oil content. Contrarily our findings showed no remarkable change in essential oil components by drying methods.

Some compounds of the oil were affected by harvest time. Thymol was the highest at 18:00, 09:00 and 12:00 before and after flowering, respectively. It was higher up to noon at both full flowering and after flowering. Late harvesting in a day resulted in harvest of higher thymol percentage compared to early harvest.

In conclusion, the harvest stage was found to affect both quality and quantity of essential oils of oregano and was determined as the most important criterion, with rare effects of drying methods on some components. Harvest time in a day on quality quantity of the oil. It is concluded that harvest stage along with drying of fresh plant material under shade should be given consideration in the absence of equipped drying machine.

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(*Received*: 16 February 2007; *Accepted*: 4 October 2007) AJC-5970