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Seasonal variation study of the volatile oils of *Origanum Cyrenaicum* in Libya

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ABSTRACT

A total of 11 samples of the aerial part of Origanum cyrenaicum were analysed fresh and dry for their essential oil contents and for the effect of seasonal variation on the concentration of these oils. Compounds characterized by gas chromatography and mass spectrometry were divided into 4 groups according to their molecular structure. The first group which contain monoterpenes hydrocarbon This group was in the highest concentration in spring during the month of May. The second group was the oxygenated form showed the highest concentration in spring during the month of May. While the third and fourth groups were the sesquiterpene hydrocarbon and the oxygenated. Showed high concentrations in the fall season during the month of October. Most compounds found were (D-germacren-4-ol, 33.57%)-(caryophyllene oxide, 28.49%) - (trans-caryophyllene, 24.76%) - (epizonarene, 21.94%) - (germacrene-D, 17.43%) The high concentration of compound D-germacren-4-ol, (33.57%) occurred in October in fall season. The results of this study indicate that Origanum cyrenaicum is rich sesquiterpene hydrocarbons and oxygenated sesquiterpenes oils specially during the fall season.

Key words: Origanum cyrenaicum, essential oils, seasonal variation, D-germacren-4-ol, caryophyllene oxide, trans-caryophyllene, epizonarene, germacrene-D

INTRODUCTION

The Origanum species are sub shrubs or perennial herbs with several stems, ascending or erect, sub sessile or petiolate leaves and flowers in verticillasters aggregated in dense or loose spikes which are arranged in a paniculate or corymbiform inflorescence. Origanum plants are widely used all over the world as a very popular spice, under the vernacular name 'Oregano'. They are of great economic importance which is not only related to their use as a spice. In fact, as recent studies have pointed out, oregano is used traditionally in many other ways as their essential oils have antimicrobial, cytotoxic and antioxidant activity [1,2] reviewed the chemosystematic investigation on the mono- and sesquiterpenoids in the genus *Origanum* (Labiatae) and published their findings in phytochemistry and stated that they have examined the volatiles of *Origanum* species native to Crete together with two naturally occurring hybrids. The main volatiles found were compared with all the existing published analyses for *Origanum* and the taxonomic significance of volatile oil composition was assessed. Results and the existing data together showed convincingly that most *Origanum* species are rich either in sabinyl compounds or cymyl compounds but never both. In Croatia [3] the volatile constituents of Origanum vulgare L.ssp. grown wild in Croatia were studied and the result showed that samples of *Origanum vulgare* ssp . were collected from the same geographic area in the south of Croatia at different seasons of growth. Have maximum concentration fluctuations for the main components of fresh plant material: thymol [149.2-1124.4mg (100g)-1], carvacrol [51.6-564.3 mg (100g)-1], p-cymene [20.2-220.9 mg (100g)-1] and γ-terpinene [50.1-217.5 mg (100g)-1]. The oregano that was analysed belonged to a thymol/carvacrol chemotype. The season of collecting affected the qualitative and quantitative composition of the essential oil. The most impressive difference was the increase of *p*-cymene content in August. After the drying of the plant material, all samples showed a minor in essential oil yields when compared with fresh plants. Drying at room temperature had no effect on the qualitative composition of oregano oil. Because of the variability of essential oil compositions from seasonally collected fresh and dried oregano, it would be important to check the quantity and quality of such components, [4] studied the impact of both the season of collection and drying on the volatile.

MATERIALS AND METHODS

The plant collected during the period 11/4/2003 - 9/3/2004 from the Green Mountain, Number of collected samples were 11 of the wild grown plant of *O. cyrenaicum.* Identified by the Botany department. The leaves were the only part screened in this study. Two sections: fresh section - frozen the other section was dried at room temperature. The collected plant material was air-dried at room temperature for 10 days resulting in a totally dry plant material. Fresh leaves were cut into small pieces and immersed in water, and then 5ml of glycerin was added and left for 24 hours without distillation to facilitate the liberation of aromatic oil associated with glycosides through the degeneration of enzymes. The quantity of the plant sample extracted (100 g) were subjected to hydro-distillation for 7 h using a Clevenger-type apparatus to extract oils. Storing essential oils in dark glass bottles with suitable caps in cool place away from light.

Table 1 Summary of collections

No.	Date of collected	Plant used as	Weight of plant extracted	Method of extracted	Volume of oil in ml
1	25/04/2003	Fresh	100 g	Hydro distillation	0.3
2	09/05/2003	Fresh	100 g	Hydro distillation	0.3
		Dry			0.4
3	16/05/2003	Dry	100 g	Hydro distillation	0.35
4	30/05/2003	Fresh	100 g	Hydro distillation	0.14
		Dry			0.1
5	06/06/2003	Dry	100 g	Hydro distillation	0.23
6	13/06/2003	Fresh	100 g	Hydro distillation	0.18
		Dry			0.25
7	08/08/2003	Fresh	100 g	Hydro distillation	0.11
		Dry			0.22
8	15/08/2003	Fresh	100 g	Hydro distillation	0.18
		Dry			0.12
9	04/09/2003	Fresh	100 g	Hydro distillation	0.15
		Dry			0.15
10	19/09/2003	Fresh	100 g	Hydro distillation	0.26
		Dry			0.2
11	09/10/2003	Fresh	100 g	Hydro distillation	0.2
		Dry			0.2

RESULTS AND DISCUSSION

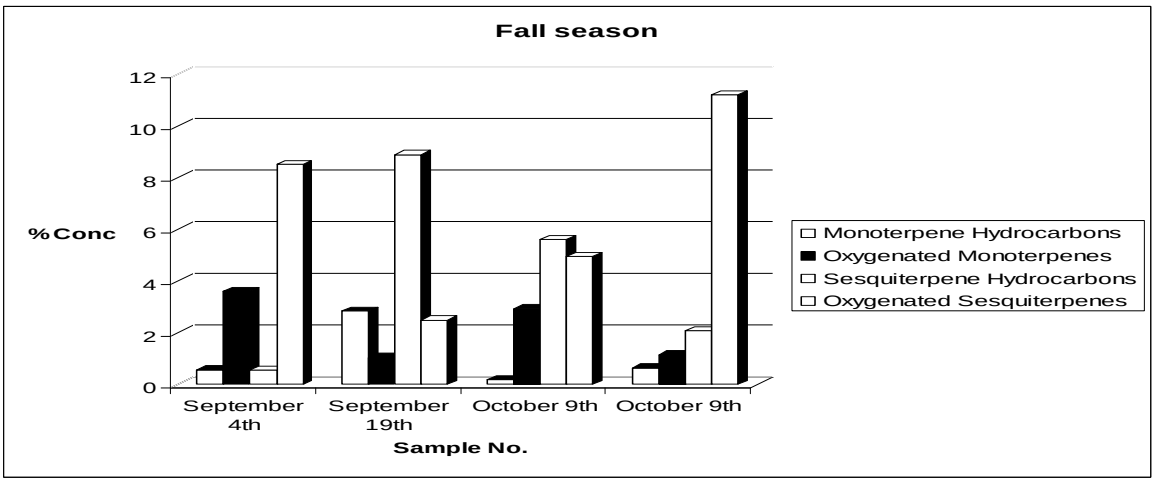
The oil samples showed in GC analysis presence of peaks at retention times and percentage areas. Analysis of the oil samples by using gas chromatography and gas chromatography / mass spectrometry gave the qualitative and the quantitative results for all compounds found in oil samples by measuring the area under each peak by the GC and examining each peak by mass spectra. Finalizing the result is by comparing the results from the mass spectra with a computerized data base for all essential oils. For similar results another technique was used to distinguish between the results is by applying the retention index formula for two known peaks located before and after the unknown peak. By using these indexes, all compounds were identified.

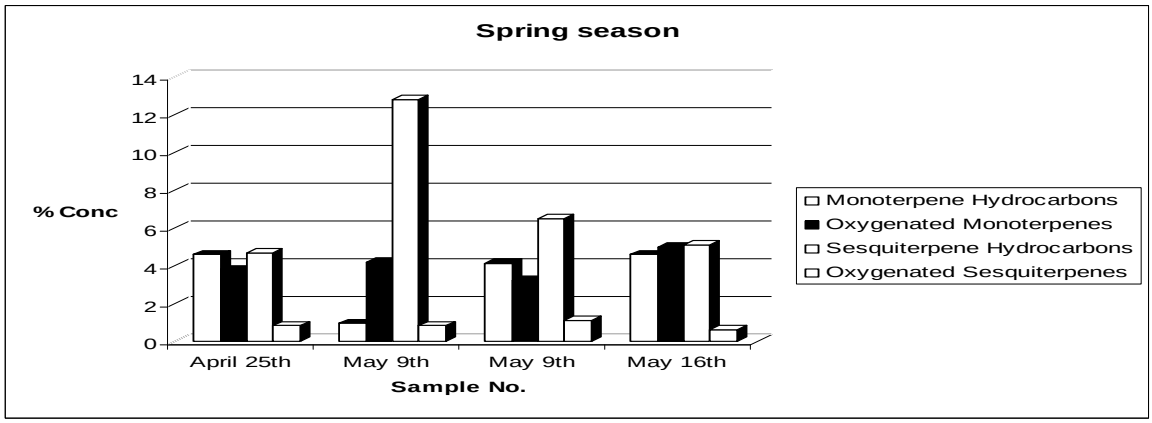
The total compounds identified to be present in all samples are divided into four groups:
a- Monoterpene hydrocarbon
b- Monoterpene with oxygen (oxygenated).
c- Sesquiterpene hydrocarbon
d- Sesquiterpene with oxygen (oxygenated).

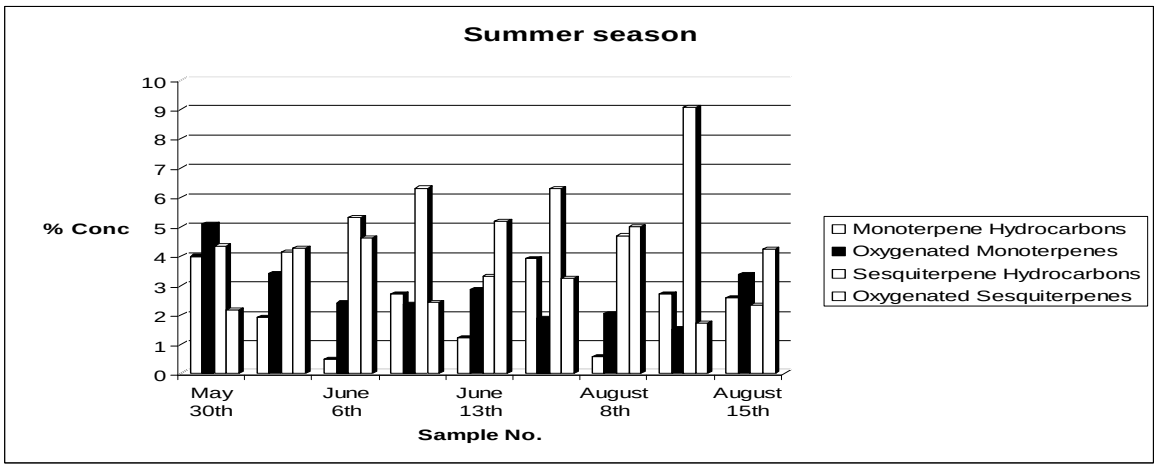
Discussing all compounds according to season would not be practical because of the many compounds identified with very low percentage concentration. Choosing the highest percentage compounds and studying them according to their concentration in different seasons and according to their percentage in the dry and fresh samples would give a clearer picture of the comparisons data.

The summer season samples
This season starts at 28th to May and ends on the 28th of August. Nine samples were collected in this season, four samples were analyzed as fresh samples and five were dry. Volumes of oil extracted from each sample are presented in (Table 1). The monoterpenes were fairly highly concentrated except in dry sample collected on 8/8. The average of the percentage concentration of the samples under this category was highest on the collection date of 30/5 which showed the highest concentration of α-pinene (9.05%) of all collections and the lowest percentage on the collection date of 8/8. Oxygenated monoterpenes were highly concentrated in these samples. The collection date of 30/5 gave

the highest average percentage concentration and the compound carvacrol was the highest in this collection and in all collections under this category (14.59 %).







Sesquiterpene hydrocarbons showed the highest in concentration in all categories with average percentage of 9.06 % at the collection date of 15/8 which showed also the highest percentage concentration of compound D-germacrene (17.43%). Oxygenated sesquiterpenes the collection date of 13/6 showed the highest average percentage concentration and represents the highest concentration of compound D-germaceren-4-ol (20.08%) on the same collection date.

The fall season samples: This season starts on 28th of August and ends on 28th of November. Four samples were collected in this season two dry and two fresh samples were studied. Monoterpenes were quite low in concentration during this season which can be understood because of hot summer season just passed and most of the light monoterpenes had evaporated. Fresh sample collected on the nineteenth of September showed the highest

concentration of monoterpene α-pinene (6.01%) and the same collection showed the highest average concentration of 2.84 % others were poor in monoterpenes. Same effects were noticed for the Monoterpenes oxygenated category with some increase in concentration. The collection dated on fourth of September showed 4-terpenol representing the highest concentration with 6.95 % and highest average concentration of 3.61 % and the disappearing of many oxygenated monoterpenes compounds were clear in this category.

Sesquiterpene hydrocarbons the concentration start increasing in this category because of high evaporation temperature needed for this type of compounds the sesquiterpene *trans*-caryophyllene was the most found terpene in this category with 16.11% in the collection date of the fourth of September which also showed the highest average concentration 8.89 %. Oxygenated sesquiterpenes this category was the highest produced in this season. Most concentrations were fairly high. The highest was D-germaceren-4-ol on the collection date ninth of October with 33.57 % and the highest average concentration was for the same date with 11.19%.

The spring season samples

Most of the spring samples were poor in oil production because the plant was not mature enough to produce the essential oils. Monoterpene hydrocarbons Dry sample collected on sixteenth of May was having α-pinene with concentration of 9.07% which also represent the highest average concentration 4.61%.While the same average concentrations were found in the sample collected on twenty-fifth of April with comparable concentrations of monoterpenes. Oxygenated monoterpenes the same sample showed the highest average concentration (5%) and carvacrol was the highest oil in the category (13.09%).

The Sesquiterpene *trans*-caryophyllene was on the top of the concentration ranking with 24.76% on the ninth of May this sample showed the highest in average concentration of 12.81%. Oxygenated sesquiterpenes this category was poorly presented by all spring samples; this very low concentration explained may be by the immaturity of plant in this season.

CONCLUSION

The oils of *Origanum cyrenaicum* were analyzed by GC/MS and confirmed the assessment of the constituents of oils, with acceptable comparison with previously reported oils of other *Origanum* species. The highest concentrations were (D-germacren-4-ol, 32.08%)-(caryophyllene oxide, 28.49%)-(trans-caryophyllene, 24.76%)-(epizonarene, 21.94%)-(germacrene-D, 17.43%)-(carvacrol, 14.59%)-(4-terpineol, 12.67%)-(α-pinene, 9.07%)-(β-thujopsan-2-ol, 8.1%)-(cadinol <epi-α->, 7.53%)-(γ-terpinene, 7.27%)-(β-pinene, 7.07%)-(sabinene, 7.03%)-(isopulegol, 6.69%)-(α-thujopsan-2-ol, 6.34%)-(2-hexenyl benzoate E, 6.09%)-(linalool, 5.86%)-(α-cadinol, 5.39%)-(octanedioic acid, diethyl ester, 4.87%)-(p-cymene, 4.82%)-(thymol, 4.31%)-(β-bourbonene, 4.24%)-(α-terpineol, 2.60%)-(β-phellandrene, 1.95%) and (camphene, 1.77%). This is the first report of oils from the Libyan endemic plant *Origanum cyrenaicum*

The effect of season was studied in brief and the monoterpenes concentration was changing were varying with high concentrations in spring season and decreasing gradually with the lowest concentration in fall season. The oxygenated monoterpenes were showing similar pattern as the monoterpenes with some different concentrations. Sesquiterpenes showed a falling trend in concentration while oxygenated sesquiterpenes (especially from dry extract) showing a clear gradual increase in concentration in the samples collected from April to October.

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