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Source / Izvornik: **Acta Pharmaceutica, 1995, 45, 517 - 522**

Journal article, Published version
Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: https://urn.nsk.hr/urn:nbn:hr:163:019490

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Download date / Datum preuzimanja: **2024-07-29**

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Acta Pharm. 45 (1995) 517–522 Original scientific paper

Variations in yields and composition of immortelle (*Helichrysum italicum*, Roth Guss.) essential oil from different locations and vegetation periods along Adriatic coast

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Immortelle was collected at nine different locations along the Adriatic coast. One location was chosen to study variations in oil yields and composition in different vegetative stages (six samples). The oil yield of the samples collected from different locations ranged from 0.08% to 0.32%, and for samples in different stages of development it ranged from 0.06% to 0.35%. The composition of the oils was analyzed by GC and GC/MS.

Keywords: Helichrysum italicum, essential oil composition, oil yield, ontogenetic variation

Received March 15, 1995

Helichrysum italicum (Roth) Guss. (everlasting or immortelle) is a plant of Mediterranean region. It is widespread along the East coast and on the islands of the Adriatic sea (1, 2). The essential oil is a characteristic component of the plant because it is present in all of the green parts of the plant. To obtain the oil, generally, freshly cut plants are used for distillation. However, sometimes partially dried material is used as well because of the distance between the areas where the plants are harvested and the location of the distilleries.

By gas chromatography the immortelle oil composition, originating from Esterele, France, and former Yugoslavia was comparatively examined by Peyron and Roubaud (3). They detected 54 significant peaks and characterized only 15.

Weyerstahl and coworkers (4, 5) studied essential oil of immortelle to clear the structure of unknown sesquiterpenes and to analyse the most interesting olfactoric fractions. They distilled off the terpenes and identified them by comparison with the known compounds. The sesquiterpenes were separated into polar and unpolar fractions, which were analysed subsequently using GC/MS and after separation into individual compounds also by ^{1}H-NMR and ^{13}C-NMR spectra. They found curcumens as the most abundant sesquiterpenes, but they also resolved the structure of four unknown sesquiterpenes: italicene, *iso*-italicene, helifolene and *iso*-helifolene.

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We have examined the samples of *H. italicum* collected from different locations along the Croatian coast and the two islands. From one location (Vela Luka on island Korčula), we have examined the quantity and composition of oils obtained from plants harvested at different development stages.

EXPERIMENTAL

Plant material. – Aboveground (aerial) parts of *H. italicum* were collected during flowering time at the sites shown in Table I. The plant material consisted of stems (15–25 cm) with leaves and flower heads. For examination of quantity and composition of essential oil at different vegetation stages, the plant material was collected at the location No. 1 (Vela Luka). All the samples were air dried in shadow and before distilling cut into pieces smaller than 1 cm. Distillation of essential oil was done by a modified apparatus according to *Ph. Jug. IV* (6). After distillation and cooling down, the essential oil was taken into pentane. The solution was dried over Na_2SO_4 sicc., filtered and pentane evaporated at room temperature. The residue obtained was dried in a vacuum desiccator. Essential oil quantification was done gravimetrically.

The composition of the oils was determined by capillary gas chromatography. The analysis was performed on a Pye Unicam PU 4550 gas chromatograph equipped with FID coupled to PU 4810 integrator. A 25 m × 0.32 mm WCOT fused silica capillary column CP-Sil 8CB (= SE 54 CB) was used at following temperatures: injection port temperature 220 °C, detector temperature 250 °C and the oven (column) programmed as follows: 60 °C (1 min), 60–220 °C at 4 °C min^{-1}. H_2 was used as a carrier gas at a flow rate of 0.3 mL min^{-1}. GC/MS analyses were performed on a Shimadzu QP 1000 GC/MS coupled to a data station. Individual peaks were identified by comparing their retention times to those of standard compounds, as well as by comparing their mass spectra to those stored in the data library. The quantitative data were obtained by peak normalization technique using integrated FID responses.

RESULTS AND DISCUSSION

The quantities of immortelle essential oil from different locations along the Adriatic coast and two islands are presented in Table I. The highest amount of oil is obtained from the sample collected during its flowering period at the location No. 5 (Ljubuški) 30 km far from the coast. In Table II the quantities of essential oil obtained at different vegetation stages are presented. The highest value has the sample of new shoots grown after lot of rain in late summer. Among other samples, the highest quantity of oil has been found in the sample collected just before flowering, as characteristic for many other aromatic plants.

In Table III the composition of essential oil from different locations is given, while in Table IV the results of examination of essential oil composition in different vegetation stages of the plant are presented.

Table I. Yield and proportion of main groups of compounds present in immortelle essential oils from different locations

Location	Yield (%)	Type of compounds (%)			
		Monoterpenic hydrocarbons	Monoterpenic alcohols, esters, phenols	Sesquiterpenes	Diterpenes or similar compounds
1. Vela Luka	0.16	5.38	15.38	75.94	3.10
2. Stobreč	0.11	12.62	25.61	58.24	3.55
3. Benkovac	0.08	41.37	21.07	34.37	2.19
4. G. Poljice	0.11	15.02	27.63	53.55	2.89
5. Ljubuški	0.32	30.15	24.22	44.95	0.68
6. Doli	0.14	0.64	14.42	81.77	2.07
7. Ličtica	0.16	0.36	25.99	68.05	5.09
8. Trogir	0.21	4.93	20.17	73.47	1.83
9. Rab	0.27	1.40	18.24	73.29	7.09

Table II. Yield and proportion of main groups of compounds present in immortelle essential oils from the plants harvested in different vegetation stages (location No. 1, Vela Luka)

Vegetation stage of plant	Yield (%)	Type of compounds (%)			
		Monoterpenic hydrocarbons	Monoterpenic alcohols, esters, phenols	Sesquiterpenes	Diterpenes or similar compounds
A. Early shoots	0.15	30.61	21.08	40.28	8.04
B. Corymb forming	0.06	35.27	16.32	46.31	2.10
C. Before flowering	0.21	17.86	15.37	63.81	2.98
D. In flowering	0.17	5.38	14.78	75.94	3.10
E. After flowering	0.15	6.38	21.60	67.88	3.81
F. Late summer shoots	0.35	23.10	20.17	56.19	0.51

As seen from Table III, the essential oils from different locations are very similar as regards their qualitative composition, but in quantity of particular components they differ greatly.

The amount of α-pinene is very high in the samples from Benkovac and Ljubuški (29.90% and 25.18%), but very low in the samples from Doli and Ličtica (0.1% and 0.44%, respectively). The portion of γ-curcumene is very high in sample No. 6 (Doli) (22.02%), but there is none whatsoever in the sample No. 5 (Ljubuški) or very low in the sample No. 4 (G. Poljice) *i.e.* 4.88%.

The amount of nerol which is a characteristic component of the oil was found in the range of 0.66 to 3.75%. Neryl acetate, also a characteristic component of this oil, was found in the range of 4.13 to 13.51%. The highest amount of this compound was found in the sample No. 5 (Ljubuški), which as regards the oil content was the richest sample.

As well, the composition of essential oil studied at different plant vegetation stages was qualitatively almost the same, but the amounts of particular components differ a

Table III. Composition of immortelle essential oil harvested on different locations of Croatian Adriatic coast and islands (%)

Component	Location[a]									Identification
	1	2	3	4	5	6	7	8	9	
α-pinene	4.15	2.29	29.90	10.06	25.18	0.44	0.10	3.47	0.43	a, b, c
Camphene	–	0.89	1.24	0.59	–	–	–	0.10	0.07	a, b, c
β-pinene	–	–	0.47	–	0.64	–	–	0.10	0.11	a, b
Myrcene	0.29	–	0.43	–	0.16	–	–	–	–	a, b
α-terpinene	–	0.30	0.14	0.32	–	–	–	–	–	a, b
α-fenchene	–	–	0.12	–	–	–	–	–	–	a, b
p-cymene	0.46	–	0.17	–	1.11	–	0.16	0.88	–	a, b
Limonene+cineole	0.39	5.69	6.23	4.05	2.75	0.20	0.05	0.21	0.60	a, b
γ-terpinene	–	–	0.21	–	0.31	–	–	–	0.15	a, b
Terpinolene	0.09	3.45	2.46	–	–	–	0.05	0.17	0.04	a, b
Linalool	0.35	1.96	2.59	1.76	0.42	1.39	0.14	3.34	1.01	a, b, c
Borneol	0.08	0.50	0.86	0.54	1.55	0.31	0.53	0.52	0.90	a, b, c
α-terpineol	10.14	0.79	1.09	0.95	0.92	0.21	0.42	0.12	–	a, b
Nerol	1.40	2.16	1.03	0.66	2.43	1.43	3.75	2.04	2.01	a, b, c
Geraniol	0.20	0.40	3.29	4.99	0.81	0.81	0.18	0.27	0.05	a, b, c
Thymol	0.07	0.41	0.51	–	0.40	0.33	0.32	0.08	0.16	a, b, c
Carvacrol	0.12	0.35	0.40	–	–	0.14	–	0.10	0.07	a, b
Neryl acetate	6.22	11.79	4.13	13.03	13.51	5.89	7.53	6.73	11.99	a, b
α-cubebene	1.32	1.58	0.33	–	2.15	1.17	2.88	1.50	1.35	a, b
Geranyl acetate	5.52	2.12	1.69	2.58	2.91	3.91	6.28	3.14	0.46	a, b
β-caryophyllene	0.20	3.26	1.82	10.81	0.38	1.08	0.95	1.09	–	a, b
α-cedrene	16.67	3.52	0.24	5.69	9.32	8.38	7.09	8.96	14.72	a, b
i-italicene	–	–	0.69	6.45	8.41	5.21	4.93	6.28	9.85	a, b
Italicene	1.65	–	1.31	1.29	9.33	2.60	1.33	1.22	1.39	a, b
α-curcumene	28.64	14.50	0.96	10.23	9.29	25.06	23.31	17.87	7.83	a, b
γ-curcumene	12.03	9.89	9.61	4.88	–	22.02	12.02	12.23	15.42	a, b
δ-cadinene	2.93	4.88	0.55	1.37	2.60	1.43	0.32	0.93	1.20	a, b
Nerolidol	1.05	3.52	2.81	0.87	0.99	1.70	0.59	1.15	2.15	a, b
Caryophyllene oxide	0.37	–	1.37	1.19	–	–	3.67	3.73	3.92	a, b
Spathulenol	13.15	3.64	1.10	1.21	–	–	0.29	1.58	0.28	a, b
T-cadinol	1.04	1.14	2.38	0.42	0.52	4.48	1.29	–	0.43	a, b
α-cadinol	0.49	0.71	0.87	0.34	–	0.72	–	0.73	0.18	a, b
Unidentified comp.	11.36	19.29	18.00	14.81	3.91	11.09	20.56	21.86	23.25	

[a] See Table I.

Mode of the identification of individual compounds: a = RT/GC, b = GC/MS, c = peak enrichment.

lot. In stages of plant shoots and corymb forming, alpha-pinene appears in high amount (25.48 or 28.86%), *i.e.* a long period preceding the flowering stage. This component is relatively low in the stages of flowering and those after flowering. In the shoots alpha--curcumene is present at 0.44% and in flowering stage at 28.06%, whereas γ-curcumene is present in the shoots with 16.55% and in flowering stage at 12.03%.

In the stage after flowering, nerol is present in the highest amount (2.52%) and its lowest value is reached in the plant shoots and corymb forming (0.38 and 0.40%, respectively). The quantity of neryl acetate is highest in the plant shoots (9.03%), *i.e.* in the

Table IV. Composition of immortelle essential oil in different vegetation stages of plant development (%)

Component	Vegetative stages[a]						Identification
	A	B	C	D	E	F	
α-pinene	24.58	28.86	14.58	4.15	4.36	17.36	a, b, c
Camphene	0.91	–	0.03	–	0.09	0.11	a, b, c
β-pinene	–	0.17	0.21	–	0.15	0.56	a, b, c
Myrcene	0.35	0.44	0.11	0.29	0.11	–	a, b
α-terpinene	0.20	0.35	0.07	–	0.06	–	a, b
α-fenchene	–	0.24	0.18	–	0.03	–	a, b
p-cymene	0.14	0.22	0.11	0.46	–	–	a, b
Limonene+cineole	3.79	4.38	1.92	0.39	1.35	4.15	a, b
γ-terpinene	0.23	–	0.46	–	0.04	0.68	a, b
Terpinolene	0.41	0.61	0.19	0.09	0.19	0.24	a, b
Linalool	0.93	0.64	0.16	0.35	0.31	0.80	a, b, c
Borneol	0.15	0.20	0.17	0.08	0.14	0.78	a, b, c
α-terpineol	0.82	0.67	0.44	0.14	0.86	0.80	a, b
Nerol	0.38	0.40	1.95	1.40	2.52	1.50	a, b, c
Geraniol	2.30	2.32	0.12	0.20	0.30	3.33	a, b, c
Thymol	0.48	0.57	0.22	0.07	0.09	0.56	a, b, c
Carvacrol	0.51	0.66	0.17	0.12	0.17	–	a, b
Neryl acetate	9.02	6.26	5.95	6.22	5.57	7.37	a, b
α-cubebene	0.20	0.29	2.08	1.32	2.67	0.88	a, b
Geranyl acetate	2.20	1.24	3.90	5.52	7.83	3.38	a, b
β-caryophyllene	3.39	1.82	0.71	0.20	0.29	0.20	a, b
α-cedrene	0.38	0.19	4.05	16.67	4.34	4.36	a, b
i-italicene	2.40	10.42	3.63	–	5.49	3.10	a, b
Italicene	1.89	0.65	–	1.65	1.01	–	a, b
α-curcumene	0.44	11.97	25.83	28.06	26.86	13.43	a, b
γ-curcumene	16.65	10.97	9.12	12.03	7.85	13.83	a, b
δ-cadinene	2.64	3.89	2.12	2.93	1.37	5.02	a, b
Nerolidol	0.71	0.80	5.64	1.05	3.21	2.10	a, b
Caryophyllene oxide	0.74	0.17	–	0.37	0.56	–	a, b
Spathulenol	0.20	–	2.47	3.15	2.50	–	a, b
T-cadinol	1.29	1.12	0.20	1.04	0.38	0.90	a, b
α-cadinol	1.22	0.55	0.67	0.49	0.70	0.70	a, b
Unidentified comp.	20.46	8.93	12.56	10.70	18.13	13.83	

[a] See Table II.

Mode of the identification of individual compounds: a = RT/GC, b = GC/MS, c = peak enrichment.

stages far from the flowering stage. However, it is found at 5.57% in the stage just after flowering and at 0.02% in the plant shoots. This is probably a rule regarding the portion share of this component in immortelle essential oil: the quantity of neryl acetate is the highest in the youngest plant parts (shoots) and the lowest in the oldest plant parts (after flowering). The shoots grown late in summer are considered as young plant parts although they appear just before autumn.

In Tables I and II the percentages of main groups of compounds present in the immortelle essential oils from different locations or at different vegetative stages are sum-

marized. In both cases the sesquiterpene type compounds are predominant, with sample No. 3 being the only exception in which monoterpenic hydrocarbons are present in the highest amount. It should be pointed out that the high percentage of monoterpenic hydrocarbons is present in early stages of growth (A, B), as well as in late summer shoots which appear in autumn after rainy season and therefore they might be considered as young parts of the plant.

Acknowledgements. – We are very much indebted to I. Pitarević, B. Sc., and M. Plazibat, M. Sc., for collecting the plant material. As well our special thanks are due to Mr. F. Mirošević for having carefully collected the plant material at different vegetative stages of growth.

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S A Ž E T A K

Varijacije u iskorištenjima i sastavu eteričnog ulja smilja (*Helichrysum italicum*, Roth Guss.) ubranog na različitim lokacijama i u različitim vegetacijskim razdobljima uzduž jadranske obale

NIKOLA BLAŽEVIĆ, JOVAN PETRIČIĆ, GORDANA STANIĆ i ŽELJAN MALEŠ

Uzorci smilja sakupljeni su na devet različitih lokacija uzduž jadranske obale. Na jednoj lokaciji (Vela Luka) studirane su varijacije u iskorištenju i sastavu ulja u različitim vegetacijskim stadijima (6 uzoraka). Iskorištenja ulja u uzorcima sakupljenima na različitim lokacijama kretala su se od 0,08% do 0,32%, a uzorci sakupljeni u različitim stadijima razvoja dali su iskorištenja ulja od 0,06% do 0,35%. Sastav ulja analiziran je plinskom kromatografijom i vezanim sustavom: plinska kromatografija – spektrometrija masa. Unatoč zamjetnoj promjenljivosti udjela pojedinih komponenata u ispitanim uzorcima ulja, može se kao zajedničko obilježje istaknuti visoki udio seskviterpenskih spojeva. Posebice je zanimljivo da u ranom stadiju razvoja biljke prevladavaju monoterpeni dok su seskviterpeni dominantni u vrijeme i nakon cvjetanja biljke.

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