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## Variations in the yield and composition of the essential oil of *Crithmum maritimum* L.

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Variations of the yield and composition of the essential oil from aerial parts of *Crithmum maritimum* L. collected from the same locality in Croatia in different growth stages are reported. Essential oil composition was analysed by GC and GC-MS. The main essential oil components of all samples were monoterpenes: limonene (33.1–49.9%), sabinene (26.4–43.5%), thymol methyl ether (4.4–8.6%) and  $\gamma$ -terpinene (2.6–5.3%).

**Keywords:** *Crithmum maritimum* L. (*Apiaceae*), essential oil, GC, GC-MS

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*Crithmum maritimum* L. (*Apiaceae*) sea fennel is a woody below, glabrous, up to 50 cm high, very aromatic, branched perennial. It has 1- to 2-pinnate leaves, deltoid in outline, with subterete, fleshy segments, while its ovoid-oblong fruits are 5–6 mm, yellowish or purplish. This plant can be found on maritime rocks, rarely on sand or shingle. It occurs on the Atlantic coast of Europe, on the Mediterranean and Black sea coasts (1). *C. maritimum* is used as an antiscorbutic and diuretic (2).

Chemical investigations of *C. maritimum* revealed the presence of essential oil (2), flavonoids (3) and amino acids (4). Previous studies of the composition of the essential oil obtained from the plants growing in France, Italy and Portugal determined the presence of monoterpenes as major components (2, 5–7).

In this paper, we have examined the quantity and composition of the essential oils obtained from the aerial parts of *C. maritimum* collected at the same locality in Croatia but in different growth stages of the plant.

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\* Correspondence

## EXPERIMENTAL

### *Plant material*

The aerial parts of *C. maritimum* were collected in different growth stages: before flowering, at the beginning of flowering and at full flowering, near Zadar (Croatia) in 1999. Voucher specimens (No. 98256–98258) have been deposited in the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy and Biochemistry (University of Zagreb, Croatia).

### *Distillation of the essential oil*

The samples were air dried in the shadow and cut into small pieces before distilling. Hydrodistillation of the essential oil was done for 4 h in a Clevenger type apparatus. After distillation and cooling, the isolated oil was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and stored at 4–6 °C (8).

### *GC and GC–MS analysis*

The analysis was performed with a Pye Unicam PU 4550 GC (Pye Unicam, UK), equipped with a FID coupled to a PU 4810 integrator, column: Supelco SPB-5 30 m  $\times$  0.25 mm i.d., coating thickness 0.13  $\mu\text{m}$ . Working conditions: injector temperature 220 °C, detector temperature 250 °C, oven temperature program 60 °C (1 min), 60–220 °C at 4 °C  $\text{min}^{-1}$ , carrier gas:  $\text{H}_2$ , flow rate: 0.3 mL  $\text{min}^{-1}$ , split ratio 1 : 50. GC/MS analyses were performed on a Shimadzu QP 1000 GC/MS-EI 70 eV apparatus (Shimadzu, Japan) coupled to a data station.

Components were identified by comparing their retention indices to those of standard compounds, peak enrichment by co-injection with standards wherever possible, as well as by comparing their MS spectra with literature data. Quantitative data were obtained by the peak normalisation technique using integrated FID responses (9–13).

## RESULTS AND DISCUSSION

The highest amount of essential oil (2.7%  $V/m$ ) was obtained from the sample collected during its flowering period, while the samples collected before flowering and at the beginning of flowering contained much lower but very similar amounts of oil of 0.7 and 0.8%  $V/m$ , respectively.

As it can be seen from Table I, the oils contained monoterpenes and sesquiterpenes. All essential oils examined contained monoterpenes as the major components, while sesquiterpenes were present in relatively small amounts. Although all monoterpenes showed fluctuations in their relative amounts, the most conspicuous ones were recorded for limonene (33.1–49.9%), sabinene (26.4–43.5%), thymol methyl ether (4.4–8.6%) and  $\gamma$ -terpinene (2.6–5.3%). The highest amounts of limonene and  $\gamma$ -terpinene were found in the sample collected before flowering, while in the stage of full flowering, sabinene appea-

Table 1. Composition of the essential oil of *Crithmum maritimum* L. collected in different growth stages (%)

Component	KRI <sup>a</sup>	Before flowering	Beginning of flowering	Full flowering
α-Thujene	985	0.9	1.2	0.6
α-Pinene	1007	2.0	1.1	3.2
Sabinene	1039	26.4	35.7	43.5
β-Pinene	1070	1.3	1.5	1.8
β-Myrcene	1075	0.2	0.2	0.1
p-Cymene	1155	1.5	0.7	1.7
Limonene	1202	49.9	38.1	33.1
β-Phellandrene	1229	1.2	0.5	0.8
γ-Terpinene	1252	5.3	2.6	5.0
α-Terpinolene	1268	0.7	0.7	0.7
Linalool	1278	0.6	0.7	0.6
Nonanal	1305	0.5	0.9	0.5
Terpinene-4-ol	1340	0.1	0.2	0.1
Thymol methyl ether	1373	4.4	8.6	6.1
Thymol	1395	–	0.2	–
Carvacrol	1408	–	0.3	–
Neryl acetate	1435	–	0.4	–
β-Caryophyllene	1453	0.3	0.1	–
<i>trans</i> -α-Bergamotene	1468	0.3	0.2	–
α-Curcumene	1523	0.3	0.3	–
α-Farnesene	1623	0.2	0.3	–
α-Bisabolene	1685	0.2	0.1	0.2
Total		96.3	94.6	98.0

<sup>a</sup> Kováts retention indices relative to C<sub>9</sub>–C<sub>28</sub> *n*-alkanes

red in its highest quantity. The highest portion of thymol methyl ether was found in the sample collected at the beginning of flowering.

The differences determined in comparison with the results of other reports on the essential oil of *C. maritimum* (5–7) suggest the occurrence of different chemotypes.

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## S A Ž E T A K

### Različitosti u količini i sastavu eteričnog ulja petrovca – *Crithmum maritimum* L.

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Utvrđene su različitosti u količini i sastavu eteričnog ulja nadzemnih dijelova petrovca – *Crithmum maritimum* L., skupljenima u različitim vegetacijskim stadijima s istog nalazišta u Hrvatskoj. Sastav eteričnog ulja analiziran je metodom plinske kromatografije, te kombiniranom tehnikom plinske kromatografije i spektrometrije masa. Glavne sastavnice eteričnih ulja svih uzoraka bili su monoterpeni: limonen (33,1–49,9%), sabinen (26,4–43,5%), timol metil eter (4,4–8,6%) i  $\gamma$ -terpinen (2,6–5,3%).

**Ključne riječi:** *Crithmum maritimum* L. (*Apiaceae*), eterično ulje, plinska kromatografija, plinska kromatografija-spektrometrija masa

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