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CHEMICAL COMPOSITION OF LEAF AND FLOWER ESSENTIAL OILS OF *Conium maculatum* FROM SERBIA

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Conium maculatum L., a member of the Apiaceae (formerly Umbelliferae) family of rhizomal plants [1], is an annual, biennial, or, in favorable conditions, perennial plant, usually 120-180 cm high. *C. maculatum* (hemlock, poison hemlock) is a very common and worldwide plant species. It is one of the most toxic plants known [1]. Poison hemlock is native to Europe and western Asia and has been brought to America and Oceania as an ornamental plant [2]. A "cocktail" of an extract from *C. maculatum*, mixed with opium has been reported to be the lethal poison which the Greek philosopher Socrates was condemned to drink in the year 399 B.C. [3].

Despite being a worldwide renowned plant species and being a member of the family of numerous aromatic plant species (some of them containing significant quantities of volatile constituents), the essential oils of this plant species were the subject of only two previous studies. Only recently was the chemical composition of the Iranian *C. maculatum* essential oil published [4]. Previously, a study concentrating on antifeedant compounds from *C. maculatum* reported only the major volatile constituents of this species [5].

Having in mind the scarce data on the volatile constituents of *C. maculatum* (and the genus *Conium* in general) and the non-existence practically of any information on plant part specification of the essential oil, we decided to investigate the chemical composition of the hydrodistilled leaf and flower essential oils of Serbian *C. maculatum*.

The yields of yellowish, transparent essential oils of noxious odor obtained from fresh leaf and inflorescence of *C. maculatum* were 0.04 and 0.06% (v/w), respectively. The essential oils were analyzed by GC and GC-MS and the resulting data on the qualitative and quantitative chemical composition are presented in Table 1. Twenty-three and fifty-seven constituents were identified in the leaf and flower oils of *C. maculatum*, accounting for 96.2 and 97.5% of the total oils, respectively.

The major constituent in both flower and leaf oils was germacrene D (27.2 and 41.0%, respectively). The two runners-up in the leaf oil were the acyclic monoterpenes (*Z*)-β-ocimene (7.1%) and (*E*)-β-ocimene (22.3%), while in the inflorescence oil the second and third most abundant components were (*Z*)-β-ocimene (14.3%) and β-myrcene (9.3%). The relative amounts of (*E*)-b-ocimene (7.7%) and (*E*)-nerolidol (7.1%) in the flower oil deserve mention as well. The monoterpene and sesquiterpene fractions of the oils were comparable in their relative amounts (flower oil: 40.1% monoterpenes versus 46.3% sesquiterpenes, leaf oil: 33.6% monoterpenes versus 54.6% sesquiterpenes Table), and the number of identified monoterpenes and sesquiterpenes followed the same trend (13 and 19). However, within the fractions a highly uneven distribution between the hydrocarbons and oxygenated derivatives was observed, with a prevalence of non-oxygenated compounds (Table 1).

The leaf and flower oils were characterized by the presence of "green-leaf" volatiles, formed by unsaturated fatty acid oxidative degradation [6], most probably as the plants response to mechanical stress during the collection and cutting of plant material. Another possible role of these volatiles, especially the esters (the corresponding octanoates and 3-hexenyl- esters) present in the flower oil, could be the attraction of insect pollinators [7]. Coniine and related volatile alkaloids (for which the poisonous hemlock is well known [1]), probably existing as salts in the plant material, and hence non-volatile under hydrodistillation conditions, were not detected in the essential oils. Compared to the bulk of the other identified components, a relatively high number of alkanes (8) was detected (most probably those constituting the exterior boundary of the leaves and flowers of *C. maculatum*).

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TABLE 1. Percentage Composition of the Leaf and Inflorescence Oils of *Conium maculatum*

Compound	RI	Percentage		Compound	RI	Percentage	
		Leaf oil	Inflorescence oil			Leaf oil	Inflorescence oil
(*E*)-3-Hexen-1-ol	851	Tr.	-	*β*-Bisabolene	1509	0.7	1.5
(*E*)-2-Hexenal	854	0.5	-	*δ*-Cadinene	1524	0.5	1.3
(*Z*)-3-Hexen-1-ol	857	2.6	0.3	Cadina-1,4-diene	1532	-	0.1
Hexanol	867	-	0.3	(*Z*)-3-Hexenyl octanoate	1560	-	0.9
Styrene	895	0.2	0.1	(*E*)-Nerolidol	1564	4.8	7.1
α-Pinene	939	-	0.4	Hexyl octanoate	1566	-	1.6
Sabinene	976	-	0.7	Caryophyllene oxide	1581	-	0.3
β-Pinene	980	-	1.6	Cedrol	1596	-	0.7
β-Myrcene	991	3.9	9.3	*α*-Cadinol	1653	-	0.1
(*Z*)-3-Hexenyl acetate	1007	3.0	0.8	*α*-Bisabolol	1683	-	0.1
β-Phellandrene	1031	0.3	3.9	Mint sulfide	1740	1.1	-
(*Z*)-*β*-Ocimene	1040	7.1	14.3	Benzyl octanoate	1754	-	0.4
(*E*)-*β*-Ocimene	1050	22.3	7.7	Octyl octanoate	1767	-	Tr.
Octanol	1070	-	0.4	Hexadecanal	1815	0.2	-
trans-Sabinene hydrate	1097	Tr.	-	2-Phenylethyl octanoate	1830	-	0.1
Nonanal	1102	-	0.4	Nonadecane	1900	-	0.1
(*E*,*E*)-Alloocimene	1129	-	0.1	(*Z*)-Falcarinol	2028	-	0.4
Terpinen-1-ol	1134	-	0.7	4-Methyleicosane	2057	-	2.4
cis-*β*-Terpineol	1144	-	1.2	Octadecanol	1082	-	0.1
Nonanol	1171	-	0.3	Heneicosane	2100	-	0.1
cis-Piperitol	1193	-	0.1	(*E*)-Phytol	2112	1.5	0.1
Safranal	1201	-	0.1	Nonadecanol	2181	-	Tr.
trans-Piperitol	1205	-	0.1	Docosane	2200	-	1.9
(*Z*)-3-Hexenyl 2-methylbutanoate	1231	-	0.1	Tricosane	2300	-	Tr.
(*Z*)-3-Hexenyl 3-methylbutanoate	1240	-	0.1	5-Methyltricosane	2347	-	Tr.
Tridecane	1300	-	0.1	Hexacosane	2600	-	Tr.
α-Cubebene	1351	2.6	0.1	Total		96.2	97.5
α-Copaene	1376	Tr.	2.4	Monoterpenes		33.6	40.1
β-Bourbonene	1384	0.2	0.3	Hydrocarbons		33.6	38.0
β-Cubebene	1390	1.6	2.0	Oxygenated		Tr.	2.1
β-Elemene	1391	-	Tr.	Sesquiterpenes		54.6	46.3
β-Caryophyllene	1418	0.5	2.0	Hydrocarbons		48.7	38.0
Calarene	1432	-	0.3	Oxygenated		5.9	8.3
Aromadendrene	1439	-	0.5	Diterpenes		1.5	0.1
Germacrene D	1480	41.0	27.2	Fatty acid derived compounds		6.3	5.8
(*E*,*E*)-*α*-Farnesene	1508	1.6	0.3	Others		0.2	5.2

*Experimentally determined retention indices on a DB-5 column (relative to C_8-C_{26}); -: the compound was not detected in the essential oil.
Tr.: trace amount (<0.1%).

Falcarinol (polyacetylene alcohol) and mint sulfide (sulfur - containing sesquiterpene) were identified for the first time in the hydrodistilled flower and leaf essential oils of *C. maculatum*, respectively. Falcarinol was previously detected in *C. maculatum* solvent extracts as one of the oviposition stimulants of the carrot fly (*Psila rosae*) [8].

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