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VARIABILITY IN COMPOSITION OF THE ESSENTIAL OIL OF *CALAMINTHA NEPETA*

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KeyWord Index—*Calamintha nepeta* ssp. *nepeta*; *Calamintha nepeta* spp. *glandulosa*; Lamiaceae; essential oil composition.

Abstract—*C. nepeta* ssp. *nepeta* and *C. nepeta* ssp. *glandulosa* are able to produce the same volatiles with the *p*-menthane skeleton oxygenated in C-3. The compositions of the essential oils range from the very simple, containing almost exclusively piperitone oxide and piperitenone oxide, to the relatively complex, containing the former oxides, pulegone, menthones, menthols and their acetates. As such they cannot be used to distinguish between the two subspecies.

Table 1. Essential oil composition (%) of *C. nepeta* subspecies

	Glandulosa			*Nepeta*						
	[1]	A	B	[3]	C	D	E	F	G	H
α-Pinene	0.1	0.4	0.3	0.1	0.6	0.6	0.5	0.5	0.4	0.2
Sabinene	0.2	0.2	0.2	tr	0.4	0.2	0.3	0.4	0.3	0.1
β-Pinene	0.2	0.5	0.3	0.3	0.6	0.8	0.5	0.6	0.5	0.2
Myrcene	0.4	0.7	0.8	0.2	0.8	0.9	0.8	1.1	0.7	0.3
Octan-3-ol	2.4	1.1	1.3	—	0.1	0.2	0.2	0.3	0.1	0.2
α-Terpinene	tr	0.2	tr	—	0.4	0.3	0.5	0.4	0.2	tr
Limonene	4.3	4.5	5.5	1.8	2.2	3.9	2.5	4.6	3.9	0.7
cis-β-Ocimene	—	tr	tr	—	0.8	0.2	0.2	0.9	0.3	0.1
trans-β-Ocimene	—	tr	tr	—	0.2	0.1	tr	0.5	tr	—
γ-Terpinene	0.3	0.4	0.1	—	0.9	0.4	0.7	0.7	0.5	0.2
trans-Sabinene hydrate	1.7	0.2	0.4	—	2.4	0.1	0.1	0.2	1.5	0.7
Terpinolene	0.3	0.1	—	—	0.2	0.1	tr	0.3	tr	—
cis-Sabinene hydrate	1.2	0.2	—	—	0.1	tr	tr	tr	tr	—
Menthone	—	4.0	12.1	0.2	6.3	8.2	6.6	8.9	8.1	4.9
Isomenthone	—	3.8	0.6	24.4	tr	3.3	0.9	6.7	0.3	0.2
Neomenthol + terpinen-4-ol	2.6	1.4	4.1	0.6	2.2	1.8	3.3	5.4	29.8	1.5
Menthol	—	—	0.5	—	3.0	1.7	3.0	2.7	7.5	1.4
Isomenthol + α-terpineol	0.4	0.2	0.1	7.1	0.9	0.8	0.7	1.7	0.5	0.5
Pulegone	—	17.0	68.0	57.7	21.0	23.1	33.2	28.5	11.5	28.9
Piperitone oxide	30.7	12.8	1.1	—	9.9	17.0	9.8	10.1	8.4	11.2
Isopiperitenone (?)	—	0.7	—	—	0.6	0.7	0.7	0.5	—	—
Neomenthyl acetate	—	—	—	—	—	—	—	—	1.9	0.6
Menthyl acetate	—	—	0.1	—	—	—	—	—	2.5	0.7
4-Hydroxypiperitone	1.4	0.8	—	—	0.4	1.2	1.4	1.4	0.2	0.1
Isomenthyl acetate	—	—	—	1.6	—	—	—	—	—	—
Piperitenone	—	3.8	1.6	2.2	0.9	2.1	3.8	0.8	0.4	1.3
Piperitenone oxide	42.4	—	0.5	—	32.6	25.0	22.7	13.3	5.9	37.8
β-Caryophyllene	2.3	1.3	0.2	0.3	1.8	1.7	1.4	2.3	6.2	1.4
α-Humulene (+ β-Farnesene)	0.1	0.6	—	—	0.2	0.2	0.4	0.5	0.6	0.4
Germacrene-D	0.8	2.3	0.7	0.3	0.9	0.4	0.7	1.0	1.6	0.6
α-Elemene	—	—	—	0.3	0.2	0.1	—	0.4	0.6	—

tr = trace, < 0.1%; − = < 0.05%; ? = tentative.

INTRODUCTION

The essential oil of *C. nepeta* (L.) Savi ssp *glandulosa* (Req.) P. W. Ball grown from seeds in the Botanical Garden of the State University of Gent (Belgium) is particularly rich in the oxides of piperitone and piperitenone, and is free of pulegone, menthones and menthols [1]. *C. nepeta* (L.) Savi ssp. *nepeta* on the other hand mainly contains the latter substances [2, 3]. Because the morphological characteristics of these subspecies as described in *Flora Europaea* tend to overlap [4], it appeared possible that the composition of the essential oils might be used to separate them. However, it is clear that before drawing any such conclusions, more specimens, preferably collected in the wild, had to be studied.

RESULTS AND DISCUSSION

The first indication that the composition of the essential oil of *C. nepeta* ssp. *glandulosa* prepared from plants raised in our Botanical Garden [1] might be an extreme case, was gleaned when a new specimen, grown from the original supply of fruits, afforded a more complex oil, containing the menthones, pulegone and the oxides of piperitone and piperitenone (Table 1A).Further plant material was then collected in the wild. Referring to the earlier findings [1–3], GC analysis gave rather unexpected results: six samples, identified as *C. nepeta* ssp. *nepeta* yielded oils which not only contained pulegone, the menthones and menthols, but were also rich in the oxides of piperitone and piperitenone (Table 1C-H). The essential oil of the last sample (Table 1B), identified as *C. nepeta* ssp. *glandulosa*, has a composition which, save for the presence of some piperitone and piperitenone oxides, is identical to the published composition of *C. nepeta* ssp. *nepeta* [2, 3]. This shows quite clearly that the same oils can be produced by both subspecies, and this rules out their use for chemotaxonomic purposes.

EXPERIMENTAL

Essential oils were prepared by hydrodistillation in a semi-micro Likens-Nickerson apparatus, and analysed by GC and GC-MS on WCOT and FSOT SE-52 columns in circumstances as described before [1]. Plant material was collected in Tanneron (Alpes Maritimes, France; sample B), near Le Lauzet-Ubaye (samples C-F), the Réservoir de Serre-Ponçon (Les Demoiselles Coiffées; sample G) and La Fresquière (sample H) (Alpes de Provence, France). Voucher specimens were deposited in the herbarium Gent: A = PG5463; PGB = 5616; C-F = PG 5609–5612; G = PG 5608; H = PG 5607.

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CARYOPHYLLENE DERIVATIVES FROM *PULICARIA ARABICA*

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Key Word Index—*Pulicaria arabica*; Compositae; sesquiterpenes; caryophyllene derivatives.

Abstract—The aerial parts of *Pulicaria arabica* afforded in addition to known caryophyllene derivatives seven new ones. The configuration at C-11 of previously reported derivatives has to be corrected as followed from the observed NOEs.

INTRODUCTION

The relatively large genus *Pulicaria* (Compositae, tribe Inuleae, subtribe Inulinae) has been studied by several groups. In addition to widespread compounds two species gave diterpenes [1, 2], two others unusual caryophyllene derivatives [3, 4] and one species, which has been placed in the *Francoeuria*, afforded different types of sesquiterpene lactones [5]. We now have reinvestigated *P. arabica* (L.) Cass.; the results are discussed in this paper.

RESULTS AND DISCUSSION

Pulicaria arabica has been investigated previously and from the aerial parts several flavones and flavone glyco-