Volatile constituents of *Nepeta cataria* L., *N. glechoma* Benth. and *N. parviflora* M. Bieb. from Hungary

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Key words: Nepeta cataria, N. parviflora, N. glechoma, essential oil, citral, geraniol, β -caryophyllene, β -cubebene, β -selinene, davanone, α -cubebene, patchoulene, spathulenol

Summary: In the temperate zone live about 150 species of the Nepeta genus. Our investigations covered the examinations of the volatile oil containing species of the genus endemic in Hungary, Nepeta cataria and Nepeta parviflora. Latter is a relict of the ancient steppe-flora and endemic in Hungary as well. Phytochemical examination of the volatile oil containing plant material has also been carried out. Catnip growing in the Botanical Garden of PTE Department of Botany contained 0,67% volatile oil in May and 0,14% in November. Chemical character of the volatile oils were measured by gas chromatography/mass spectrometry and citronellol, citral-A, citral-B and geraniol components were identified. The composition of the oil of November samples shifted towards citronellol (65%). In both samples insecticide and repellent activity bearing compounds (+)-cis-p-menthane-3,8-diol, and (-)-trans-p-menthane-3,8-diol in 2–2.5 and 4–4.5% amount have been found. The catnip sample deriving from Germany contained a small amount of anetol, citronellol, neral, geraniol and geranial (6–13%), and possibly two isomers of nepetalactone in 23–31%.

The Nepeta parviflora endemic in the Nagyvölgy valley near Nagykarácsony consisted of the same compounds in the investigated years (1998-2000). Its limonene, methyl chavicol, b-cariophyllene, b-selinene, b-cubebene, davanone, germacrene-D constituents have been identified. In the year 2000 different GC % of these compounds were detected in the different organs of the plants.

The closely related species *Nepeta cataria var. citriodora* contained 83% citral, and the *N. glechoma* (= *Glechoma hederacea*) contained 41% a-cubebene, 20% patchoulenol, 7,7% spathulenol respectively. These compounds were identified by gas chromatography and gas chromatography / mass spectrometry.

Introduction

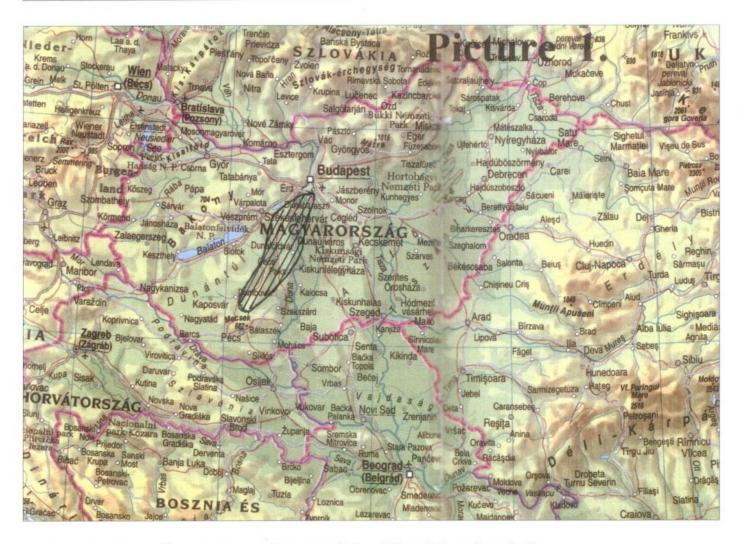
Nepeta species belong to the Lamiaceae family in the Lamiales order. In temperate zone live about 150 species of Nepeta genus. Our research covered the investigation of the volatile oil content of the wild living Nepeta cataria L. (catnip) found in North and Middle Europe and the fairly rare N. parviflora M. Bieb (small flowered catnip).

N. ucranica (blue flowered catnip) is the closest relative of N. parviflora, the species is endemic in Bulgaria, Romania and in East and Southeast Europe. N. parviflora did not appear in the Carpathian basin for a long time. In 1871 it was discovered by Gy. Tauscher nearby Ercsi village. On his later collecting travels he found four habitats

more (Pusztaszabolcs, Perkáta, Szentágota, Alsószentiván). Hungarian habitats of the species support the hypothesis that the small flowered catnip is endemic in the Hungarian flora and is a relict of the ancient steppe-flora. During the last 120 years its existence in the Hungarian flora has been questioned by some of the botanists that is why Lendvai's activity in this field was of great importance (*Lendvai* 1993).

In 1992 Lendvai found a great population at Mezőföld, near Nagykarácsony, in Nagyvölgy valley, where it occurred typically on the most arid west and southwest slopes of the hill only. This area and the great ancient grassland remnant found alongside the Dinnyés-Kajtor canal (Picture 1. at the green area) present habitats to this small-height Labiatae

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species, to the *N. parviflora*. In Hungary there are other relatives of it, the *N. cataria var. citriodora* (Becker) Balb. and *N. glechoma* Benth. (=Glechoma hederacea L.). Recently latter species are classified to an other genus and used for covering soil and as a medicinal herb (Keville 1991).

Nepeta species contain volatile oils of different scent character and chemical composition (Héthelyiné 2000), that is why the determination of the volatile oil composition by gas chromatography/mass spectrometry is of great significance. Herbs and extracts for phytotherapy purposes can be used only after the determination of the composition in accord with the results.

The volatile oil of *N. flavida* endemic in Turkey is rich in linalool (37%) and cineol (23%) (*Baser* 1998), the main component of *N. nuda* is 1,8-cineol (43–64%) (*Chalchat* 1998), *N. fissa* contains caryophyllene oxide in 24 percent (*Baser* 2000) and *N. trachonitica* is a species rich in spathulenol (*Tümen* 1999).

The volatile oil composition of endemic in Iran *Nepeta* species is investigated as well. So, the volatile oil of *N. denudata* contains 48% cincol, *N. cephalotes* 28% eucalyptol and 35% nepetalactone. In the volatile oil of *N. racemosa* 65% nepetalactone has been found (*Rustalyan* 2000).

Materials and methods

In our experiments the investigated catnip plant individuals were collected in full blossom stage in the Botanical Garden of the Pécs University of Science in May and November of 2000. In both cases the volatile oil was produced from air-dry plant raw material. Since we have not found nepetalactone in the examined nepeta oils yet, Katzenminze drug has been asked for from Germany.

We have been investigating the volatile oil of *N. parviflora* since 1998. The plant material was collected always in the same stadium of growth. In 2000 not only the spray of blossom but other parts of the plant were also investigated and the chemical character of the volatile oil was determined by GC-MS measurements. The plant material was collected in the Nagyvölgy valley by associate professor Kevey B. of the PTE Botany Department (on the Picture 1.).

From the 2000, year autumn collection, the volatile oil content of the air-dry raw plant material deriving from Bisse was examined by gas chromatography as well.

Preparation of the volatile oils: for gas chromatography/mass spectrometry measurements they were prepared by steam distillation of the air-dry drugs in a modified Clevenger apparatus. Gas chromatographic analysis: the determination of the area percent composition of the essential oils was performed by a Shimadzu gas chromatography dedicated to capillary work.

Instrument: Shimadzu GC-14b, Gas Chromatography, quare kapillary column: 30 m \times 0,25 mm ID \times 0,25 μ m SE-30 film thickness, Nitrogen gas 1 ml/min, Splitter 75:1 , IB.: 220 °C, FID detector, temp.:Det.: 250 °C,

Oven temp.: 110 °C, (IT 3 min.), 8 °C/min. to 220 °C (FT 5 min), Time: 21,45 min.

Shimadzu Class – VP Chromatography Data System, Version 4,2 PC System,

ACER IBM-PC, XEROX Colour Printer,

The identification of the compounds has been carried out by standards deriving from Roth, in some cases it was completed by gas chromatography/mass spectrometry. Hewlet-Packard 5960 and Finnigan Matt GCQ Mass Spectrometer instruments.

Results and Discussion

The N. cataria herb collected in May in the botanical garden bore a pleasant citral scent and contained 0,66% volatile oil. This sensation has been supported by the gas chromatographic results, that showed 17,3% citronellal, 10% neral, 21,3% citronellol, 12,8% geraniol and 13,6% geranial in the oil. The catnip collected in November contained 0,14% essential oil, had a pleasant fragrance but the ratio of the compounds shifted towards citronellol. 65% citronellol, 4% neral, 4,5% geraniol and 6,3% geranial was found. In Table 1 the results of the volatile oil of Nepeta cataria can be seen. In both samples peaks appear with 13,20 and 14,15 minute retention time, their amounts almost doubled in the autumn samples but they are missing from the German sample. The identification of these peaks was carried out by Aldrich standards and by component addition method. The peak at 13,20 min. proved to be (+)-cis-p-

Table I Essential oil content and main compounds of Nepeta cataria

Compound	PTE-1 Catnip	PTE-2 Catnip	German Katzenminze
Methylchavicol	3,8	2,6	
Citronellal	17,3	4,1	7.8
Unknown	5,7	20000	1000000
Citral-A	10.1	4,1	6,1
Citronellol	21,3	65,1	10,3
Citral-B	13,6	6,3	6,8
Anethol			3,9
7 the trio	5.9	1,6	
Geraniol	12.8	2,3	5,8
Cubebene			5,8
Nepetalactone-I.			21.8
cis-p-Menthane-3,8-diol	1.9	4,4	
trans-p-Menthane-3.8-dio	2.4	4,1	
Nepetalactone-II.			31,2
Unknown			3,2
CONTENT:	0.67%	0,14%	0,05%

Notice: PTE-1 originated from Pécs, Botanical Garden 27, 05, 2000. PTE-2 originated from Pécs, Botanical Garden 17, 11, 2000. Menthane-3,8-diol, while the one at 14,15 min. was the (–)-trans-p-Menthane-3,8-diol. Both isomers have insecticide and repellent activity. The German Katzenminze drog had to be extracted by hexane because it contained too small amount of oil. According to the gas chromatographic analysis 7,8% citronellal, 6% citral-A, 10,3% citronellol, 6,8% citral-B as known compounds have been identified and two more unknown components in 21,8% and 28,5% were determined. They are assumed to be the two isomer nepetalactone contained by the catnip (*N. cataria*) in 40% due to literature. This cyclopentanoid monoterpene nepetalactone amounts to the 40% of the volatile oil. This component can be found in 95% in the volatile oil of *N. caesarea* species (*Aydin* 1998).

The nepetalactone content of the volatile oils has been considered a drawback for a long time but recently research aiming at the replacement of opium and morfinan based analgesics turned into the direction of determining the analgesic activity of herb originating agents and put nepetalactone to good account. These facts have changed the judgement on their presence in the essential oils of *Nepeta* species (*Aydin* 1998).

The blossom spray of *Nepeta parviflora* contained the same components in all three years investigated, but in a slightly different GC %. In the year of 2000 the volatile oil from all of the plant parts above ground has been manufactured in our laboratory, volatile of the flower, the leaf and the stem as well. Their composition was determined by gas chromatography. The results can be found in *Table 2*, from their the evidence can be judged that the flower oil is the most similar to the one prepared from the whole plant. The following components: limonene (6.8-8.7%), estragol (3.1-6.3%), β -caryophyllene (7.3-13.1%), β -selinene (30.9-35.1%), β -cubebene (14.1-23.7%), davanone (4.2-8.4%) and germacrene (0.3-6.8%) have been identified.

Table 2 Main compounds of the different organs from the oil of Nepeta parviflora

Content	Flower	Leaves	Stem	Whole plant
Limonene	8,7	tr	tr	6.8
Methyl chavicol	6,3	5,5	4,4	3.1
Unknown		2,5		
Unknown		2,1		
Caryophyllene	13,1	12,9	12,5	7.3
Selinene	30,9	35,1	33,7	34,4
Cubebene	14,3	19,2	23,7	14,1
Unknown	11,2	8.1	20,8	9,9
Davanone	4,2	8,4	4,9	4,4
Germacrane-D	4,6	6,8	0.3	3,2

Notice: wild plant material originated from Nagykarácsony (Nagyvölgy) tr = trace

The air-dry herb of the autumn-collected *Nepeta* glechoma (= Glechoma hederacea) from Bisse contained nearly 0.1% volatile oil. By gas chromatography the presence of 1.4% β-pinene, 5,3% 1,8-cineol, 1,3% methyl chavicol have been proved so far. Its 41,8% a-cubebene,

20% patchoulene and 7,7% spatulenol content has also been identified by gas chromatography / mass spectrometry.

As far as we know, the decoction or tea of *N. cataria* is capable of alleviating and ceasing the gastric- and bowelpain and spasm. It is very useful as a night tea for children with hyperactivity syndrome. It acts as an analgesic in a high-toned nerve state. There have been found no data yet in the literature on the chemical characteristic's or pharmacological and phytoterapeutical investigation of *N. parviflora*.

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