

Sensory and Instrumental Evaluation of Catnip (*Nepeta cataria* L.) Aroma

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The present study investigates the composition of volatile constituents and sensory characteristics of catnip (*Nepeta cataria* L.) grown in Lithuania. Hydrodistillation, simultaneous distillation–solvent extraction, static headspace, and solid phase microextraction methods were used for the isolation of aroma volatiles. Geranyl acetate, citronellyl acetate, citronellol, and geraniol were the major constituents in catnip. Differences in the quantitative compositions of volatile compounds isolated by the different techniques were considerable. A sensory panel performed sensory analysis of the ground herb, pure essential oil, and extract; aroma profiles of the products were expressed graphically, and some effects of odor qualities of individual compounds present in catnip on the overall aroma of this herb were observed.

KEYWORDS: *Nepeta cataria* L.; Labiatae; catnip; essential oil; sensory evaluation; headspace; solid phase microextraction

INTRODUCTION

Catnip or catmint (*Nepeta cataria*) is a perennial herb belonging to the mint family, Labiatae. This plant is spread from Central Europe to the Iranian plateaus and in Central Asia (1). Catnip has been used for ornamental and culinary purposes and as a domestic folk-medicine remedy. The leaves and shoots have been used in sauces, soups, and stews. Leaves and flowers are used in herbal teas, especially for a strong mint odor note (1). Different anatomical parts of catnip have been used as a flavoring in several patented beverages (2–5), fruit table wines (6, 7), medium-sweet liqueurs (8), and shashlik sauce production (9), particularly to reduce the cost and improve the quality and sensory properties. Catnip herb and essential oil possess strong antimicrobial activities (10–12); its extracts have been reported to have an antioxidative power as well (13–16). In medicinal preparations catnip has been used as an antispasmodic, carminative, diaphoretic, emmenagogue, nervine, stomachic, stimulant, and mild sedative component. Its use in the treatment of diarrhea, colic, the common cold, and cancer was also reported (1). In the early 17th century the plant was used as a tonic and/or a disinfectant for rhinitis (17).

The flavor composition of *N. cataria* has been reported in several papers (10, 18–23). Bourrel et al. (10) determined that the essential oil of catnip consists of 4 α ,7 α ,7 α β -nepetalactone (11.4–56.9%), β -caryophyllene (6.2–24.6%), caryophyllene

oxide (14.3–18.2%), 4 α ,7 α ,7 α -nepetalactone (1.3–2.8%), and 3,4 β -dihydro-4 α ,7 α ,7 α -nepetalactone (1.7–2.0%) depending on vegetation period. The oil of *N. cataria* L. from two different Bulgarian origins was constituted mainly of terpenoids, such as 4 α ,7 α ,7 α -nepetalactone (11.0 and 6.0%) and 4 α ,7 α ,7 β -nepetalactone (24.0 and 78.0%); nepetalic acid (1.2 and 1.6%), 3,4 β -dihydro-4 α ,7 α ,7 β -nepetalactone (10.0%), and 3,4 α -dihydro-4 α ,7 α ,7 β -nepetalactone (15.0%) were reported as new compounds in the species (18). Tittel et al. (19) found that the main constituents of *N. cataria* var. *citriodora* were citronellol (15.6%), elemol (11.9%), geraniol (9.5%), β -elemene (7.5%), β -caryophyllene oxide (4.5%), α -cadinol (5.0%), nerol (3.7%), isopulegol (3.3%), cadinol (2.6%), citronellal (2.6%), hexahydrofarnesyl acetone (2.2%), linalool (1.8%), and neral (1.5%). Venskutonis (20) examined the same variety and reported nerol (22.73%), citronellol (17.36%), geraniol (16.72%), and caryophyllene oxide (7.26%) as the main constituents. The essential oil of catnip grown in Cordoba province (Argentina) consisted mainly of nepetalactone (57.30%), caryophyllene oxide (19.35%), β -caryophyllene (8.10%), dihydronepetalactone (3.43%), β -farnesene (2.14%), humulene oxide (1.63%), and α -humulene (1.27%) (21). The essential oil of *N. cataria* var. *citriodora* from the Drome region of France was found to comprise mainly geraniol (25.13–31.00%), nerol (19.95–30.70%), citronellol (11.44–16.73%), and geraniol (4.93–11.05%) (22). Osinska and Suchorska (23) described the main constituent of essential oil of catnip (lemon catmint) as 1,8-cineole (28–48%).

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Publications on catnip volatile oil clearly demonstrate that chemical polymorphism is characteristic of this species; the composition depends on variety, growing site, climatic conditions, and analysis method (10, 18–23). In general, two main chemotypes of catnip can be distinguished: one with nepetalactones as the dominating oil compounds and another with citral derivatives as the major components. Therefore, it was of interest to study the aroma and essential oil profile of catnip cultivated in Lithuania. It was also considered that the use of different isolation techniques, such as hydrodistillation (HD), simultaneous distillation–solvent extraction (SDSE), static headspace (SH), and solid phase microextraction (SPME) could provide more comprehensive information on the flavor of this plant. It should be emphasized that so many techniques for the study of aromatic plants and catnip in particular have not been performed previously. Also, a comprehensive comparison of instrumental and sensory results obtained by using free choice and descriptor's list assessments was not earlier performed for catnip or for many other aromatic herbs. Therefore, the comparison of the techniques applied was also considered as one of the goals of the present study.

MATERIALS AND METHODS

Plant Material and Isolation of Volatiles. Catnip (*N. cataria* L.) was grown in the Kaunas Botanical Garden, Lithuania, and harvested in 1999 at full flowering stage. The herb was dried at room temperature and stored in glass containers in the dark.

The two following methods were used for the complete isolation of volatile compounds: (i) HD in a Clevenger-type apparatus (24) and (ii) SDSE in a Likens–Nickerson apparatus (25). In the latter case, 30 g of dried catnip herb was distilled in a 250 mL round-bottom flask to which 100 mL of distilled water was added and extracted with 15 mL of CH_2Cl_2 (ACS 99.5%, Acros Organics, Geel, Belgium) during 1.5 h. The extract was dried over MgSO_4 and concentrated under a stream of nitrogen to ~ 2 mL just before GC and coupled GC-MS analysis. Each analysis of HD and SDSE procedures was replicated twice.

SPME and HS Analysis. SPME was performed with three different fibers, namely, polydimethylsiloxane (PDMS, 100 μm), polydimethylsiloxane–divinylbenzene (PDMS-DVB, 65 μm), and carboxen–polydimethylsiloxane (CAR-PDMS, 75 μm), all from Supelco (Bellefonte, PA). For headspace SPME sampling, 1 g of dried ground catnip herb was placed in a 20 mL vial, closed with an open hole cap faced with a PTFE/white silicone septum, and equilibrated in a Gerber Liebisch-Bielefeld 14 thermostat (Gerber Instruments, Effretikon, Germany) at 40 °C for 1 h. The fiber was exposed to the headspace of the herb during 5 min at 40 °C. Afterward, the fiber was withdrawn into the housing, the SPME device was removed from the sample vial, and the fiber was desorbed into the GC injector.

For conventional SH 20 μL of catnip oil was placed into a 20 mL HS vial that was sealed hermetically with a PTFE/butyl-coated septum and silver aluminum cap. The samples were equilibrated for 1 h at 40 °C, and 1 mL of headspace gases was withdrawn using a 5.0 mL gastight syringe (SGE Co., Ringwood, Australia) and injected into the GC.

Gas Chromatography (GC). The oil diluted in diethyl ether (1% v/v) and the SDSE extract were analyzed on a Fisons 8000 series gas chromatograph (Fisons Instruments Inc., Rodano MI, Italy) equipped with a flame ionization detector (FID) and a DB-5 fused silica capillary column (polydimethylsiloxane, 5% phenyl, 50 m length, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA). The carrier gas was helium at a linear flow velocity of 43 cm s^{-1} at 50 °C, which was equivalent to a 2.35 mL min^{-1} volumetric flow; the detector temperature was 320 °C, and the oven temperature was programmed from 50 °C (for 2 min) to 280 °C (hold 10 min) at the rate of 5 °C min^{-1} . A split/splitless injector was used at 250 °C in split mode at a ratio of 1:5; the injection volume was 1 μL . The content of the eluted compounds was expressed as a GC peak area percentage; mean values were calculated from three to five injections. The coefficient of variation

is defined as the ratio of the corresponding standard deviation (%RSD) to the average value from three to five replicate injections.

For the analyses of the headspace of the essential oil (HS-EO) split mode was used at a ratio of 1:5 and an injector temperature of 250 °C. Thermal desorption of volatile analytes adsorbed on the SPME fibers was carried out in the GC injector port at 250 °C for 3 min in splitless mode. The oven temperature was programmed as described above.

Gas Chromatography—Mass Spectrometry (GC-MS). GC-MS analyses were performed on an HP 5890 (II) gas chromatograph coupled to an HP 5971 series mass selective detector (Hewlett-Packard, Avondale, PA) in the electron impact ionization mode at 70 eV; the mass range was m/z 30–550. Volatile compounds were separated using an HP5-MS capillary column (polydimethylsiloxane, 5% phenyl, 30 m length, 0.25 mm i.d., 0.25 μm film thickness, Hewlett-Packard). The temperature was programmed from 40 °C (2 min) to 100 °C at 12 °C min^{-1} (2 min hold), then further increased to 150 °C at 12 °C min^{-1} (2 min hold), and finally increased to 260 °C at 15 °C min^{-1} (5 min hold). Helium was used as a carrier gas at a linear flow velocity of 36.2 cm s^{-1} at 40 °C or 1.01 mL min^{-1} volumetric flow.

The components were identified by comparison of their Kovats retention indices (KI) relative to C_8 – $\text{C}_{30,32}$ *n*-alkanes (Sigma Chemical Co., St. Louis, MO), obtained on a nonpolar DB-5 column with those provided in the literature (26) and by comparison of their mass spectra with the data provided by the NIST, NBS 75K, and EPA mass spectral libraries. Positive identification was assumed when a good match of mass spectrum and KI was achieved; otherwise, it was considered to be tentative.

Sensory Analysis. Sensory evaluation was performed by a panel consisting of 25–30 assessors. All of them were staff members and students of the Department of Food Technology at Kaunas University of Technology (between 20 and 50 years of age) with some experience in sensory analysis, and a few of them were registered panel members at the Kraft Foods Lithuania company. Sensory assessment was performed during two separate panel sessions: during the first one the panelists had to use their own descriptors (free choice assessment) and during the second they were provided with a list of selected descriptors and had to attribute them to the odor of the samples assessed (descriptor's list assessment). Dried herb, pure essential oil, and SDSE extracts were evaluated in separate panel sessions.

RESULTS AND DISCUSSION

Composition of Volatile Compounds Isolated by Different Methods. The flavor compositions of the EO, the SDSE, and the headspace above the oil (HS-EO) are presented in **Table 1**. Among 71 compound, 55 were identified positively and 16 tentatively. All of the identified compounds have already been reported in catnip (10, 18–23). They constituted >98% of the total integrated GC peak area. The total content of essential oil in the dried catnip herb was rather low 0.36 ± 0.06 mL 100 g^{-1} . The major constituents in the volatile oil of catnip were characteristic for this species; however, their percentages were quite different as compared with published results (10, 18–23). The major compound geranyl acetate constituted more than half in the oil (54.8%), followed by citronellyl acetate (13.4%), citronellol (6.9%), and geraniol (5.5%). Germacrene D (1.9%), caryophyllene oxide (1.8%), and spathulenol (1.1%) were the most abundant sesquiterpenes in the essential oil. The chemical formulas of some constituents, as representatives of different groups of volatiles identified in catnip, are provided in **Figure 1**.

The percentage composition of the volatiles in the SDSE was different as compared to hydrodistilled oil. The content of geranyl acetate and citronellyl acetate were lower in the SDSE, 1.6 and 1.5 times, respectively, whereas the content of monoterpene hydrocarbons, oxygenated monoterpenes, and some other compounds was higher in the SDSE. For example, the content of 1,8-cineole in SDSE was 7.7% (EO = 0.4%), that

Table 1. Composition of Catnip (*N. cataria* L.) EO, SDSE, and HS-EO, GC Peak Area Percent

constituent	KI on DB5	identification	GC peak area percentage ^a			odor note
			EO	SDSE	HS-EO	
hex-3-en-1-ol	856	KI, MS	0.1	0.2	nd	powerful fresh, green, grass odor (29, 30)
α -thujene	934	KI, MS	nd	0.1	nd	na ^c
α -pinene	944	KI, MS	tr	0.4	2.0	woody, piney, and turpentine-like, with a slight cooling camphoraceous nuance and a fresh herbal lift (31)
camphene	964	KI, MS	nd	0.1	tr	camphoraceous, cooling, piney woody with terpy nuances; it has citrus, green minty and green spicy notes (31)
sabinene	971	KI, MS	tr	0.2	0.5	woody, terpy, citrus, pine-like with a spice nuance (32)
β -pinene	990	KI, MS	0.2	0.4	1.0	cooling, woody, piney, and turpentine-like with a fresh minty, eucalyptus and camphoraceous note with a spicy peppery and nutmeg nuance (31)
6-methyl-5-hepten-2-one	994	KI, MS	tr	1.0	3.3	fruity, apple, musty, ketonic and creamy with slight cheesy and banana nuances (33)
δ -3-carene ^b	1007	KI	nd	tr	0.8	na
α -phellandrene	1011	KI, MS	tr	tr	0.9	minty, herbaceous (29); citrus, terpenic, slightly green, black-pepper-like (34)
α -terpinene	1015	KI, MS	0.1	0.4	0.3	green-grassy, lemon-like (29); citrusy, woody, terpy with camphoraceous and thymol notes; spicy and juicy citrus nuances (31)
<i>p</i> -cymene	1031	KI, MS	0.1	0.4	4.6	weak, citrus odor (29); harsh chemical, woody, and terpy-like with an oxidized citrus lemon notes; spicy nuances reminiscent of cumint, oregano, and cilantro (31)
β -phellandrene	1034	KI, MS	tr	tr	3.5	minty, herbaceous (29)
1,8-cineole	1048	KI, MS	0.4	7.7	15.4	camphoraceous, sharp, cool, spicy (29)
<i>cis</i> - β -ocimene	1054	KI, MS	0.1	0.6	1.6	tropical, green, terpy and, woody with vegetable nuances (35)
<i>trans</i> - β -ocimene	1061	KI, MS	tr	0.5	nd	mild, citrus, sweet, orange, lemon (29)
γ -terpinene	1069	KI, MS	tr	0.6	0.5	terpy, herbaceous, oily, woody, sweet, citrus with tropical and cooling lemon/lime-like nuances (32, 34)
<i>cis</i> -linaloloxide	1083	KI, MS	1.3	3.3	9.9	woody, floral, cooling, terpy, and slightly green (36)
<i>trans</i> -linaloloxide	1098	KI, MS	0.8	1.9	4.6	na
linalool	1109	KI, MS	0.6	1.1	1.3	floral, berry, and sweet with a waxy musty and woody nuance (37); floral, sweet, green, rosy, woody with a spicy tropical nuance (38)
<i>cis</i> -rose oxide	1121	KI, MS	0.8	4.2	3.0	very pure rose oxide with high <i>cis</i> content (30)
<i>cis</i> - <i>p</i> -menth-2-en-1-ol ^b	1131	KI	tr	0.2	tr	light minty, woody (29)
<i>trans</i> -rose oxide	1140	KI, MS	0.1	1.2	1.6	na
terpinen-1-ol	1147	KI, MS	tr	0.4	na	na
camphor	1156	KI, MS	nd	0.1	nd	camphoraceous, medicinal, mentholic with a cooling green nuance (39); aromatic, woody, medicinal (29)
citronellal	1165	KI, MS	0.3	0.9	0.8	citrus with lemon nuance (29); clean lemony floral odor (30)
borneol	1177	KI, MS	tr	0.7	0.2	camphoraceous, piney (29)
menthol ^b	1185	KI	tr	0.1	tr	cooling, menthol, minty, and ethereal with a penetrating, spicy eucalyptus nuance (40)
terpinen-4-ol	1191	KI, MS	tr	0.2	tr	sweet, green, citrus, cooling lime-like with a tropical terpy nuances (41); slightly minty, floral, wet straw-like aroma (42)
α -terpineol	1200	KI, MS	0.2	0.4	0.7	fragrant, floral, lilac (29)
myrtenal	1215	KI, MS	nd	tr	nd	cooling, green, minty with spicy woody notes (43)
<i>trans</i> -carveol	1218	KI, MS	0.4	1.2	0.5	caraway, spearmint (29)
isodihydrocarveol	1223	KI, MS	tr	0.1	nd	na
citronellol	1240	KI, MS	6.9	7.2	3.5	fresh, clean floral, rosy, sweet, citrus with green fatty terpene nuances (30, 38)
neral	1256	KI, MS	0.7	0.9	0.6	na
carvone	1252	KI, MS	0.1	tr	nd	warm, herbaceous, spearmint, peppermint (29); characteristic caraway and rye odor (30)
geraniol	1265	KI, MS	5.5	5.1	1.3	very high quality rose/lemon odor (30); green, citrus-like with a floral woody nuance (38); floral, sweet, rosey, fruity, berry and citronella-like with a citrus/lemon nuance (40, 44)
linalyl acetate ^b	1270	KI	0.3	0.7	0.6	citrus, floral, sweet, green with waxy and woody nuances (35)
geranial	1285	KI, MS	1.0	1.9	0.7	green floral weedy woody notes (30)
citronellyl formate	1295	KI, MS	0.2	0.4	nd	tropical fruity, rose odor (30); sweet, green, waxy, floral, apricot, citrus, fruity and mandarin (45)
neryl formate ^b	1307	KI	0.1	0.2	nd	rose herbaceous green character (30); green, metallic, sweet, fruity, floral, citrus and tropical (41)

Table 1. (Continued)

constituent	KI on DB5	identification	GC peak area percentage ^a			odor note
			EO	SDSE	HS-EO	
geranyl formate	1322	KI, MS	0.7	0.5	0.2	fresh, dry, ethereal green odor (30)
α -terpinyl acetate ^b	1336	KI	0.1	0.1	nd	herbal, citrus, spicy, woody, floral, waxy, and clean (46)
citronellyl acetate	1357	KI, MS	13.4	8.7	10.3	citrus, reminiscent of lemon peel, rose (29); fresh, rose, fruity odor (30); floral, rosy, green, fatty, citrus lemon, and bois-de-rose-like, waxy pear and apple-like on dry out (37); floral, green, sweet, fruity, citrus with woody tropical fruit nuances (47)
neryl acetate	1366	KI, MS	0.3	0.5	0.2	sweet floral, orange, citrus, fresh rose odor (30); floral, rosy, sweet, soapy, citrus, grapefruit, fruity with a tropical nuance (36)
geranyl acetate	1390	KI, MS	54.8	34.2	22.1	rose, green odor with lavender undertones (30); floral, rosy, waxy, herbal and green with a slight cooling nuance (48)
α -cubebene	1396	KI, MS	0.2	0.2	0.2	na
isocaryophyllene	1407	KI, MS	0.4	0.3	0.5	na
α -gurjunene	1419	KI, MS	0.1	0.2	0.3	na
β -caryophyllene	1431	KI, MS	0.1	0.2	0.4	terpene odor, woody, spicy (29)
β -gurjunene ^b	1442	KI	0.1	tr	nd	na
<i>cis</i> - β -farnesene	1448	KI, MS	0.6	0.3	0.8	woody green vegetative odor with a lavender background (32)
α -humulene	1462	KI, MS	0.5	1.9	0.2	sweat, fruity, honey-like (29)
<i>trans</i> - β -farnesene	1471	KI, MS	0.2	0.2	nd	na
<i>allo</i> -aromadendrene ^b	1477	KI	0.1	0.1	nd	na
γ -gurjunene ^b	1485	KI	0.1	0.2	nd	na
germacrene D	1496	KI, MS	1.9	1.1	0.5	na
β -ionone	1503	KI, MS	0.4	0.1	nd	warm, woody, balsamic, floral, rose, violet on dilution (29); sweet, fruity, berry-like with a green berry background (49)
α -muurolene ^b	1519	KI	0.1	0.5	0.1	na
β -bisabolene	1525	KI, MS	0.5	0.5	nd	berry, somewhat spicy citrus note (30)
γ -cadinene ^b	1530	KI	0.1	0.3	nd	na
δ -cadinene	1540	KI, MS	0.3	0.4	nd	na
<i>cis</i> -nerolidol ^b	1554	KI	0.1	0.2	nd	rose, apple, green, citrus, slightly woody, waxy (29)
germacrene B	1569	KI, MS	0.1	0.1	nd	na
spathulenol	1591	KI, MS	1.1	0.7	nd	na
caryophyllene oxide	1596	KI, MS	1.8	1.1	0.2	herbaceous (29)
γ -eudesmol ^b	1646	KI	0.1	0.1	nd	na
β -eudesmol ^b	1653	KI	0.1	0.1	nd	na
α -cadinol ^b	1669	KI	0.1	0.1	nd	na
α -bisabolol ^b	1701	KI	0.1	0.2	nd	sweet, waxy, orange peel, floral odor (30)
2 <i>cis</i> ,6 <i>cis</i> -farnesol	1730	KI, MS	0.1	0.1	nd	delicate, floral, oily (29); delicate, fresh, green muguet note (30)
phytol	1984	KI, MS	tr	tr	nd	delicate, floral, balsamic (29)
total			98.3	98.2	99.2	
RSD ^d (%)			9.8	19.6	24.1	

^a Average peak areas of three to five replicates. nd, not detected; tr, $\leq 0.04\%$. ^b Tentatively identified components. ^c na, not available. ^d RSD (%), mean of percentage relative standard deviation.

of *cis*-linalol oxide 3.3% (EO = 1.3%), that of *cis*-rose oxide 4.2% (EO = 0.8%), that of *trans*-rose oxide 1.2% (EO = 0.1%), that of citronellal 0.9% (EO = 0.3%), and that of *trans*-carveol 1.2% (EO = 0.4%). The percentage of major sesquiterpenes in EO was almost 2 times higher as compared to SDSE (Table 1). Differences in the composition between EO and SDSE were also reported by other researchers (27), but the exact reason for this phenomenon has not been comprehensively explained.

The RSD was calculated for each compound. In the analysis of EO components it was from 0.4% (citronellyl acetate) to 22.7% (β -pinene); for most of the constituents it was in the range of 2–9%. The RSD of SDSE varied from 1.3% (geraniol) to 33.1% (γ -gurjunene); for most of compounds it was <16%. The RSD of HS-EO ranged between 6.0% (γ -terpinene) and 57.2% (β -pinene), and for the most of the constituents it was below 20%. The mean value of all calculated RSDs is provided in Table 1 for EO, SDSE, and HS-EO, respectively.

The contents of the main groups of catnip constituents in EO, SDSE, and HS-EO are compared in Figure 2. Although geranyl acetate was dominating in all samples, there were significant differences in its content between analyzed products. It is interesting to note that the highest percentage of geranyl acetate was in the EO (54.8%), whereas in the SDSE and HS-EO it was 34.2 and 22.1%, respectively. Monoterpene hydrocarbons are more volatile constituents than oxygenated compounds; therefore, their content in the HS-EO was significantly higher than in the pure oil. For instant, traces (tr $\leq 0.04\%$) of such monoterpenes, as α -pinene, sabinene, and α -phellandrene, were detected in EO, whereas their contents in the headspace of oil were 2.0, 0.5, and 0.9%, respectively. Only traces of 6-methyl-5-hepten-2-one were found in the EO, whereas its contents in SDSE and HS-EO were 1.0 and 3.3%, respectively; the content of *p*-cymene in the HS-EO was >65 times higher than in the EO. This is in agreement with previously reported results obtained during the analysis of thyme and sage (27).

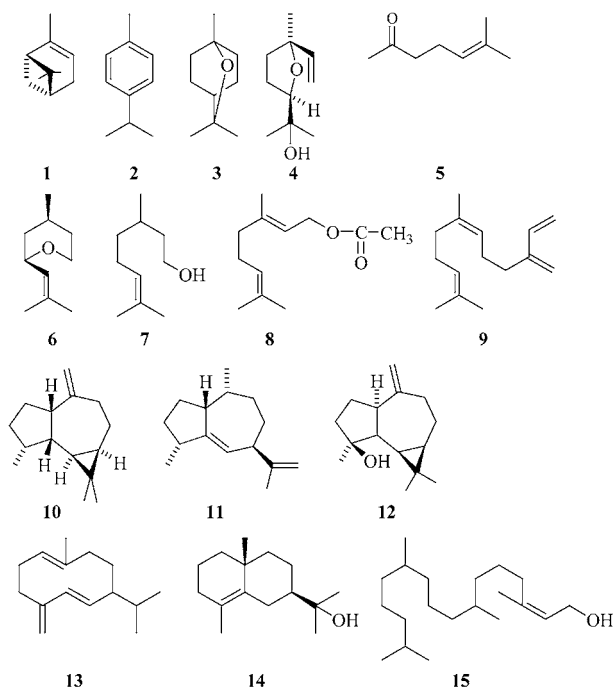


Figure 1. Chemical structures of some constituents identified in catnip: 1, α -pinene; 2, *p*-cymene; 3, 1,8-cineole; 4, *cis*-linalool oxide; 5, 6-methyl-5-hepten-2-one; 6, *cis*-rose oxide; 7, citronellol; 8, geranyl acetate; 9, *cis*- β -farnesene; 10, *allo*-aromadendrene; 11, γ -gurjunene; 12, spathulenol; 13, germacrene D; 14, γ -eudesmol; 15, phytol.

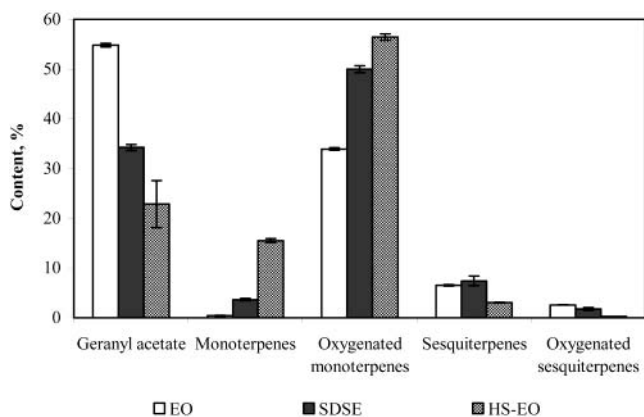


Figure 2. Content of geranyl acetate and the main terpene groups in catnip EO, SDSE, and HS-EO, in GC peak area percentage.

In general, catnip (*Nepeta cataria*) grown in Lithuania and analyzed in the present study depends on citral chemotype, containing terpene ester geranyl acetate as a dominating constituent, other quantitatively important components being citronellol acetate, citronellol, and geraniol. The composition of catnip volatile components strongly depended on their isolation method: the percentage of aliphatic monoterpenes was higher in the extracts obtained by simultaneous distillation–solvent extraction, whereas the contents of major oxygenated terpenes, such as citronellol and geranyl acetates, and most sesquiterpenes were higher in the essential oil hydrodistilled according to a standard procedure.

Analysis of Volatile Compounds by SPME. A headspace SPME technique has been introduced by Zhang and Pawliszyn (50). Volatile sample constituents are adsorbed on a thin, fused silica fiber, coated with a layer of an organic polymer placed in the headspace above the sample, and subsequently thermally desorbed inside a GC injection port. In comparison with solvent

extraction, SDSE, conventional solid phase extraction, or purge-and-trap sampling, which are the most frequently used sample preparation techniques employed in flavor analysis, SPME is simple, rapid, solvent-free, and inexpensive (51).

The SPME coatings can be classified by polarity, extraction type (absorbent or adsorbent), or size exclusivity (52). Three different SPME-coated fibers, PDMS (nonpolar absorbent-type), combined PDMS-DVB (bipolar adsorbent-type), and CAR-PDMS (bipolar adsorbent type), were used in this study. Each coating offers particular advantages; for example, the PDMS is a nonpolar coating that has been known to work very effectively on a wide range of analytes, both polar and nonpolar (53, 54); on the contrary, the polyacrylate coating is more polar phase, which readily extracts more polar analytes (54). When the porous polymer DVB is suspended in PDMS, the polarity is relatively low; however, it has been demonstrated that this fiber extracts such polar components as amines (52). Carboxen is essentially bipolar because the pores are the primary mechanism for extracting and retaining the analytes. When CAR is suspended in PDMS, the resulting fiber coating is moderately polar and extracts solvents, such as ethanol and acetonitrile, even at 20 ppb level in water (52).

Figure 3 illustrates the percentage distribution of the main components extracted by different fiber coatings from catnip herb headspace. It is evident that the contents of various compounds absorbed by the used coatings were remarkably different. The volatile profile of catnip consists mainly of oxygenated and aliphatic terpenes. Aliphatic terpenes, such as α -pinene, camphene, β -pinene, α -phellandrene, and *p*-cymene, are nonpolar compounds; however, their percentage was higher in the combined PDMS-DVB and CAR-PDMS coatings. For example, the content of nonpolar *p*-cymene on combined PDMS-DVB- and CAR-PDMS-coated fibers constituted 2.7 and 1.9%, respectively, whereas the content of this compound on nonpolar PDMS-coated fiber was 1.0%. The content of the most abundant 1,8-cineole was highest on the nonpolar PDMS coating (39.2%) compared to PDMS-DVB (29.5%) and CAR-PDMS (22.6%) fibers; the percentage of geranyl and citronellol acetates was >3 times higher on the moderately polar CAR-PDMS than on the relatively nonpolar PDMS-DVB-coated fiber.

The precision of SPME measurements was estimated by running six replicate extractions. The corresponding RSD was calculated for these extractions with each used fiber. For PDMS extractions it varied from 0.8% (citronellol) to 11.69% (β -pinene) and for most of the constituents was <6%; for PDMS-DVB it was from 0.4% (α -terpinene) to 33.1% (camphene), being for most of the volatiles below 12%; for the CAR-PDMS fiber it was from 0.5% (citronellol) to 19.0% (caryophyllene oxide), and for most of the volatiles it was <10%. Error bars are provided in **Figures 3** and **4** for every SPME analysis.

The concentrations of the main compounds extracted from catnip herb headspace by different fibers were also expressed in arbitrary units related to the peak area, which provides more comprehensive information about extraction efficiency as long as they are directly related to the absolute amount of a particular compound absorbed by the matrix. Such data can be more closely related to the sensory properties of catnip oil and herb. The results depicted in **Figure 4** show that the highest enrichment of catnip volatile compounds was obtained with the CAR-PDMS-coated fiber (4165 ± 307) $\times 10^3$ au. The PDMS-DVB and PDMS coatings extracted approximately 1.6 [(2595 ± 217) $\times 10^3$ au] and 1.7 [(2407 ± 543) $\times 10^3$ au] times lower amounts of aroma constituents, respectively. The results also demonstrate that the peak areas of analytes extracted with the

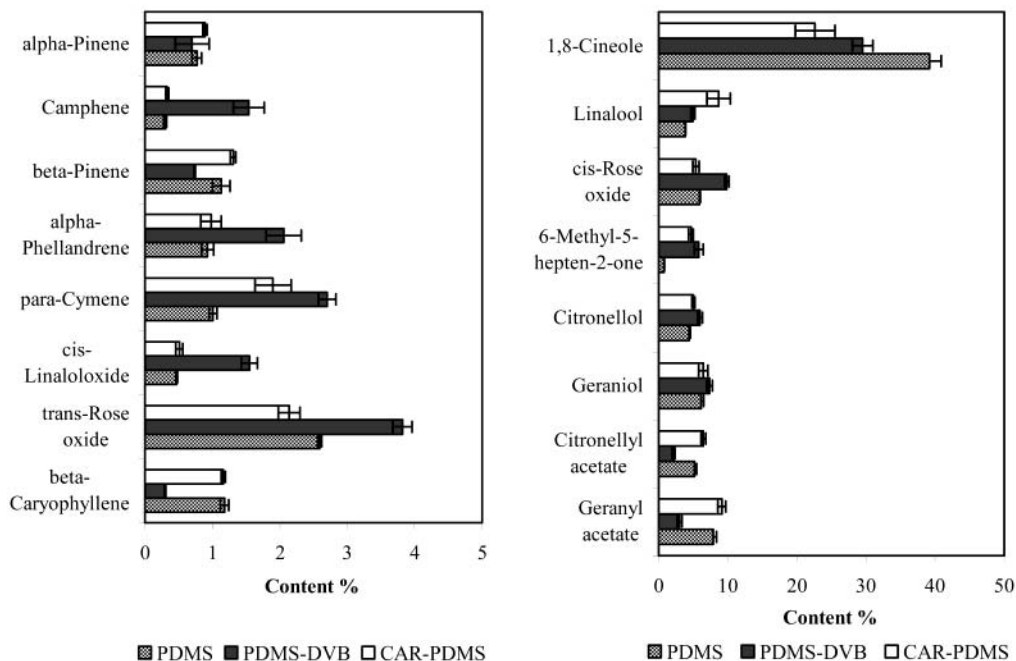


Figure 3. Composition of volatile compounds extracted by different SPME fibers in dried catnip headspace, in GC peak area percentage.

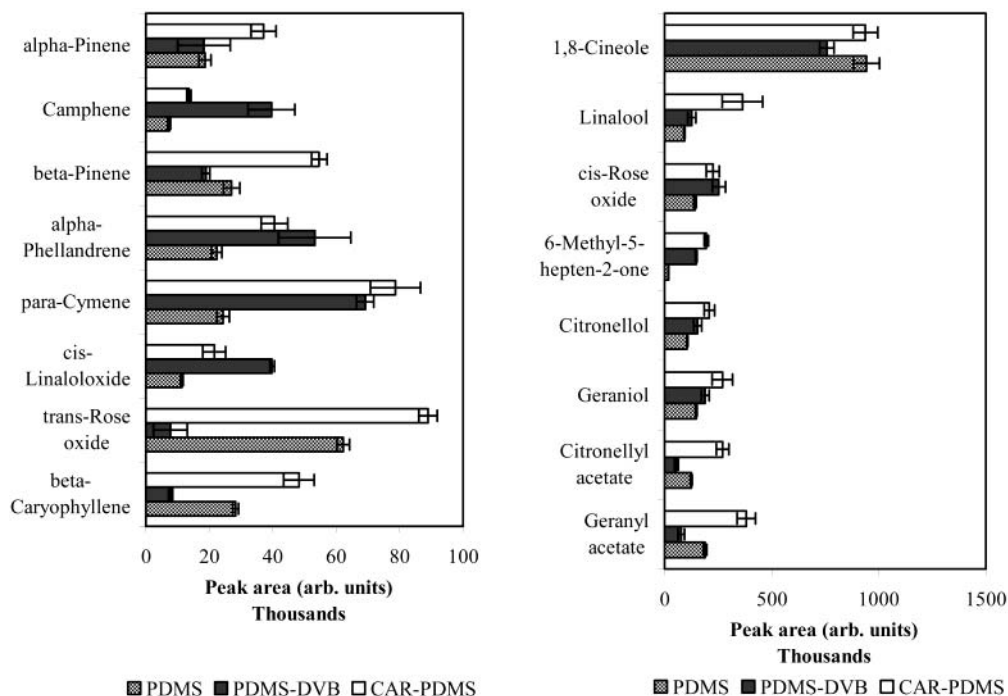


Figure 4. Amount of volatile compounds extracted by different SPME fibers in dried catnip headspace, in arbitrary GC peak area units.

CAR-PDMS fiber were much bigger than those extracted with other fibers. Popp (55) obtained similar results when comparing a CAR-PDMS fiber to other fibers for the extraction of volatile compounds in model systems. Carboxen 1006 (the type of carboxen used in the fiber) acts as an adsorbent, whereas a liquid phase performs mainly by partitioning or as an absorbent. Smaller size analytes are not well retained by the fibers coated with only liquid phases, whereas the pores in carboxen are designed to retain smaller analytes. Due to the better efficiency of the CAR-PDMS fiber in extracting small analytes, it is more suitable for trace-level analysis. The fiber coatings containing DVB, which is also an adsorbent type fiber, extracted better than the fiber coatings with only liquid phase; however, the amount of analyte extracted with DVB was lower compared to

CAR. This difference is likely to be primarily due to the pore size. Carboxen is a mixture of micro-, meso-, and macropores, whereas DVB is mesoporous. Mesopores only slightly retain lower molecular weight analytes (56). In general, the strong adsorbent CAR extracted these volatiles better than the weaker adsorbent DVB, which extracted better than the absorbent or liquid phase coated PDMS fibers. It can be expected that higher polarity fibers will better extract polar analytes. The results obtained indicate that nonpolar PDMS did not extract higher amounts of many nonpolar analytes in comparison with the relatively polar CAR-PDMS. Therefore, the amount of *p*-cymene or β -caryophyllene was considerably lower on nonpolar PDMS fiber compared to the relatively polar CAR-PDMS fiber (Figure 4). The contents of extracted 1,8-cineole were similar both on

PDMS [(942 ± 60) × 10³ au] and on CAR-PDMS [(938 ± 58) × 10³ au]; a slightly lower amount of this compound was extracted on PDMS-DVB [(757 ± 33) × 10³ au]. In the case of some aliphatic terpenes, CAR-PDMS was more effective than nonpolar PDMS. These findings indicate that the effect of fiber polarity on the extraction of aliphatic and oxygenated terpenes was minimal, that is, the polar fiber did not extract more of the polar analytes than the nonpolar one. However, the polar fiber extracted much less of the nonpolar analytes than nonpolar fibers. Therefore, the polar fibers provide better selectivity for polar analytes.

The efficiencies of the SPME fibers applied to collect volatiles in the catnip headspace were quite different, both in terms of percentage composition of the extracted volatiles and in terms of their absolute amounts. The obtained results indicate that the effect of fiber polarity on the extraction of terpenic compounds from catnip headspace was not remarkable. The SPME method strongly depends on experimental conditions and sample matrix (51). Additionally, for compounds of the same class, the adsorption on SPME fibers generally varied with different molecular sizes (57). The CAR-PDMS fiber was more efficient in terms of extracted volatiles from dried catnip herb and their absolute amounts. However, to obtain a more comprehensive explanation of the differences in extraction efficiencies obtained in our study, more detail investigations with model systems (e.g., pure compounds) should be performed.

Differences between headspace composition of dried catnip herb and its essential oil can be observed and should be briefly commented on. First, it is evident that the content of geranyl and citronellyl acetates was lower in the headspace of dried herb (as determined with all three SPME fibers) than in the headspace of the essential oil (as determined by the SH method). The percentages of *p*-cymene, *cis*- and *trans*-linalol oxides, and some other terpenes were also higher in the essential oil headspace as compared with the dried herb. However, the content of such constituents as 1,8-cineole and linalool was considerably higher in the headspace of dried catnip herb than in HS-EO. Such differences could have an important influence on the changes of the sensory aroma profile between dried herb and its essential oil.

Sensory Assessment of Catnip Flavor. During processing and other handling of aromatic herbs the flavor profile could undergo bigger or smaller changes (28). For instance, the aroma of fresh herb changes after drying due to losses of the most volatile constituents and consequently “green aroma notes”; the essential oil aroma profile also differs from that of freshly cut or dried herbs. The effect of processing is important in terms of flavor profiles of the products obtained. In this study the effect of processing is demonstrated on catnip dried herb, EO and SDSE. Sensory odor profiles of *N. cataria* ground herb, E, and SDSE are presented in **Figure 5**.

It can be observed that the results of free choice and descriptor’s list assessments were quite similar. The most prevailing descriptors of catnip herb were “citrus, lemon”, “floral, sweet”, “fruity, esteric”, “herbaceous, spicy”, and “minty”. The aroma profile depends on the composition of volatile constituents in the product headspace, which is defined by the amount of the compounds in the matrix and their properties, for example, boiling temperature, vapor pressure, binding capacity to other food matrix components, and, consequently, the rate of release from that matrix. Also, the odor threshold of a particular compound plays an important role in the aroma perception. Geranyl acetate, 1,8-cineole, citronellyl acetate, *cis*- and *trans*-linalol oxides, *p*-cymene, and some other

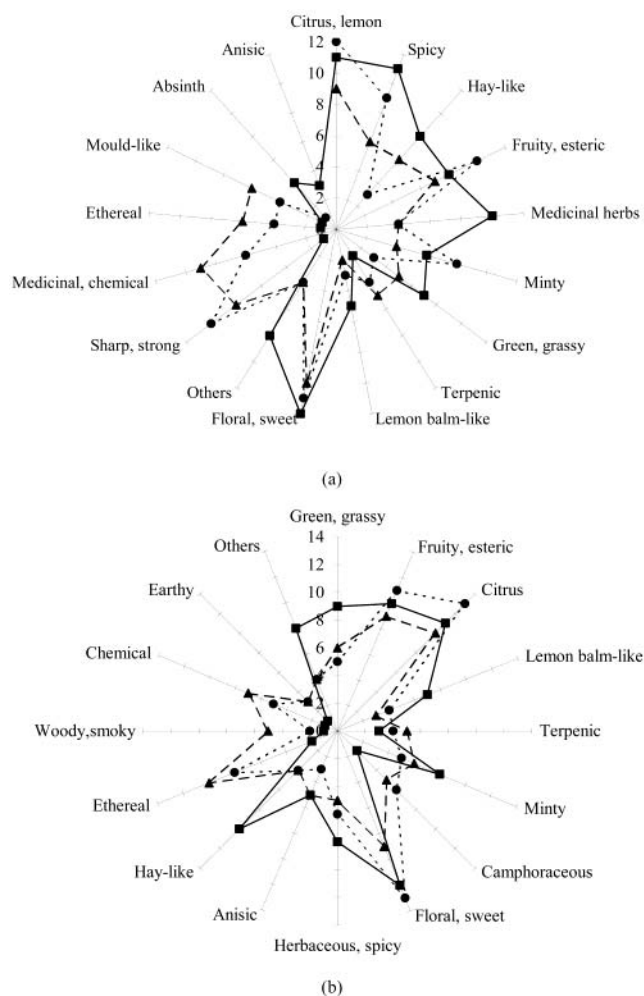


Figure 5. Sensory odor profiles of ground catnip herb (■), EO (●), and SDSE (▲): (a) free choice assessment; (b) descriptor’s list assessment.

terpenes were the most abundant constituents in the headspace of catnip herb, and therefore it is most likely that these compounds are important to the overall herb aroma profile. In general, it is in agreement with aroma assessment of these compounds, provided in various literature sources. “Floral, sweet” and “fruity, esteric” aroma notes have been attributed to linalol oxide, linalool, citronellol, geraniol, citronellyl and neryl formates, linalyl, citronellyl, neryl and geranyl acetates, and some other catnip compounds (**Table 1**); these notes were prevailing both in the free choice (**Figure 5a**) and in the descriptor’s list assessments (**Figure 5b**). For instance, *p*-cymene was reported to possess a citrus odor (30); 11 panelists recognized such a note while assessing catnip dried herb during the free choice sessions. Geranyl and citronellyl acetates, terpinen-4-ol, and α -terpinene can provide “green, grassy” aroma notes, which were prevailing in the descriptor’s list assessment sessions (**Figure 5b**). α - and β -phellandrenes, β -pinene, *cis*-*p*-menth-2-en-1-ol, terpinen-4-ol, menthol, and myrtenal were reported to possess “minty” aroma notes (**Table 1**), which were pointed out by several assessors. The impact of the mentioned odor characteristics, first of all such as “green, grassy”, “medicinal herbs”, “hay-like”, “spicy”, and “lemon balm-like”, were reduced after hydrodistillation, in the case of both EO and SDSE, whereas such aroma notes as “citrus, lemon”, “fruity, esteric”, “terpenic”, “camphoraceous”, “floral, sweet”, and some others were more frequently attributed to the processed catnip products, especially EO. Some specific odor notes of catnip such

as "lemon balm-like" were weaker after distillation, whereas "terpenic" (typical to α -terpinene, α -pinene, β -pinene, *p*-cymene, 1,8-cineole, camphor, and borneol) and "caraway" (typical to carveol and carvone) after distillation were stronger in the case of both free choice and descriptor's list assessments. A more general descriptor, "sharp, strong" (1,8-cineole, γ -terpinene, terpinolene, and β -caryophyllene), was frequent in a free choice assessment, and it was also more often attributed to the concentrated products than to the dried herb. This finding can be explained by the increase of the concentration of strongly smelling compounds after distillation. Some odor notes can be directly related to the presence of particular constituents in catnip products. For instance, "floral, sweet" notes are typical of the major constituent geranyl acetate and some other catnip compounds, for example, citronellyl acetate, citronellol, geraniol, and linalool.

Such descriptors as "chemical", "ethereal", "woody, smoky", and "mold-like" were more frequent in assessment of EO and especially SDSE. It is reasonable considering the increase of the concentration of strong odor impact natural volatile compounds; some of them, for example, sabinene, β -pinene, *cis*-*p*-menth-2-en-1-ol, and β -caryophyllene, were reported to possess the above-mentioned odor qualities (Table 1). The residues of organic solvent in the case of SDSE also have to be taken into account. Some panel members recognized "camphoraceous" aroma notes in the descriptor's list assessment, which were more characteristic of concentrated products and could be imparted by the presence of camphene, α -terpinene, β -pinene, α -pinene, 1,8-cineole, camphor, borneol, and some other minor constituents. The "catnip" aroma note was not included in the descriptor's list deliberately (most of the panelists were not familiar with such odor), and nobody recognized "catnip" aroma during assessing.

It can be concluded that sensory assessment revealed some differences in odor profiles between dried herb and distilled and/or extracted volatile concentrates during both free choice and descriptor's list assessment sessions. Odor profiles of catnip and their changes during isolation procedure in many cases can be closely linked to the odor characteristics of pure compounds present in catnip.

ABBREVIATIONS USED

HD, hydrodistillation; SDSE, simultaneous distillation–solvent extraction; SH, static headspace; SPME, solid phase microextraction; PDMS, polydimethylsiloxane; DVB, divinylbenzene; CAR, carboxen; EO, essential oil; HS-EO, the headspace above the essential oil; KI, Kovats retention indices; RSD, relative standard deviation; au, arbitrary units.

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