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Volatile constituents from aerial parts and roots of *Cichorium intybus* L. (chicory) grown in Lithuania

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The composition of volatile fraction from overground parts and roots of *Cichorium intybus* L. has been studied. The plants were collected in five different locations of Lithuania in 2007 during flowering stage. Volatile compounds were obtained by hydrodistillation of dried material and analysed by GC/MS. Octane, n-nonadecane, pentadecanone, hexadecane and a tentatively identified compound (pentenyl salicilate?) have been found as principal components among all volatile constituents. The amounts of octane and the tentatively identified compound were significantly higher in roots (34.3–69.8% and 4.8–22.7%, respectively) than in overground parts of the chicory (8.0–25.6% and 0–0.9%, respectively). An opposite relation was observed for nonadecane, its content being higher in the aerial parts (5.1–46.9%) than in roots (0.3–3.9%). Aliphatic compounds and their derivatives comprised the main fraction (63.2–76.9% and 64.1–81.3%, respectively in the aerial parts and roots), while terpenoids were minor constituents. Thirty and twenty-eight identified compounds comprised 75.2–84.7% and 83.4–95.1% of the total content in the aerial parts and roots, respectively.

Key words: *Cichorium intybus*, Asteraceae, secondary metabolites, aliphatic compounds, sesquiterpenes

INTRODUCTION

Chicory is the common name given to the flowering plants from the genus *Cichorium* of the family Asteraceae (tribe Cichorieae). There are two cultivated and ten wild species in the world.

Common chicory (*Cichorium intybus*), native to Eurasia, is a bushy perennial plant with white, blue or pink-blue flowers, can reach 170 cm in height. Common chicory is also known as blue sailors, succory and coffeeweed.

Two species of chicory grow in Lithuania: *C. intybus* is a widespread weed, while *C. endivia* is a rare, mostly cultivated species. The habitats of *C. intybus* are roadsides, railroads, disturbed sites and waste grounds, flowering period lasts from June to October. Several subspecies (*intybus*, *sativum*) and varieties of *C. intybus* grow in Lithuania [1].

Since the 16th century the herb has been used in food preparation (boiled and fresh). Root chicory (*Cichorium intybus* var. *sativum*) has been cultivated in Europe as a coffee substitute for a long time. The roots are baked, ground, and used as a coffee substitute and additive. Around 1970 it was found that the root contains up to 40% inulin (polysaccharide), which has a minimal impact on blood sugar and for this reason is suitable for diabetics. Inulin is a valuable food additive, used as a sweetener in the food industry (with a sweetening power 30% higher than that of sucrose) and is sometimes added to yoghurts as a probiotic. Since then, new strains have been created, giving root chicory an inulin content comparable to that of sugar beet.

Flowers of chicory (*Cichorii flos*) contain saccharides, methoxy coumarin cichorine, flavonoides (anthocyanins, flavonols, flavones) and essential oils. Chicory roots (*Cichorii radix*) are free of harmful ingredients and have a large content of three sugars (pentose, levulose and dextrose) along with taraxarcine (the bitter principle of dandelion) [2]. The roots have the potential to be used for the production of biomass for industrial use. They are rich in the starch inulin which can easily be converted to alcohol. A dried and powdered mixture of several herbs can be added to a compost heap in order to enhance bacterial activity and thus shorten the time needed to make the compost. Chicory herb would be a potential source of functional feed additives for domestic animals [3].

Chicory has a long history of medicinal herbal use and is especially of great value for its tonic effect upon the liver and digestive tract [4]. The roots and the leaves are appetizers, digestives, cholagogues, depuratives, diuretics, hypoglycaemics, laxatives and tonics [5–11]. Chicory, especially its flowers, was used as a herbal treatment for everyday ailments as a tonic and appetite stimulant, and as a treatment for gallstones, gastro-enteritis, sinus problems, cuts and bruises. The roots are the most medicinally active part of the plant [11]. Extracts of roots ameliorate blood circulation and at the same time help to eliminate possible fat concentrations and toxins from the vessels, while inulin reduces blood pressure. A decoction of the root has proved to be of benefit in the treatment of jaundice, liver enlargement, gout and rheumatism [4]. The juice is said to be a folk remedy for cancer of the uterus and for tumours. Antibacterial, antimalarial, cytotoxic, anti-diabetic, no-mutagenic and other activities were evaluated [12–16].

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Various compound classes such as pigments (anthocyanins), tannins, sesquiterpene lactones, coumarins, inulin, cinnamic acid derivatives (such as chicoric, caffeic and chlorogenic acids) have been investigated in chicory [17–19], while data on essential oils or other volatile constituents of the plant are very limited [20, 21].

The aim of the study was to investigate volatile compounds from the aerial parts and roots of *C. intybus* grown in Lithuania.

EXPERIMENTAL

Samples of *Cichorium intybus* were collected at flowering stage from five localities in Lithuania (in 2007): A – Salantai (Kretinga district), B – Vilnius city, C – Vilkaviškis, D – Kaunas and E – Marcinkonys (Varėna district). Overground parts (including flowers and leaves) are indicated by the letter *o* and roots by *r* in Table. The roots were separated before drying from the rest part of the plants, samples were dried at room temperature (~20 °C) and crushed. The volatile fraction was isolated by hydrodistillation for 2 h with the Clevenger type apparatus; a mixture of pentane and diethyl ether (1 : 1) was used as a collecting solvent. The yield of the volatile fraction was ~0.02–0.04% (v/w) on the dry weight basis.

GC/MS analyses were performed using an HP 5890II chromatograph interfaced with an HP 5971 mass spectrometer (ionization voltage 70 eV, m/z scan rage 35–350 Da, scan time 0.6 s) and equipped with a DB-5 capillary column (50 m × 0.32 mm, film thickness 0.25 μm). The oven temperature was held at 60 °C for 2 min, then programmed from 60–160 °C at a rate of 5 °C/min, held for 1 min, increased up to 250 °C at the rate 10 °C/min and was kept at the final temperature for 3 min, using He as a carrier gas (1.0 ml/min, split ratio 1 : 20). The injector and detector temperatures were 250 °C. The number of analyses was no less than two repetitions.

The percentage composition of the oils was computed from GC peak areas without correction factors. Qualitative analysis was based on a comparison of retention times, indices and mass spectra with the corresponding data in the literature [22, 23] and computer mass spectra libraries (Wiley and NBS 54K).

RESULTS AND DISCUSSION

The chemical composition of the volatile compounds of *C. intybus* L. growing in Lithuania was determined. In the course of the study, ten samples of succory aerial parts and roots were analysed by GC/MS. Volatile compounds obtained by hydrodistillation of the dried material were presented in Table. Thirty and twenty-eight identified compounds formed 75.2–84.7% and 83.4–95.1% of the total content in the aerial parts and roots, respectively.

Octane, n-nonadecane, n-hexadecane, pentadecanone and the tentatively identified compound (pentenyl salicilate?) were found as the majors.

Living organisms frequently contain hydrocarbons which are directly derived from fatty acids. Hydrocarbons are found at the outer surface in higher plants, in insects and several marine organisms. These compounds serve as a barrier to water penetration in the organism, as sex attractants (or anti-aphrodisiacs), affect the absorption of chemicals and microorganisms.

Aliphatic hydrocarbons and their derivatives were the predominant fraction (63.2–76.9% and 64.1–81.3%, respectively, in the aerial parts and roots), while the quantities of terpenoids were minor. The amounts of octane and the tentatively identified compound were significantly higher in the roots (34.3–69.8% and 4.8–22.7%, respectively) than in overground parts of the chicory (8.0–25.6% and 0–0.9%, respectively). An opposite relation was observed for nonadecane whose content was higher in the aerial parts (5.1–46.9%) than in roots (0.3–3.9%). One sample of roots (Ar) was characterized by a high content of hexadecane (18.1%), while another three samples of aerial parts (Ao, Co and Do) contained appreciable amounts of 2–pentadecanone (6.5–14.9%). A high content of aliphatic derivatives was also characteristic of the roots and overground parts of numerous plants from different countries, investigated earlier. Some aliphatic hydrocarbons have fixative effects and therefore are responsible for a longer-lasting odour of the essential oils or perfumes.

Low amounts of monoterpenoids were determined in the aerial parts of chiccory. Except that, notable quantities of β-ionone and geranyl acetone were found in some samples of overground parts (1.3–3.0% and 0.7–3.2%, respectively), while the contents of these constituents were minor in roots (0–0.5% and 0–0.6%, respectively). Only several sesquiterpene hydrocarbons (β-elemene, β-ylangene, trans-caryophyllene, allo- and dehydro-aromadendrenes, (E)-β-farnesene and trans-β-guaiene) were identified in *C. intybus* roots. Minor amounts of sesquiterpenes could be explained by the influence of enzymes present in chicory roots on terpene conversion. According to [24], the enzymes in the presence of NADH (nicotanamide adenine dinucleodite phosphate oxidase) impact terpenoid biosynthesis and catalyse the hydroxylation of various sesquiterpene olefins into sesquiterpene alcohols and lactones. In the above work, there were investigated sixteen different terpenes, and most of them were hydroxylated due to the microsomal pellet of chicory roots. Hydroxylation of terpenes is important to the flavour and fragrance industry in the search of new production methods and new compounds. During the above investigations, was found an unexpected conversition of valencene into nootkatone, a valuable substance widely used in the food and perfumery industry because of its pleasant grapefruit flavour. Nootkatone is an expensive compound, for this reason new possibilities for its (bio) synthesis have been studied intensively. The above-established conversion catalysed by the microsomal pellet of chicory might be of interest, particularly because the undesired side products are hardly formed [24].

CONCLUSIONS

The overground parts and roots of *Cichorium intybus* L. grown in Lithuania biosynthesise small amounts of volatile compounds, among which the most predominant are aliphatic hydrocarbons and their derivatives. A very small quantity of terpenoids in the volatile fraction could be explained by the presence of active enzymes in chicory roots, which impact terpenoid biosynthesis and catalyse the hydroxylation of various sesquiterpene hydrocarbons into sesquiterpene alcohols and lactones.

Table. **Volatile constituents (%) of chicory (*Cichorium. intybus* L.) aerial parts and roots grown in Lithuania (2007)**

Compound	RI	Ao	Ar	Bo	Br	Co	Cr	Do	Dr	Eo	Er
Octane	800	25.6	34.3	9.2	56.7	23.0	64.5	8.0	69.8	21.4	69.6
Octen-3-ol-1	979	tr			tr	0.3					
2-Pentyl furan	988	2.2		tr		1.8	0.2	1.1	0.3	2.6	tr
(2E, 4E)-Heptadienal	1007	2.5		tr	tr	1.9	1.0	2.0		2.6	
1,8-Cineole	1032	tr		0.1		0.9		1.0			
Benzene acetaldehyde	1042	1.5		1.2		4.5		1.0		1.0	
n-Nonanal	1100	6.5	0.6	2.1	tr	2.5	0.6	4.5	1.2	2.7	
Camphor	1146							1.4			
(2E, 6Z)-Nonadienal	1154	0.6									
(2E)-Nonen-1-al	1161	0.9									
n-Decanal	1201	1.7		0.8		1.3		1.5		0.8	
(2E, 4E)-Nonadienal	1212	tr						0.4			
n-Decanol	1269		tr		tr	0.9	tr				
(2E, 4Z)-Decadienal	1293	0.5	0.8	0.5		1.3	0.9	1.3	0.8	1.3	0.9
n-Tridecane	1300	tr					0.3		0.4		0.4
(2E, 4E)-Decadienal	1316	1.9	3.0			1.5	2.9		2.2		3.4
β-Elemene	1390			tr			0.6		0.3		
(E)-Caryophyllene	1419						tr		0.4		tr
β-Ylangene	1420		0.7		0.6				0.3		
Geranyl acetone	1455	2.6	tr	0.7		2.0	0.6	3.2		1.4	
(E)-β-Farnesene	1456		2.2						0.4		
allo-Aromadendrene	1460						tr		3.9		
dehydro-Aromadendrene	1462								0.6		
β-Ionone	1488	3.0		1.3		2.2	0.5	1.4		1.9	
Pentadecane	1500		1.8								tr
trans-β-Guaiene	1502		0.5	tr	0.7						
(2E)-Undecenol acetate	1504		1.3		1.9						
Sesquicineole	1516					tr			0.8		
(2E)-Tridecanol	1570	6.3					0.5		2.6		tr
Pentenyl salicilate?	1580	0.9	22.1		22.7	tr	6.8		4.8		9.6
n-Hexadecane	1600	4.3	18.1	0.9	1.7	1.4			2.6	5.9	
Tetradecanal	1611			1.0		1.5	2.7	2.8	1.3	2.8	1.1
Tetradecanol	1672			0.8		0.8					
2-Pentadecanone	1697	6.5	1.3		0.4	14.9		10.1	0.8	4.2	
(E)-2-Hexylcinnamaldehyde	1749			0.4							
Octadecane	1800			0.5		0.5					
n-Nonadecane	1900	13.3	3.0	46.9	0.3	5.1	1.0	31.1	1.2	29.7	3.9
(5E, 9E)-Farnesyl acetone	1913	1.5		0.8		0.6		2.3		0.9	
n-Eicosane	2000	1.3		1.1	5.1	2.9		1.5		0.9	2.1
n-Octadecanol	2077					1.0		0.3			
n-Heicosane	2100			8.0		2.5	0.4	8.2	0.5	4.5	
Total		83.4	89.6	76.4	90.1	75.2	83.4	83.0	95.1	84.7	90.9

RI – retention index on nonpolar column DB-5, tr – traces (≤0.05%), overground parts of chicory indicated by letter *o* and roots by *r*.
Growing localities indicated by the letters: A – Salantai (Kretinga district), B – Vilnius city, C – Vilkaviškis, D – Kaunas and E – Marcinkonys (Varėna district). Mass spectrum of tentatively identified compound (pentenyl salicilate?): 120 (100), 162 (67), 93 (53), 105 (46), 41 (45), 79 (41), 147 (29), 55 (27), 67 (21), 206 (19), 133 (11), 191 (7).

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LAKIŲJŲ JUNGINIŲ, GAUTŲ IŠ LIETUVOJE AUGANČIOS CIKORIJOS (*CICHORIUM INTYBUS* L.) ANTŽEMINĖS DALIES IR ŠAKNŲ, SUDĖTIS

Santrauka

Išanalizuoti lakieji junginiai cikorijos antžeminės dalies ir šaknų mėginiuose, surinktuose penkiose įvairiose Lietuvos vietovėse 2007 m. Lakioji frakcija gauta panaudojus hidrodistiliaciją Klevendžerio tipo aparatu. Kiekybinė ir kokybinė analizė atlikta dujų chromatografijos / masių spektrometrijos metodu. Vyravo alifatiniai angliavandeniliai ir jų dariniai. Pagrindiniai komponentai tarp visų lakiųjų junginių: oktanas, nonadekanas, pentadekanonas, heksadekanas ir numanomas junginys (pentenilo salicilatas?). Oktano ir numanomo junginio buvo nustatyta kur kas daugiau šaknyse (atitinkamai 34,3–69,8% ir 4,8–22,7%) nei antžeminėje dalyje (atitinkamai 8,0–25,6% ir 0–0,9%). Priešinga priklausomybė nustatyta nonadekanui, jo kiekis didesnis antžeminėje dalyje (5,1–46,9%), nei šaknyse (0,3–3,9%). Terpenoidai sudarė labai mažą dalį, tai galėtų būti paaiškinta fermentų, esančių šaknyse, aktyviu poveikiu terpenoidų sintezei, kuomet terpeniniai angliavandeniliai virsta sudėtingesnės struktūros junginiais (alkoholiais ir laktonais).