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Content and Composition of Essential oils from *Solidago canadensis* L. and *Solidago virgaurea* L. Growing in Estonia

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Abstract

Both invasive Canadian goldenrod (*Solidago canadensis* L.) and Common goldenrod (*S. virgaurea* L., Asteraceae) are recognised in traditional medicine as folk remedies for the treatment of kidney, urinary tract, and liver diseases, among others; however, their pharmaceutical potential remains largely unexplored. The aim of the study was to compare the yield and composition of essential oils (EO) of flowering tops (20 cm long) of *S. canadensis* and *S. virgaurea*. The yield of EOs, hydrodistilled from *S. canadensis* (n=8) and *S. virgaurea* (n=5) herbs using the European Pharmacopoeia method, ranged from 2.7 to 14.9 mL/kg. The average EO yield in both goldenrod species was similar, but the composition differed. 82 constituents were identified and semiquantified by GC-MS in the EOs of both *Solidago* species, eight of which have been found in these species for the first time. α-Pinene, *(Z)*-β-ocimene, D-limonene, and *(E)*-β-ocimene were the principal compounds in *S. canadensis* herb EO; and α-pinene, l-β-pinene, β-myrcene, and humulene in S. *virgaurea* EO. It contained, on average, 39 times more benzyl salicylate than the EO from *S. canadensis*. Also, the amounts of viridiflorol (more in *S. virgaurea*), or L-β-bourbonene and (E)-β-ocimene (more in *S. canadensis*) can be used as a chemical fingerprint of both goldenrod species studied. The qualitative composition of the EO of both goldenrods was very similar, only the content of α-muurolene may be a chemical marker for distinguishing them. The pharmaceutical perspective of *V. canadensis* as an invasive species is not yet sufficiently clear. Chemical composition of different species of goldenrod and their relationship to biological activity, as well as the potential for internal and external use, remains a topic of ongoing interest.

Keywords: Canadian goldenrod; Common goldenrod; essential oil; benzyl salicylate; viridiflorol; α-muurolene

1. Introduction

Goldenrod (*Solidago*) is a plant belonging to the Asteraceae family, with approximately 150 different species, subspecies, and hybrids within this plant family [1]. Common goldenrod (*Solidago virgaurea* L.), Canadian goldenrod (*S. canadensis* L.) and autumn goldenrod (*S. gigantea* Aiton) occur naturally in Estonia [2], but the latter is very rare in local flora.

S. canadensis (Figure 1) is native to North America but is now widely distributed in Europe, being able to adapt to most habitats and surfaces [3]. Canadian goldenrod, which has spread rapidly in Estonia, grows in clumps up to 1.5 m high; the stems of the plant are mostly bare, although they may be slightly hairy at the top. The leaves are needle-like, the inflorescences are arranged in erect

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compound inflorescences up to 1 cm in diameter [3,4]. Originally introduced to Europe in the 1600s as an ornamental plant, it has since become one of the most aggressive invaders across Europe, China, and other regions [5,6]. Its rapid colonization and tendency to form dense, single-species stands pose serious risks to biodiversity by suppressing native flora and disrupting ecosystem processes. The species' expansion is supported by traits such as prolific seed production and allelopathic effects. Compounds released from its roots strongly inhibit the germination and growth of surrounding plants [5,6]. In addition, *S. canadensis* modifies soil properties, leading to nutrient depletion and reduced soil quality [6]. Today, the species has spread worldwide, thriving under diverse soil conditions, though it shows optimal growth in fertile, moist, and heavier soils. Its ease of cultivation ensures a reliable supply of biomass. Despite its invasive nature, the plant also contributes positively to ecosystems by providing abundant nectar for pollinators [6,7]. Beyond ecological roles, *S. canadensis* has economic importance, serving as a source of natural pesticides, dyes, pharmaceuticals, and even biofuels [6,8]. With a long tradition of use in folk medicine, the species warrants further scientific investigation, and its potential applications in modern medicine remain promising.

S. virgaurea (Figure 2) is also widespread in Europe and Asia, North Africa and prefers sunny locations in moderately moist soil [3,9]. The mature plant is 30-70 cm tall and up to 1 m in diameter. The oblong leaves are three-lobed, the inflorescences are yellow, 4-6 mm long and 3-4 mm in diameter, flowering lasts from June to September. The branches of the compound inflorescence are perpendicular to the stem, the stem is short-haired at the top [3,4,9].

A B

Figure 2. *Solidago canadensis* L. – an invasive plant species (photo: A – A.Raal; B - A. Doll).

The European Pharmacopoeia defines goldenrod herb as "Whole or cut, dried, flowering aerial parts of *Solidago gigantea* Aiton or *Solidago canadensis* L., their varieties or hybrids and/or mixtures of these", which must contain not less than 2.5 per cent of flavonoids, expressed as hyperoside (dried drug) [10]. Goldenrod contains flavonoids, which are attributed to antioxidant and anti-inflammatory properties, and the herb has also been studied for antimicrobial activity and hepatoprotective effects [11,12]. In addition to flavonoids, chlorogenic acid, caffeic acid, vanillic acid, and camphor have been identified in goldenrod [8,13,14].

The composition of goldenrod essential oil (EO) is mostly monoterpenoids, sesquiterpenoids, and oxidised compounds. The components of the EO of different *Solidago* species are similar, but differences occur in the quantitative proportions of the substances. Terpenoids are associated with the anti-inflammatory activity and antibacterial effect of goldenrod [15,16]. The use of goldenrod extract in combination with antibiotics for treating cystitis has also been studied [17]. *S. virgaurea* saponins create an unfavourable growth environment for *Candida albicans* fungi, affecting its reproduction and biofilm formation, which allows, for example, the use of mouthwash containing goldenrod extract to prevent oral candidiasis in cases of xerostomia [18]. The foaming properties of saponins may also be one of the reasons for the rapid spread and invasiveness of *S. canadensis*, as they inhibit the spread of molds that damage plants [19]. *S. virgaurea* extracts have been studied and found to have cytotoxic activity of saponins on various tumor cells [20].

In America, goldenrod has historically been used to increase appetite and stimulate gastric secretions [21]. It has also been used to treat colds, reduce cough, and treat inflammatory skin diseases, as well as promote diuresis in cases of cystitis and kidney stones [22,23]. In traditional Chinese medicine, goldenrod is used to relieve cold symptoms, treat malaria, and address conditions such as trauma, cellulitis, and athlete's foot. It is said to have cooling, expectorant, and anti-oedema properties [24–26]. The historical Estonian folk medicine botanical database Herba does not contain the term "kuldvits" ("goldenrod”) or the name form “Solidago” [27]. The reason is likely the recent spread of goldenrod to Estonia, which occurred only in the second half of the 20th century. Consequently, the tradition of using goldenrod in folk medicine has not yet developed in Estonia. Since then, the *S. canadensis* has also started to spread in Estonia as an invasive species. Considering this, it is advisable to investigate the chemical composition of the raw material of these plants that have spread in Estonia, which may subsequently allow the identification of certain regularities in their chemical profile depending on geographical and ecological factors.

The best-known property of goldenrod is its diuretic effect, as well as its use in the prevention of urinary tract infections. Its effect on microbes and biofilm formation has been thoroughly studied and proven. Flavonoids and saponins contained in goldenrod species affect the permeability of cell membranes and thereby change the ion balance [14]. *S. virgaurea* extracts with spasmolytic activity inhibit bladder contractions by affecting muscarinic-type receptors [28]. In addition, general inhibition of smooth muscle contractions has also been described, which could make goldenrod extracts potential candidates for relieving urinary incontinence [29]. The antimicrobial effect of goldenrod extracts and EO has been studied quite thoroughly, finding it to have potential in the treatment and prevention of infections of various origins [30–33].

Considering the utilization of these plants in other sectors of the national economy, it should be noted that goldenrod flowers produce yellow, orange and brown dyes, which have also been used to dye fabrics and yarns made of various materials [34]. Due to the rapid spread of *S. canadensis*, the potential applications of using it for cellulose production and as a biopesticide have been investigated [35,36]. Goldenrod is important as a late summer pollen plant and has high honey productivity. This honey has been attributed to antioxidant, antimicrobial and antifungal effects [37].

The aim of this study was to compare the yield and chemical composition of EOs obtained from *S. canadensis* and *S. virgaurea* herbs growing in Estonia, to identify novel constituents and potential chemical markers for species differentiation, and to provide a basis for further investigations into the relationship between EO composition, biological activity, and ecological adaptation in goldenrod species.

2. Materials and Methods

2.1. Plant Materials

Seven *S. canadensis* samples were collected from Estonia and one from Latvia, as well as five *S. virgaurea* samples from Estonia (Table 1). The plant research material was collected in 2024 during the flowering period (July–September), by cutting off the upper (approximately 20 cm long) flowering tops (n=10) from the plants in dry weather. The drugs were dried in a dark, well-ventilated room at room temperature for 10 days. The dried samples were stored in closed paper bags in a dry environment, avoiding temperature fluctuations and direct light. Before distillation of the EO, woody stem parts were removed from the plant material, and the resulting samples were ground into particles of 1-3 mm. The Estonian plant identifier was used for species identification [38]. The voucher specimen is stored at the Institute of Pharmacy, University of Tartu, Estonia (No Ast/S_cana 1 and Ast/S_virg 1).

Table 1. The growing locations and essential oil yields of *Solidago* species studied.

No	Species	Origin	Yield of essential oil (mL/kg)
1.	*Solidago canadensis*	Maltsa village, Viljandi municipality, Viljandi county	14.7 ±0.5

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2.		Vägeva, Jõgeva municipality, Jõgeva county	14.9 ± 0.5
3.		Ergeme village, Ergeme municipality, Vidzeme region, Läti	2.7 ± 0.1
4.		Luunja alevik, Tartu municipality, Tartu county	2.9 ± 0.1
5.		Pudisoo village, Kuusalu municipality, Harju county	9.6 ± 0,3
6.		Tallinn city	11.5 ±0.4
7.		Kibuna village, Saue municipality, Harju county	4.8 ± 0.2
8.		Tartu city	8.5 ± 0.3
		Average	8.7 ± 0.3
9.	*Solidago virgaurea*	Kuusalu alevik, Kuusalu municipality, Harju county	6.1 ± 0.2
10.		Ivaste village, Kambja municipality, Tartu county	9.5 ± 0.3
11.		Malla village, Viru-Nigula municipality, Lääne-Viru county	9.0 ± 0.3
12.		Tallinn city	8.0 ± 0.3
13.		Kibuna village, Saue municipality, Harju county	11.3 ± 0.4
		Average	8.8 ± 0.3

2.2. Distillation of Essential Oils

The EO was hydrodistilled from the dried flowering tops of both *Solidago* spp. using the method described in the European Pharmacopoeia [10]. The flowering tops of S. *canadensis* and *S. virgaurea* (20 g) with 400 mL of purified water were distilled in a 1000 mL round-bottom flask for 2 hours (3–4 mL/min). Hexane (0.5 mL) was added to a graduated tube to remove the distilled EO.

2.3. Gas Chromatography-Mass Spectrometry

The samples of EO were analysed by gas chromatography with mass detection (GC-MS), using an Agilent 6890/5973 GC-MS system controlled by a mass spectrometry detector (MSD) Chemstation. 1 µL of the sample was injected at an injector temperature of 280°C in split mode (150:1), using helium as the carrier gas, onto an Agilent HP-5MSI column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness). The carrier gas was held at a constant flow rate of 1 mL/min. The oven was held at 50 ^{o}C for 2 min, followed by a ramp of 4 ^{o}C/min to a final temperature of 280 ^{o}C and held at 280 ^{o}C for 5 minutes. The MSD was operated in EI mode at 70 eV. Mass spectra were recorded in the range of 29 – 400 m/z with a delay time of 4 min and a scan speed of 3.8 scans per second. The data were analysed by the deconvolution algorithm of the Agilent Masshunter Software package using different window size factors. Obtained compounds were identified by using NIST23 library with Match Factor ≥ 90 and by retention indexes (relative to n-alkanes C8 – C30) either made available in the literature [39] or obtained by the analysis of the reference compounds. The area percentages of each peak were calculated from the total areas in the chromatograms without using correction factors. The same method has been successfully used in the analyses of EO of several plants [40–42].

3. Results

The EOs yield was 2.7-14.9 mL/kg from *S. canadensis* herb and 4.4-11.3 mL/kg from *S. virgaurea* herb (Table 1). Considering the average contents in both *Solidago* species, the yield is practically the same; however, in the case of *S. canadensis*, a greater variability in the EO content is observed between the minimum and maximum values.

In total, 82 volatile compounds were identified in *S. canadensis* and *S. virgaurea* EOs (Table 2). The sample GC-MS chromatograms are given in Figures 3 and 4.).

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Figure 3. *Solidago virgaurea* L. (Photo: A. Doll).

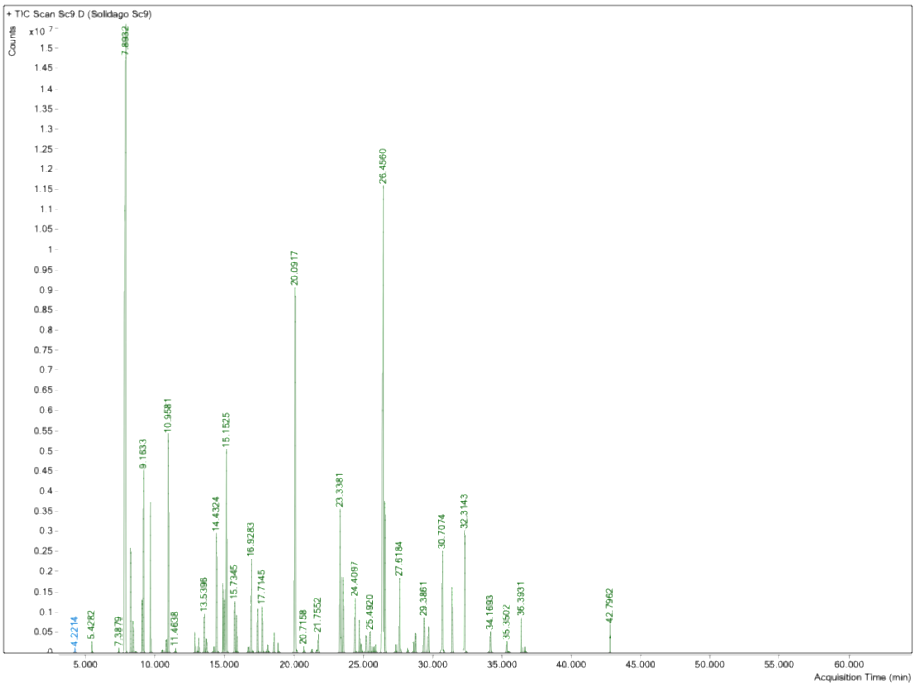

Figure 3. GC-MS chromatogram of essential oil from *Solidago canadensis* herb.

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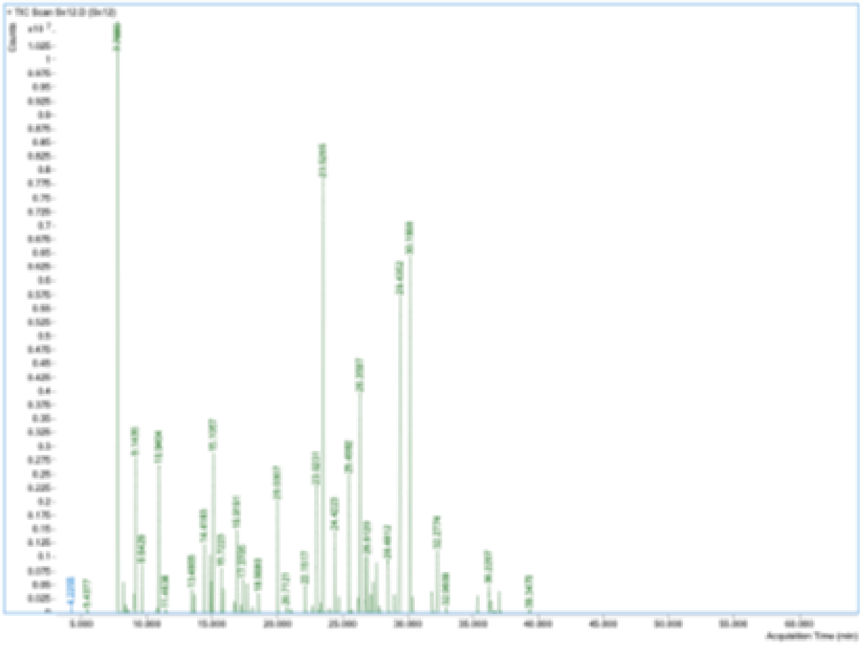

Figure 4. GC-MS chromatogram of essential oil from *Solidago virgaurea* herb.

Table 2. The composition of essential oils from *Solidago canadensis* and *Solidago virgaurea* flowering tops.

No	Compound	Retention index Experimental	Retention index NIST 23	Structure	Content. % *S. canadensis* 1	2	3	4	5	6	7	8	9	*S.virgaurea* 10	11	12	13
1	Hexanal	800	801	$C_6H_{12}O$	0.03	0.01	0.03	0.03	0.03	0.05	0.03	0.09	0.11	0.07	0.10	0.07	0.07
2	α-Pinene	936	937	$C_{10}H_{16}$	25.70	19.42	13.94	22.28	21.48	18.23	24.26	33.35	17.34	31.68	25.41	24.02	19.04
3	L-β-Pinene	976	978	$C_{10}H_{16}$	7.92	4.88	4.10	3.49	6.27	6.81	4.11	7.47	11.68	8.03	7.79	5.29	7.72
4	Bornane	976	980	$C_{10}H_{18}$	0.02	0.01	0.01	0.01	0.03	0.14	0.03	0.01	0.23	0.16	0.16	0.03	0.15
5	Sulcatone	987	986	$C_8H_{14}O$	0.01	0.01	0.29	0.01	0.03	0.02	0.01	0.02	0.04	0.02	0.06	0.04	0.03
6	β-Myrcene	992	991	$C_{10}H_{16}$	2.10	1.14	13.76	0.26	2.44	5.29	9.47	2.38	11.37	8.35	4.85	1.13	8.65
7	α-Phellandrene	992	1005	$C_{10}H_{16}$	2.10	1.14	13.76	9.03	2.44	5.29	9.47	2.38	11.37	0.90	4.85	1.13	8.65
8	p-Cymene	1024	1025	$C_{10}H_{14}$	0.18	0.09	0.09	0.60	0.28	0.73	0.28	1.18	0.46	0.34	0.41	0.23	0.16
9	D-Limonene	1029	1031	$C_{10}H_{16}$	7.03	5.01	5.44	9.83	9.68	4.58	2.38	4.47	2.45	1.72	2.97	2.58	1.10

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10	*(Z)*-β-Ocimene	1038	1038	C10H16	6.64	4.53	5.28	9.03	9.15	4.17	2.31	4.09	3.16	0.19	0.34	2.23	0.13
11	Salicylaldehyde	1042	1047	C7H6O2	0.24	0.16	0.19	0.34	0.35	0.15	0.08	0.15	0.10	0.13	0.28	0.18	0.22
12	*(E)*-β-Ocimene	1048	1049	C10H16	6.64	4.53	5.28	9.03	9.14	4.17	2.31	4.09	0.76	1.06	0.19	0.26	1.18
13	γ-Terpinene	1058	1060	C10H16	0.15	0.08	0.06	0.04	0.00	0.15	0.07	0.02	0.08	0.11	0.10	0.06	0.06
14	Terpinolene	1088	1088	C10H16	0.12	0.06	0.08	0.02	0.04	0.07	0.05	0.03	0.26	0.48	0.08	0.05	0.06
15	Linalool	1100	1099	C10H18O	0.19	0.10	0.24	0.49	0.09	0.17	0.08	0.11	0.54	0.36	0.18	0.40	0.24
16	Nonanal	1104	1104	C9H18O	0.05	0.03	0.04	0.05	0.02	0.07	0.03	0.04	0.27	0.20	0.28	0.26	0.19
17	*(E)*-4.8-Dimethylnona-1.3.7-triene	1117	1116	C11H18	0.15	0.08	0.30	0.02	0.05	0.12	0.14	0.04	0.17	0.16	0.13	0.05	0.06
18	α-Campholenal	1126	1125	C10H16O	0.71	0.39	0.39	2.10	1.14	4.37	1.53	2.29	0.95	0.32	1.89	2.26	1.17
19	*(Z)*-*p*-Mentha-2.8-dien-1-ol	1139	1133	C10H16O	0.04	0.04	0.03	0.16	0.15	0.33	0.13	0.19	0.10	0.05	0.19	0.22	0.14
20	*(E)*-L-Pinocarveol	1139	1139	C10H16O	0.31	0.18	0.10	0.57	0.48	1.18	0.44	0.75	0.39	0.17	0.67	0.87	0.65
21	*(Z)*-L-Verbenol	1141	1141	C10H16O	0.10	0.06	0.07	0.31	0.21	0.79	0.26	0.53	0.18	0.08	0.31	0.36	0.16
22	*(E)*-Verbenol	1146	1144	C10H16O	0.78	0.46	0.53	2.51	1.53	4.86	1.80	3.34	1.23	0.50	1.67	2.43	1.11
23	Pinocarvone	1163	1162	C10H14O	0.38	0.20	0.15	0.56	0.49	1.05	0.47	0.73	0.39	0.17	0.69	0.73	0.48
24	α-Phellandrene-8-ol	1167	1167	C10H16O	0.12	0.07	0.11	0.47	0.31	1.02	0.37	0.94	0.31	0.14	0.51	0.58	0.22
25	Terpinen-4-ol	1177	1177	C10H18O	0.17	0.10	0.06	0.04	0.10	0.13	0.06	0.09	0.07	0.09	0.07	0.08	0.07
26	L-α-Terpineol	1191	1190	C10H18O	0.08	0.05	0.04	0.11	0.05	0.11	0.04	0.06	0.16	0.20	0.09	0.23	0.10
27	(1R)-(-)-Myrtenal	1196	1203	C10H14O	0.89	0.52	0.29	1.49	1.23	2.60	1.04	1.82	0.90	0.41	1.42	1.96	1.39
28	Decanal	1205	1206	C10H20O	0.04	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.13	0.09	0.15	0.08	0.10
29	(1S)-(-)-Verbenone	1209	1204	C10H14O	0.18	0.10	0.12	0.61	0.43	0.90	0.56	0.85	0.33	0.08	0.46	0.57	0.21

30	*(E)*-Carveol	1219	1217	C10H16O	0.35	0.18	0.10	0.86	0.77	1.15	0.35	0.63	0.23	0.09	0.33	0.59	0.20
31	*(Z)*-Carveol	1231	1229	C10H16O	0.06	0.03	0.01	0.14	0.13	0.08	0.03	0.06	0.01	0.00	0.03	0.06	0.01
32	L-Carvone	1244	1245	C10H14O	0.64	0.35	0.11	1.24	1.18	0.61	0.24	0.50	0.09	0.04	0.20	0.52	0.11
33	Geraniol	1255	1255	C10H18O	0.06	0.03	0.04	0.15	0.03	0.06	0.03	0.02	0.29	0.71	0.15	0.17	0.10
34	*(E.E)*-2.4-Decadienal	1316	1317	C10H16O	1.08	0.72	0.05	0.10	0.05	0.11	0.06	0.09	0.27	0.16	0.19	0.18	0.21
35	δ-Elemene	1339	1338	C15H24	0.15	0.06	0.16	0.35	0.25	0.54	0.58	0.11	0.10	0.21	0.21	0.05	0.04
36	α-Cubebene	1351	1351	C15H24	0.04	0.02	0.01	0.01	0.09	0.03	0.04	0.02	0.00	0.35	0.10	0.55	0.29
37	Copaene	1378	1376	C15H24	0.25	0.41	0.21	0.06	0.21	2.08	0.35	0.14	0.08	1.15	0.60	2.44	1.47
38	Geranyl acetate	1385	1382	C12H20O2	0.19	0.12	0.22	0.02	0.08	0.18	0.13	0.06	0.17	0.73	0.09	0.15	0.09
39	L-β-Bourbonene	1387	1384	C15H24	1.28	0.67	2.20	0.25	0.71	4.46	1.18	1.22	0.22	0.14	0.17	0.20	0.15
40	Bicyclosesquiphellandrene	1393	1489	C15H24	1.50	3.28	1.09	0.40	0.43	0.35	0.69	0.43	0.17	6.69	3.31	2.45	2.00
41	β-Elemene	1394	1398	C15H24	2.03	6.96	5.75	1.09	3.90	0.87	6.03	1.14	0.51	0.54	0.42	17.15	11.55
42	Dodecanal	1409	1409	C12H24O	0.12	0.16	0.16	0.01	0.01	0.01	0.15	0.00	0.04	0.05	0.05	0.04	0.07
43	Caryophyllene	1423	1419	C15H24	1.74	1.00	0.93	0.30	0.53	0.35	1.16	0.26	1.79	2.28	1.64	0.77	0.90
44	β-Copaene	1432	1432	C15H24	1.80	0.63	0.94	0.32	0.38	1.21	1.30	0.32	0.42	0.51	0.50	0.52	0.45
45	γ-Elemene	1436	1434	C15H24	0.16	0.09	0.15	0.24	0.16	0.15	1.39	0.09	0.57	0.72	0.07	0.06	0.15
46	*(E)*-α-Bergamotene	1438	1435	C15H24	1.64	0.94	1.41	0.08	1.42	0.07	1.28	0.16	0.09	0.07	0.09	0.04	0.04
47	Germacrene D	1446	1448	C15H24	0.26	0.10	0.20	0.10	0.07	0.39	0.25	0.07	0.11	0.09	0.13	0.03	0.03
48	Humulene	1461	1454	C15H24	6.29	3.87	7.59	0.80	0.88	0.54	2.05	0.78	9.57	9.64	1.34	4.91	6.09
49	*(E)*-β-Farnesene	1460	1457	C15H24	0.21	0.10	0.24	0.92	0.04	1.56	0.36	0.09	1.50	1.10	1.93	0.70	0.93
50	β-Selinene	1488	1486	C15H24	3.89	9.52	5.70	6.65	6.29	1.28	9.65	0.52	9.67	6.17	7.18	0.06	2.48

51	a-Muurolene	1499	1502	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.68	0.31	1.15	0.09
52	Bicylogermacrene	1500	1496	$C_{15}H_{24}$	0.46	0.49	0.29	0.04	0.09	0.83	1.41	0.09	0.06	1.12	0.16	0.55	0.38
53	α-Farnesene	1510	1508	$C_{15}H_{24}$	0.52	0.81	0.50	0.15	0.25	0.82	0.29	0.07	0.55	0.62	0.66	0.15	0.20
54	Cubenene	1535	1532	$C_{15}H_{24}$	0.06	0.03	0.02	0.01	0.01	0.03	0.03	0.03	0.02	0.13	0.04	0.14	0.07
55	α-Calacorene	1546	1542	$C_{15}H_{20}$	0.08	0.04	0.02	0.14	0.04	0.18	0.09	0.18	0.04	0.02	0.06	0.11	0.05
56	Elemol	1552	1549	$C_{15}H_{26}O$	0.03	0.02	0.13	0.05	0.01	0.03	0.07	0.01	0.02	0.01	0.02	0.02	0.13
57	Hedycaryol	1556	1553	$C_{15}H_{26}O$	0.03	0.10	0.13	0.05	0.02	0.28	0.08	0.04	0.02	0.10	0.25	0.04	0.15
58	E-Nerolidol	1567	1564	$C_{15}H_{26}O$	0.27	0.16	0.42	0.28	0.18	0.28	0.13	0.18	0.11	0.18	0.25	0.14	0.10
59	4.8-Epoxyazulene	1570	1573	$C_{15}H_{24}O$	0.28	0.16	0.06	0.81	0.14	0.30	0.33	0.68	0.06	0.03	0.05	0.11	0.10
60	Palustrol	1570	1568	$C_{15}H_{26}O$	0.14	0.07	0.03	0.39	0.07	0.15	0.17	0.52	0.03	0.02	0.02	0.08	0.03
61	(Z)-3-Hexenyl benzoate	1575	1570	$C_{13}H_{16}O_2$	0.04	0.03	0.01	0.23	0.03	0.50	0.04	0.29	0.85	0.99	1.93	0.72	1.50
62	Spathulenol	1583	1576	$C_{15}H_{24}O$	0.21	0.12	0.05	0.04	0.13	0.03	0.85	0.44	0.04	0.61	0.43	0.16	0.84
63	Viridiflorol	1589	1591	$C_{15}H_{26}O$	0.20	0.28	0.10	0.02	0.21	0.08	0.04	0.24	0.63	0.56	1.30	3.57	2.40
64	Mintketone	1598	1595	$C_{15}H_{24}O$	0.48	0.28	0.22	0.52	0.19	1.00	0.55	1.39	0.28	0.15	0.27	0.61	0.46
65	Humulene epoxide I	1614	1604	$C_{15}H_{24}O$	0.26	0.14	0.17	0.05	0.07	0.12	0.13	0.08	0.10	0.10	0.30	0.35	0.16
66	Junenol	1623	1620	$C_{15}H_{26}O$	0.14	0.09	0.04	0.08	0.03	0.10	0.10	0.05	0.07	0.06	0.04	4.58	2.64
67	Benzophenone	1632	1635	$C_{13}H_{10}O$	0.03	0.02	0.01	0.80	0.03	0.57	0.18	0.50	0.14	0.04	0.18	0.14	0.06
68	Isospathulenol	1632	1638	$C_{15}H_{24}O$	0.08	0.05	0.05	1.88	0.08	1.39	0.43	1.14	0.25	0.29	0.44	0.49	0.18
69	τ-Muurolol	1644	1642	$C_{15}H_{26}O$	0.38	0.23	0.09	0.04	0.03	0.10	0.14	0.03	0.15	0.35	0.16	0.23	0.17
70	α-Cadinol	1658	1653	$C_{15}H_{26}O$	0.71	0.38	0.16	0.11	0.20	0.35	0.20	0.25	0.26	0.24	0.19	0.36	0.27

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71	*(Z)*-3-Hexenyl salicylate	1671	1669	$C_{13}H_{16}O_3$	0.04	0.01	0.04	0.02	0.02	0.02	0.01	0.03	0.10	0.09	0.23	0.07	0.08
72	Bulnesol	1670	1667	$C_{15}H_{26}O$	0.07	0.06	0.25	0.01	0.03	0.07	0.02	0.03	0.03	0.01	0.03	0.12	0.08
73	5-Cyclodecen-1-ol	1690	1690	$C_{15}H_{24}O$	0.59	0.35	0.32	0.54	0.17	1.49	0.78	1.99	0.35	0.17	0.41	0.67	0.40
74	1-Pentadecanal	1715	1715	$C_{15}H_{30}O$	0.01	0.00	0.01	0.02	0.00	0.01	0.01	0.01	0.04	0.07	0.13	0.06	0.06
75	β-Nootkatol	1721	1714	$C_{15}H_{24}O$	0.16	0.09	0.04	0.05	0.11	0.08	0.08	0.07	0.01	0.04	0.01	0.02	0.01
76	Benzoic acid	1767	1763	$C_{14}H_{12}O_2$	0.07	0.02	0.03	0.13	0.19	0.35	0.14	3.06	0.31	0.16	0.98	0.16	0.48
77	14-Hydroxy-δ-cadinene	1805	1803	$C_{15}H_{24}O$	0.16	0.09	0.06	0.12	0.11	0.21	0.13	0.11	0.09	0.10	0.11	0.29	0.26
78	Neophytadiene	1840	1837	$C_{20}H_{38}$	0.06	0.03	0.09	0.03	0.10	0.46	0.18	0.10	0.11	0.14	0.15	0.27	0.34
79	Hexahydrofarnesyl acetone	1846	1844	$C_{18}H_{36}O$	0.09	0.05	0.11	0.34	0.06	0.62	0.12	0.17	0.24	0.19	0.10	0.19	0.21
80	β-Phenylethyl benzoate	1857	1856	$C_{15}H_{14}O_2$	0.07	0.04	0.05	0.01	0.04	0.43	0.03	0.06	0.29	0.89	0.82	0.11	0.70
81	Benzyl salicylate	1873	1871	$C_{14}H_{12}O_3$	0.24	0.14	0.09	0.04	0.03	0.03	0.03	0.06	1.43	2.09	11.99	0.09	0.08
82	Phytol	2107	2114	$C_{20}H_{40}O$	0.22	0.12	0.16	0.06	0.10	0.72	0.10	0.08	0.02	0.08	0.03	0.03	0.11

Note: nd - not detected

4. Discussion

Among the 82 volatile compounds identified in the EOs of *S. canadensis* and *S. virgaurea* (Table 2), the predominant constituent was α-pinene. The highest content of α-pinene was found in *S. canadensis* EO samples collected in Estonia (average 22.33%). This compound has also been the main component in *S. canadensis* EO growing in Ukraine, where we have found seven pinene-rich chemotypes [43]. Other main components found in *Solidago* species growing in Estonia include D-limonene (average 6.05%), α-pellandrene (5.70%), *(E)*-β-ocimene (5.65%), *(Z)*-β-ocimene (5.65%), L-β-pinene (5.63%) and β-selinene (5.44%). *S. virgaurea* EO also contained the highest amount of α-pinene (average 23.50%), as well as L-β-pinene (8.10%), β-mycrene (6.87%), humulene (6.31%), β-elemene (6.03%), α-phellandrene (5.38%), and β-selinene (5.11%).

Differences in the composition of *S. canadensis* and *S. virgaurea* EOs are indicated by the average concentrations of some substances, the difference of which is more than twofold (Table 3). The EOs of *S. canadensis* contained, on average, nearly 9 times more L-β-bourbonene and about 8 times more (E)-β-ocimene than *S. virgaurea*. In contrast, the EOs studied from *S. virgaurea* contained as much as 39 times more benzyl salicylate and about 11 times more viridiflorol than those from *S. canadensis*. The higher concentration of benzyl salicylate in the EOs of *S. virgaurea* is also found by other researchers [32,44]. It is likely that the content of benzyl salicylate could be used as a chemical fingerprint of the two species, based on, among other things, the content of the other substances just mentioned.

The qualitative composition of the EOs from the two goldenrods studied is nearly identical. The only difference was that we were able to detect a relatively low content of α-muurolene (0.09-1.15%) in the EO of *S. virgaurea*. However, in addition to the *S. canadensis* samples, we did not find α-muurolene in any of the *S. virgaurea* samples. Therefore, the content of α-muurolene remains a somewhat vague chemical marker for distinguishing the two goldenrod species (Table 2).

Table 3. The quantitative variability in the composition of the EO of two *Solidago* species.

Compound	Average content, %		Ratio of averages
	S. canadensis	***S. virgaurea***	
D-Limonene	6.05	2.17	2.8
(Z)-β-Ocimene	5.65	1.21	4.7
(E)-β-Ocimene	5.65	0.69	8.2
L-α-Terpineole	0.07	0.16	2.3
Decanal	0.02	0.11	5.5
L-Carvone	0.61	0.19	3.2
Geraniol	0.05	0.29	5.8
Cubebene	0.03	0.08	2.7
L-β-Bourbonene	1.50	0.17	8.8
4.8-Epoxyazulene	0.34	0.07	4.9
(Z)-3-Hexenyle benzoate	0.15	1.20	8
Viridiflorol	0.15	1.69	11.3
(Z)-3-Hexanyl salicylate	0.02	0.11	5.5
1-Pentadecanal	0.01	0.07	7
β-Nootkatol	0.09	0.02	4,5
Benzyl salicylate	0.08	3.14	39.3

Comparison of EOs of two *Solidago* species has also been described in other similar studies [16,39,45,46]. We have determined, for the first time in *Solidago* species, the content of *(Z)*- and *(E)*-β-ocimene, l-β-bourbonene, *(Z)*-3-hexenylbenzoate, *(Z)*-3-hexenylsalicylate, 1-pentadecanal, β-nootcatol, and benzyl salicylate.

The determination of the difference in the content of many minor components (<0.1%) of EO is of no practical medical or pharmaceutical importance. However, these differences are important in a biological context, for example, in the aroma profile of the plant EO. In addition, some compounds act as repellents and participate in the plant's defense mechanisms. It is precisely these minor differences that allow us to distinguish between plant species. This is particularly valuable in distinguishing between the species *S. canadensis* and *S. virgaurea*, where confusion often arises.

S. canadensis EO contains higher amounts of D-limonene and *(Z)*- and *(E)*-β-ocimene, which may be one of the reasons for the rapid spread and invasiveness of Canadian goldenrod, inhibiting the growth of other species, but also repelling some protozoa and insects [6,47,48]. *S. virgaurea*, at the same time, contains high concentrations of benzyl salicylate, which has insecticidal activity against mosquitoes and other insects [49,50].

Viridiflorol is one of the substances whose content in *S. virgaurea* EO samples was particularly high compared to *S. canadensis*. Viridiflorol has been demonstrated in studies to possess strong anti-inflammatory activity, as well as antioxidant activity and an inhibitory effect on the development of mycobacteria [51]. *S. virgaurea* also contained more *(Z)*-3-hexenyl benzoate and salicylate than *S. canadensis*, which could affect the plant's odor and are used as a fragrance [52].

The high concentration of α-pinene supports the biological activity of *S. canadensis* drugs against various bacteria and fungi, since compared to β-pinene, which is also used in the composition of EO, it has much greater activity against *C. albicans*, *C. neoformans* and MRSA [53].

Both isomers of β-ocimene are attributed to importance in the biological processes and defence mechanisms of the plant itself [54]. This monoterpenoid is also found, for example, in honeybees, where *(E)*-β-ocimene helps to spread information between insects within the colony [55]. In pharmaceuticals, β-ocimene is of interest as a potential leishmaniasis drug, inhibiting *L. amazonesis* at different stages of development: directly by changing the membrane permeability and indirectly by activating the human immune system [56].

The β-selinene in goldenrod has been most studied as a source of its oxidation products, which confer high resistance to fungi in plants containing them. Selenene derivatives are effective against the varroa mite, which infects honeybees [57,58].

D-limonene is the active form of limonene, which has found use as a flavouring agent, as well as a food supplement. Several in vitro and in vivo studies demonstrate the activity of D-limonene as an antioxidant, anti-inflammatory agent, and mediator of the immune response [59–61]. On the other hand, contact dermatitis due to the oxidised form of D-limonene has been observed and studied, especially in patients who are constantly exposed to perfumed cleaning products [62,63].

5. Conclusions

The yield and chemical composition of EOs obtained from *S. canadensis* and *S. virgaurea* herbs growing in Estonia has been studied. The yield of EOs from *S. canadensis* and *S. virgaurea* herb was equivalent, but the composition of EOs was different. 82 constituents were identified in the EOs of both *Solidago* species, eight of which have been found in these species for the first time. More than half of the EO components are monoterpenoid hydrocarbons. The main components of *S. canadensis* EO are α-pinene, *(Z)*-β-ocimene, D-limonene, *(E)*-β-ocimene and β-selinene, while *S. virgaurea* contains α-pinene, l-β-pinene, β-myrcene, humulene and β-elemene as principal compounds. The benzyl salicylate content in particular can be used as a chemical fingerprint to distinguish between *S. canadensis* and *S. virgaurea*, taking into account also the significant differences in viridiflorol, L-β-bourbonene, and (E)-β-ocimene content in the EOs of these two plant species. The quantitative composition of the EOs of both goldenrods is very similar, and the content of α-muurolene seems to be a chemical marker for distinguishing them. In the future, the research could be expanded by including other species of goldenrod and analysing the relationship between composition and mechanisms of biological activity and ecological adaptation. The pharmaceutical perspective of *V. canadensis* as an invasive species, and thus the valorization of its natural resource, is not yet clear.

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