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ORIGINAL PAPER

Evaluation of two invasive plant invaders in Europe (*Solidago canadensis* and *Solidago gigantea*) as possible sources of botanical insecticides

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Abstract

Solidago gigantea and *Solidago canadensis* (Asteraceae) are two invasive weeds native to North America and introduced in Europe and Asia, where they are spreading quickly threatening the stability of local secondary ecosystems. These two plant invaders may represent an ideal bioresource to be exploited for production of green pesticides. Therefore, herein we evaluated the efficacy of the essential oils (EOs) obtained from their different parts, i.e. leaves, inflorescences and roots, against *Culex quinquefasciatus*, *Spodoptera littoralis* and *Musca domestica*. The essential oil composition was investigated by gas chromatographic–mass spectrometry (GC–MS) analysis. *S. canadensis* leaf EO was the most toxic to *C. quinquefasciatus*, with a LC_{50} of 89.3 µl L^{-1}. The two most effective oils against *M. domestica* adults were *S. canadensis* leaf and flower EOs, with LD_{50} values of 206.9 and 207.1 µg $adult^{-1}$, respectively. Three EOs highly toxic to *S. littoralis* were also identified, namely *S. gigantea* leaf EO, *S. canadensis* leaf EO and *S. gigantea* flower EO, with LD_{50} values of 84.5, 98.9 and 107.4 µg $larva^{-1}$, respectively. Since the *S. canadensis* leaf EO was the only green product effective against all the tested insect pests, we selected it for non-target toxicity assays on *Eisenia fetida* earthworms, along with the leaf EO from *S. gigantea*. Both the *S. canadensis* and *S. gigantea* leaf EOs did not led to mortality of *E. fetida* adult earthworms, at variance with the positive control α-cypermethrin, allowing us to propose them for pest control purposes in IPM and organic farming.

Keywords Essential oil · *Culex quinquefasciatus* · Insect pest · Mosquito vector control · *Musca domestica* · *Spodoptera littoralis*

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Key message

- *Solidago* invasive species may represent an ideal green resource to be exploited for production of green pesticides
- *Solidago gigantea* and *S. canadensis* essential oils from various plant parts were tested on three insect pests
- *Solidago canadensis* leaf oil was the most toxic to *Culex quinquefasciatus* and *Musca domestica*
- *Solidago gigantea* leaf oil was the most toxic to *Spodoptera littoralis* larvae
- *Solidago* essential oils were not toxic to non-target earthworms, *Eisenia fetida*

Introduction

The eco-friendly management of insect pests is a timely challenge nowadays (Isman 2006; Desneux et al. 2007; Benelli 2015, 2018a, b; Athanassiou et al. 2018). In this framework, essential oils extracted from plants may represent a promising reservoir of effective products for pesticide development (Pavela 2016; Stevenson et al. 2017; Benelli and Pavela 2018a, b; Pavela et al. 2018), due to a wide number of favourable characteristics that are compatible with Integrated Pest Management (IPM) criteria, including multiple mechanisms of action and low toxicity to vertebrates (Isman 2000, 2015; Pavela and Benelli 2016a, b).

Solidago canadensis L. (Canada goldenrod) and *Solidago gigantea* Aiton (giant goldenrod) are rhizomatous, long-lived, perennial herbs native to North America. When introduced to Europe and Asia, they became invasive and, by their increased dominance, threatened the stability of local secondary ecosystems (Ledger et al. 2015; Pal et al. 2015). *Solidago canadensis* and *S. gigantea* are generally described as having a broad tolerance with respect to soil moisture, light, nutrient contents, temperature or pH range, although they prefer ruderal habitats, where they are dominant (Werner et al. 1980; Weber and Jakobs 2005). However, their ecological needs overlap and regularly coexist both in their native and in the introduced range: *S. canadensis* prefers loose and drier soils than *S. gigantea*; hence, *S. canadensis* occurs near to urban areas, roadsides and railways more often and *S. gigantea* occurs mainly on riverside and embankments (Botta-Dukát and Dancza 2004).

Solidago species (both the two-aforementioned species and *S. virgaurea* L., which is native to Europe) are well known for their medicinal use in Europe: they are ingredients of the so-called *Herba Solidaginis* included in the ESCOP publication (Kalemba and Thiem 2004). This preparation is used to treat disorders of urinary tract, prostate and kidney. Regarding the secondary metabolites, several groups are reported in the two species, mainly flavonoids, phenolic acids, diterpenes, saponosides, and essential oils (Apáti et al. 2003; Kołodziej et al. 2011; Kraujalienė et al. 2017; Zihare and Blumberga 2017). These compounds have been shown to exert anti-inflammatory, antimicrobial, antioxidant, antispasmodic and diuretic properties (Liu et al. 2016).

Although these species are close relatives, they have distinct chemical profiles suggesting a possible influence of the geographic origin, genetics (e.g. polyploidy level) and plant part investigated (Radusiene et al. 2018; Kalemba and Thiem 2004; Gruľová et al. 2016; Shelepova et al. 2018; Kalemba et al. 2001; Hull-Sanders et al. 2009a, b).

Solidago gigantea and *S. canadensis* are consumed by many specialist herbivores in their native range (Pilson and Rausher 1995; Carson and Root 2000; Meyer et al. 2005). On the other hand, in their introduced ranges there are only few generalist insects consuming them (Botta-Dukát and Dancza 2004; Jakobs et al. 2004), suggesting that there are no specialist herbivores in the place of introduction. However, Hull-Sanders et al. (2009a) reported lower foliar concentrations of monoterpenes and diterpenes in the introduced *S. gigantea* populations than in the native ones. The same authors found a higher growth rate of a generalist herbivore, *Spodoptera exigua* (Hübner), fed on introduced plants than on native ones, while the specialist *Trirhabda virgata* LeConte was not influenced (Hull-Sanders et al. (2009b). In contrast, in a common garden experiment, Nagy et al. (2017) found a higher insect resistance of *S. gigantea* populations introduced in Europe compared with native ones. This might support the potential of introduced *Solidago* populations under natural conditions as a source of insecticidal compounds.

Since *S. gigantea* and *S. canadensis* may represent an ideal bioresource to be exploited for production of highly-valued products, in the present work we evaluated the insecticidal efficacy of the EOs obtained from their different parts (i.e. leaves, inflorescences and roots), whose compositions were analysed by gas chromatography–mass spectrometry (GC–MS). For the purpose, we assayed them on larvae of the filariasis and Zika virus vector *Culex quinquefasciatus* Say (Benelli and Romano 2017) and the tobacco cutworm *Spodoptera littoralis* (Boisduval), as well as against adults of the housefly, *Musca domestica* L. The most effective essential oils were tested to evaluate potential non-target effects on adult earthworms, *Eisenia fetida* (Savigny). The insecticidal effects of *Solidago* EOs from different plant parts of the two studied species were compared, linking their bioactivity against insects to the chemical profiles obtained.

Materials and methods

Plant material and sample preparation

The sample collection was performed in the flowering phenophase of *S. canadensis* and *S. gigantea*, during a three-week period in August 2017 (Fig. 1). Weather conditions were sunny and slightly windy, and there was no rainfall for 48 h before each sampling day. Sample collection took place in the introduced range of both species, i.e. a semi-humid meadow close to an agricultural field and a canal in Szentlőrinc, Hungary (46°02′47.3″N; 17°58′37.4″E; elevation: 114.5 m above sea level). The selection of goldenrod populations was based on the high dominance of both species (alone or together at least 70% vegetation cover), open, unshaded vegetation and the co-occurrence of the investigated species to exclude the effect of different environmental

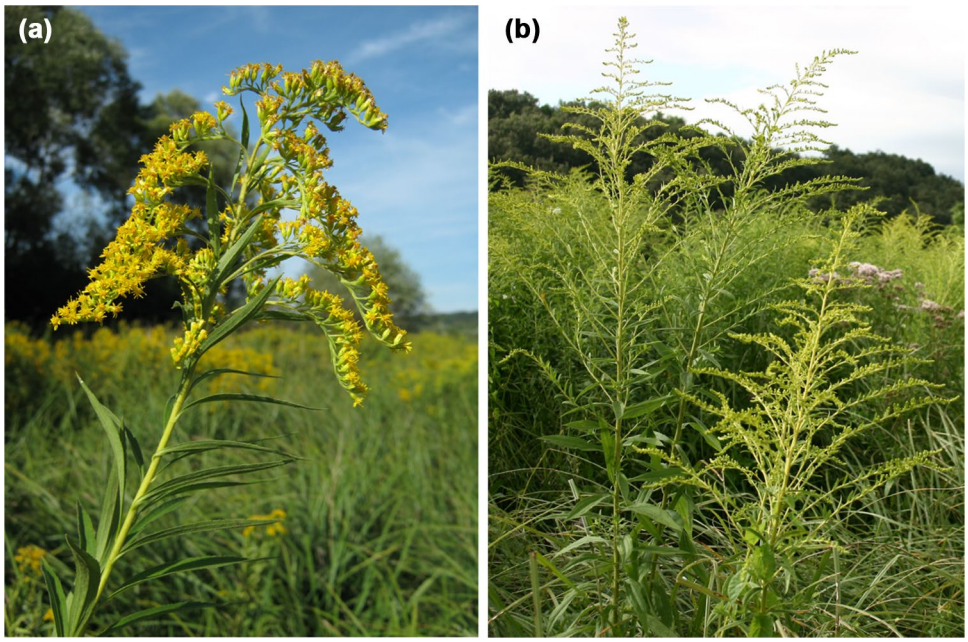

Fig. 1 *Solidago gigantea* (**a**) and *S. canadensis* (**b**) in the collection site (Szentlőrinc, Hungary)

conditions on the overall chemical composition. An area of 400 × 500 m was sampled randomly throughout its entire range. For the analyses, young and intact (without any injury or infection) materials were collected from around 50–100 individuals of both species, which were located at least 5 m apart from another, to reduce the risk of resampling the same clone. Individuals were removed, using a hand shovel; rhizomes, leaves and inflorescences were separated immediately with secateurs and placed separately into plastic bags. Collection continued until 2 kg fresh mass was reached from all organs except for roots of *S. canadensis* (1 kg). After collections, samples were air-dried separately, at 24–28 °C in a storage room, without direct light, for 1 month. The herbarium specimens of the two species were deposited in the Herbarium of the University of Pécs, Hungary, under the codes JPU 82/3630 (*S. gigantea*) and JPU 82/3631 (*S. canadensis*).

Chemicals

Analytical standards of some essential oil constituents (Table 1) were purchased from Sigma-Aldrich (Milan, Italy) and used for GC–MS peak assignment. Viridiflorol was kindly furnished by Michael Russell, Department of Primary Industries, Industry and Investment NSW, Wollongbar, NSW, Australia. A mix of *n*-alkanes, ranging from octane (C_8) to triacontane (C_{30}), was obtained from Supelco (Bellefonte, CA, USA) and injected using the analytical conditions reported below to determine the temperature-programmed retention index (RI) according to the following formula:

$$RI_x = 100_n + 100(t_x - t_n)/(t_{n+1} - t_n),$$

where n is the number of carbon atoms of the alkane eluting before the compound x, t_n and $t_n + 1$ are retention times of the reference alkanes eluting before and after compound x and tx is the retention time of the compound × (Van den Dool and Kratz 1963). All compounds were of analytical standard grade. Analytical grade *n*-hexane solvent was bought from Carlo Erba (Milan, Italy) and distilled by a Vigreux column before use.

Isolation of *Solidago* essential oils

Different amounts of dry plant organs of *S. gigantea* and *S. canadensis*, namely roots (700 and 625 g, respectively), leaves (650 and 500 g, respectively) and inflorescences (200 and 300 g, respectively), were reduced into small pieces and inserted in 10-L flasks filled with 5–6 L of deionized water, then subjected to hydrodistillation using a Clevenger-type apparatus for 4 h. The EOs were decanted, separated from water and dehydrated using anhydrous Na_2SO_4. They were stored in amber vials capped with PTFE-faced silicon septa at 4 °C until analysed. The yield was calculated as g of EO/100 g of dry matter.

GC–MS analysis

Chemical analysis of the EOs from various plant parts of the two *Solidago* species was performed by using an Agilent 6890 D gas chromatograph coupled to a single-quadrupole 5973-N mass spectrometer. Separation was achieved on a HP-5 MS (5% phenylmethylpolysiloxane, 30 m, 0.25 mm i.d., 0.1 µm film thickness; J&W Scientific, Folsom) capillary column. The temperature programme used was as

Table 1 Chemical composition of the essential oils obtained from leaves, inflorescences and roots of *Solidago gigantea* and *Solidago canadensis*

No	Component[a]	RI exp.[b]	RI Lit.[c]		*Solidago gigantea* (%)[d]			*Solidago canadensis* (%)[d]			ID[e]
			ADAMS	NIST 17	Leaves	Flowers	Roots	Leaves	Flowers	Roots	
1	1-Octene,7-methyl	847		847			0.9 ± 0.2			0.2 ± 0.0	b,c
2	2,6-Dimethyl-1,3,6-heptatriene	861		858			0.6 ± 0.1			3.0 ± 0.6	b,c
3	1-Nonene	888		889	0.1 ± 0.0	0.1 ± 0.0	13.1 ± 2.5			1.6 ± 0.3	b,c
4	Tricyclene	916	921	921					0.1 ± 0.0		b,c
5	α-Thujene	921	924	922		0.1 ± 0.0		tr[f]	tr	tr	b,c
6	α-Pinene	926	932	925	1.5 ± 0.3	8.1 ± 1.5	0.2 ± 0.0	4.6 ± 0.9	29.5 ± 4.5	2.9 ± 0.6	a,b,c
7	Camphene	939	946	940	0.5 ± 0.1	0.7 ± 0.2		1.0 ± 0.2	1.9 ± 0.5	0.2 ± 0.0	a,b,c
8	Thuja-2,4(10)-diene	945	953	945	tr	0.2 ± 0.0		0.1 ± 0.0	1.4 ± 0.4		b,c
9	Sabinene	967	969	968	tr	0.4 ± 0.1	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	1.0 ± 0.2	a,b,c
10	β-Pinene	968	974	968	0.4 ± 0.1	1.3 ± 0.3	4.6 ± 0.9	1.2 ± 0.3	2.4 ± 0.5	31.3 ± 4.0	a,b,c
11	1-Octen-3-ol	977	974	978			tr				a,b,c
12	2-Pentyl-furan	987	984	990			0.1 ± 0.0	tr	0.1 ± 0.0		b,c
13	Myrcene	989	988	988	0.3 ± 0.0	0.6 ± 0.2	2.1 ± 0.4	tr		1.5 ± 0.3	a,b,c
14	α-Phellandrene	1003	1002	1003	0.1 ± 0.0	0.2 ± 0.0	0.4 ± 0.1	tr		1.8 ± 0.4	a,b,c
15	*p*-Methyl-anisole	1009	1015	1009			0.1 ± 0.0			tr	b,c
16	α-Terpinene	1014	1014	1014		0.1 ± 0.0	tr		tr	0.1 ± 0.0	b,c
17	*p*-Cymene	1022	1020	1020	0.4 ± 0.1	3.5 ± 0.7	2.5 ± 0.5	0.2 ± 0.0	1.5 ± 0.3	2.3 ± 0.4	a,b,c
18	Limonene	1025	1024	1025	0.2 ± 0.0	0.6 ± 0.2	3.1 ± 0.6	1.0 ± 0.2	5.1 ± 1.1	32.7 ± 5.0	a,b,c
19	1,8-Cineole	1027	1026	1027			0.3 ± 0.1			0.6 ± 0.2	a,b,c
20	2-Ethyl-hexanol	1030		1031			0.1 ± 0.0			tr	b,c
21	Benzene acetaldehyde	1043	1036	1042	tr						a,b,c
22	(*E*)-β-ocimene	1047	1044	1047					tr		a,b,c
23	γ-Terpinene	1055	1054	1055		0.1 ± 0.0	tr		0.1 ± 0.0	0.1 ± 0.0	a,b,c
24	1-Nonen-3-ol	1080		1081			0.7 ± 0.2				b,c
25	Terpinolene	1085	1086	1085		tr	tr		tr	0.1 ± 0.0	a,b,c
26	*p*-Cymenene	1087	1089	1089	tr	0.1 ± 0.0		tr	0.2 ± 0.0	tr	b,c
27	3-Nonanone	1087		1089			0.6 ± 0.1			tr	b,c
28	1-Undecene	1091		1093			0.6 ± 0.1				b,c
29	3-Nonanol	1098		1099			0.2 ± 0.0				b,c
30	Linalool	1101	1095	1100	tr	0.1 ± 0.0			0.1 ± 0.0		a,b,c
31	*endo*-Fenchol	1109	1114	1110						0.1 ± 0.0	b,c
32	*trans-p*-Mentha-2,8-dien-1-ol	1118	1119	1117					0.1 ± 0.0		b,c
33	α-Campholenal	1123	1122	1123	0.1 ± 0.0	0.6 ± 0.2		0.3 ± 0.0	1.5 ± 0.3	tr	b,c
34	*trans*-Pinocarveol	1133	1135	1133	0.1 ± 0.0	0.7 ± 0.2	tr	0.4 ± 0.1	2.1 ± 0.4	0.2 ± 0.0	a,b,c
35	*cis*-Verbenol	1138	1137	1139	tr	0.5 ± 0.1		0.2 ± 0.0	1.1 ± 0.3		b,c
36	*trans*-Verbenol	1141	1140	1142	0.2 ± 0.0	1.7 ± 0.4		1.4 ± 0.3	3.9 ± 0.8		b,c

Table 1 (continued)

No	Component[a]	RI exp.[b]	RI Lit.[c]		*Solidago gigantea* (%)[d]			*Solidago canadensis* (%)[d]			ID[e]
			ADAMS	NIST 17	Leaves	Flowers	Roots	Leaves	Flowers	Roots	
37	Isoborneol	1151	1155	1151						tr	a,b,c
38	*trans*-Pinocamphone	1155	1158	1156		0.1 ± 0.0			0.1 ± 0.0		b,c
39	Pinocarvone	1157	1160	1164	tr	0.3 ± 0.0	tr	0.2 ± 0.0	0.8 ± 0.2	0.3 ± 0.1	b,c
40	Borneol	1160	1165	1160	0.4 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	a,b,c
41	*p*-Mentha-1,5-dien-8-ol	1164	1166	1165	0.1 ± 0.0	0.5 ± 0.1		0.2 ± 0.0	3.8 ± 0.7		b,c
42	(2*E*)-Nonenol	1170	1163	1171			0.2 ± 0.0				b,c
43	Terpinen-4-ol	1173	1174	1174	tr	0.3 ± 0.0	0.1 ± 0.0		0.2 ± 0.0	0.2 ± 0.0	a,b,c
44	*n*-Nonanol	1174	1165	1174			0.1 ± 0.0				b,c
45	*p*-Cymen-8-ol	1184	1179	1184	tr	0.1 ± 0.0	tr	tr	0.3 ± 0.1	tr	b,c
46	α-Terpineol	1187	1186	1186	tr	0.1 ± 0.0	0.1 ± 0.0		0.1 ± 0.0	0.5 ± 0.1	a,b,c
47	Myrtenal	1190	1195	1190	0.1 ± 0.0	0.3 ± 0.1	tr	0.3 ± 0.1	1.1 ± 0.3	0.3 ± 0.0	a,b,c
48	Myrtenol	1191	1194	1191	0.1 ± 0.0	0.4 ± 0.1	tr	0.2 ± 0.0	1.1 ± 0.2	0.1 ± 0.0	a,b,c
49	Verbenone	1205	1204	1205	tr	0.1 ± 0.0		0.2 ± 0.0	0.7 ± 0.2		a,b,c
50	*trans*-Carveol	1216	1215	1216	tr	0.1 ± 0.0		0.1 ± 0.0	0.9 ± 0.2		b,c
51	*cis*-Carveol	1228	1226	1229					tr		b,c
52	Thymol, methyl ether	1234	1232	1235			tr			0.1 ± 0.0	b,c
53	Cumin aldehyde	1235	1238	1235		0.1 ± 0.0	tr		tr		b,c
54	Carvacrol, methyl ether	1243	1242	1244			0.1 ± 0.0			0.1 ± 0.0	b,c
55	Carvone	1241	1239	1241	tr	tr		tr	0.7 ± 0.1	tr	a,b,c
56	Methylcamphenoate	1248		1250			0.2 ± 0.0			3.2 ± 0.7	b,c
57	Bornyl acetate	1282	1287	1281	13.7 ± 2.5	11.4 ± 2.4	tr	13.4 ± 2.8	12.2 ± 2.0	0.2 ± 0.0	a,b,c
58	Lavandulyl acetate	1293	1288	1292		tr					b,c
59	Carvacrol	1302	1298	1302	tr	0.1 ± 0.0	tr		tr	tr	a,b,c
60	Silphiperfol-5-ene	1325	1326	1330			0.1 ± 0.0				b,c
61	Methyl decanoate	1327	1323	1328			tr				b,c
62	δ-Elemene	1332	1335		0.1 ± 0.0	0.1 ± 0.0	0.3 ± 0.1	tr		tr	b,c
63	7-*epi*-Silphiperfol-5-ene	1343	1345	1348			0.1 ± 0.0				b,c
64	α-Cubebene	1344	1345	1345	0.1 ± 0.0	0.1 ± 0.0	0.4 ± 0.1	tr	tr	tr	b,c
65	Eugenol	1355	1356	1355	tr	tr		tr	tr		a,b,c
66	α-Ylangene	1363	1373	1364	0.1 ± 0.0	tr	0.2 ± 0.0				b,c
67	α-Copaene	1368	1376	1367	0.1 ± 0.0	0.1 ± 0.0	0.4 ± 0.1	0.1 ± 0.0	0.1 ± 0.0		a,b,c
68	Modheph-2-ene	1374	1383	1376						0.2 ± 0.0	b,c
69	α-Isocomene	1376	1387	1376			tr				b,c
70	β-Bourbonene	1376	1387	1376	0.2 ± 0.0	0.1 ± 0.0		0.3 ± 0.1	0.1 ± 0.0		b,c
71	β-Cubebene	1383	1387	1383	0.1 ± 0.0	tr	0.2 ± 0.0	0.1 ± 0.0	tr		b,c

Table 1 (continued)

No	Component[a]	RI exp.[b]	RI Lit.[c]		*Solidago gigantea* (%)[d]			*Solidago canadensis* (%)[d]			ID[e]
			ADAMS	NIST 17	Leaves	Flowers	Roots	Leaves	Flowers	Roots	
72	β-Elemene	1386	1389	1387	0.6 ± 0.2	0.2 ± 0.0	0.1 ± 0.0	1.7 ± 0.4	0.7 ± 0.2	3.4 ± 0.7	a,b,c
73	α-Gurjunene	1400	1409	1400	2.6 ± 0.5	2.3 ± 0.4	3.0 ± 0.7	1.3 ± 0.3	1.3 ± 0.4	0.2 ± 0.0	a,b,c
74	(*E*)-caryophyllene	1409	1417	1412	0.5 ± 0.1	0.8 ± 0.2	1.1 ± 0.2	0.8 ± 0.2	0.2 ± 0.0	0.1 ± 0.0	a,b,c
75	β-Copaene	1420	1430	1424	0.2 ± 0.0	0.2 ± 0.0	0.4 ± 0.1	0.2 ± 0.0	tr		b,c
76	α-*trans*-Bergamotene	1431	1432		0.1 ± 0.0	0.1 ± 0.0	0.5 ± 0.1	tr	tr	tr	b,c
77	6,9-Guaiadiene	1436	1442		tr		tr	tr			b,c
78	α-Humulene	1443	1452	1444	0.2 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	0.1 ± 0.0	tr	a,b,c
79	Geranyl acetone	1453	1453	1453	0.1 ± 0.0			0.1 ± 0.0			b,c
80	*cis*-Cadina-1(6),4-diene	1453	1461			0.2 ± 0.0					b,c
81	γ-Gurjunene	1463	1475	1465	1.3 ± 0.3	0.9 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	0.6 ± 0.2		b,c
82	γ-Muurolene	1470	1478	1469	1.2 ± 0.2	0.8 ± 0.2	0.1 ± 0.0			0.1 ± 0.0	b,c
83	Germacrene D	1472	1484	1473	6.3 ± 1.1	9.0 ± 1.6	14.4 ± 2.8	11.0 ± 2.2	1.0 ± 0.2	3.9 ± 0.8	b,c
84	β-Selinene	1476	1489	1476	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	0.8 ± 0.0	1.6 ± 0.3	0.4 ± 0.1	b,c
85	*epi*-Cubebol	1487	1493	1488				0.2 ± 0.0			b,c
86	α-Selinene	1487	1498	1488	0.2 ± 0.0	0.1 ± 0.0	0.3 ± 0.0			0.1 ± 0.0	b,c
87	Bicyclogermacrene	1488	1500	1490	0.7 ± 0.2	0.5 ± 0.1	1.2 ± 0.3				b,c
88	α-Muurolene	1494	1500	1494	0.2 ± 0.0	0.1 ± 0.0	0.3 ± 0.1	0.1 ± 0.0	tr		b,c
89	δ-Amorphene	1500	1511		0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0				b,c
90	β-Bisabolene	1505	1505	1505					tr		b,c
91	γ-Cadinene	1506	1513	1507	0.7 ± 0.2	1.2 ± 0.3	1.5 ± 0.3	0.1 ± 0.0		0.1 ± 0.0	b,c
92	*trans*-Calamenene	1517	1521	1517	1.5 ± 0.3	0.1 ± 0.0	0.2 ± 0.0			0.1 ± 0.0	b,c
93	δ-Cadinene	1518	1522	1520	1.5 ± 0.4	1.2 ± 0.3	2.6 ± 0.5	0.3 ± 0.1	0.2 ± 0.0	0.2 ± 0.0	b,c
94	β-Sesquiphellandrene	1519	1521	1520						0.1 ± 0.0	b,c
95	*trans*-Cadina-1,4-diene	1524	1533	1525	tr		tr				b,c
96	α-Cadinene	1530	1537	1533	tr	0.2 ± 0.0	0.1 ± 0.0				b,c
97	α-Calacorene	1534	1542	1535	0.4 ± 0.1	0.3 ± 0.1	0.2 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	tr	b,c
98	*epi*-Torilenol[g]	1546	1546		1.7 ± 0.3	2.1 ± 0.3	1.3 ± 0.3	2.1 ± 0.4	0.5 ± 0.1		b,c
99	epoxysalvial-4(14)-ene	1556		1557	4.1 ± 0.7	3.0 ± 0.6	1.5 ± 0.3	1.8 ± 0.4	2.5 ± 0.5	0.1 ± 0.0	b,c
100	β-Calacorene	1556	1564	1555			0.2 ± 0.0				b,c
101	(*E*)-Nerolidol	1562	1561	1562	0.3 ± 0.0	0.1 ± 0.0		0.3 ± 0.0	0.1 ± 0.0		a,b,c
102	Spathulenol	1568	1576	1570	4.3 ± 0.8	3.4 ± 0.7	4.6 ± 0.9	2.1 ± 0.4	1.1 ± 0.3	tr	b,c
103	Caryophyllene oxide	1571	1583	1571	0.9 ± 0.2	1.8 ± 0.4	0.6 ± 0.2	2.1 ± 0.5	2.1 ± 0.5		a,b,c
104	Eudesm-4(15)-en-1-one[g]	1575	1574		0.7 ± 0.1	1.0 ± 0.2	0.6 ± 0.1	0.6 ± 0.1	0.1 ± 0.0		b,c
105	Viridiflorol	1581	1592	1583	0.4 ± 0.1	0.2 ± 0.0	2.0 ± 0.4	0.8 ± 0.2	0.4 ± 0.1	tr	a,b,c
106	Salvial-4(14)-en-1-one	1583	1594	1584	2.0 ± 0.4	1.4 ± 0.3	1.5 ± 0.3	3.0 ± 0.6	0.7 ± 0.1	0.3 ± 0.0	b,c

Table 1 (continued)

No	Component[a]	RI exp.[b]	RI Lit.[c]		*Solidago gigantea* (%)[d]			*Solidago canadensis* (%)[d]			ID[e]
			ADAMS	NIST 17	Leaves	Flowers	Roots	Leaves	Flowers	Roots	
107	Ledol	1592	1602	1593	2.9 ± 0.6	1.7 ± 0.4	0.5 ± 0.1	2.6 ± 0.5	1.1 ± 0.3	0.1 ± 0.0	b,c
108	Rosifoliol	1597	1600	1595			0.5 ± 0.1			0.2 ± 0.0	b,c
109	Humulene epoxide II	1597	1608	1596	1.3 ± 0.3	1.3 ± 0.3		1.7 ± 0.4	0.7 ± 0.1		a,b,c
110	Torilenol[g]	1601	1599		0.5 ± 0.1	2.5 ± 0.4	1.4 ± 0.3	4.1 ± 0.7	0.6 ± 0.1	0.1 ± 0.0	b,c
111	Isospathulenol	1621	1622	1621	3.0 ± 0.6	2.8 ± 0.6	3.6 ± 0.7	2.4 ± 0.5	0.8 ± 0.2	0.3 ± 0.1	b,c
112	*epi*-α-Cadinol	1633	1640	1633	0.3 ± 0.1	0.2 ± 0.0	0.2 ± 0.0	0.1 ± 0.0		tr	b,c
113	*epi*-α-Muurolol	1634	1640	1635	0.3 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.1 ± 0.0		tr	b,c
114	Opposita-4(15),7(11)-dien-1β-ol[g]	1636	1633		1.4 ± 0.3	1.2 ± 0.3	0.8 ± 0.2	2.1 ± 0.4	0.3 ± 0.0	0.1 ± 0.0	b,c
115	α-Cadinol	1646	1652	1646	0.7 ± 0.2	0.6 ± 0.1	0.8 ± 0.2			0.3 ± 0.1	a,b,c
116	Cadalene	1666	1675	1665	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.0			0.1 ± 0.0	b,c
117	Eudesma-4(15),7-dien-1β-ol	1676	1687	1674	4.4 ± 0.9	4.6 ± 0.9	2.8 ± 0.6	7.1 ± 1.5	1.2 ± 0.3	0.3 ± 0.0	b,c
118	10-*nor*-Calamenen-10-one	1692		1702	0.1 ± 0.0	0.1 ± 0.0					b,c
119	Cyclocolorenone	1748		1748	15.6 ± 3.1	6.4 ± 1.3	0.2 ± 0.0	8.8 ± 1.6	2.9 ± 0.6 ± 0.0	0.2 ± 0.0	b,c
120	Phytone	1844		1845	tr	0.4 ± 0.1		tr	0.1		b,c
121	Kaurene	2028	2025	2030			0.3 ± 0.1				b,c
	Oil yield (%)				0.16	0.15	0.06	0.20	0.18	0.04	
	Total identified (%)				83.3	88.1	83.5	85.5	94.3	96.2	
	Grouped compounds (%)										
	Monoterpene hydrocarbons				3.5	16.0	12.9	8.3	42.3	74.0	
	Oxygenated monoterpenes				15.1	17.7	1.2	17.2	30.8	6.2	
	Sesquiterpene hydrocarbons				19.5	19.1	29.2	17.9	5.9	9.0	
	Oxygenated sesquiterpenes				45.1	34.5	23.1	42.1	15.2	2.0	
	Others				0.1	0.5	17.4	tr	0.1	5.0	

[a]Compounds are listed in order of their elution from a HP-5MS column. [b]Linear retention index on HP-5MS column, calculated according to Van den Dool and Kratz equation (1963) using homologous series of C_8–C_{30} alkanes. [c]Linear retention index taken from Adams (2007) and NIST 17 (2017). [d]Relative percentage values are means of three determinations ± SD. [e]Identification methods: a, based on comparison with authentic compounds; b, based on comparison with WILEY, ADAMS, FFNSC2 and NIST 17 MS databases; c, based on comparison of calculated RI with those reported in ADAMS, FFNSC 2 and NIST 17. [f] tr, % below 0.1%. [g]RI and MS taken from Kalemba et al. (2001)

follows: 5 min at 60 then 4 °C min^{-1} up to 220 °C, then 11 °C min^{-1} up to 280 °C, held for 15 min. Injector and detector temperatures: 280 °C; carrier gas: He; flow rate: 1 ml min^{-1}; split ratio: 1:50; acquisition mass range: 29–400 *m/z*; mode: electron-impact (EI, 70 eV). The EO was diluted 1:100 in *n*-hexane, and 2 µl of the solution was injected into the GC–MS system twice. The MSD ChemStation software (Agilent, Version G1701DA D.01.00) and the NIST Mass Spectral Search Program for the NIST/EPA/NIH EI and NIST Tandem Mass Spectral Library v. 2.3 were used to analyse data. For identification of EO components, co-injection with the above standards was used, together with correspondence of retention indices and mass spectra with those of ADAMS, NIST 17 and FFNSC2 libraries (Adams 2007; NIST 17 2017; FFNSC2 2012). Some oxygenated sesquiterpenes were identified by comparison of RI and MS with those reported by Kalemba et al. (2001). Semi-quantification of EO components was made by peak area normalization considering the same response factor for all volatile components. Percentages values were the mean of two independent chromatographic analyses.

Insect and earthworm rearing

Culex quinquefasciatus third-instar larvae and *M. domestica* adult females were reared as reported by Benelli et al. (2018a, b). *Spodoptera littoralis* early third-instar larvae were reared following Sut et al. (2017). Insects were maintained at 25 ± 1 °C, 70 ± 3% R.H. and 16:8 h (L:D).

Eisenia fetida adults (weight 350–500 mg) were reared as reported by Pavela (2018) in artificial soil (OECD 1984). Room temperature was 20 ± 1 °C. Soil maximum water-holding capacity (35%) was monitored weekly.

Toxicity on *Culex quinquefasciatus* larvae

In insecticidal assays, we tested the EOs extracted from various plant parts of *S. canadensis* and *S. gigantea*, except for the root EO of *S. canadensis*, since the yield of this one was too scarce to be considered in insecticidal assays (see paragraph 3.1). The five *Solidago* EOs were diluted in dimethyl sulfoxide (DMSO), formulated at the concentration of 100 ml L^{-1}, then tested on *C. quinquefasciatus* third-instar larvae following Benelli et al. (2017). Based on preliminary assays, we tested dilution series ranging from 50 to 200 ml L^{-1} to estimate the EO lethal concentration values. For each concentration, we conducted four duplicate trials. Negative control was distilled water with the same amount of DMSO used testing *S. canadensis and S. gigantea* EOs. α-cypermethrin (Vaztak®) was tested as positive control (Benelli et al. 2018c). Larval mortality was noted after 24 h.

Toxicity on *Musca domestica* adults

Topical application tests were conducted to evaluate the acute toxicity of five EOs extracted from various plant parts of *S. canadensis* and *S. gigantea* on *M. domestica* adult females (3–6 days old). According to Benelli et al. (2018b), 1 µL of acetone (Sigma-Aldrich, Germany), carrying a given *Solidago* EO at the dose of 200 µg $adult^{-1}$ (each replicated at least 4 times), was applied through a microelectric applicator on the pronotum of fly adults anesthetized using CO_2. Acetone without the *Solidago* EO served as negative control. α-Cypermethrin (Vaztak®) was tested as positive control (Benelli et al. 2018c). Houseflies were then moved to a recovery box (10 × 10 × 12 cm, 26 ± 1 °C 16:9 L:D) for 24 h, before checking mortality rates. The EOs were tested at dilution series ranging from 50 to 400 µg $adult^{-1}$ to estimate the lethal doses.

Toxicity on *Spodoptera littoralis* larvae

Toxicity of the five EOs extracted from various plant parts of *S. canadensis* and *S. gigantea* on third-instar larvae of *S. littoralis* was evaluated through topical application of the EO diluted in acetone, as detailed by Sut et al. (2017). Larvae were treated on the dorsum with 1 µL of acetone containing the selected *Solidago* EO at dose of 150 µg $larva^{-1}$. We did four duplicate replicates ($n = 20$ larvae per replicate) for each tested *Solidago* EO concentration. Acetone without EO served as negative control. α-Cypermethrin (Vaztak®) was tested as positive control (Benelli et al. 2018c). Then, *S. littoralis* larvae were moved to a recovery box (10 × 10 × 7 cm, with thin holes on each wall to avoid fumigation effects, 26 ± 1 °C, 70 ± 3% R.H., and 16:8 L:D) for 24 h, before checking mortality. The EOs were tested using dilution series ranging from 30 to 250 µg $larva^{-1}$ to estimate the lethal doses.

Toxicity on non-target earthworms

Since the *S. canadensis* leaf EO was the only tested product effective against the three selected insect pests, it was selected for non-target tests, along with the leaf EO from *S. gigantea*. The standard OECD (1984) method was followed to test the *Solidago* leaf EO toxicity on *E. fetida* adult earthworms. The artificial soil had the same composition and pH as described for *E. fetida* rearing; the soil was prepared by adding the *Solidago* EOs at concentrations of 200, 100 and 50 mg kg^{-1}, mixed with Tween 80 (ratio 1:1 v:v), equivalent to 100, 50 and 25 mg EO a.i. per kg of dry weight basis soil. *α*-Cypermethrin at 50.0, 25.0 and 12.5 mg kg^{-1} of dry soil [i.e. Vaztak® at 1000, 500 and 250 µL kg^{-1} (v/v)] was the positive control. Distilled water with Tween 80 at

concentration of 100 mg kg^{-1} of dry soil was used as negative control. An aqueous formulation containing the leaf EO from the two studied *Solidago* species, pure water or α-cypermethrin was mixed with the soil (650 g), and 10 *E. fetida* adults were added. Treated and control soil samples were stored in glass pots (1 L) covered with gauze to ensure aeration. *Eisenia fetida* mortality was noted 7 and 14 days post-exposure to the treatments at 20 ± 1 °C, R.H. 80–85%, 16:8 (L:D) and 600 lux (Pavela 2018).

Statistical analysis

If control mortality was > 20%, the treatment mortality rates were corrected by the Abbott's formula (Abbott 1925). Lethal dose $LD_{50(90)}$ or concentration $LC_{50(90)}$ values, with associated 95% LCL and UCL, were estimated by probit analysis (Finney 1971) using BioStat version 5.

Results

Chemical analysis of *Solidago* essential oils

The hydrodistillation of leaves, inflorescences and roots of *S. gigantea* and *S. canadensis* gave similar EO yields, with leaf and flower being richer (0.15–0.16 and 0.18–0.20%, respectively) than root (0.06 and 0.04%, respectively). The GC analysis performed by using a combination of MS and RI and, whenever possible, co-elution with available standards, allowed us to identify 121 volatile compounds in the six EOs from the two *Solidago* species (Table 1). Overall, the chemical profiles of leaves of *S. gigantea* and *S. canadensis* species were quite similar, whereas those of inflorescences (Fig. 2a, b) and, to a major extent, roots exhibited noteworthy differences (Fig. 2c–f).

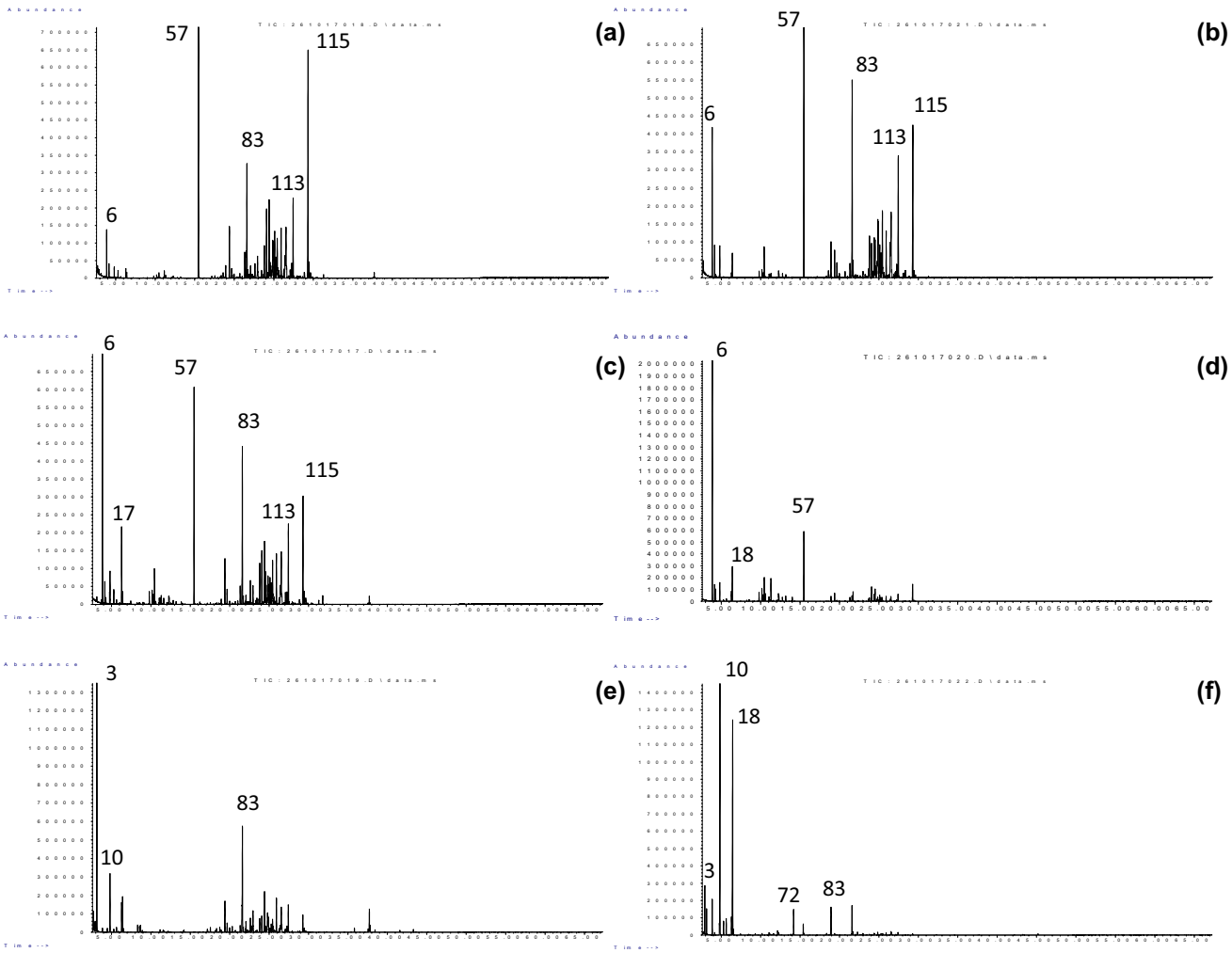

Fig. 2 TIC-GC/MS chromatograms of the essential oils extracted from leaves, inflorescences and roots of *Solidago gigantea* (**a**, **c**, **e**, respectively) and *Solidago canadensis* (**b**, **d**, **f**, respectively). Numbers of main peaks refer to those reported in Table 1

A total of 80 volatile components were identified in the leaf EO from *S. gigantea*, accounting for 83.3% of the total. This EO was dominated by oxygenated sesquiterpenes (45.1%), followed by sesquiterpene hydrocarbons (19.5%) and oxygenated monoterpenes (15.1%), with cyclocolorenone (15.6%), bornyl acetate (13.7%) and germacrene D (6.3%) as the major compounds. Other components occurring at noteworthy levels were the sesquiterpenes eudesma-4(15),7-dien-1β-ol (4.4%), spathulenol (4.3%) epoxysalvial-4(14)-ene (4.1%) and isospathulenol (3.0%). A total of 43 compounds were detected in percentages below 1% and 19 at trace levels (< 0.1%).

Solidago canadensis leaf EO yielded a total of 66 components, corresponding to 85.5% of the total composition. The oxygenated sesquiterpenes (42.1%) were still the major fraction of this oil, along with similar levels of sesquiterpene hydrocarbons (17.9%) and oxygenated monoterpenes (17.2%), and minor amounts of monoterpene hydrocarbons (8.3%). The most abundant components were again bornyl acetate (13.4%), germacrene D (11.0%) and cyclocolorenone (8.8%), accompanied by minor components like eudesma-4(15),7-dien-1 β-ol (7.1%), α-pinene (4.6%), torilenol (4.1%) and salvial-4(14)-en-1-one (3.0%). Thirty-two compounds were present in percentages lower than 1% and 13 at trace levels.

The EO from inflorescences of *S. gigantea* showed a chemical profile (84 identified components accounting for 88.1% of the EO) similar to that of leaf EO of the same species, with oxygenated sesquiterpenes (34.5%), sesquiterpene hydrocarbons (19.1%) and oxygenated monoterpenes (17.7%), and an additional occurrence of monoterpene hydrocarbons (16.0%). Here, the major components were bornyl acetate (11.4%), germacrene D (9.0%), α-pinene (8.1%) and cyclocolorenone (6.4%). Minor contributions derived from eudesma-4(15),7-dien-1 β-ol (4.6%), *p*-cymene (3.5%), spathulenol (3.4%) and epoxysalvial-4(14)-ene (3.0%). A total of 56 components were present in percentages below 1% and 6 at trace levels.

A different profile was found in the EO from inflorescences of *S. canadensis,* where a total of 71 compounds, accounting for 94.3% of the total, were identified. Here, monoterpenoids (monoterpene hydrocarbons 42.3%, oxygenated monoterpenes 30.8%) dominated over sesquiterpenes (oxygenated sesquiterpenes 13.6%, sesquiterpene hydrocarbons 5.9%). The major compounds were α-pinene (29.5%) and bornyl acetate (12.2%), with minor contributions of limonene (5.1%), *trans*-verbenol (3.9%) and *p*-mentha-1,5-dien-8-ol (3.8%). Main leaf volatile components such as cyclocolorenone and germacrene D were here poorer (2.9 and 1.0%, respectively). A total of 34 components were present in percentages lower than 1.0% and 14 at trace levels.

The chemical profiles of the two *Solidago* root EOs differed considerably from each other. In *S. gigantea* EO, we identified 88 compounds accounting for 83.5% of the total composition. Sesquiterpene hydrocarbons (29.2%) were the most abundant fraction, followed by oxygenated sesquiterpenes (23.1%), alkenes (14.5%) and monoterpene hydrocarbons (12.9%). Germacrene D (14.4%) and 1-nonene (13.1%) were the most abundant constituents, with minor amounts of β-pinene (4.6%), spathulenol (4.6%), isospathulenol (3.6%), limonene (3.1%) and α-gurjunene (3.0%). A total of 53 constituents were present in percentages below 1% and 12 at trace levels. *Solidago canadensis* EO showed a different profile, with a total of 69 constituents, corresponding to 96.2% of the oil. The EO was dominated by monoterpene hydrocarbons accounting for 74.0% of the total composition. The remaining compounds comprised sesquiterpene hydrocarbons (9.0%), oxygenated monoterpenes (6.2%) and alkenes (4.9%). The oil composition was dominated by two components, namely limonene (32.7%) and β-pinene (31.3%), whereas germacrene D (3.9%), β-elemene (3.4%), methyl-camphenoate (3.2%) and 2,6-dimethyl-1,3,6-heptatriene (3.0%) were present in low concentrations. Thirty-eight constituents were below 1% and 19 at trace levels. 1-nonene, i.e. one of the major volatile constituents in the roots of *S. gigantea*, was here present at scant amounts (1.6%).

Insecticidal activity and toxicity on non-target earthworms

The acute toxicity of the EOs extracted from various plant parts of *S. canadensis* and *S. gigantea* varied consistently among the tested insect pests. Tables 2, 3 and 4 show the bioactivity of the tested five EOs on *C. quinquefasciatus*, *M. domestica* and *S. littoralis*, respectively. At the maximum tested concentration, i.e. 100 µl L^{-1}, mortality rates on *C. quinquefasciatus* third-instar larvae varied from 22.0% (*S. gigantea* root EO) to 61.0% (*S. canadensis* leaf EO). According to the criteria exposed by Pavela (2015a, b), *Solidago* EOs achieving mortality rates lower than 50% when tested at the highest concentration of 100 µl L^{-1} were excluded from probit analysis. Therefore, the only *Solidago* EO of interest for developing *C. quinquefasciatus* larvicides was from *S. canadensis* leaves, with a LC_{50} of 89.3 µl L^{-1} and a LC_{90} of 189.6 µl L^{-1} (Table 2).

Concerning toxicity assays on *M. domestica* adults, *Solidago* EOs tested at the maximum dose of 200 µg $adult^{-1}$ led to fly mortality rates ranging from 30% (*S. gigantea* flower EO) to 67.5% (*S. canadensis* flower EO) (Table 3). The two most effective EOs were those from *S. canadensis* leaf and flowers, with LD_{50} values of 206.9 and 207.1 µg $adult^{-1}$, respectively. LD_{90} values were 355.6 and 426.4 µg $adult^{-1}$, respectively (Table 3).

Furthermore, three out of the five tested *Solidago* EOs showed relevant toxicity against third-instar larvae of *S. littoralis*. EOs tested at the highest dose of 150 µg larva^{-1} led to caterpillar mortality rates ranging from 33.3% (*S. canadensis* flower EO) to 93.5% (*S. gigantea* leaf EO) (Table 4). Three highly effective EOs were identified, including *S. gigantea* leaf EO, *S. canadensis* leaf EO and *S. gigantea* flower EO, with LD_{50} values of 84.5, 98.9 and 107.4 µg larva^{-1}, respectively. LD_{90} values were 149.4, 200.4 and 264.6 µg larva^{-1}, respectively (Table 4). For all the tested insect pests, the toxicity results achieved testing α-cypermethrin as positive control are provided in Tables 2, 3 and 4.

Since the *S. canadensis* leaf EO was the only tested bio-product effective against the three selected tested pests, we selected it for non-target toxicity tests on *E. fetida*

Table 2 Acute toxicity of the essential oils from various plant parts of *Solidago canadensis* and *Solidago gigantea* on *Culex quinquefasciatus* third-instar larvae

Treatment	Mortality at 100 µl L^{-1}	LC_{50} µl L^{-1}	CI95	LC_{90} µl L^{-1}	CI95	Chi square
Solidago gigantea flowers	28.0 ± 3.3	ND	–	–	–	–
Solidago gigantea leaves	44.8 ± 3.3	ND	–	–	–	–
Solidago gigantea roots	22.0 ± 2.3	ND	–	–	–	–
Solidago canadensis flowers	38.9 ± 2.8	ND	–	–	–	–
Solidago canadensis leaves	61.0 ± 8.2	89.3	72.9–92.3	189.6	172.3–199.8	3.256 ns
Negative control	0.0 ± 0.0	–	–	–	–	–
Positive control, α-cypermethrin	100.0 ± 0.0	0.0005	0.0003–0.0007	0.0018	0.0009–0.0023	2.756 ns

ND not determined

ns not significant ($P > 0.05$)

Table 3 Acute toxicity of the essential oils from various plant parts of *Solidago canadensis* and *Solidago gigantea* on *Musca domestica* adult females

Treatment	Mortality at 200 µg adult^{-1}	LC_{50} µg adult^{-1}	CI95	LC_{90} µg adult^{-1}	CI95	Chi square
Solidago gigantea flowers	32.5 ± 2.5	ND	–	–	–	–
Solidago gigantea leaves	42.5 ± 7.5	ND	–	–	–	–
Solidago gigantea roots	30.0 ± 0.0	ND	–	–	–	–
Solidago canadensis flowers	67.5 ± 12.5	207.1	191.3–226.2	355.6	310.1–369.8	1.718 ns
Solidago canadensis leaves	57.8 ± 12.5	206.9	187.5–232.4	426.4	401.8–471.5	5.246 ns
Negative control	0.0 ± 0.0	–	–	–	–	–
Positive control, α-cypermethrin	100.0 ± 0.0	0.19	0.16–0.35	0.85	0.78–1.15	3.121 ns

ND not determined

ns not significant ($P > 0.05$)

Table 4 Acute toxicity of the essential oils from various plant parts of *Solidago canadensis* and *Solidago gigantea* on *Spodoptera littoralis* third-instar larvae

Treatment	Mortality at 150 µg larva^{-1}	LC_{50} µg larva^{-1}	CI95	LC_{90} µg larva^{-1}	CI95	Chi square
Solidago gigantea flowers	60.0 ± 8.2	107.4	94.6–118.9	264.6	173.7–316.1	0.044 ns
Solidago gigantea leaves	93.5 ± 2.5	84.5	72.9–89.5	149.4	122.7–178.5	1.787 ns
Solidago gigantea roots	40.8 ± 8.2	ND	–	–	–	–
Solidago canadensis flowers	33.3 ± 12.5	ND	–	–	–	–
Solidago canadensis leaves	73.3 ± 2.5	98.9	83.4–124.1	200.4	180.4–256.7	2.517 ns
Negative control	0.0 ± 0.0	–	–	–	–	–
Positive control, α-cypermethrin	–	0.0032	0.0022–0.0039	0.0082	0.0057–0.0105	2.482 ns

ND not determined

ns not significant ($P > 0.05$)

Table 5 Toxicity of the essential oils extracted from *Solidago canadensis* and *Solidago gigantea* leaves, and α-cypermethrin on *Eisenia fetida* earthworms

Concentration (mg kg^{-1})	7th day* (% ±SD)	14th day* (% ±SD)
Solidago canadensis 200.0	0.0 ± 0.0^{a}	0.0 ± 0.0^{b}
Solidago gigantea 200.0	0.0 ± 0.0^{a}	0.0 ± 0.0^{a}
α-Cypermethrin 50.0	100.0 ± 0.0^{c}	100.0 ± 0.0^{c}
α-Cypermethrin 25.0	100.0 ± 0.0^{c}	100.0 ± 0.0^{c}
α-Cypermethrin 12.5	75.5 ± 2.5^{b}	95.5 ± 2.5^{b}
Control	0.0 ± 0.0^{a}	5.0 ± 2.5^{a}
ANOVA $F_{5,18}$, P	358.15; 0.001	459.22; 0.001

Herein, the *S. canadensis* leaf essential oil was the only tested product effective against the three selected tested pests; therefore, it was selected for non-target tests, along with the leaf essential oil from *S. gigantea*

**E. fetida* mortality (±SD) achieved on the 7th and 14th day post-application of *Solidago canadensis* and *Solidago gigantea* essential oils

Numbers within a column follower by the same letter do not differ significantly according to ANOVA, Tukey's HSD test at $P < 0.05$

earthworms, along with the leaf EO from *S. gigantea*. Results, given in comparison with the positive control α-cypermethrin, are provided in Table 5. Notably, neither of the EOs produced any earthworm mortality on adults of the *E. fetida* earthworms, at variance with the positive control α-cypermethrin, which led to 100% mortality when applied at 25 and 50 mg kg^{-1} in the soil (Table 5).

Discussion

Chemical analysis of *Solidago* essential oils

Results highlighted a chemical polymorphism in the vegetative and reproductive organs of the two *Solidago* species, with bornyl acetate, germacrene D and cyclocolorenone as marker compounds of the leaf EOs, α-pinene, bornyl acetate and germacrene D characterizing the inflorescence EOs, and 1-nonene, germacrene D, β-pinene and limonene as markers of the root EOs (Fig. 3).

Germacrene D is a ubiquitous sesquiterpene occurring in many plant EOs (Casiglia et al. 2017). It is a chiral compound arising from the methylerythritol phosphate pathway and playing an important role in the plant cell metabolism as the precursor of many sesquiterpenes (Steliopoulos et al. 2002). In addition, it has been recognized as an important sex stimulant for the males of *Periplaneta americana* L. (Kitamura et al. 1976) and has been indicated as a useful compound for pest control (Stranden et al. 2002; Zihare and Blumberga 2017). Bornyl acetate is an ester of the monoterpenoid borneol having camphoraceous smell and occurring in many EOs such as those of conifers and valerian (Matsubara et al. 2011). This compound has been proved to exert anti-inflammatory activity (Tung et al. 2008). Interestingly, bornyl acetate is used by some insects, such as *Corythucha marmorata* (Uhler) (Hemiptera: Tingidae), as a source of sex pheromones (Watanabe and Shimizu 2017). 1-Nonene is a linear alkene occurring in the defensive secretions of tenebrionid beetles (Tschinkel 1975). Cyclocolorenone is a tricyclic sesquiterpene ketone occurring also in other species, namely *Pseudowintera colorata* (Raoul) Dandy, *Ledum palustre* L., *Magnolia grandiflora* L. and *S. canadensis* (Kalemba et al. 2001). This compound has been also reported as an allopathic and antimicrobial agent (Jacyno et al. 1991).

When comparing our data on Hungarian *Solidago* species with those of previously published reports, we found both similarities and differences. For instance, Kalemba et al. (2001) examined a population of *S. gigantea* growing in Poland and reported germacrene D (23.5%) and cyclocolorenone (32.4%) as the major essential oil constituents of aerial parts. The same authors examined the chemical profile of the EO from inflorescences of Polish *S. canadensis* and reported α-pinene (13.0%), limonene (12.0%) and γ-cadinene (27.1%) as the most abundant constituents (Kalemba et al. 1990). The same group also analysed the volatile fraction of micropropagated plants of *S. gigantea* and *S. canadensis* and found α-gurjunene (16.6%), germacrene D (12.8%) and cyclocolorenone (32.8%) as the major compounds in the former, and α-pinene (59.5%), limonene (9.7%) and germacrene D (15.2%) in the latter (Kalemba and Thiem 2004). Fujita (1980) reported germacrene D (66–77%) and bornyl acetate (5–7%) as the major components of S. *gigantea* EO. Weyerstahl et al. (1993) studied the chemical profile of the EO from *S. canadensis* growing in Poland and found α-pinene (14.7%), germacrene D (19.8%) and β-sesquiphellandrene (10.4%) as the most abundant constituents. Synowiec et al. (2017) reported α-pinene (26.0%), limonene (11.5%) and germacrene D (27.5%) as the major EO constituents of Polish *S. canadensis*. Gruľová et al. (2016) analysed Slovak populations of *S. gigantea* and *S. canadensis* and found a significant chemical polymorphism depending on the collection site and species. *S. gigantea* was found rich in sesquiterpenes, namely curlone (14.4%), tumerone (14.0%) and δ-cadinene (5.4%); on the other hand, *S. canadensis* contained α-pinene (36.3%), limonene (7.8%) and germacrene D (9.9%) as the main EO constituents. Shelepova et al. (2018) studied different populations of *S. canadensis* growing in Europe (i.e. Austria, Ukraine, Kazakhstan and Russia) and found α-pinene (12.6–52.4%), germacrene D (2.9–36.2%), bornyl acetate (3.4–26.3%) and limonene (6.4–22.5%) as the major EO components. Watanabe and Shimizu (2017) reported bornyl acetate (20.2%) and germacrene D (54.0%) as the major EO components of

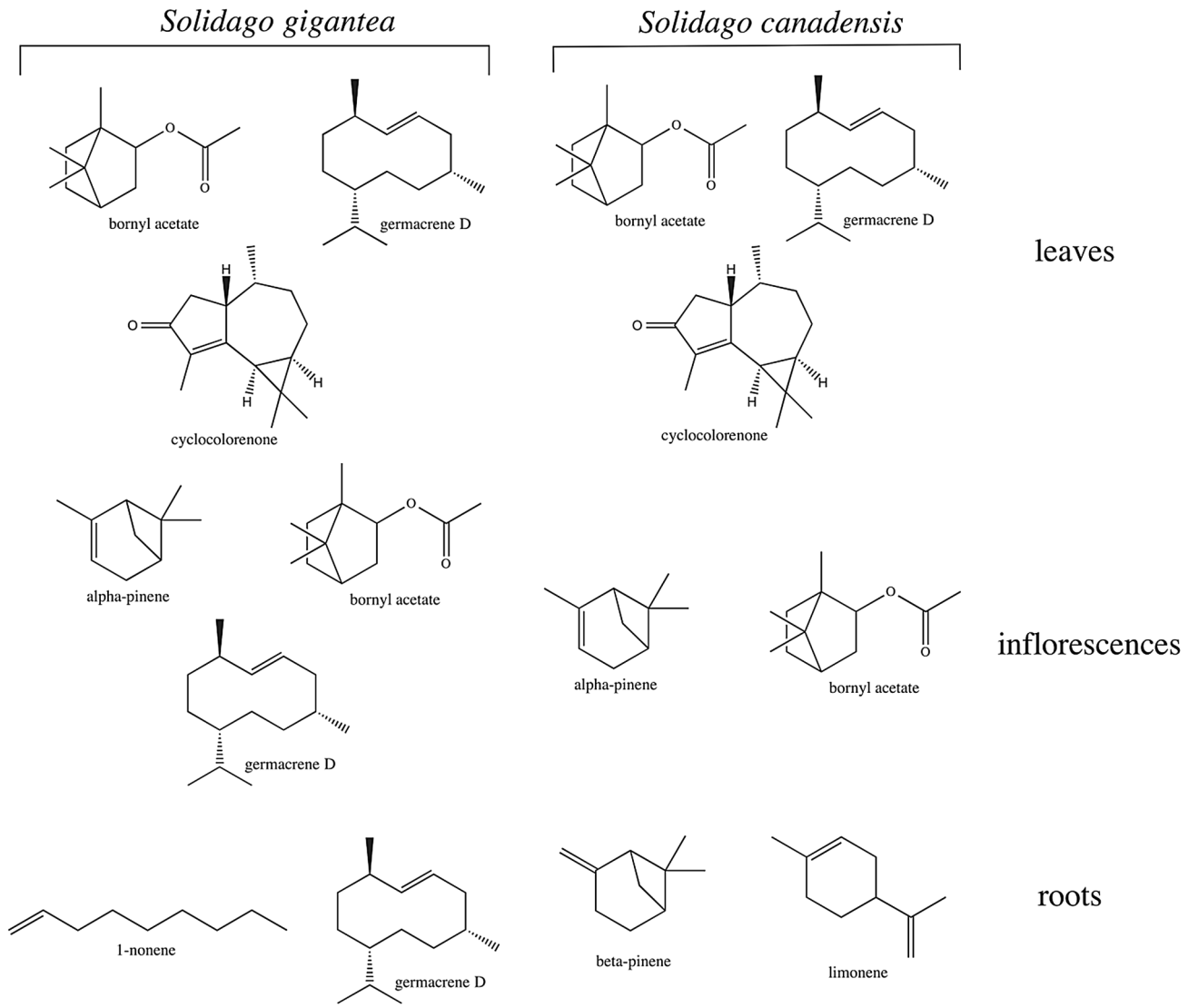

Fig. 3 Marker volatile compounds in the essential oils extracted from different plant parts of *Solidago gigantea* and *Solidago canadensis*

S. canadensis growing in Japan. This oil was slightly phytotoxic against four common weeds (Synowiec et al. 2017). Chanotiya and Yadav (2008) analysed Indian *S. canadensis* and found limonene (0.2–12.5%) and germacrene D (56.7–75.5%) as the main EO constituents. Liu et al. (2016) examined the EO from leaves of Chinese *S. canadensis* and found α-pinene (53.6%) as the major compound followed by germacrene D, limonene and β-pinene.

In conclusion, EOs from these two invasive species show significant variability that can be linked to several factors, such as the geographic origin of samples, together with the cytotype, phenological stage and part studied (see also Pavela and Benelli 2016b).

Insecticidal activity and toxicity on non-target earthworms

The insecticidal efficacy of botanical insecticides based on EOs depends on multiple factors, such as the size and species of target organisms, mode of application, post-application temperature and, in particular, chemical composition and mutual ratios of major substances, which may exhibit both synergistic and antagonistic relationships (Pavela 2015a, b; Pavela and Benelli 2016b; Pavela and Sedlák 2018). Herein, the efficacies of the five tested *Solidago* EOs were different. *Solidago canadensis* leaf EO was most toxic to *C. quinquefasciatus*, with an LC_{50} of 89.3 µl L^{-1}. Therefore, it can be viewed as promising for the development of botanical larvicides, given that EOs are generally considered as prospective if their LC_{50} is lower than 100 ppm (Pavela

2015a). The two most effective EOs against *M. domestica* adults were *S. canadensis* leaf and *S. canadensis* flower EOs, with LD_{50} values of 206.9 and 207.1 µg adult^{-1}, respectively. Three EOs highly toxic to *S. littoralis* were also identified, namely *S. gigantea* leaf EO, *S. canadensis* leaf EO and *S. gigantea* flower EO, with LD_{50} values of 84.5, 98.9 and 107.4 µg larva^{-1}, respectively.

Although these lethal concentrations were relatively higher compared to other EOs or plant extracts (Pavela et al. 2008, 2017; Benelli et al. 2018b), they can still be considered as suitable for the development of botanical insecticides, particularly the *S. canadensis* leaf EO, which showed efficacy against all three tested insect species.

The *Solidago* EOs studied here contained a high number of various substances of which none exhibited a major share exceeding 50% (Table 1). No major constituents can thus be identified, which could be believed to be responsible for the insecticidal efficacy. However, it can be noted that the efficacy was related to the overall amount of oxygenated sesquiterpenes, where the EO efficacy rose correspondingly with increasing amounts of these substances. The closest relationship between oxygenated sesquiterpenes and achieved mortality rate was found for the EOs applied in the dose of 150 µg larva^{-1} against *S. littoralis* larvae, while a significant linear relationship was observed (Fig. 4). Based on this finding, it is likely that oxygenated terpenes are substances with a significantly higher insecticidal efficacy compared to non-oxygenated terpenes, which agrees with earlier research (Bakkali et al. 2008; Pavela 2014, 2015b). The position of the functional group in the molecule and the shape of the molecule both result in diverse mechanisms of action. The compounds exert their activities on insects through neurotoxic effects involving several mechanisms, notably through GABA, octopamine synapses, and the inhibition of acetylcholinesterase (Pavela and Benelli 2016a, b; Jankowska et al. 2017).

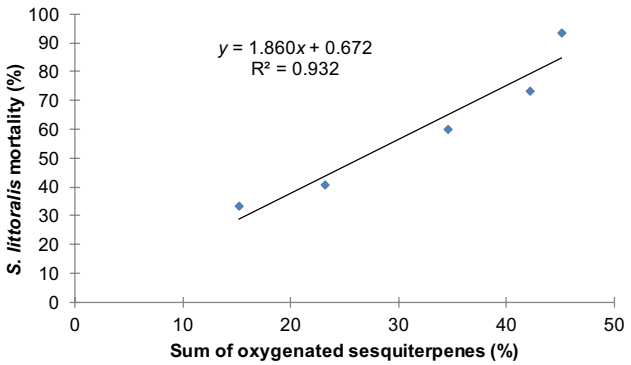

Fig. 4 A relationship between *Spodoptera littoralis* larval mortality and the oxygenated sesquiterpene content characterizing the five tested *Solidago* essential oils (all at 150 µg larva^{-1}) was observed. A significant linear relationship was noted ($P=0.001$). The same was not observed analysing *C. quinquefasciatus* data

Developing eco-friendly pesticides is important in (IPM) (Isman 2017; Lucchi and Benelli 2018), as well as a One Health perspective (Benelli and Duggan 2018). Herein, since the *S. canadensis* leaf EO was the only tested bioproduct effective against the three selected tested pests, we selected it for non-target toxicity tests on *E. fetida* earthworms, along with the leaf EO from *S. gigantea*. Both the *S. canadensis* and *S. gigantea* leaf EOs did not led to mortality when used to treat *E. fetida* adult earthworms, at variance with the positive control α-cypermethrin. This fact is very important, given that earthworms rank among significant soil organisms. Earthworms are necessary for the development and maintenance of the nutritional value and structure of soil (Datta et al. 2016), and they play an important role in the conversion of biodegradable materials and organic waste to vermicast, which is rich in nutrients (Jansirani et al. 2012). Protection of these organisms is thus clearly important.

Even though earthworms can consume a wide range of contaminated organic materials including sewage sludge and industrial waste (Lim et al. 2016), they are very sensitive to insecticides (Datta et al. 2016; Vasantha-Srinivasan et al. 2017). Generally, insecticides exhibit a negative effect on the survival of earthworms, especially in concentrations over 25 mg kg^{-1} (Datta et al. 2016).

More in general, it is expected that *S. gigantea* and *S. canadensis* EOs are harmless against pollinators and natural predators such as honeybees and ladybird beetles, respectively. In this regard, it has been reported that goldenrod is an important source of nectar for honeybees (Stefanic et al. 2003). Besides, the fact that some major leaf volatile constituents of *S. gigantea* and *S. canadensis* EOs, such as germacrene D and bornyl acetate, are sex stimulants or pheromones within species belonging to cockroaches and lacewings (Kitamura et al. 1976; Watanabe and Shimizu 2017), should give a low risk from an ecotoxicological standpoint. Notably, *Solidago* spp. have used as feed for cattle and other mammalian herbivores (Botta-Dukát and Dancza 2004; Werner et al. 1980). Furthermore, *Solidago* spp. host beneficial invertebrates, such as aphid predators, e.g. *Harmonia axyridis* (Pallas) (Genung et al. 2012; Kamo et al. 2010). Regarding the impact on aquatic ecosystems, it has been reported that the *S. canadensis* extracts exert low toxicity on *Daphnia magna* Straus and zebrafish, *Danio rerio* Hamilton (Huang et al. 2014).

In a broader perspective, the relatively high tolerance of insect pollinators, including social bees, to plant EOs used for pest management purposes has been confirmed by several researches (Umpierrez et al, 2017; Ribeiro et al. 2018; Palmer-Young et al. 2018). In addition, this is also substantiated by the fact that EOs are used at relatively high concentrations to protect bees against *Varroa destructor*

(Andreson and Trueman) (Acari: Varroidae) (Ramzi et al., 2017). Besides, the selectivity of EOs was also determined against other non-target organisms including native predators of pests (Castilhos et al 2018; Pavela 2018) or larvivorous fish (Govindarajan et al. 2016a, b; AlShebly et al. 2017; Pavela and Govindarajan 2017).

It has been earlier noted that *S. gigantea* and *S. canadensis* can represent a serious threat for the preservation of local secondary ecosystems. However, the high biomass produced by them may be a resource to be exploited for fair purposes. Indeed, they are extremely common in Europe, North America and Asia so that they can satisfy a huge demand for the manufacture of insecticides. In this regard, their distribution throughout several regions, namely British Isles, Germany, North America and Europe, is mapped on several websites (http://www.floraweb.de/webkarten/karte.html?taxnr=5680; http://www.brc.ac.uk/plantatlas/plant/solidago-gigantea; http://www.brc.ac.uk/plantatlas/plant/solidago-canadensis; https://www.cabi.org/isc/datasheet/50575#toDistributionMaps; https://www.cabi.org/isc/datasheet/50599). Therefore, we believe that the production of botanical insecticides from these two plant invaders may be scalable since both species are renewable resources being able to easily regenerate from their rhizomes. Cooperation among agrochemical industry and landscape managers will be a key point to make the production of botanical insecticides from goldenrod sustainable through a correct management of mowing.

Overall, from a natural product research standpoint, herein we have succeeded in finding these two *Solidago* EOs as prospective, environmentally acceptable and active ingredients utilizable in botanical insecticides to be employed in IPM.

Author contributions

GB, RP and FM conceived and designed research. All authors conducted experiments and/or analysed data. GB, RP and FM wrote the manuscript. All authors read and approved the manuscript.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

Animals and human rights All applicable international and national guidelines for the care and use of animals were followed. All procedures performed in studies involving animals were in accordance with the ethical standards of the institution or practice at which the studies were conducted.

Ethical approval This article does not contain any studies with human participants performed by any of the authors.

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