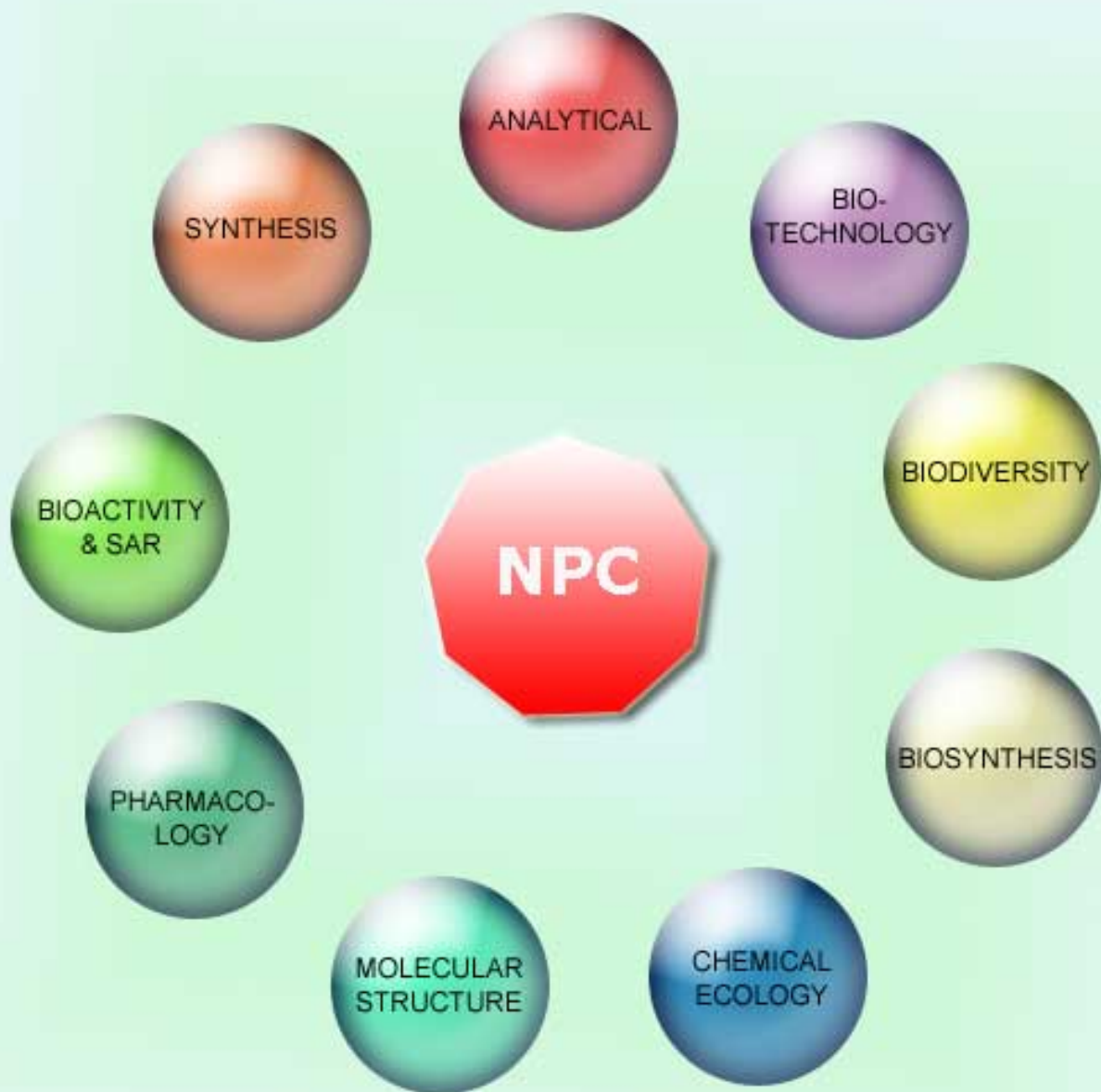


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## Natural Variability in Enantiomeric Composition of Bioactive Chiral Terpenoids in the Essential Oil of *Solidago canadensis* L. from Uttarakhand, India\*

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The natural variability in the enantiomeric distribution of biologically active chiral terpenoids in *Solidago canadensis* L. essential oil from Kumaon was evaluated by enantioselective capillary GC, capillary GC, and GC-MS. Germacrene D, a sesquiterpene hydrocarbon, was noticed as the major compound, contributing 56.7%, 75.5% and 69.7% to the samples, while other constituents with variable compositions were limonene (0.2 to 12.5%), bornyl acetate (2.1 to 2.9%),  $\delta$ -elemene (2.4 to 3.2),  $\beta$ -elemene (1.3 to 1.8%), and elemol (1.4 to 2.6%). The enantiomeric excess has been determined for germacrene D with (+)-enantiomer (>41.8% to >47%) dominating over the (-)-enantiomer in all the samples. Furthermore, there has been above 95% enantiomeric excess for (*R*)-(+)-limonene (>95.1% to >99%), whereas moderate to low excess for (1*R*)-(+)- $\alpha$ -pinene (>47.9%), and (1*S*)-(-)- $\beta$ -pinene (>30.3%) was established. Notably, only (-)-bornyl acetate was found as a single enantiomer with >99% enantiomeric excess. However, for all the identified chiral terpenoids, the enantiomeric distribution varied within only a narrow range in all the samples.

**Keywords:** *Solidago canadensis* L., Asteraceae, chiral terpenoid, essential oil composition, (+)-germacrene D, enantiomeric excess.

*Solidago canadensis* L. or goldenrod (family Asteraceae), mostly grown as an ornamental plant, was introduced in the Kumaon hills of India from North America during the British period. The plant is cultivated throughout India and is distributed on hill slopes, up to 1800 m, along road sides, near human settlements and along water courses [1]. *S. canadensis* and *S. gigantea* are widely distributed in most European countries as well. The medicinal raw material, known as Herba Solidaginis, includes *S. canadensis*, *S. gigantea* and *S. virgaurea* [2].

Several research papers have been published on the essential oil compositions of *Solidago* species from many countries other than India. The oil compositions of *S. canadensis*, *S. gigantea*, *S. graminifolia* and *S. virgaurea* have been reported from Poland [3a-3e]. That of micropropagated *S. canadensis* contained  $\alpha$ -pinene (59.5%), germacrene D (15.2%) and limonene (9.7%) [3d]. Enantiomeric

variations in (-)-germacrene D (21.6 to 23.5%) have been reported in *S. gigantea* [3e]. Overall, the essential oil obtained from *Solidago* species is not only a rich source of enantiomeric germacrene D, but it also possesses significant antibacterial activity [3f] and acts as a good neuron receptor in the moth, *Helicoverpa armigera* [3g].

The odor and specific character of terpenoids are often related to their stereochemistry. Capillary gas chromatography using modified cyclodextrins as stationary phase has proved a reliable technique in the determination of the enantiomeric composition of terpenoids [4a,4b]. Most sesquiterpenes are chiral molecules, but usually only one of the two possible enantiomers is produced in a single species. *S. canadensis* is an exception to this rule, because it contains the sesquiterpene enantiomers, (+)-germacrene D (29a) and (-)-germacrene D (29b) in approximately equal amounts. The responsible two sesquiterpene synthases, viz., (+)-germacrene D

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**Table 1:** Compositions (in %) of essential oils of *Solidago canadensis*. Detection: A, RI on Equity-5 capillary column; B, GC/MS; C, co-injection with standards; † tentatively identified (see Experimental Part).

Entry	Compounds	RI <sub>1</sub> *	RI <sub>2</sub> *	<i>Solidago canadensis</i> Aerial parts			Detection
				Sample I	Sample II	Sample III	
1	$\alpha$ -Pinene	938	1018	5.0	t	0.4	A, B, C
2	Camphene	952	1059	0.2	-	t	A, B, C
3	Sabinene	976	1116	2.4	-	0.2	A, B
4	$\beta$ -Pinene	980	1104	1.2	-	0.2	A, B, C
5	$\beta$ -Myrcene	991	1158	2.8	t	0.4	A, B
6	$\alpha$ -Phellandrene	1007	1161	0.2	-	-	A, B
7	<b><math>\alpha</math>-Terpinene</b>	<b>1018</b>	-	t	-	-	A, B
8	<i>p</i> -Cymene	1025	1274	t	-	-	A, B
9	<b>Limonene</b>	<b>1031</b>	<b>1191</b>	<b>12.5</b>	0.2	2.6	A, B, C
10	Benzene acetaldehyde	1040	-	0.6	t	0.2	A, B
11	( <i>E</i> )- $\beta$ -Ocimene	1048	1268	t	-	-	A, B
12	<b><math>\gamma</math>-Terpinene</b>	<b>1059</b>	<b>1247</b>	t	-	-	A, B
13	<i>cis</i> -Sabinene hydrate	1069	-	t	-	t	A, B
14	<b>Terpinolene</b>	<b>1090</b>	<b>1295</b>	t	-	t	A, B
15	Linalool	1099	1546	0.1	t	t	A, B, C
16	Terpinen-4-ol	1178	1585	0.2	0.2	0.2	A, B, C
17	$\alpha$ -Terpineol	1189	1695	t	t	t	A, B
18	Bornyl acetate	1286	1557	2.1	2.2	2.9	A, B, C
19	$\delta$ -Elemene	1339	1573	2.4	3.2	3.2	A, B
20	<b><math>\alpha</math>-Copaene</b>	<b>1376</b>	<b>1497</b>	t	t	t	A, B
21	$\beta$ -Bourbonene	1384	1521	t	t	t	A, B
22	<b><math>\beta</math>-Cubebene</b>	<b>1387</b>	-	t	t	0.1	A, B
23	$\beta$ -Elemene	1390	1567	1.3	1.8	1.8	A, B
24	<b><i>cis</i>-Jasmone</b>	<b>1394</b>	-	0.1	0.1	0.2	A, B
25	$\beta$ -Caryophyllene	1421	1591	0.7	0.8	1.0	A, B
26	$\beta$ -Gurjunene	1433	-	0.4	0.6	0.5	A, B
27	$\gamma$ -Elemene	1435	-	0.3	0.4	0.3	A, B
28	$\alpha$ -Humulene	1454	1644	0.7	0.9	0.8	A, B
29	<b>Germacrene D</b>	<b>1480</b>	<b>1691</b>	<b>56.7</b>	<b>75.5</b>	<b>69.7</b>	A, B, C
30	<b><i>epi</i>-Cubebol</b>	<b>1496</b>	-	0.2	0.3	0.2	A, B
31	$\alpha$ -Muurolene	1499	1709	0.3	0.4	0.4	A, B
32	<i>trans</i> - $\beta$ -Guaiene†	1502	-	0.1	0.3	0.2	A, B
33	$\beta$ -Bulnesene	1508	-	0.1	0.2	0.1	A, B
34	$\gamma$ -Cadinene	1515	1740	0.2	0.1	0.1	A, B
35	Cubebol	1515	-	0.1	0.2	0.2	A, B
36	$\delta$ -Cadinene	1519	1748	0.6	0.7	0.5	A, B
37	$\alpha$ -Cadinene	1538	1772	t	t	t	A, B
38	Elemol	1550	1801	1.4	2.5	2.6	A, B, C
39	Germacrene B	1559	-	0.4	0.2	0.2	A, B
40	Germacrene D-4-ol	1575	-	t	0.2	0.3	A, B
41	Guaiol†	1594	-	0.1	0.2	0.3	A, B
42	1- <i>epi</i> -Cubebol	1616	-	0.5	1.0	1.2	A, B
43	<i>epi</i> - $\alpha$ -Cadinol	1643	2154	0.5	0.7	0.4	A, B
44	<b><math>\beta</math>-Eudesmol</b>	<b>1653</b>	-	0.2	0.5	0.4	A, B
45	Selin-11-en-4- $\alpha$ -ol	1653	-	0.6	0.7	0.5	A, B
	<b>Total identified</b>			<b>95.2</b>	<b>94.1</b>	<b>92.3</b>	

RI<sub>1</sub>, retention indices relative to homologous series of *n*-alkanes (C<sub>8</sub>-C<sub>25</sub>) hydrocarbons on Equity-5 capillary column, RI<sub>2</sub>, retention indices relative to homologous series of *n*-alkanes (C<sub>8</sub>-C<sub>25</sub>) hydrocarbons (Polyscience Corp. Niles IL) on CP-Wax 52 CB capillary column.

synthase and (-)-germacrene D synthase, have been reported from *S. canadensis*. Furthermore, it was established that both synthases catalyze the formation of enantiomerically pure products [4c,4d]. No previous work has been reported on the essential oil and enantiomeric composition of *S. canadensis* from India. In the present communication, we report the essential oil composition and enantiomeric differentiation of chiral terpenoids of *S. canadensis* growing in the Kumaon region of India.

The comparative composition of *S. canadensis* oil is depicted in Table 1. Germacrene D (Entry 29) was characterized as the main constituent, but with varied

composition 56.7, 75.5, and 69.7%, respectively in the three oil samples. Other significant compounds were limonene (Entry 9, 0.2 to 12.5%),  $\alpha$ -pinene (Entry 1, t to 5%),  $\beta$ -myrcene (Entry 5, t to 2.8%), sabinene (Entry 3, 0.2 to 2.4%), and bornyl acetate (Entry 18, 2.1 to 2.9%). Apart from the above, other sesquiterpene hydrocarbons, such as  $\delta$ -elemene,  $\beta$ -elemene,  $\beta$ -caryophyllene,  $\alpha$ -humulene, and  $\delta$ -cadinene and oxygenated sesquiterpenes, including elemol, have also been detected in significant percentages. Similarly, among the oxygenated monoterpenes, bornyl acetate (Entry 18), terpinen-4-ol (Entry 16), and linalool (Entry 15) have been noticed.

**Table 2:** Enantiomeric excess (in %) of predominant enantiomer of chiral terpenes in *Solidago canadensis* essential oil by enantioselective capillary gas chromatography (eGC) using permethylated  $\beta$ -cyclodextrin as stationary phase (see Experimental).

Entry	Enantiomers*	<i>Solidago canadensis</i> Aerial parts (%)					
		Sample I		Sample II		Sample III	
		eGC-FID	enantiomeric excess	eGC-FID	enantiomeric excess	eGC-FID	enantiomeric excess
(1a)	(1S)-(-)- $\alpha$ -pinene	1.2					
(1b)	(1R)-(+)- $\alpha$ -pinene	3.4	>47.9	-	-	-	-
(4a)	(1R)-(+)- $\beta$ -pinene	0.4					
(4b)	(1S)-(-)- $\beta$ -pinene	0.7	>30.3	-	-	-	-
(5a)	( $\pm$ )- $\beta$ -myrcene	2.5	-	-	-	-	-
(3a)	( $\pm$ )-sabinene	1.8	-	-	-	-	-
(9a)	(S)-(-)-limonene	0.3	-	-	-	-	-
(9b)	(R)-(+)-limonene	12.7	>95.1	-	-	3.8	>99
(18a)	(-)-bornyl acetate	2.4	>99	4.7	>99	5.3	>99
(29a)	(+)-germacrene D	37.3	>41.8	50.5	>47	49	>45.3
(29b)	(-)-germacrene D	15.3		18.2		18.4	

\*Compounds are listed in elution order from SUPELCO  $\beta$ -DEX 110 capillary column, enantiomeric excess (in %) calculated only for predominant enantiomer.

Enantioselective capillary gas chromatography of all three oils showed variation in terms of enantiomeric ratios and enantiomeric excess among the different enantiomeric pairs. The enantiomeric distributions have been reported in terms of their enantiomeric excess (ee) with respect to the predominant isomers (Table 2). Among monoterpenes, only limonene showed high optical purity, the (+)-enantiomer prevailing (more than 97%, i.e., 95% ee) in sample I and 99% ee in sample III, while sample II did not contain any one of them, even in traces.  $\alpha$ -Pinene showed optical purity (74%) for the (1R)-(+)-enantiomer, which is equivalent to 47.9% in terms of ee, and (1S)-(-)- $\beta$ -pinene was found to be with a lowest optical purity (30.3%) in sample I and was not observed in the other samples. In contrast to these pairs, (-)-bornyl acetate was an exception, as it was noticed as a single enantiomer with ee >99% in all three samples, but the presence of a small proportion of (+)-bornyl acetate could not be excluded. The (+)- and (-)-germacrene D enantiomers appear with 70.9 and 29.1% optical purity, which corresponds to 41.8% enantiomeric excess for the (+)-enantiomer in sample I. On the other hand, in the other two samples, ee corresponding to >47% and >45% have been recorded for the (+)-enantiomer. However, both enantiomers have been reported previously in equal amounts from *S. canadensis*.

Interestingly, these reports do not agree with our results. Therefore, the enantiomeric ratios for our oil samples are new. Furthermore, the enantiomeric compositions revealed four pairs of bioactive chiral terpenoids, viz., (1S)-(-)- $\alpha$ -pinene (Entry 1a), and (1R)-(+)- $\alpha$ -pinene (Entry 1b), (1R)-(+)- $\beta$ -pinene (Entry 4a), and (1S)-(-)- $\beta$ -pinene (Entry 4b), (S)-(-)-limonene (Entry 9a), and (R)-(+)-limonene (Entry 9b), and (+)-germacrene D (Entry 29a), and

(-)-germacrene D (Entry 29b) in *S. canadensis*. Only (-)-bornyl acetate (Entry 18a) was observed as a single enantiomer. However, compositional variations have been observed in all *S. canadensis* oil samples. GC and GC-MS results showed high percentages of germacrene D (56.7 to 75.5%), along with limonene (0.2 to 12.5%) in all the oil samples. An earlier report revealed a high  $\alpha$ -pinene (59.5%) content, besides germacrene D (19.8%) and limonene (9.7%) [3d], while another reported curlone (23.5%), germacrene D (19.8%),  $\alpha$ -pinene (14.7%),  $\beta$ -sesquiphellandrene (10.4%), limonene (9.3%), and myrcene (4.2%) [3a]. Notably, these have previously been erroneously identified as  $\gamma$ -cadinene and  $\delta$ -cadinene [5]. However, the absence of curlone and  $\beta$ -sesquiphellandrene makes the essential oil composition entirely different.

In conclusion, enantioselective capillary GC is an efficient method for stereochemical assignments of the chiral terpenoids present in essential oils. *S. canadensis* growing wild in the Kumaon region contained (+/-)-germacrene D in variable enantiomeric ratios, with an overall predominance of the (+)-form. Therefore, the enantiomeric ratio for the major enantiomer appears to be independent of the geographical origin of the plant and thus, any variation in the characteristic value may be regarded as adulteration. These results also support the usefulness of the enantiomeric ratios and enantiomeric excess of bioactive chiral terpenes in authenticity studies of the essential oil.

## Experimental

**General:** A PerkinElmer Autosystem XL gas chromatograph was used, fitted with an EQUITY-5 column (60 m x 0.32 mm, film thickness 0.25  $\mu$ m, SUPELCO). The column temperature ranged from

70-250°C, programmed at 3°C/min, with a final hold time of 2 min., using H<sub>2</sub> as carrier gas at 10 psi constant pressure, a split ratio of 1: 30, an injection size of 0.03 µL neat, and injector and detector (FID) temperatures of 250°C and 280°C, respectively. The enantioselective capillary GC analysis was conducted on a Varian CP-3800 GC fitted with a β-DEX 110 fused silica capillary column (30 m x 0.25 mm x 0.25 µm film thickness, SUPLECO). The column temperature of 60°C -180°C was programmed at 3°C/min with an initial hold time of 2 min., then 180°C-220°C at a rate of 3.5°C/min, with a final hold time of 7 min. using H<sub>2</sub> as carrier gas at 10 psi constant pressure, split ratio 1:100, an injection size 0.06 µL neat, and injector and detector (FID) temperatures of 220°C and 250°C, respectively. GC/MS utilized a PerkinElmer Autosystem XL GC interfaced with a Turbomass Quadrupole Mass spectrometer fitted with an EQUITY-5 (SUPELCO) fused silica capillary column (60 m x 0.32 mm; 0.25 µm film coating). The oven temperature program was the same as that used in GC, while the injector, transfer line and sources temperatures were 250°C. The injection size was 0.03 µL neat, and a split ratio of 1:30 was used with He as carrier gas at 10 psi constant pressure. MS were taken at 70 eV with a mass range of m/z 40-450. Characterization was achieved on the basis of retention time, Kovats Index, relative retention index using a homologous series of *n*-alkanes (C<sub>8</sub>-C<sub>25</sub> hydrocarbons, Polyscience Corp.

Niles IL), coinjection with enantiomeric standards (Sigma Aldrich), mass spectra library search (NIST and Wiley), and by comparing with the mass spectral literature data [6a]. The relative amounts of individual components were calculated based on GC peak areas without using correction factors.

**Plant material:** The aerial parts of three *Solidago canadensis* plants were collected in June 2007 at the young stage of development from three different locations in Bhimtal (1500 m), Kumaon, India. The plant identifications (voucher specimens CSC 62301 to 62303) were confirmed by Prof. YPS Pangtey, and deposited in the Botany Department, Kumaun University, Nainital, India.

**Extraction and isolation of oils:** The aerial parts of fresh plants of all the three samples were subjected to hydrodistillation in a Clevenger type apparatus (0.2 kg each) for 3 h [6b]. The distillate was saturated with NaCl and the oil was extracted with *n*-hexane and dichloromethane. The solvent phase was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then the solvent distilled off in a thin film rotary vacuum evaporator at 35°C. The oil samples were stored at -20°C until analyzed. The oil yields of sample I to III were 0.35%, 0.32% and 0.30%, respectively.

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