

Cyclodextrin based Gas Chromatography and GC/MS methods for determination of chiral pair constituents in mint essential oils

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Supplementary Material

Materials and Methods

Method 2

A β -DEX 110 (Supelco, Bellefonte, PA) chiral column consist of 10% 2,3,6-trimethyl- β -cyclodextrin (wt %) in 35% diphenyl/65% dimethylpolysiloxane (PM- β -CD) fused silica capillary column with dimensions of 30 m x 0.25 mm id and film thickness of 0.25 μ m was used in method 1. Injector temperature was 220°C and carrier gas was at 1.8 mL/min constant flow with a split ratio of 1:140. The FID detector temperature was 250°C. The column oven was initially at 60°C with a hold time of 2 mins and increased at the rate of 3°C/min to 180°C (hold for 2 min) and further increased at the rate of 3.5°C/min upto 220°C with final hold time of 5 min.

Method 3

A γ -DEX 120 (Supelco, Bellefonte, PA) chiral column comprised of 20% 2,3,6-trimethyl- γ -cyclodextrin (wt%) in 35% phenyl/65% dimethylsiloxane (PM- γ -CD) fused silica capillary column with dimensions of 30 m x 0.25 mm id and film thickness of 0.25 μ m was used in method 3. Injector temperature was 240°C and carrier gas flow rate at 1.4 mL/min constant flow with split ratio of 1:140. The FID detector temperature was 240°C. The column oven was initially at 40°C and increased at the rate of 3°C/min to 100°C (hold for 15 min), and further increased at the rate of 5°C/min to 220°C (hold for 2 min).

Method 4

A RtTM- β -DEXsa (Restek U.S., Bellefonte, PA) chiral column consist of 2,3-diacetoxy-6-*tert*-butyldimethylsilyl- β -cyclodextrin with 14% cyanopropylphenyl/86% dimethyl polysiloxane (TBDA- β -CD) fused silica capillary column with dimension of 30m x 0.25 mm id and film thickness of 0.25 μ m. Injector temperature was 220°C with carrier gas flow rate at 2 mL/min constant flow and split ratio of 1:140. The FID detector temperature was 230°C. The column oven was initially at 70°C then increased at the rate of 3°C/min to 110°C (hold for 5 min), and further at the rate of 1°C/min to 120°C and increased at the rate of 5°C/min to 220°C.

Method 5

A RtTM- γ -DEXsa (Restek U.S., Bellefonte, PA) chiral column made up of 2,3-diacetoxy-6-*tert*-butyldimethylsilyl- γ -cyclodextrin added into 14% cyanopropylphenyl/86% dimethyl polysiloxane (TBDA- γ -CD) fused silica capillary column with dimension of 30m x 0.25 mm id and film thickness of 0.25 μ m was used in method 4. The carrier gas flow rate was kept at 1.4 mL/min constant flow with a split ratio of 1:140 and injector temperature was maintained at 220°C. The FID detector temperature was kept at 230°C. The column oven temperature was initially at 70°C and increased at the rate of 3°C/min to 100°C and further increased at the rate of 4°C/min until 220°C with a final hold time of 2 min.

Table S1 Relative percentage of identified essential oils constituents of *Mentha arvensis* cultivars

Compound	RI ₁ *	RI ₂ *	Kosi	CIM	Kalka	Kushal	Sambhav	Saksham	Damroo	Himalaya	Gomti	Shivalik
α -Pinene	1015	936	0.7 $\pm$ 0.1	0.7 $\pm$ 0.0	0.7 $\pm$ 0.1	0.7 $\pm$ 0.0	0.6 $\pm$ 0.0	0.7 $\pm$ 0.2	0.7 $\pm$ 0.0	0.7 $\pm$ 0.1	0.7 $\pm$ 0.1	0.7 $\pm$ 0.0
α -Thujene	1019	928	nd	t	t	nd	t	t	t	t	nd	nd
Diethyl tetrahydrofuran	1032	-	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	t	0.1 $\pm$ 0.1	0.1 $\pm$ 0.0	0.2 $\pm$ 0.1	nd	0.1 $\pm$ 0.0
C ₁₀ H ₁₆	-	-	nd	t	t	nd	t	t	t	t	nd	nd
Camphene	1041	951	t	t	t	nd	nd	nd	nd	t	nd	nd
β -Pinene	1100	981	0.8 $\pm$ 0.0	0.7 $\pm$ 0.1	0.8 $\pm$ 0.1	0.8 $\pm$ 0.1	0.6 $\pm$ 0.1	0.8 $\pm$ 0.2	0.8 $\pm$ 0.0	0.8 $\pm$ 0.1	0.8 $\pm$ 0.0	0.8 $\pm$ 0.0
Sabinene	1113	975	0.3 $\pm$ 0.1	0.3 $\pm$ 0.0	0.3 $\pm$ 0.0	0.3 $\pm$ 0.0	0.4 $\pm$ 0.1	0.3 $\pm$ 0.1	0.3 $\pm$ 0.0	0.3 $\pm$ 0.0	0.3 $\pm$ 0.1	0.3 $\pm$ 0.0
β -Myrcene	1157	991	0.6 $\pm$ 0.1	0.6 $\pm$ 0.1	0.6 $\pm$ 0.0	0.6 $\pm$ 0.1	0.6 $\pm$ 0.1	0.5 $\pm$ 0.1	0.6 $\pm$ 0.1	0.6 $\pm$ 0.0	0.6 $\pm$ 0.0	0.6 $\pm$ 0.1
Limonene	1188	1031	2.9 $\pm$ 0.2	3.1 $\pm$ 0.1	3.2 $\pm$ 0.6	1.9 $\pm$ 0.4	2.4 $\pm$ 0.2	1.7 $\pm$ 0.6	1.3 $\pm$ 0.3	1.9 $\pm$ 0.2	1.2 $\pm$ 0.1	1.2 $\pm$ 0.4
1,8-Cineole	1200	1034	0.1 $\pm$ 0.1	0.1 $\pm$ 0.1	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.4 $\pm$ 0.1	0.3 $\pm$ 0.1
(Z)- β -Ocimene	1228	1035	nd	nd	t	nd	t	t	t	nd	t	nd
γ -Terpinene	1234	1060	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
(E)- β -Ocimene	1258	1045	nd	t	t	nd	t	t	t	nd	nd	nd
Terpinolene	1269	1091	nd	t	nd	t	nd	nd	nd	nd	nd	nd
Cis-3-Hexenol	1383	851	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1	0.1 $\pm$ 0.0	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.1 $\pm$ 0.0	0.2 $\pm$ 0.1	0.1 $\pm$ 0.0	t	0.1 $\pm$ 0.1
3-Octanol	1394	997	0.3 $\pm$ 0.0	0.3 $\pm$ 0.1	0.2 $\pm$ 0.1	0.9 $\pm$ 0.1	0.3 $\pm$ 0.0	0.8 $\pm$ 0.1	0.5 $\pm$ 0.1	0.8 $\pm$ 0.1	0.9 $\pm$ 0.1	0.4 $\pm$ 0.2
Menthone	1450	1161	4.6 $\pm$ 0.4	4.9 $\pm$ 0.5	6.2 $\pm$ 2.2	6.1 $\pm$ 0.8	7.7 $\pm$ 1.4	4.7 $\pm$ 1.1	9.4 $\pm$ 2.3	5.3 $\pm$ 0.8	11.2 $\pm$ 2.1	6.2 $\pm$ 2.2
Isomenthone	1475	1170	3.2 $\pm$ 0.1	3.1 $\pm$ 0.1	3.3 $\pm$ 0.1	3.1 $\pm$ 0.1	3.3 $\pm$ 0.3	2.9 $\pm$ 0.1	3.8 $\pm$ 0.2	3.1 $\pm$ 0.4	3.3 $\pm$ 0.2	4.4 $\pm$ 0.3
Cis -3-hexenyl isovalerate	1480	1236	0.3 $\pm$ 0.0	0.3 $\pm$ 0.0	0.3 $\pm$ 0.1	0.4 $\pm$ 0.0	0.2 $\pm$ 0.0	0.3 $\pm$ 0.1	0.2 $\pm$ 0.1	0.3 $\pm$ 0.0	0.2 $\pm$ 0.0	0.2 $\pm$ 0.1
β -Bourbonene	1495	1391	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	t	nd	t	t	nd	nd	0.1 $\pm$ 0.0
Dihydroedulan	1499	1298	0.1 $\pm$ 0.0	t	t	t	nd	t	nd	nd	nd	nd
Unknown		-	nd	t	t	nd	nd	t	nd	nd	nd	nd
Menthyl acetate & Linalool ^s	1550	1296& 1098	5.0 $\pm$ 2.4	5.4 $\pm$ 2.6	6.3 $\pm$ 5.7	2.3 $\pm$ 0.8	4.0 $\pm$ 1.3	3.8 $\pm$ 0.6	t	2.2 $\pm$ 0.7	3.4 $\pm$ 0.3	2.1 $\pm$ 0.3
Unknown	1554	-	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.1 $\pm$ 0.0	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.0	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1
Isopulegol	1559	1150	0.8 $\pm$ 0.1	0.7 $\pm$ 0.1	0.8 $\pm$ 0.1	0.6 $\pm$ 0.2	0.4 $\pm$ 0.1	0.5 $\pm$ 0.1	0.8 $\pm$ 0.1	0.5 $\pm$ 0.1	0.4 $\pm$ 0.1	0.7 $\pm$ 0.1
Isomenthyl acetate	1563	-	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.3 $\pm$ 0.2	t	0.2 $\pm$ 0.1	0.1 $\pm$ 0.1	t	0.1 $\pm$ 0.0	nd	0.1 $\pm$ 0.1
β -Caryophyllene	1570	1426	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1	0.3 $\pm$ 0.0	0.3 $\pm$ 0.1	0.4 $\pm$ 0.11	0.3 $\pm$ 0.1	0.3 $\pm$ 0.0	0.3 $\pm$ 0.1	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1
Neomenthol	1588	1170	2.1 $\pm$ 0.2	2.1 $\pm$ 0.3	2.1 $\pm$ 0.1	2.5 $\pm$ 0.3	2.1 $\pm$ 0.1	2.1 $\pm$ 0.7	1.8 $\pm$ 0.6	2.5 $\pm$ 0.2	1.8 $\pm$ 0.1	2.3 $\pm$ 0.4
Terpinen-4-ol	1592	1178	c	c	c	c	c	c	c	c	c	c
Neoisomenthol	1617	1193	0.3 $\pm$ 0.0	0.3 $\pm$ 0.1	0.3 $\pm$ 0.1	0.3 $\pm$ 0.1	0.2 $\pm$ 0.1	0.3 $\pm$ 0.1	0.2 $\pm$ 0.0	0.3 $\pm$ 0.1	0.1 $\pm$ 0.0	0.4 $\pm$ 0.1

Pulegone	1626	1242	0.2±0.1	0.2±0.1	0.2±0.1	t	t	t	0.4±0.3	t	0.1±0.0	0.1±0.0
Menthol	1636	1181	74.7±1.9	73.7±2.9	71.9±7.1	76.3±1.8	74.3±0.9	77.3±3.1	76.0±2.1	77.5±1.1	71.9±2.2	75.3±2.8
Unknown	1655	-	0.1±0.0	0.1±0.0	0.1±0.0	0.1±0.0	t	t	t	t	nd	0.2±0.1
Isomenthol	1659	1188	0.1±0.1	0.1±0.1	0.1±0.0	0.3±0.3	0.2±0.1	0.4±0.2	0.2±0.1	0.3±0.2	0.2±0.2	0.2±0.1
Germacrene D	1680	1488	0.5±0.1	0.6±0.1	0.5±0.1	0.4±0.0	0.2±0.1	0.3±0.1	0.4±0.0	0.4±0.1	0.4±0.2	0.8±0.3
α -Terpineol	1690	1195	0.1±0.1	0.2±0.1	0.2±0.1	0.2±0.1	0.1±0.1	0.2±0.1	0.2±0.0	0.2±0.0	0.1±0.0	0.3±0.1
C ₁₀ H ₁₈ O	1703	-	0.1±0.0	t	t	t	t	t	0.1±0.0	t	t	t
Piperitone	1706	1258	0.5±0.1	0.4±0.0	0.5±0.1	0.6±0.1	0.8±0.1	0.5±0.1	0.3±0.0	0.6±0.1	0.6±0.1	0.3±0.1
Carvone	1708	1248	t	t	t	t	t	t	t	t	t	t
Total			99.5	99.1	99.8	99.4	99.5	99.0	99.0	99.4	99.1	98.8

Retention Index: RI₁ on Supelcowax 10 capillary column and RI₂ on DB-5 capillary column, both using a homologous series of *n*-alkane (C₆-C₂₈) hydrocarbons, Polyscience Corp. Niles IL); *: Comparison of experimental and literature reported RI are listed in Table S2; -: RI not reported or unknown, t: trace (< 0.1%), nd: not detected; ^scoeluting with previous compound; CIM: CIM Saryu.

Table S2. Relative percentage of identified essential oils constituents of *Mentha piperita* cultivars

Compound	RI _{1a}	RI _{1b}	RI _{2a}	RI _{2b}	Percentage composition				
					CIM-Indus	CIM-Madhuras	Pranjai	Kukrail	Tushar
α -Pinene	1015	1027	936	932	0.7 $\pm$ 0.1	0.8 $\pm$ 0.0	0.8 $\pm$ 0.1	0.8 $\pm$ 0.1	0.9 $\pm$ 0.0
α -Thujene	1019	1030	928	924	nd	t	nd	nd	nd
2,5-Diethyl tetrahydrofuran	1032	nr	-	-	nd	nd	t	t	t
Camphene	1041	1070	951	946	nd	t	nd	t	t
β -Pinene	1100	1110	981	974	1.1 $\pm$ 0.0	1.1 $\pm$ 0.1	1.2 $\pm$ 0.0	1.2 $\pm$ 0.0	1.3 $\pm$ 0.1
Sabinene	1113	1123	975	969	0.6 $\pm$ 0.0	0.6 $\pm$ 0.1	0.7 $\pm$ 0.0	0.6 $\pm$ 0.0	0.7 $\pm$ 0.1
β -Myrcene	1157	1167	991	988	0.3 $\pm$ 0.0	0.2 $\pm$ 0.0	0.3 $\pm$ 0.0	0.3 $\pm$ 0.0	0.3 $\pm$ 0.0
α -Terpinene	1168	1181	1019	1014	0.2 $\pm$ 0.1	2.4 $\pm$ 0.2	0.2 $\pm$ 0.1	0.3 $\pm$ 0.1	0.2 $\pm$ 0.0
Limonene	1188	1199	1031	1024	2.2 $\pm$ 0.1	5.0 $\pm$ 0.5	2.7 $\pm$ 1.0	2.3 $\pm$ 0.3	2.9 $\pm$ 0.9
1,8-Cineole	1200	1212	1034	1026	4.9 $\pm$ 0.1	0.2 $\pm$ 0.1	6.2 $\pm$ 0.1	5.7 $\pm$ 0.3	7.0 $\pm$ 0.4
(Z)- β -Ocimene	1228	1239	1035	1032	0.2 $\pm$ 0.2	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.3 $\pm$ 0.1
γ -Terpinene	1234	1249	1060	1054	0.4 $\pm$ 0.1	0.4 $\pm$ 0.0	0.3 $\pm$ 0.1	0.4 $\pm$ 0.2	0.4 $\pm$ 0.0
(E)- β -Ocimene	1258	1252	1045	1044	t	nd	nd	t	0.1 $\pm$ 0.0
p-Cymene	1259	1276	1026	1020	0.1 $\pm$ 0.0	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1
Terpinolene	1269	1286	1091	1086	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0
Cis-3-Hexenol	1383	1391	851	850	0.1 $\pm$ 0.0	0.1 $\pm$ 0.1	0.1 $\pm$ 0.0	0.1 $\pm$	0.1 $\pm$ 0.0
3-Octanol	1394	1394	997	988	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0
Menthone	1450	1460	1161	1148	30.8 $\pm$ 4.6	28.9 $\pm$ 2.5	22.5 $\pm$ 0.4	28.9 $\pm$ 1.2	20.5 $\pm$ 6.0
Cis-sabinene hydrate	1461	1463	1069	1065	1.0 $\pm$ 0.7	0.8 $\pm$ 0.5	1.3 $\pm$ 0.3	1.1 $\pm$ 0.9	0.7 $\pm$ 0.2
Menthofuran	1466	1483	1170	1159	3.8 $\pm$ 2.0	5.4 $\pm$ 4.0	4.5 $\pm$ 1.1	5.0 $\pm$ 2.7	3.0 $\pm$ 1.0
Unknown	1471	-	-	-	t	0.1 $\pm$ 0.0	0.1	0.1	0.1
Isomenthone	1475	1488	1170	1158	4.7 $\pm$ 0.2	4.4 $\pm$ 0.1	3.9 $\pm$ 0.6	4.3 $\pm$ 0.0	3.8 $\pm$ 0.4
Cis-3-hexenyl isovalerate	1480	nr	1236	1232	nd	nd	nd	t	nd
β -Bourbonene	1495	1508	1391	1387	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.2 $\pm$ 0.0	0.1 $\pm$ 0.1	0.2 $\pm$ 0.0
Dihydroedulan	1499	1496	1298	1293 ^{JCB}	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0
Neomenthyl acetate	1516	nr	1277	1271	0.3 $\pm$ 0.3	0.3 $\pm$ 0.2	0.4 $\pm$ 0.1	0.4 $\pm$ 0.2	0.5 $\pm$ 0.2
Trans-sabinene hydrate	1543	1562	-	-	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.1	0.1 $\pm$ 0.0
Menthyl acetate +Linalool ^S	1550	1537	1296	1294&	4.1 $\pm$ 2.5	4.1 $\pm$ 1.4	5.7 $\pm$ 0.6	4.2 $\pm$ 1.3	6.7 $\pm$ 2.0
		1535	&1098	1095					
Unknown	1554	-	-	-	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0
Isopulegol	1559	1574	-	-	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0	0.1 $\pm$ 0.0
Isomenthyl acetate	1563	nr	-	-	0.2 $\pm$ 0.2	0.2 $\pm$ 0.1	0.4 $\pm$ 0.0	0.3 $\pm$ 0.1	0.4 $\pm$ 0.0
β -Caryophyllene	1570	1590	1426	1417	2.5 $\pm$ 0.1	2.5 $\pm$ 0.4	3.1 $\pm$ 0.4	2.6 $\pm$ 0.5	2.9 $\pm$ 0.1

Neomenthol	1588	1595	1170	1161	3.0±0.1	2.7±0.3	3.0±0.3	3.0±0.3	3.1±0.4
Terpinen-4-ol	1592	1606	1178	1174	1.0±0.2	1.0±0.4	0.8±0.1	1.1±0.4	1.1±0.1
Neoisomenthol	1617	nr	1193	1184	0.4±0.1	0.4±0.1	0.6±0.1	0.4±0.0	0.6±0.1
Pulegone	1626	1646	1242	1233	1.2±0.2	1.6±1.0	1.3±0.6	1.6±1.0	1.0±0.5
Menthol	1636	1650	1181	1167	30.8±0.9	31.2±0.7	33.8±2.0	29.3±1.1	34.9±1.9
α -Humulene	1641	1675	1460	1452	0.2±0.1	0.1±0.1	0.2±0.1	0.1±0.1	0.2±0.2
Unknown	1655	-	1396	-	0.3±0.0	0.4±0.1	0.4±0.1	0.4±0.1	0.4±0.0
Isomenthol	1659	1673	1188	1179	0.1±0.0	0.1±0.0	0.2±0.0	0.1±0.0	0.2±0.1
(Z)- β -Farnesene	1665	1671	1458	1440	0.2±0.0	0.2±0.0	0.2±0.0	0.3±	0.3±0.1
Germacrene D	1680	1701	1488	1484	1.8±0.5	1.8±0.8	2.3±0.8	2.0±0.9	2.1±0.3
α -Terpineol	1690	1697	1195	1186	0.4±0.0	0.5±0.0	0.5±0.1	0.4±0.0	0.5±0.1
C ₁₀ H ₁₈ O	1703	-	-	-	0.4±	0.2±0.2	0.4±	0.3±0.2	0.3±0.2
Piperitone	1706	1725	1258	1249	0.5±0.3	0.6±0.2	0.3±0.3	0.6±0.1	0.6±0.1
Bicyclogermacrene	1727	1756	1494	1500	t	t	0.2±	0.2	0.1±
Viridiflorol	2050	2042	1590	1592	0.4±0.2	0.4±0.3	0.6±0.32	0.5±0.3	0.5±0.1
Total					99.8	99.5	99.9	99.9	99.6

Compounds listed as per their elution in Supelcowax 10 column. Retention Index (RI): (RI_{1a}) on Supelcowax 10 capillary column and (RI_{2a}) on DB-5 capillary column using a homologous series of *n*-alkane (C₆-C₂₈) hydrocarbons, Polyscience Corp. Niles IL; (RI_{1b}) and (RI_{2b}) reported in literature (SR1, SR2, SR3, SR4) on similar stationary phases; -: RI not reported or unknown, nr: RI not reported and identified based on mass spectrum, t: trace (< 0.1%), nd: not detected; ^scoelution observed in Supelcowax 10.

Table S3. Chiral Relative Retention Index values (cRRI) of enantiomers present in the essential oils of *M. arvensis* and *M. piperita*

Compounds	cRRI ^a	cRRI ^b	cRRI ^c	cRRI ^e	cRRI ^d
(1R)-(+)- α -Pinene	922	1015	{989}	{926}	993
(1S)-(-)- α -Pinene	924	1009			1000
(1R)-(+)- β -Pinene	954	1068	{1053}	{984}	{1052}
(1S)-(-)- β -Pinene	962	1073			
(+)-Sabinene	981	1043	{1044}	1005	1040
(-)-Sabinene	992	1052		1009	1037
(4S)-(-)-Limonene	1059	1100	{1101}	{1059}	{1078}
(4R)-(+)-Limonene	1073	1103			
(+)-Menthone	1214	{1273}	1291	1280	1345
(-)-Menthone	1210		1294	1274	1361
(+)-Isomenthone	1204	1286	1309	1277	1371
(-)-Isomenthone	1216	1294	1311	1280	1385
(+)-Terpinen-4-ol	1266	1349	1349	{1320}	{1362}
(-)-Terpinen-4-ol	1269	1353	1346		
(+)-Neomenthol	1276	1334	1340	1319	1365
(-)-Neomenthol	1285	1340	1345	1316	1370
(1R, 2S, 5R)-(-)-Menthol	1299	{1354}	1368	{1338}	1380
(1S, 2R, 5S)-(+)-Menthol	1302		1364		1374
(-)- α -Terpineol	1316	1387	1386	1373	1404
(+)- α -Terpineol	1326	1390	1390	1379	1408
(1R)-(-)-Menthyl acetate	1309	1374	1394	1368	1388
(1S)-(+)-Menthyl acetate	1331	1402	1395	1366	1385
(4R)-(-)-Piperitone	1346	1406	1446	1424	1514
(4S)-(+)-Piperitone	1352	1411	1451	1426	1547
(R)-(+)-Pulegone	1331	1381	1402	1374	1425
(S)-(-)-Pulegone	1335	1384	1404	1374	1427
(+)-Germacrene D	1490	1569	1581	{1536}	{1554}
(-)-Germacrene D	1495	1580	1583		

Note: Chiral relative retention index was calculated using a homologous series of n-alkanes.

Column : a - TBDE- β -CD; b - PM- β -CD; c -PM- γ -CD; d - TBDA- β -CD and e - TBDA- γ -CD chiral capillary columns. Parentheses show the co-elution of the enantiomers.

Table S4. Comparison of current method with published/ literature reports.

Compounds	Current work	Lit. 1	Lit. 2	Lit. 3
α -Pinene	ES, BER, CR	ES	ES	-
β -Pinene	ES, BER, CR	ES	ES	-
Sabinene	ES, BER, CR	ES	-	-
Limonene	ES, BER, CR	ES	ES	-
Menthone	ES, BER, CR	ES	ES	ES, BER
Isomenthone	ES, BER, CR	-	ES	ES, BER
Neomenthol	ES, BER, CR	-	-	ES, BER
Terpinen-4-ol	ES, BER, CR	-	-	-
Menthol	ES, BER, CR	ES	ES	ES, BER
Menthyl acetate	ES, BER, CR	ES	-	ES, BER
α -Terpineol	ES, BER, CR	ES	-	-
Pulegone	ES, BER, CR	-	ES	-
Piperitone	ES, BER, CR	-	-	-
GermacreneD	ES, BER, CR	-	-	-
Thujene	-	ES	-	-
Phellandrene	-	ES	-	-
Isomenthol	-	ES	ES	-
β -Caryophyllene	-	ES	-	-
Neoisomenthol	-	-	-	ES, BER
Chiral phases used	1	2	1	1
Enantiomers separated	14	12	8	6
Technique	Es-GC	Es-GC	Es-GC	MDGC

Note: ES – enantiomers separated, BER – both enantiomers reported, CR – chiral relative retention index reported for both separated enantiomers, Lit. 1 - Ruiz del Castillo et al., 2004; Lit. 2 – Bicchi et al., 1997; Lit. 3 - Faber et al., 1994

Table S5 . Matrix data for *Mentha arvensis* cultivars

Kosi	CIM *	Kalka	Kushal	Sambhav	Saksham	Damroo	Himalaya	Gomti	Shivalik
1.0000000									
0.6750000	1.0000000								
0.7250000	0.6500000	1.0000000							
0.4750000	0.5500000	0.5750000	1.0000000						
0.4250000	0.4500000	0.4000000	0.4500000	1.0000000					
0.5000000	0.4750000	0.6000000	0.5750000	0.4750000	1.0000000				
0.4500000	0.4750000	0.5500000	0.6500000	0.5250000	0.5500000	1.0000000			
0.4750000	0.5250000	0.5500000	0.7250000	0.4250000	0.6750000	0.5750000	0.5750000		
1.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.4250000	0.4750000	
0.4250000	0.4000000	0.4750000	0.5500000	0.6000000	0.4750000	0.6000000	0.4250000	0.4250000	0.6000000
0.5000000	1.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.5500000	0.5000000	0.0000000
0.5000000	0.5000000	0.5500000	0.4750000	0.4250000	0.4750000	0.5500000	0.4750000	0.4500000	0.4250000
0.4750000	0.5500000	1.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.0000000	0.5000000	0.0000000

*CIM: CIM Saryu

Table S6 . Matrix data for five *Mentha piperita* cultivars

CIM Indus	CIM Madhuras	Pranjal	Kukrail	Tushar
1.0000000				
0.5454545	1.0000000			
0.3409091	0.3636364	1.0000000		
0.3863636	0.5227273	0.4318182	1.0000000	
0.2500000	0.3181818	0.4545455	0.4090909	1.0000000

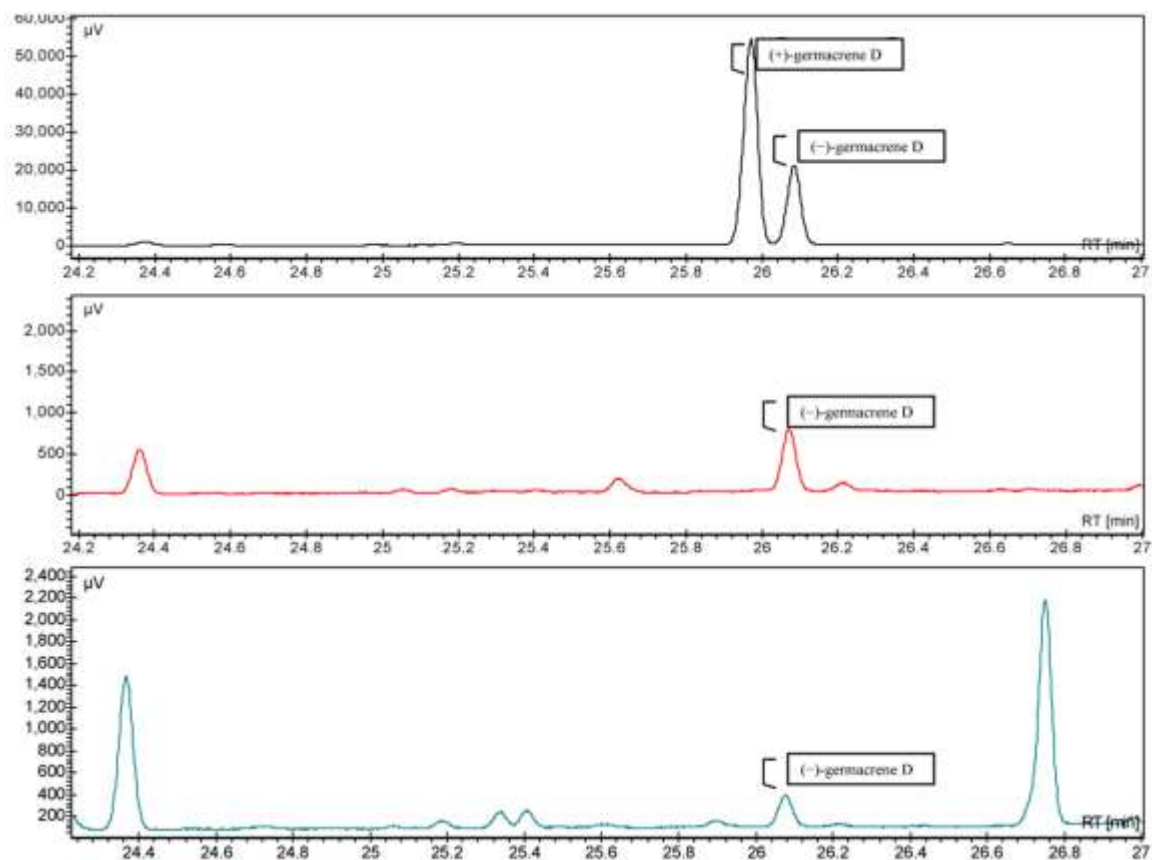
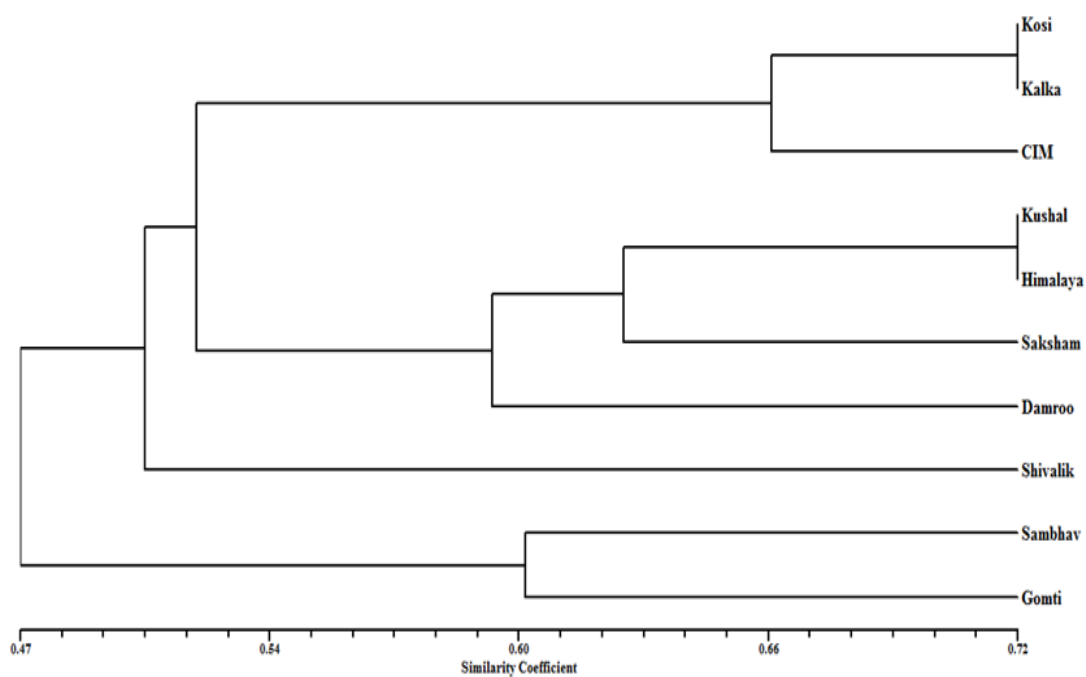


Fig. S1 Resolution of germacrene D enantiomers in TBDE- β -CD column

Note: Separation of germacrene D enantiomers in *Solidago canadensis* (Presence of both germacrene D enantiomers (top); Chiral chromatogram of *M. arvensis* essential oil ((+)-germacrene D not detected) (middle); Chiral chromatogram of *M. piperita* essential oil ((+)-germacrene D not detected) (bottom)



*CIM: CIM Saryu

Fig. S2 Enantiomeric ratio based dendrogram depicting relationship among different *Mentha arvensis* cultivars

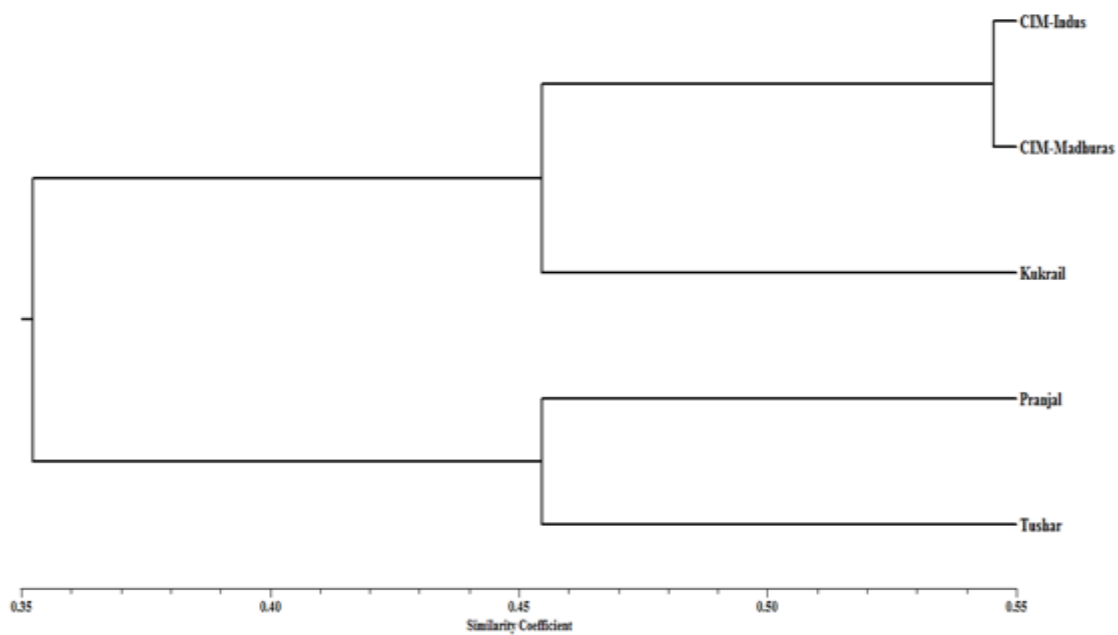


Fig. S3 Enantiomeric ratio based dendrogram depicting relationship among different *Mentha piperita* cultivars

Supplementary References

SR1.

K-J. Kim, Y-H. Kim, H-H. Yu, S-I. Jeong, J-D. Cha, B-S. Kil, Y-O. You, Antibacterial activity and chemical composition of essential oil of *Chrysanthemum boreale*. *Plant Medica*, 69, 274-277 (2003).

SR2.

R.S. Verma, V. Pandey, R.C. Padalia, D. Saikia, B Krishna, Chemical composition and antimicrobial potential of aqueous distillate volatiles of Indian peppermint (*Mentha piperita*) and spearmint (*Mentha spicata*). *Journal of Herbs, Spices & Medicinal Plants*, 17, 258–267 (2011).

SR3.

R.C. Padalia, R.S. Verma, A. Chauhan, V. Sundaresan, C.S. Chanotiya, Essential oil composition of sixteen elite cultivars of *Mentha* from western Himalayan region, India. *Maejo International Journal of Science and Technology*, 7(01), 83-93, (2013).

SR4.

M. Cirlini, P. Mena, M. Tassotti, K.A. Herrlinger, K.M. Nieman, C. Dall'Asta, D.D. Rio, Phenolic and volatile composition of a dry spearmint (*Mentha spicata* L.) extract. *Molecules*, 21, 1007, 1-15 (2016).