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Chemical compositions and enantiomeric distributions of leaf essential oils of three conifers from Oregon

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Abstract
Essential oils from conifers have been shown to be valuable in aromatherapy as well as topical medications. In this work, the leaves (needles) of *Abies procera* (noble fir), *Pinus contorta* subsp. *murrayana* (Sierra lodgepole pine), and *Tsuga heterophylla* (western hemlock) were collected from northern Oregon and the essential oils obtained by hydrodistillation. The essential oils were analyzed by gas chromatography – mass spectrometry (GC-MS) as well as chiral GC-MS. (–)-Limonene dominated the essential oil of *A. procera* (44.0%). The major components of *P. contorta murrayana* were β-phellandrene (37.2%; 99.6% (–)-enantiomer), β-pinene (17.0%; 97.8% (–)-enantiomer), and α-terpineol (11.6%; 96.6% (–)-enantiomer). *Tsuga heterophylla* essential oil showed α-terpineol (10.2%; 86.9% (–)-enantiomer), (+)-pulegone (7.6%), and beyerene (13.3%) as major constituents. This is the first characterization of the leaf volatiles from *A. nobilis*, *P. contorta murrayana*, and *T. heterophylla* from Oregon.

Keywords: Pinaceae, *Abies procera*, Pinus contorta, *Tsuga heterophylla*, essential oil composition, chiral GC-MS

1. Introduction
Several essential oils derived from the Pinaceae are commercially important for use in aromatherapy and topical therapy applications. These include *Abies balsamea* IL.) Mill. (balsam fir), *Abies sibirica* Ledeb. (Siberian fir), *Picea mariana* (Mill.) Britton, Sterns & Poggenb. (Black spruce), *Pinus sylvestris* L. (Scotch pine), and *Pseudotsuga menziesii* (Mirb.) Franco (Douglas fir). The Cascade Range of Oregon is home to several common members of the Pinaceae, including *Abies grandis* (Douglas ex D. Don) Lindl. (Grand fir), *Abies lasiocarpa* (Hook.) Nutt. (Subalpine fir), *Abies procera* Rehder (noble fir), *Pinus contorta* Douglas ex Loudon (lodgepole pine), *Tsuga heterophylla* (Raf.) Sarg. (Western hemlock), *Tsuga mertensiana* (Bong.) Carrière (mountain hemlock), and *P. menziesii* (Douglas fir) [1].
Abies procera Rehder, syn. *Abies nobilis* (Douglas ex D. Don) Lindl. (Pinaceae), Figure 1, is commonly called noble fir, red fir, and Christmas tree. The tree is native to the Cascade Range of Oregon and Washington [2]. It is a popular Christmas tree and has been cultivated as an exotic in suitable climates in northern Europe, including Denmark [3], Norway [4], Germany [5], Poland [6], Ireland [7], and Great Britain [8]. Paiute Native Americans used the leaves of *A. procera* as a remedy for colds [9]. Zavarin and co-workers had carried out an extensive examination of *A. procera* cortical oleoresin volatiles [10].

Fig 1: *Abies nobilis* from northern Oregon. A: Leaves (needles) and cones. B: bark.

Pinus contorta Douglas ex Loudon (Pinaceae) is native to western North America. There are three recognized subspecies of *P. contorta*: *P. contorta* subsp. *contorta*, shore pine, which ranges along the Pacific coast from southern Alaska, south to northwestern California; *P. contorta* subsp. *latifolia* (Engelm.) Critchf, Rocky Mountain lodgepole pine, which is found in the Rocky Mountains from the Yukon, south through Colorado; and *P. contorta* subsp. *murrayana* (Balf.) Engelm., Figure 2, Sierra lodgepole pine, found along the Cascade Range from Washington, through Oregon, and into northern California, and the Sierra Nevada Range in California [11, 12]. This tree has become a troublesome invasive in several locations, including New Zealand [13] and southern South America [14, 15].

Fig 2: *Pinus contorta* subsp. *murrayana* from northern Oregon.
A: Leaves (needles) and cone. **B:** bark.

Tsuga heterophylla (Raf.) Sarg., Figure 3, western hemlock (Pinaceae) is native to the northern Pacific Coast of North America from southern Alaska south to northern California, and an inland population found in the Rocky Mountains of British Columbia and northern Idaho [16]. Bella Coola and Hesquiat Native Americans used a poultice of *T. heterophylla* leaves to treat burns [9].

Fig 3: *Tsuga heterophylla* from northern Oregon.
A: Leaves (needles) and cone. **B:** bark.

The purpose of this investigation was to examine previously understudied conifers of the Pacific Northwest to add to our understanding of conifer volatile compositions. As far as we are aware, this is the first report of the leaf essential oils of *A. nobilis*, *P. contorta* subsp. *murrayana*, and *T. heterophylla* from Oregon.

2. Materials and Methods

2.1 Plant Material

Fresh plant material was collected from individual mature trees located in the Hoyt Arboretum near Portland, Oregon. The trees were identified by the staff of the Hoyt Arboretum and confirmed by E. Ankney using the field guide by Turner and Kuhlmann [1]. The fresh leaves (needles) of each tree species were hydro distilled for 3 h using a Likens-Nickerson apparatus with continuous extraction with dichloromethane to give colorless essential oils (Table 1).

Table 1: Collection and hydro distillation details of three conifers collected in Oregon.

Tree species	Collection site	Date, time	Mass leaves	Mass essential oil
Abies procera	45° 30′ 46″ N, 122° 42′ 49″ W, elev. 276 m	9-7-20, 12:57 pm	41.45 g	376.9 mg
Pinus contorta subsp. *murrayana*	45° 30′ 57″ N, 122° 42′ 47″ W, elev. 261 m	9-7-20, 12:30 pm	57.53 g	220.2 mg
Tsuga heterophylla	45° 30′ 59″ N, 122° 43′ 03″ W, elev. 230 m	9-7-20, 1:07 pm	21.36 g	223.9 mg

2.2 Gas Chromatography – Mass Spectrometry (GC-MS)

The leaf essential oils of *A. procera*, *P. contorta*, and *T. heterophylla* were subjected to gas chromatographic–mass spectral (GC–MS) analysis, as previously reported [17]: Shimadzu GCMS-QP2010 Ultra, electron impact (EI) mode with electron energy = 70 eV, scan range = 40–400 atomic mass units, scan rate = 3.0 scans/s, and Shimadzu GC-MS solution software v. 4.45 (Shimadzu Scientific Instruments, Columbia, MD, USA); ZB-5ms fused silica capillary GC column Phenomenex, Torrance, CA, USA; (5% phenyl)-polymethylsiloxane stationary phase, 0.25 µm film thickness; helium carrier gas, column head pressure = 552 kPa, flow rate = 1.37 mL/min; injector temperature = 260 °C, ion source temperature = 260 °C; GC oven temperature program: initial temperature = 50 °C, temperature increased 2 °C/min to 260 °C. For each sample, a 5% w/v solution in CH_2Cl_2 was prepared, and 0.1 µL was injected using a split ratio of 30:1. Identification of the individual components of the essential oils was determined by comparison of the Kovats retention indices, determined using a series of *n*-alkanes, in addition to comparison of the mass spectral fragmentation patterns with those found in the MS databases [18-21], using the LabSolutions GCMS solution software version 4.45 (Shimadzu Scientific Instruments, Columbia, MD, USA) and with matching factors > 90%.

2.3 Chiral GC-MS

Chiral GC–MS of the three leaf essential oils was carried out, as reported previously [17]: Shimadzu GCMS-QP2010S (Shimadzu Scientific Instruments, Columbia, MD, USA), electron impact (EI) mode, electron energy = 70 eV; scan range = 40–400 amu, scan rate = 3.0 scans/s; Restek B-Dex 325 chiral capillary GC column (Restek Corp., Bellefonte, PA, USA) (30 m × 0.25 mm ID × 0.25 µm film thickness). Oven temperature program: starting temperature = 50 °C, temperature increased 1.5 °C/min to 120 °C, then 2 °C/min to 200 °C, and kept at 200 °C for an additional 5 min; carrier gas was helium, flow rate = 1.8 mL/min. For each essential oil sample, a 3% w/v solution in CH_2Cl_2 was prepared, and 0.1 µL was injected using a split ratio of 1:45. The enantiomers of the monoterpenoids were identified by comparison of retention times with authentic samples obtained from Sigma-Aldrich (Milwaukee, WI, USA). The enantiomer percentages were determined from peak areas.

3. Results and Discussion

3.1 *Abies procera*

Hydrodistillation of the fresh leaves of *A. procera* gave a colorless essential oil in 0.909% (w/w) yield. The chemical composition of the essential oil is presented in Table 2. A total of 82 compounds were identified in the essential oil accounting for 100% of the composition. Monoterpene hydrocarbons dominated the essential oil with limonene (44.0%), β-phellandrene (19.9%), β-pinene (9.2%), and α-pinene (6.2%) as the major components. Although accounting for only 8.9% of the essential oil composition, there were 23 oxygenated monoterpenoids identified in *A. procera* leaf essential oil.

Table 2: Chemical composition of *Abies procera* leaf essential oil.

RI_{calc}	RI_{db}	Compound	% Composition	ED, (+):(–)
879	880	Santene	tr	
921	923	Tricyclene	0.1	
923	925	α-Thujene	0.1	57.1:42.9
931	932	α-Pinene	6.2	42.8:57.2
945	948	α-Fenchene	tr	
947	950	Camphene	1.1	100:0
970	971	Sabinene	0.1	
976	978	β-Pinene	9.2	2.4:97.6
987	989	Myrcene	2.8	
1003	1004	*p*-Mentha-1(7),8-diene	tr	
1005	1006	α-Phellandrene	1.5	75.3:24.7
1007	1008	δ-3-Carene	0.4	100:0
1013	1015	1,4-Cineole	0.1	
1015	1017	α-Terpinene	0.4	100:0
1023	1025	*p*-Cymene	0.2	
1029	1030	Limonene	44.0	0:100
1031	1031	β-Phellandrene	19.9	2.2:97.8
1033	1034	(*Z*)-β-Ocimene	0.2	
1056	1057	γ-Terpinene	0.7	
1083	1086	Terpinolene	1.8	
1089	1090	2-Nonanone	tr	
1098	1099	Linalool	tr	
1099	1099	*trans*-Sabinene hydrate	tr	
1117	1119	*endo*-Fenchol	0.1	
1122	1124	*cis*-*p*-Menth-2-en-1-ol	0.7	
1124	1126	α-Campholenal	tr	
1133	1136	Terpin-3-en-1-ol	tr	
1140	1142	*trans*-*p*-Menth-2-en-1-ol	0.5	
1145	1145	Camphor	tr	
1153	1156	Camphene hydrate	0.1	
1162	1158	Menthone	0.1	
1169	1170	Borneol	0.1	0:100
1178	1180	Terpinen-4-ol	0.9	47.7:52.3
1184	1185	Cryptone	tr	
1193	1195	α-Terpineol	2.2	8.4:91.6
1194	1196	*cis*-Piperitol	0.2	
1197	1200	γ-Terpineol	tr	
1204	1206	Decanal	tr	
1207	1208	*trans*-Piperitol	0.3	
1227	1229	Thymol methyl ether	tr	
1235	1237	Pulegone	0.2	100:0
1247	1250	Thymoquinone	tr	
1251	1254	Piperitone	tr	
1275	1277	Phellandral	tr	
1281	1282	Bornyl acetate	1.6	0:100
1287	1289	Thymol	0.2	
1290	1293	2-Undecanone	0.1	
1295	1296	Carvacrol	tr	
1332	1335	δ-Elemene	0.1	
1347	1349	Citronellyl acetate	tr	
1356	1361	Neryl acetate	tr	
1375	1378	Geranyl acetate	1.7	
1386	1390	*trans*-β-Elemene	tr	
1407	1409	Dodecanal	0.1	
1415	1417	(*E*)-β-Caryophyllene	0.1	
1451	1453	α-Humulene	tr	
1472	1480	Widdra-2,4(14)-diene	tr	
1475	1482	α-Amorphene	tr	

1477	1483	Germacrene D	tr	
1483	1488	δ-Selinene	tr	
1485	1487	β-Selinene	0.1	
1492	1497	α-Selinene	tr	
1498	1504	Epizonarene	tr	
1501	1503	(*E*,*E*)-α-Farnesene	tr	
1509	1512	γ-Cadinene	tr	
1514	1518	δ-Cadinene	tr	
1544	1546	α-Elemol	tr	
1557	1561	(*E*)-Nerolidol	0.3	55.7:44.3
1623	1629	*iso*-Spathulenol	0.2	
1627	1632	γ-Eudesmol	0.1	
1638	1638	τ-Cadinol	0.1	
1639	1640	τ-Muurolol	tr	
1651	1652	α-Eudesmol	0.6	
1653	1659	Selin-11-en-4α-ol	0.1	
1683	1686	α-Bisabolol	0.2	
1688	1692	(2*Z*,6*Z*)-Farnesol	0.1	
1692	1696	Juniper camphor	tr	
1711	1713	(2*E*,6*Z*)-Farnesol	0.3	
1864	1869	Benzyl salicylate	tr	
1927	1931	Beyerene	0.1	
2222	2222	Abietadienone	0.1	
2299	2297	4-*epi*-Abietal	tr	
		Monoterpene hydrocarbons	88.5	
		Oxygenated monoterpenoids	8.9	
		Sesquiterpene hydrocarbons	0.2	
		Oxygenated sesquiterpenoids	2.0	
		Diterpenoids	0.1	
		Others	0.2	
		Total identified	100.0	

RI_{calc} = Retention indices calculated in reference to a homologous series of *n*-alkanes on a ZB-5ms column. RI_{db} = Retention indices obtained from the databases [18-21]. ED = enantiomeric distribution (dextrorotatory enantiomer: levorotatory enantiomer). tr = "trace" (< 0.05%).

The monoterpenoid distribution of *A. procera* leaf essential oil is comparable to the oleoresin monoterpenoid distributions previously reported [10]. That is, *A. procera* oleoresins from Oregon were composed largely of α-pinene (14.7-42.3%), β-pinene (7.8-25.2%), limonene (2.8-37.8%), and β-phellandrene (13.8-52.2%).

The traditional use of *A. procera* to treat colds can be attributed to the activities of the major monoterpenes present. Thus, for example, α-pinene has shown antitussive effects in a Guinea pig model [22], both (–)-α-pinene and (–)-β-pinene have shown inhibitory activity against infectious bronchitis virus (IBV) [23], limonene has shown antibacterial activity against the respiratory pathogens *Streptococcus pyogenes*, *Streptococcus pneumoniae*, and *Haemophilus influenzae* [24] as well as activity against *Mycobacterium tuberculosis* [25].

3.2 *Pinus contorta* subsp. *murrayana*

Pinus contorta leaf essential oil was obtained as a colorless oil in 0.383% (w/w) yield. The leaf essential oil composition is summarized in Table 3. Fifty compounds were identified in *P. contorta* subsp. *murrayana* essential oil accounting for 99.8% of the composition. The major components were the monoterpene hydrocarbons β-phellandrene (37.2%) and β-pinene (17.0%) and the monoterpene alcohol α-terpineol (11.6%).

Table 3: Chemical composition of *Pinus contorta* subsp. *murrayana* leaf essential oil.

RI_{calc}	RI_{db}	Compound	% Composition	ED, (+):(–)
782	782	Prenol	1.2	
921	923	Tricyclene	tr	
931	932	α-Pinene	3.0	20.3:79.7
947	950	Camphene	0.3	
970	971	Sabinene	0.1	
975	978	β-Pinene	17.0	2.2:97.8
987	989	Myrcene	1.6	
1005	1006	α-Phellandrene	1.1	0:100
1007	1008	δ-3-Carene	3.4	100:0
1015	1017	α-Terpinene	0.4	100:0
1022	1024	*p*-Cymene	0.2	
1027	1030	Limonene	2.2	0:100
1028	1031	β-Phellandrene	37.2	0.4:99.6
1033	1034	(*Z*)-β-Ocimene	0.6	
1055	1057	γ-Terpinene	0.5	
1068	1069	*cis*-Linalool oxide (furanoid)	0.5	49.8:50.2

1083	1086	Terpinolene	2.2	
1084	1086	*trans*-Linalool oxide (furanoid)	0.6	
1098	1099	Linalool	0.4	0:100
1117	1119	*endo*-Fenchol	0.4	
1122	1124	*cis*-*p*-Menth-2-en-1-ol	1.6	
1140	1142	*trans*-*p*-Menth-2-en-1-ol	1.3	
1152	1156	Camphene hydrate	0.3	
1162	1158	Menthone	0.5	100:0
1167	1169	*cis*-Linalool oxide (pyranoid)	0.2	
1169	1170	Borneol	0.4	0:100
1178	1180	Terpinen-4-ol	1.9	39.9:60.1
1185	1186	*p*-Cymen-8-ol	0.3	
1193	1195	α-Terpineol	11.6	3.4:96.6
1194	1196	*cis*-Piperitol	0.4	
1207	1208	*trans*-Piperitol	0.7	
1235	1237	Pulegone	0.9	100:0
1251	1254	Piperitone	0.1	100:0
1275	1277	Phellandral	0.1	
1281	1282	Bornyl acetate	2.2	0:100
1284	1285	(*E*)-Anethole	0.2	
1287	1289	Thymol	0.3	
1290	1293	2-Undecanone	0.2	
1386	1390	*trans*-β-Elemene	0.2	0:100
1484	1487	β-Selinene	0.3	
1491	1494	α-Selinene	0.2	
1514	1518	δ-Cadinene	0.2	
1572	1576	Spathulenol	0.3	
1581	1582	*epi*-Globulol	0.1	
1589	1590	Globulol	0.1	
1637	1640	τ-Cadinol	0.4	
1639	1644	τ-Muurolol	0.5	
1642	1644	α-Muurolol (= δ-Cadinol)	0.1	
1651	1652	α-Cadinol	1.2	
1653	1658	Selin-11-en-4α-ol	0.4	
		Monoterpene hydrocarbons	69.7	
		Oxygenated monoterpenoids	24.6	
		Sesquiterpene hydrocarbons	0.9	
		Oxygenated sesquiterpenoids	3.2	
		Diterpenoids	0.0	
		Others	1.5	
		Total identified	99.8	

RI_{calc} = Retention indices calculated in reference to a homologous series of *n*-alkanes on a ZB-5ms column. RI_{db} = Retention indices obtained from the databases [18-21]. ED = enantiomeric distribution (dextrorotatory enantiomer: levorotatory enantiomer). tr = "trace" (< 0.05%).

The leaf essential oil composition of *P. contorta* subsp. *latifolia* from Alberta, Canada, was also found to be rich in β-pinene (30.5%), β-phellandrene (34.3%), and α-terpineol (4.3%) [26]. The oleoresin samples of *P. contorta* subsp. *latifolia* from Alberta, Canada, were also dominated by β-pinene and β-phellandrene [27].

3.3 *Tsuga heterophylla*

The colorless leaf essential oil of *T. heterophylla* was obtained in a yield of 1.05% (w/w). The volatile components of *T. heterophylla* leaves are shown in Table 4. The compounds with the highest concentrations in *T. heterophylla* essential oil were the monoterpenoids α-terpineol (10.2%), pulegone (7.6%), and thymol methyl ether (5.8%), along with the sesquiterpenoid α-cadinol (5.9%), and the diterpenoid beyerene (13.3%).

Table 4: Chemical composition of *Tsuga heterophylla* leaf essential oil.

RI_{calc}	RI_{db}	Compound	% Composition	ED, (+):(–)
974	978	β-Pinene	0.2	
977	978	1-Octen-3-ol	0.8	
986	989	Myrcene	0.3	
1022	1024	*p*-Cymene	0.6	
1028	1030	Limonene	1.1	0:100
1028	1029	β-Phellandrene	1.1	0:100
1029	1030	1,8-Cineole	2.7	
1033	1034	(*Z*)-β-Ocimene	1.2	
1055	1057	γ-Terpinene	0.4	
1098	1099	Linalool	0.6	
1122	1124	*cis*-*p*-Menth-2-en-1-ol	1.7	

1139	1139	*trans*-*p*-Menth-2-en-1-ol	1.4	
1142	1145	*trans*-Verbenol	0.6	
1162	1158	Menthone	3.8	100:0
1169	1171	*p*-Mentha-1,5-dien-8-ol	0.7	
1177	1180	Terpinen-4-ol	3.1	30.2:69.8
1184	1186	*p*-Cymen-8-ol	0.6	
1189	1192	Methyl salicylate	0.8	
1192	1195	α-Terpineol	10.3	13.1:86.9
1204	1205	Verbenone	1.3	53.6:46.4
1206	1208	*trans*-Piperitol	1.0	
1226	1229	Thymol methyl ether	5.8	
1235	1237	Pulegone	7.7	100:0
1287	1289	Thymol	4.2	
1376	1378	Geranyl acetate	0.6	
1385	1390	β-Elemene	0.3	
1415	1417	(*E*)-β-Caryophyllene	0.6	
1429	1432	*trans*-α-Bergamotene	0.6	
1450	1453	α-Humulene	0.2	
1476	1480	Germacrene D	0.6	
1484	1487	β-Selinene	0.3	
1491	1494	α-Selinene	0.8	
1494	1497	α-Muurolene	0.5	
1508	1512	γ-Cadinene	0.6	
1513	1518	δ-Cadinene	3.1	0:100
1537	1540	(*E*)-α-Bisabolene	0.4	
1558	1560	(*E*)-Nerolidol	2.0	47.0:53.0
1622	1628	1-*epi*-Cubenol	1.0	
1637	1640	τ-Cadinol	3.8	
1639	1644	τ-Muurolol	3.7	
1641	1644	α-Muurolol (= δ-Cadinol)	1.4	
1650	1652	α-Cadinol	6.0	
1653	1658	Selin-11-en-4α-ol	1.6	
1673	1676	Tetradeca-(9*Z*,12*E*)-dien-1-ol	3.3	
1926	1931	Beyerene	13.6	
2298	2298	4-*epi*-Abietal	0.4	
		Monoterpene hydrocarbons	5.7	
		Oxygenated monoterpenoids	46.4	
		Sesquiterpene hydrocarbons	8.1	
		Oxygenated sesquiterpenoids	19.7	
		Diterpenoids	14.0	
		Others	4.1	
		Total identified	98.1	

RI_{calc} = Retention indices calculated in reference to a homologous series of *n*-alkanes on a ZB-5ms column. RI_{db} = Retention indices obtained from the databases [18-21]. ED = enantiomeric distribution (dextrorotatory enantiomer: levorotatory enantiomer). tr = "trace" (< 0.05%).

Von Rudloff carried out an extensive study in the 1970s of the essential oils of *T. heterophylla* from British Columbia [28]. Both the coastal population and the inland population of *T. heterophylla* from British Columbia were examined. The coastal samples from British Columbia were dominated by monoterpene hydrocarbons, α-pinene (14.6-16.9%), β-pinene (8.6-11.4%), myrcene (14.9-25.5%), limonene (1.3-11.6%), β-phellandrene (16.0-23.3%), and (*Z*)-β-ocimene (8.2-11.5%). The inland population had similar compositions, α-pinene (17.3-17.5%), β-pinene (9.1-13.3%), myrcene (15.2-25.0%), limonene (1.6-2.6%), β-phellandrene (17.4-28.7%), and (*Z*)-β-ocimene (7.8-11.1%). Thus, the leaf essential oil composition of *T. heterophylla* from Oregon is markedly different from the leaf essential oils in this early report from British Columbia [28]. There are several factors that may contribute to the different *T. heterophylla* leaf essential oil profiles, including latitude, climate, herbivory, and disease [29, 30], and it is not clear what may be responsible. Furthermore, leaves of a cultivated specimen from Kingston, Rhode Island was analyzed by solid-phase microextraction / gas chromatography – mass spectrometry [31]. The Rhode Island sample was dominated by α-pinene (18.6%), camphene (8.4%), isobornyl acetate (28.4%), β-caryophyllene (6.1%), and α-humulene (12.3%). The differences are most likely due to the adsorption characteristics of the polydimethylsiloxane (PDMS) fiber used, but there may also be variation due to the geographical location, abiotic or biotic conditions of the sample. In a study on the variation in black spruce (*Picea mariana*) oleoresin volatiles, Chang and Hanover observed no significant relationship between monoterpene concentration and temperature, latitude, or rainfall, but did observe variation based on east-west geographical location [32].

3.4 Enantiomeric Distribution

Enantiomeric distributions of several chiral essential oil components have been determined by chiral gas chromatography – mass spectrometry. In *A. procera* essential oil, (+)-α-thujene was the major enantiomer (57%), which is comparable to those observed in two subspecies of *Abies spectabilis* from Nepal, *A. spectabilis* subsp. *densa* (76% (+)-α-thujene) and *A. spectabilis* subsp. *langtangensis* (70% (+)-α-thujene) [33]. Likewise, (+)-camphene, and (–)-β-

phellandrene were the dominant enantiomers in the leaf essential oil of *A. procera*, analogous to that observed for *A. spectabilis* [33].

The ratio of (+)-α-pinene and (–)-α-pinene observed in the leaf essential oil of *P. contorta* subsp. *murrayana* (20:80) is comparable to that observed for the stem essential oil of *P. contorta* subsp. *latifolia* (40:60) [34]. Likewise, the enantiomeric distributions, (+):(–), of β-pinene (2.2:97.8), δ-3-carene (100:0), and β-phellandrene (0.4:99.6) in this work, were similar to those identified in *P. contorta* subsp. *latifolia* stem essential oil (2.8:97.2, 100:0, and 0:100, respectively).

(–)-β-Pinene was the major enantiomer in the leaf essential oils of *A. procera* (2:98), and *P. contorta* subsp. *murrayana* (2:98). The (–)-enantiomer is dominant in many *Abies* [33, 35-37] and *Pinus* [35] essential oils.

As observed in several conifer essential oils, (–)-limonene was the dominant enantiomer in the essential oils of *A. procera*, *P. contorta*, and *T. heterophylla* with 100% (–)-limonene. *Abies balsamea* [37], *Abies sachalinensis* [36], and *Pinus cembra* [35] essential oils also showed only (–)-limonene. Interestingly, however, (+)-limonene was found to be the dominant enantiomer in *Pinus sylvestris* (98:2) [35] and *P. halapensis* (94:6) [38].

Tsuga heterophylla from British Columbia showed a limonene enantiomeric distribution of 35:65 (based on the optical rotation reported) [28]. Interestingly, the ratio of (+)-β-phellandrene to (–)-β-phellandrene in *T. heterophylla* from British Columbia was 28:72 [28], whereas the sample from Oregon showed 100% (–)-β-phellandrene. British Columbian *T. heterophylla* also showed (+):(–) of α-pinene = 26:74 and (+):(–) of β-pinene = 10:90 [28], but the concentrations of these two components were too low in the Oregon sample to determine the enantiomeric distributions.

4. Conclusions

The leaf essential oil compositions and enantiomeric distributions of *A. nobilis*, *P. contorta murrayana*, and *T. heterophylla* from Oregon are reported for the first time. This work adds to our knowledge of Pinaceae essential oil compositions and these oils may be considered for commercial development for the fragrance and cosmeceutical industries.

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