Article

Essential Oil Compositions of *Pinus* Species (*P. contorta* Subsp. *contorta, P. ponderosa* var. *ponderosa*, and *P. flexilis*); Enantiomeric Distribution of Terpenoids in *Pinus* Species

Elizabeth Ankney  1, Kathy Swor  2, Prabodh Satyal  3  and William N. Setzer  3,4,*  

1 Independent Researcher, 141 W. 17th St., Lafayette, OR 97127, USA  
2 Independent Researcher, 1432 W. Heartland Dr., Kuna, ID 83634, USA  
3 Aromatic Plant Research Center, 230 N 1200 E, Suite 100, Lehi, UT 84043, USA  
4 Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35899, USA  
* Correspondence: wsetzer@chemistry.uah.edu; Tel.: +1-256-468-2862

Abstract: *Pinus* species are important in traditional medicine throughout their ranges, and pine essential oils are of interest in aromatherapy and as topical treatments. In this work, the leaf (needle) essential oils of *Pinus ponderosa* var. *ponderosa* and *Pinus contorta* subsp. *contorta* from Oregon and *Pinus flexilis* growing in Idaho, have been obtained by hydrodistillation and analyzed by gas chromatographic techniques. The leaf essential oil of *P. ponderosa* was dominated by β-pinene (21.5–55.3%), methyl chavicol (8.5–41.5%), α-pinene (3.6–9.6%), δ-3-carene (3.6–6.2%), and α-terpineol (1.4–5.3%). The major components of *P. contorta* essential oil were β-phellandrene (23.8%), terpinen-4-ol (11.0%). The essential oil of *P. flexilis* was dominated by α-pinene (37.1%), β-pinene (21.9%), bornyl acetate (12.8%), and camphene (8.5%). Chiral gas chromatography revealed the enantiomeric ratios of α-pinene and limonene to be variable, but (−)-β-pinene predominated in *Pinus* essential oils.

Keywords: ponderosa pine; shore pine; limber pine; monoterpenoids; enantiomers; chiral GC-MS

1. Introduction

Numerous members of the genus *Pinus* (Pinaceae) are used in traditional medicine in their native ranges [1] and several essential oils derived from the genus are commercially important for use in aromatherapy and topical therapy applications, such as Scots pine (*Pinus sylvestris* L.), black pine (*Pinus nigra* J.F. Arnold), jack pine (*Pinus banksiana* Lamb.), and white pine (*Pinus strobus* L.) [2]. In this work, the leaf essential oils of *Pinus ponderosa* Douglas ex C. Lawson var. *ponderosa*, *Pinus contorta* Douglas ex Loudon subsp. *contorta*, and *Pinus flexilis* E. James have been investigated for their chemical compositions and terpenoid enantiomeric distributions. In the case where essential oils are used therapeutically (e.g., aromatherapy) the different compositions and enantiomers may have very different biological activities. For commercial essential oils, the chemical compositions and enantiomeric distribution can be valuable for assessing the quality and consistency of the essential oil as well as a potential screen for adulteration or contamination.

*Pinus ponderosa*, the ponderosa pine (Figure 1), is the most widespread species of pine in western North America and ranges from British Columbia, south through the Cascade Range, the Sierra Nevada range of California, the Rocky Mountains and into the southwestern mountains of Utah, Arizona, and New Mexico. World Flora Online currently lists 11 subtaxa for the species [3], but the taxonomy is not resolved [4]. However, two varieties of the species are generally recognized: *Pinus ponderosa* var. *ponderosa*, the Pacific ponderosa pine, which ranges from southern British Columbia, south through the mountains of Washington, Oregon, and California, and *Pinus ponderosa* var. *scopulorum* Engelm., the Rocky Mountain ponderosa pine, found in eastern Montana, western North and South Dakota and Nebraska, Wyoming, Nebraska, northern and central Colorado and
Flathead Native Americans used the boughs of *P. ponderosa* in sweat lodges to treat muscular pains, while the Navajo people took a decoction of the needles for coughs and fever [6].

![Figure 1](image-url)  
**Figure 1.** *Pinus ponderosa* var. *ponderosa* from central Oregon. (A) Leaves (needles) and cone. (B) bark.

The native range of *P. contorta* is western North America, where there are three recognized subspecies: *P. contorta* subsp. *latifolia* (Engelm.) Critchf., the Rocky Mountain lodgepole pine, is found in the Rocky Mountains from the Yukon, south through Colorado; *P. contorta* subsp. *murrayana* (Balf.) Engelm., the Sierra lodgepole pine, found along the Cascade Range from Washington, through Oregon, and into northern California, and the Sierra Nevada Range in California; and *P. contorta* subsp. *contorta*, the shore pine (Figure 2), which ranges along the Pacific coast from southern Alaska, south to northwestern California [7,8]. The Haisla and Hanaksiala Native Americans used smoldering twigs of *P. contorta* subsp. *contorta* to alleviate pain and swelling of arthritic or injured joints [6].

*Pinus flexilis* (Figure 3) naturally ranges in the Rocky Mountains of western North America, from southwest Alberta and southeast British Columbia, south through Colorado and New Mexico. It is also found in the mountains of Utah, Idaho, Nevada, and California [9]. The Navajo people used *P. flexilis* as cough medicine and to reduce fever [6]. As part of our investigation into the essential oil compositions of *Pinus* species [10,11], we have examined the compositions of the leaf essential oils of *P. ponderosa* var. *ponderosa* from La Pine, Oregon, *P. contorta* subsp. *contorta* from Ona Beach, Oregon, and *Pinus flexilis* from Boise, Idaho. As far as we are aware, this is the first report on the leaf oil composition of *P. flexilis* and the first report on the enantiomeric distributions of terpenoids in these *Pinus* species.
Figure 2. *Pinus contorta* subsp. *contorta* from the central Oregon coast. (A) Leaves (needles) and cone. (B) bark.

Figure 3. *Pinus flexilis* from southwestern Idaho. (A) Leaves (needles) and cone. (B) bark.
2. Results and Discussion

2.1. Chemical Composition of Pinus ponderosa var. ponderosa

Hydrodistillation of three samples of fresh leaves of *P. ponderosa* var. *ponderosa* gave colorless essential oils in 0.321%, 0.399%, and 0.463% (w/w) yield, which are comparable to those obtained in previous studies (0.1–0.6%) [12–14]. The essential oil compositions are presented in Table 1. A total of 118 compounds were identified in the essential oils accounting for >99% of the composition. The major components in the essential oils were β-pinene (21.5–55.3%), methyl chavicol (8.5–41.5%), α-pinene (3.6–9.6%), δ-3-carene (3.6–6.2%), and α-terpineol (1.4–5.3%).

**Table 1.** Chemical composition of *Pinus ponderosa* var. *ponderosa* leaf essential oil.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                  | % Composition |
|-----------------|----------------|---------------------------|---------------|
|                 |                |                           | Tree #1 | Tree #2 | Tree #3 |
| 919             | 919            | Hashishene               | tr      | —      | —      |
| 922             | 923            | Tricyclene               | tr      | tr     | tr     |
| 925             | 926            | α-Thujene                 | tr      | tr     | tr     |
| 932             | 932            | α-Pinene                 | 3.6     | 5.7    | 9.6    |
| 946             | 948            | α-Fenchene               | tr      | tr     | tr     |
| 948             | 950            | Camphene                 | 0.1     | 0.2    | 0.3    |
| 970             | 970            | 3,7,7-Trimethyl-1,3,5-cycloheptatriene | tr | tr | tr |
| 971             | 971            | Sabinene                 | 0.1     | 0.1    | 0.1    |
| 978             | 978            | β-Pinene                 | 21.5    | 35.3   | 55.3   |
| 988             | 989            | Myrcene                  | 1.7     | 1.3    | 1.7    |
| 999             | 1000           | δ-2-Carene               | tr      | —      | —      |
| 1006            | 1006           | α-Phellandrene           | tr      | tr     | tr     |
| 1009            | 1008           | δ-3-Carene               | 3.6     | 5.5    | 6.2    |
| 1015            | 1015           | 1,4-Cineole              | tr      | tr     | tr     |
| 1016            | 1017           | α-Terpinene              | tr      | 0.1    | 0.1    |
| 1019            | 1022           | m-Cymene                 | tr      | tr     | tr     |
| 1024            | 1025           | p-Cymene                 | 0.1     | 0.1    | 0.1    |
| 1028            | 1030           | Limonene                 | 0.8     | 1.1    | 1.3    |
| 1030            | 1031           | β-Phellandrene           | 0.9     | 1.3    | 1.7    |
| 1034            | 1034           | (Z)-β-Ocimene            | 0.7     | 0.7    | tr     |
| 1045            | 1045           | (E)-β-Ocimene            | 0.1     | tr     | tr     |
| 1057            | 1057           | γ-Terpinene              | 0.1     | 0.1    | 0.1    |
| 1069            | 1069           | *cis*-Linalool oxide (furanoid) | tr | tr | tr |
| 1082            | 1082           | *p*-Mentha-2,4(8)-diene  | tr      | tr     | tr     |
| 1084            | 1086           | Terpinolene              | 0.4     | 0.7    | 0.8    |
| 1086            | 1086           | *trans*-Linalool oxide (furanoid) | 0.1 | — | 0.1 |
| 1089            | 1091           | *p*-Cymene               | tr      | —      | tr     |
| 1090            | 1090           | 2-Nonanone               | —       | 0.1    | tr     |
| 1099            | 1101           | Linalool                 | 2.1     | 0.4    | 0.3    |
| 1104            | 1104           | Nonanal                  | 0.1     | tr     | tr     |
| 1118            | 1119           | *endo*-Fenchol           | 0.1     | tr     | tr     |
| 1124            | 1124           | *cis*-p-Menth-2-en-1-ol  | tr      | tr     | tr     |
| 1126            | 1126           | α-Campholenal            | tr      | tr     | tr     |
| 1127            | 1127           | αllo-Ocimene             | —       | tr     | —      |
| 1137            | 1137           | Nopinone                 | 0.2     | tr     | 0.1    |
| 1140            | 1140           | *trans*-Pinocarveol      | 0.4     | 0.1    | tr     |
| 1142            | 1142           | *trans*-p-Menth-2-en-1-ol| —       | 0.1    | —      |
| 1145            | 1145           | Camphor                  | —       | tr     | —      |
| 1154            | 1156           | Camphene hydrate         | 0.1     | 0.1    | 0.1    |
| RI$_{\text{calc}}$ | RI$_{\text{db}}$ | Compound                     | % Composition |
|-----------------|----------------|-----------------------------|---------------|
|                 |                |                             | Tree #1 | Tree #2 | Tree #3 |
| 1155            | 1155           | Hexyl isobutyrate           | —       | —      | tr     |
| 1160            | 1160           | trans-Pinocamphone          | 0.2     | 0.2    | 0.3    |
| 1161            | 1164           | Pinocarvone                 | 0.3     | 0.1    | 0.1    |
| 1170            | 1170           | (2E)-Nonen-1-ol             | 0.1     | tr     | 0.1    |
| 1171            | 1171           | $p$-Menta-1,5-dien-8-ol      | 0.1     | tr     | tr     |
| 1175            | 1176           | cis-Pinocamphone            | 0.2     | 0.2    | 0.2    |
| 1180            | 1180           | Terpinen-4-ol               | 0.4     | 0.3    | 0.2    |
| 1187            | 1186           | $p$-Cymen-8-ol              | 0.3     | 0.1    | —      |
| 1196            | 1195           | $\alpha$-Terpineol          | 5.3     | 1.4    | 3.0    |
| 1199            | 1197           | Methyl chavicol (= Estragole) | 41.5 | 27.4 | 8.5 |
| 1206            | 1206           | Decanal                     | —       | 0.1    | 0.1    |
| 1208            | 1208           | Verbenone                   | tr      | tr     | —      |
| 1228            | 1229           | Thymol methyl ether         | —       | —      | tr     |
| 1252            | 1253           | (Z)-Anethole                | —       | tr     | —      |
| 1253            | 1254           | Piperitone                  | —       | tr     | —      |
| 1278            | 1276           | (2E)-Decen-1-ol             | —       | 0.1    | —      |
| 1283            | 1282           | Bornyl acetate              | 0.2     | 0.1    | 0.1    |
| 1285            | 1285           | (E)-Anethole                | 2.3     | 1.6    | 0.1    |
| 1292            | 1295           | 2-Undecanone                | —       | 0.1    | —      |
| 1313            | 1314           | Carvenolide                 | 0.1     | —      | —      |
| 1322            | 1322           | Myrtanyl acetate            | 0.1     | 0.1    | tr     |
| 1345            | 1346           | $\alpha$-Terpinyacetate     | 0.3     | 0.3    | 0.2    |
| 1372            | 1370           | (2E)-Undecen-1-ol           | 0.7     | 0.3    | 0.3    |
| 1375            | 1375           | $\alpha$-Copaene            | 0.1     | 0.2    | 0.2    |
| 1383            | 1382           | $\beta$-Bourbonene          | —       | tr     | —      |
| 1387            | 1387           | $\beta$-Cubebene            | tr      | 0.1    | tr     |
| 1389            | 1390           | trans-$\beta$-Elemene       | 0.1     | —      | —      |
| 1389            | 1389           | (5Z)-Decen-1-yl acetate     | —       | 0.5    | 0.4    |
| 1399            | 1403           | Methyl eugenol              | 0.1     | tr     | —      |
| 1409            | 1410           | Dodecanol                   | 0.1     | 0.1    | 0.1    |
| 1419            | 1417           | (E)-$\beta$-Caryophyllene   | 0.5     | 0.5    | 0.1    |
| 1429            | 1430           | $\beta$-Copaene             | tr      | tr     | tr     |
| 1432            | 1432           | trans-$\alpha$-Bergamotene  | 0.5     | 0.1    | 0.1    |
| 1438            | 1438           | Aromadendrene               | 0.3     | tr     | 0.2    |
| 1442            | 1442           | Guai-6,9-diene               | —       | —      | tr     |
| 1447            | 1447           | Geranyl acetone             | —       | tr     | —      |
| 1448            | 1448           | cis-Muurola-3,5-diene        | —       | tr     | tr     |
| 1452            | 1452           | (E)-$\beta$-Farnesene       | 0.1     | tr     | —      |
| 1455            | 1454           | $\alpha$-Humulene           | 0.1     | 0.1    | tr     |
| 1459            | 1457           | allo-Aromadendrene          | —       | —      | tr     |
| 1461            | 1463           | cis-Muurola-4(14),5-diene    | 0.1     | 0.1    | tr     |
| 1467            | 1469           | Ethyl (E)-cinnamate         | 0.2     | —      | 0.1    |
| 1469            | 1470           | (2E)-Undecenyl acetate      | 0.1     | 0.3    | tr     |
| 1471            | 1472           | trans-Cadina-1(6),4-diene    | tr      | 0.1    | 0.1    |
| 1474            | 1475           | $\gamma$-Murolene           | 0.2     | 0.4    | 0.2    |
| 1480            | 1480           | Germacrene D                | 0.4     | 0.9    | 0.3    |
| 1488            | 1489           | $\beta$-Selinene            | 0.4     | 0.1    | 0.2    |
| 1491            | 1492           | trans-Muurola-4(14),5-diene  | 0.1     | 0.1    | 0.1    |
| 1495            | 1495           | 2-Tridecanone               | —       | 0.3    | —      |
| 1496            | 1497           | Bicyclogermacrene           | 0.8     | —      | 0.5    |
| 1498            | 1497           | $\alpha$-Murolene           | 0.3     | 0.5    | 0.3    |
| 1512            | 1512           | $\gamma$-Cadinene           | 0.9     | 1.5    | 1.0    |
| 1518            | 1518           | $\delta$-Cadinene           | 1.6     | 2.8    | 1.9    |
| 1519            | 1519           | trans-Calamene              | tr      | tr     | 0.1    |
| 1522            | 1521           | Zonarene                    | tr      | tr     | 0.1    |
Table 1. Cont.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                                      | Tree #1 | Tree #2 | Tree #3 |
|-----------------|----------------|-----------------------------------------------|---------|---------|---------|
| 1532            | 1533           | trans-Cadina-1,4-diene                         | tr      | 0.1     | 0.1     |
| 1536            | 1538           | α-Cadinene                                    | 0.1     | 0.1     | 0.1     |
| 1540            | 1541           | α-Calacorene                                   | tr      | tr      | tr      |
| 1561            | 1561           | (E)-Nerolidol                                  | —       | 1.0     | —       |
| 1561            | 1560           | Dodecanolic acid                               | 0.5     | 0.2     | 0.3     |
| 1574            | 1574           | Germacrene D-4α-ol                             | —       | 0.6     | —       |
| 1577            | 1576           | Spathulenol                                    | 1.0     | —       | 0.6     |
| 1581            | 1582           | Caryophyllene oxide                            | 0.2     | 0.1     | tr      |
| 1586            | 1590           | Globulol                                       | 0.1     | 0.1     | 0.1     |
| 1593            | 1598           | Ethyl dodecanoate                              | 0.1     | —       | —       |
| 1625            | 1624           | Muurola-4,10(14)-dien-1β-ol                    | tr      | 0.1     | tr      |
| 1627            | 1628           | 1-epi-Cubenol                                  | tr      | 0.1     | 0.1     |
| 1642            | 1643           | γ-Cadinol                                      | 0.3     | 0.5     | 0.3     |
| 1644            | 1644           | γ-Muurolol                                     | 0.3     | 0.6     | 0.5     |
| 1655            | 1655           | α-Cadinol                                      | 0.5     | 0.7     | 0.5     |
| 1664            | 1664           | Brevifolin (= Xanthoxylin)                     | 0.1     | —       | —       |
| 1675            | 1670           | (6Z)-Pentadecen-2-one                          | 0.1     | 0.2     | —       |
| 1765            | 1769           | Benzyl benzoate                                | —       | 0.1     | tr      |
| 1794            | 1796           | (9Z)-Hexadecenal                               | —       | 0.1     | tr      |
| 1816            | 1817           | Hexadecanal                                    | tr      | 0.1     | 0.1     |
| 1866            | 1869           | Benzyl salicylate                              | —       | 0.1     | —       |
| 1991            | 1998           | Manoyl oxide                                   | 0.2     | 0.1     | 0.1     |
| 1995            | 1997           | 9β-Isopimaraz,15-diene                         | —       | 0.1     | 0.1     |
| 2290            | 2297           | Methyl isopimarate                             | 0.1     | 0.1     | tr      |

RI<sub>calc</sub> = Retention indices calculated in reference to a homologous series of n-alkanes on a ZB-5ms column. RI<sub>db</sub> = Retention indices obtained from the databases [15–18]. tr = “trace” (<0.05%). — = not detected.

There have been several investigations into the essential oil composition of *P. ponderosa* from different geographical locations, including California (USA) [13,14], British Columbia (Canada) [19], Washington (USA) [20], Poland [21], and Arizona (USA) [22]. Although there is much variation in the concentrations, the major components of *P. ponderosa* leaf essential oils reported in the literature have been α-pinene (10.2–69.3%), β-pinene (2.1–66.0%), myrcene (1.4–7.4%), δ-3-carene (up to 41.8%), α-terpineol (up to 7.5%) and methyl chavicol (1.8–20.4%). Thus, the essential oil compositions of Oregon *P. ponderosa*, subsp. *ponderosa* in this work are qualitatively similar to previous reports for *P. ponderosa*, and the wide chemical variations are likely due to geographical locations and/or genetic differences.

2.2. Chemical Composition of *Pinus contorta* Subsp. *contorta*

The fresh leaves of *P. contorta* subsp. *contorta* were hydrodistilled to give a colorless essential oil in 0.674% (w/w) yield. A previous report by Adams and co-workers indicated an essential oil yield of only 0.1% [23]. The essential oil composition is summarized in Table 2. A total of 55 compounds were identified accounting for 98.2% of the essential oil composition. The dominant components in the essential oil were the monoterpenoids β-phellandrene (23.8%), terpinen-4-ol (11.0%), thymol (6.6%), and chavicol (5.3%). Adams and co-workers have reported the leaf essential oils of *P. contorta* subsp. *contorta*, *P. contorta* subsp. *latifolia*, and *P. contorta* subsp. *murrayana* [23]. There are some notable differences...
between the leaf essential oil composition of the Oregon sample (this work) and those from coastal Washington [23]. The β-phellandrene concentration was lower than the Washington samples (39.2–61.5%), but γ-terpinene and terpinen-4-ol concentrations were higher than the Washington samples (0.6–1.7% and 0.3%, respectively), and neither chavicol nor thymol were detected in the Washington samples.

Table 2. Chemical composition of *Pinus contorta* subsp. *contorta* leaf essential oil.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                        | % Composition |
|------------------|-----------------|---------------------------------|---------------|
| 782              | 782             | Prenol                          | 1.1           |
| 801              | 801             | Hexanal                         | 0.6           |
| 848              | 849             | (2E)-Hexenal                    | 0.5           |
| 851              | 853             | (3Z)-Hexenol                    | 0.3           |
| 923              | 923             | Tricyclene                      | 0.1           |
| 925              | 927             | α-Thujene                       | 0.2           |
| 933              | 932             | α-Pinene                        | 1.2           |
| 949              | 950             | Camphene                        | 0.2           |
| 959              | 959             | Benzaldehyde                    | 2.0           |
| 972              | 971             | Sabinene                        | 0.2           |
| 977              | 978             | β-Pinene                        | 0.5           |
| 989              | 989             | Myrcene                         | 1.0           |
| 989              | 990             | Dehydro-1,8-cineole             | 0.1           |
| 1007             | 1006            | α-Phellandrene                  | 0.6           |
| 1009             | 1008            | δ-3-Carene                      | 0.2           |
| 1014             | 1015            | 1,4-Cineole                     | 3.7           |
| 1017             | 1017            | α-Terpine                        | 3.6           |
| 1024             | 1024            | p-Cymene                        | 1.5           |
| 1029             | 1030            | Limonene                        | 2.0           |
| 1030             | 1031            | β-Phellandrene                  | 23.8          |
| 1035             | 1034            | (Z)-β-Ocimene                   | 1.1           |
| 1057             | 1057            | γ-Terpine                       | 6.8           |
| 1069              | 1069            | cis-Linalool oxide (furanoid)    | 0.2           |
| 1085              | 1086            | Terpinolene                     | 2.2           |
| 1086              | 1086            | trans-Linalool oxide (furanoid)  | 0.4           |
| 1089              | 1091            | p-Cymene                        | 0.3           |
| 1100              | 1099            | Linalool                        | 0.1           |
| 1124              | 1124            | cis-p-Menth-2-en-1-ol            | 1.8           |
| 1135              | 1136            | Terpin-3-en-1-ol                | 2.3           |
| 1142              | 1142            | trans-p-Menth-2-en-1-ol          | 1.2           |
| 1146              | 1145            | Camphor                         | 0.6           |
| 1177              | 1179            | 2-Isopropenyl-5-methyl-4-hexenal | 0.6           |
| 1180              | 1180            | Terpinen-4-ol                   | 11.0          |
| 1187              | 1186            | p-Cymen-8-ol                    | 1.7           |
| 1187              | 1188            | trans-β-Ocimenol                | 0.3           |
| 1195              | 1195            | α-Terpineol                     | 2.4           |
| 1196              | 1197            | Estragole (= Methyl chavicol)    | 0.4           |
| 1199              | 1200            | γ-Terpineol                     | 0.9           |
| 1237              | 1237            | Pulegone                         | 0.4           |
| 1249              | 1250            | Chavicol                         | 5.3           |
| 1277              | 1277            | Phellandral                     | 0.3           |
| 1286              | 1285            | (E)-Anethole                    | 0.3           |
| 1289              | 1289            | Thymol                          | 6.6           |
| 1353              | 1356            | Eugenol                         | 0.3           |
| 1444              | 1442            | Guai-6,9-diene                   | 0.8           |
| 1483              | 1480            | Germacrene D                    | 0.2           |
| 1564              | 1560            | Dodecanoic acid                 | 1.7           |
| 1573              | 1571            | (3Z)-Hexenyl benzoate           | 1.6           |
Table 2. Cont.

| RI_{calc} | RI_{db} | Compound       | % Composition |
|-----------|---------|----------------|---------------|
| 1579      | 1576    | Spathulenol     | 0.5           |
| 1627      | 1627    | Benzophenone    | 0.2           |
| 1766      | 1769    | Benzyl benzoate | 0.5           |
| 1868      | 1869    | Benzyl salicylate| 0.5          |
| 1960      | 1958    | Palmitic acid   | 0.6           |
| 2012      | 2016    | Juivabione      | 0.6           |
| 2052      | 2053    | Manool         | 0.4           |
|           |         | Monoterpenoid   | 45.3          |
|           |         | Oxygenated monoterpenoids | 34.2 |
|           |         | Sesquiterpenoid | 0.9           |
|           |         | Oxygenated sesquiterpenoids | 0.5 |
|           |         | Diterpenoid     | 0.4           |
|           |         | Benzenoid aromatic | 11.5 |
|           |         | Others          | 5.5           |
|           |         | Total identified | 98.2          |

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 [15–18].

β-Phellandrene also dominated the essential oils of *P. contorta* subsp. *latifolia* from Alberta, Canada (34.3% β-phellandrene) [24] and *P. contorta* subsp. *murrayana* (37.2% β-phellandrene) [11]. In contrast, however, the concentration of terpinen-4-ol was relatively minor in both *P. contorta* subsp. *latifolia* (0.5%) and *P. contorta* subsp. *murrayana* (1.9%). Thymol was a minor component (0.3%) in *P. contorta* subsp. *murrayana*, and not observed in *P. contorta* subsp. *latifolia*. Chavicol was not observed either the *latifolia* or *murrayana* subspecies. Conversely, β-pinene was an abundant constituent of *P. contorta* subsp. *latifolia* (30.5%) and *P. contorta* subsp. *murrayana* (17.0%) as was α-terpineol (4.3% and 11.6%, respectively).

2.3. Chemical Composition of *Pinus flexilis*

Hydrodistillation of the fresh leaves (needles) of *P. flexilis* gave a colorless essential oil in 0.273% (w/w) yield. There have been no previous reports on *P. flexilis* essential oil yields. However, essential oils from *Pinus* species have been obtained in yields ranging from 0.08% (*P. rigida*) to 2.33% (*P. pumila*) [14]. The essential oil composition is presented in Table 3. A total of 102 compounds were identified in the leaf essential oil of *P. flexilis*, accounting for 99.7% of the composition. The major components in the essential oil were α-pinene (37.1%), β-pinene (21.9%), bornyl acetate (12.8%), and camphene (8.5%).

Table 3. Chemical composition of *Pinus flexilis* leaf essential oil.

| RI_{calc} | RI_{db} | Compound         | % Composition |
|-----------|---------|------------------|---------------|
| 801       | 801     | Hexanal          | 0.2           |
| 848       | 849     | (2E)-Hexenal     | 0.7           |
| 850       | 853     | (3Z)-Hexenal     | 0.2           |
| 863       | 867     | 1-Hexanol        | 0.1           |
| 880       | 880     | Santene          | 0.1           |
| 900       | 900     | Nonane           | tr            |
| 923       | 923     | Tricyclene       | 0.7           |
| 925       | 925     | α-Thujene        | tr            |
| 933       | 933     | α-Pinene         | 37.1          |
| 951       | 953     | Camphene         | 8.5           |
| 953       | 953     | Thuja-2,4(10)-diene | tr  |
| 972       | 972     | Sabinene         | 0.3           |
| RI$_{calc}$ | RI$_{db}$ | Compound                        | % Composition |
|-----------|---------|--------------------------------|---------------|
| 979       | 978     | β-Pinene                       | 21.9          |
| 989       | 989     | Myrcene                        | 1.5           |
| 1007      | 1007    | α-Phellandrene                 | 0.1           |
| 1017      | 1017    | α-Terpinene                    | 0.1           |
| 1024      | 1024    | p-Cymene                       | 0.1           |
| 1030      | 1030    | Limonene                       | 3.3           |
| 1031      | 1031    | β-Phellandrene                 | 2.2           |
| 1034      | 1034    | (Z)-β-Octimene                 | 0.1           |
| 1045      | 1045    | (E)-β-Octimene                 | tr            |
| 1057      | 1057    | γ-Terpinene                    | 0.2           |
| 1085      | 1086    | Terpinolene                    | 1.0           |
| 1088      | 1090    | Fenchone                       | 0.1           |
| 1093      | 1096    | p-Cymenene                     | tr            |
| 1099      | 1100    | 6-Camphenone                   | 0.1           |
| 1104      | 1104    | Undecanone                     | 0.4           |
| 1119      | 1120    | Nonanal                         | tr            |
| 1124      | 1124    | cis-p-Menth-2-en-1-ol          | tr            |
| 1126      | 1126    | α-Campholenal                  | 0.2           |
| 1138      | 1139    | Nopinone                       | tr            |
| 1140      | 1141    | trans-Pinocarveol              | 0.2           |
| 1142      | 1142    | trans-p-Menth-2-en-1-ol        | tr            |
| 1145      | 1145    | trans-Verbenol                 | 0.1           |
| 1147      | 1147    | Camphor                        | 0.1           |
| 1150      | 1150    | α-Phellandren-8-ol             | 0.1           |
| 1155      | 1156    | Camphene hydrate               | 0.1           |
| 1160      | 1160    | trans-Pinocamphone             | tr            |
| 1162      | 1164    | Pinocarvone                    | tr            |
| 1171      | 1171    | p-Menta-1,5-dien-8-ol          | 0.3           |
| 1171      | 1173    | Borneol                        | 0.2           |
| 1180      | 1180    | Terpinen-4-ol                  | 0.2           |
| 1186      | 1186    | p-Cymen-8-ol                   | 0.1           |
| 1195      | 1195    | α-Terpineol                    | 1.5           |
| 1206      | 1205    | Verbenone                      | tr            |
| 1228      | 1229    | Thymyl methyl ether            | 0.2           |
| 1286      | 1287    | Bornyl acetate                 | 12.8          |
| 1291      | 1293    | 2-Undecanone                   | 0.3           |
| 1294      | 1294    | trans-Pinocarvyl acetate       | tr            |
| 1300      | 1300    | Tridecane                      | tr            |
| 1357      | 1357    | 2-Methylundecanal              | 0.1           |
| 1376      | 1375    | α-Copaene                      | 0.1           |
| 1409      | 1410    | Dodecanal                      | 0.1           |
| 1410      | 1408    | Acora-3,7(14)-diene            | tr            |
| 1420      | 1417    | (E)-β-Caryophyllene            | 0.2           |
| 1430      | 1430    | β-Copaene                      | tr            |
| 1452      | 1152    | (E)-β-Farnesene                | 0.2           |
| 1455      | 1154    | α-Humulene                     | tr            |
| 1475      | 1175    | γ-Muurole                      | tr            |
| 1481      | 1480    | Germacrene D                   | 0.2           |
| 1494      | 1494    | 2-Tridecanone                  | 0.3           |
| 1498      | 1497    | α-Muurole                      | 0.2           |
| 1507      | 1508    | β-Bisabolene                   | 0.6           |
| 1512      | 1512    | γ-Cadinene                     | 0.1           |
| 1518      | 1518    | δ-Cadinene                     | 0.3           |
| 1548      | 1549    | α-Elemol                       | tr            |
| 1560      | 1560    | (E)-Nerolidol                  | tr            |
| 1576      | 1576    | Spathulenol                    | 0.1           |
Table 3. Cont.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound | % Composition |
|------------------|----------------|---------|--------------|
| 1627             | 1628           | 1-epi-Cubenol | tr           |
| 1641             | 1640           | τ-Cadinol | 0.1           |
| 1643             | 1644           | τ-Muurolol | 0.1           |
| 1651             | 1651           | α-Muurolol (= β-Cadinol) | tr |
| 1655             | 1655           | α-Cadinol | 0.2           |
| 1664             | 1665           | Intermedeo | tr           |
| 1668             | 1667           | (6Z)-Pentadecen-2-one | tr |
| 1683             | 1684           | epi-α-Bisabolol | tr |
| 1687             | 1688           | α-Bisabolol | 0.7 |
| 1697             | 1697           | 2-Pentadecanone | 0.1 |
| 1706             | 1707           | (2E,6Z)-Farnesol | tr |
| 1714             | 1717           | (2E,6Z)-Farnesol | 0.1 |
| 1737             | 1734           | (2E,6E)-Farnesal | tr |
| 1779             | 1782           | Dodecyl butyrate | tr |
| 1817             | 1815           | Hexadecanal | tr |
| 1832             | 1830           | Farnesyl acetate | tr |
| 1968             | 1964           | Sandaracopimara-8(14),15-diene | 0.1 |
| 1994             | 1993           | Manoyl oxide | 0.3 |
| 2007             | 2000           | 9β-Isopimara-7,15-diene | 0.1 |
| 2086             | 2085           | Abietadiene | tr |
| 2147             | 2145           | Abienol | tr |
| 2180             | 2182           | Sandaracopimarial | 0.1 |
| 2231             | 2222           | Isopimarinal | 0.2 |
| 2236             | 2230           | Palustrinal | 0.2 |
| 2238             | 2234           | Levopimarinal | tr |
| 2239             | 2241           | Methyl pimarate | tr |
| 2267             | 2262           | Dehydroabietal | tr |
| 2297             | 2292           | Methyl isopimarate | tr |
| 2302             | 2296           | Methyl levopimarate | tr |
| 2312             | 2307           | Abietal | tr |
| 2341             | 2330           | Methyl dehydroabietate | tr |
| 2366             | 2365           | Neoabietic acid | tr |

RI<sub>calc</sub> = Retention index calculated with respect to a homologous series of n-alkanes on a ZB-5ms column. RI<sub>db</sub> = Reference retention index obtained from the databases [15–18]. tr = trace (<0.05%). * Identification tentative; the MS is a good match (93% similarity match), but there is no reference RI available.

2.4. Enantiomeric Distribution of Terpenoids

The enantiomeric distributions of several terpenoid essential oil components have been determined by chiral gas chromatography-mass spectrometry. The enantiomeric distributions of terpenoid components of P. ponderosa var. ponderosa, P. contorta subsp. contorta, and P. flexilis essential oils are summarized in Table 4.

In P. ponderosa var. ponderosa essential oil, the (−)-enantiomer was the dominant stereoisomer in all monoterpenoids assessed. In the case of limonene and terpinen-4-ol, the (−)-enantiomer was only slight excess over the (+)-enantiomer, however. In the case of P. contorta subsp. contorta, the (−)-enantiomer was dominant in α-pinene, β-pinene, α-phellandrene, limonene, β-phellandrene, borneol, and α-terpineol, which is comparable to the distribution found in P. contorta subsp. murrayana [11] as well as P. ponderosa var. ponderosa (above). Interestingly, the enantiomeric distribution for terpinen-4-ol was (+)53.0:(−)47.0 in P. c. subsp. contorta, but reversed in P. c. subsp. murrayana,
(+39.9:–60.1). In *P. flexilis*, the (–)-enantiomers dominated in α-pinene, camphene, β-pinene, α-phellandrene, β-phellandrene, and α-terpineol, while the (+)-enantiomers were exclusively observed for sabinene, fenchone, and β-bisabolene. As observed in *P. ponderosa* var. *ponderosa*, the (–)-enantiomers were slightly higher than the (+)-enantiomers for limonene and for terpinen-4-ol in *P. flexilis*.

Table 4. Enantiomeric distribution of terpenoids of *Pinus ponderosa* var. *ponderosa*, *Pinus contorta* subsp. *contorta*, and *Pinus flexilis* leaf essential oils.

| Terpenoid Compound | Tree #1 | Tree #2 | Tree #3 | P. ponderosa | P. flexilis |
|--------------------|---------|---------|---------|--------------|-------------|
| α-Pinene           | 39.5:60.5 | 38.7:61.3 | 38.7:61.3 | 27.5:72.5 | 4.8:95.2 |
| Camphene           | 47.9:52.1 | 10.6:89.4 | 8.2:91.8 | —           | 1.8:98.2 |
| Sabinene           | —       | —       | —       | —           | 100:0      |
| δ-3-Carene         | 1.9:98.1 | 1.7:98.3 | 1.7:98.3 | 0:100       | 3.2:96.8   |
| β-Phellandrene     | —       | —       | —       | 8.4:91.6    | 17.2:82.8  |
| Limonene           | 2.3:97.7 | 0.9:99.1 | 1.3:98.7 | 0.6:99.4    | 3.5:96.5   |
| Fenchone           | —       | —       | —       | —           | 100:0      |
| Linalool           | 7.6:92.4 | 9.3:90.7 | 9.7:90.3 | —           | —          |
| Camphor            | —       | —       | —       | 0:100       | —          |
| Borneol            | —       | —       | —       | —           | 100:0      |
| Terpinen-4-ol      | 37.2:62.8 | 30.7:69.3 | 39.3:60.7 | 53.0:47.0 | 43.5:56.5 |
| α-Terpineol        | 2.6:97.4 | 3.6:96.4 | 2.8:97.2 | 35.5:64.5   | 8.8:91.2   |
| Pulegone            | —       | —       | —       | 100:0       | —          |
| Bornyl acetate     | 0:100   | 0:100   | 0:100   | —           | 100:0      |
| α-Terpinyl acetate | 0:100   | 0:100   | 0:100   | —           | —          |
| (E)-β-Caryophyllene| 0:100   | 0:100   | 0:100   | —           | —          |
| Germacrene D       | 0:100   | 0:100   | 0:100   | —           | —          |
| β-Bisabolene       | —       | —       | —       | —           | 100:0      |
| δ-Cadinene         | 0:100   | 0:100   | 0:100   | —           | —          |
| (E)-Nerolidol      | —       | 0.6:99.4 | —       | —           | —          |

= not detected.

The enantiomeric distributions for α-pinene, β-pinene, and limonene have been assessed for several *Pinus* species, which are listed in Table 5 for comparison. A perusal of Table 5 reveals that the enantiomeric distribution of α-pinene and limonene in *Pinus* species is variable both between species and within species. Allenspach and co-workers found that (+)-α-pinene generally predominated in primary essential oils of *P. sylvestris* and *P. cembra*, but that *P. mugo* and *P. nigra* were generally dominated by (–)-α-pinene [25]. The enantiomeric distribution in β-pinene in *Pinus* species, however, is consistently dominated by (–)-β-pinene.

Table 5. Enantiomeric distribution, (+):(–), of monoterpane hydrocarbons in *Pinus* species leaf essential oils.

| Pinus Species | Geographical Source | α-Pinene | β-Pinene | Limonene | Ref. |
|---------------|---------------------|----------|----------|---------|-----|
| *Pinus banksiana* Lamb | Eastern Canada | 74.5:25.5 | 3.0:97.0 | 8.4:91.6 | APRC |
| *Pinus cembra* L. | Italy | 64.4:35.6 | 0.8:99.2 | 0.100 | [26] |
| *Pinus contorta* subsp. *murrayana* (Balf.) Engelm. | Oregon, USA | 20.1:79.7 | 2.2:97.8 | 0.100 | [11] |
| *Pinus contorta* Douglas ex Loudon subsp. *contorta* | Oregon, USA | 27.5:72.5 | 0:100 | 13.2:86.8 | This work |
| *Pinus flexilis* E. James | Idaho, USA | 4.8:95.2 | 3.2:96.8 | 33.0:67.0 | This work |
Table 5. Cont.

| Pinus Species | Geographical Source | α-Pinene | β-Pinene | Limonene | Ref. |
|---------------|--------------------|----------|----------|----------|------|
| Pinus halepensis Mill. | Portugal | 59.1:40.9 | 4.7:95.3 | — | [27] |
| Pinus mugo Turra (syn. P. montana Mill.) | Austria | 49.2:50.8 | 0.9:99.1 | 28.1:71.9 | [26] |
| | Italy | 63.3:36.7 | 1.4:98.6 | 13.4:86.6 | |
| | Korea | 43.8:56.2 | 19.1:80.9 | 62.7:37.3 | |
| Pinus nigra J.F. Arnold | Austria | 16.9:83.1 | 6.7:93.3 | 23.8:76.2 | [26] |
| | Albania | 3.9:96.1 | 18.0:82.0 | 23.6:76.4 | APRC |
| Pinus peuce Griseb. | Germany | 26.8:73.2 | 3.7:96.3 | 29.2:70.8 | [26] |
| | Italy | 63.3:36.7 | 1.4:98.6 | 13.4:86.6 | |
| | Korea | 43.8:56.2 | 19.1:80.9 | 62.7:37.3 | |
| Pinus pinaster Aiton | Portugal | 30.3:69.7 | 0.6:99.4 | 31.0:69.0 | [27] |
| Pinus ponderosa Douglas ex C. Lawson var. ponderosa | Oregon, USA | 53.3:46.7 | 1.9:98.1 | 38.7:61.3 | This work |
| | Oregon, USA | 20.3:79.7 | 1.7:98.3 | 41.1:58.9 | |
| | Oregon, USA | 6.2:93.8 | 1.7:98.3 | 41.2:58.8 | |
| Pinus resinosa Aiton | Eastern Canada | 61.2:38.8 | 2.9:97.1 | 44.0:56.0 | APRC |
| | Eastern Canada | 63.0:37.0 | 2.5:97.5 | 38.8:61.2 | |
| Pinus strobus L. | Eastern Canada | 39.8:60.2 | 2.2:97.8 | 16.5:83.5 | APRC |
| | Eastern Canada | 40.2:59.8 | 2.4:97.6 | 16.5:83.5 | |
| Pinus sylvestris L. | Poland | 76.2:23.8 | 1.8:98.2 | 98.1:1.9 | [
| | Austria | 23.2:76.8 | 3.5:96.5 | 25.9:74.1 | 26] |
| | Italy | 13.5:86.5 | 3.6:96.4 | 29.3:70.7 | |
| | Korea | 33.4:66.6 | 4.9:95.1 | 66.7:33.3 | |
| | Portugal | 27.2:72.8 | 0.9:99.1 | — | [27] |
| | Eastern Canada | 67.1:32.9 | 2.3:97.7 | 21.8:78.2 | APRC |
| | Eastern Canada | 67.3:32.7 | 2.4:97.6 | 21.7:78.3 | |
| Pinus uncinata subsp. uliginosa (G.E.Neumann ex Wimm.) Businsky | Poland | 65.6:34.4 | 11.7:88.3 | 63.6:36.4 | [29] |
| Pinus uncinata Ramond ex DC. | Poland | 58.4:41.6 | 9.1:90.9 | 11.7:88.3 | [29] |

APRC = Data from the commercial essential oil samples from the collection of the Aromatic Plant Research Center (Lehi, Utah, USA). — = not detected.

The dominant enantiomer for α-pinene and β-pinene in *P. flexilis* were the (−)-enantiomers. α-Pinene enantiomeric distributions are generally variable in *Pinus* species, but (−)-β-pinene generally predominates in the genus (see above). The enantiomeric distribution of limonene also seems to be variable in *Pinus* species (see above), but (−)-limonene was the major enantiomer in *P. flexilis*. (−)-Camphene was the dominant enantiomer in *P. flexilis*, which was also found to be the case for *Pinus uncinata* subsp. *uliginosa* (G.E.Neumann ex Wimm.) Businsky, *Pinus uncinata* Ramond ex DC., *Pinus peuce* Griseb., *Pinus mugo* Turra, *Pinus nigra* J.F. Arnold, *Pinus pinaster* Aiton, and *Pinus cembra* L. [26]. Interestingly, the enantiomeric distribution for camphene in *Pinus sylvestris* L. is variable depending on geographical source; (−)-camphene dominated in *P. sylvestris* from Poland and from Korea, whereas (+)-camphene dominated the essential oils from Austria and Italy [26]. (−)-Borneol and (−)-bornyl acetate were the exclusive enantiomers in *P. flexilis* essential oil, which was also observed in *P. contorta* subsp. *latifolia* (Engelm.) Critchf. [11].

3. Materials and Methods

3.1. Plant Material

Fresh plant material of *P. ponderosa* was collected from three individual mature trees growing near La Pine, Oregon (#1, 43°46′28″ N, 121°32′33″ W, elev. 1288 m; #2, 43°46′24″ N, 121°32′30″ W, elev. 1283 m; #3, 43°45′51″ N, 121°31′47″ W, elev. 1294 m), on 18 May 2021. *Pinus contorta* subsp. *contorta* was collected from a mature tree near Ona Beach, Oregon (44°31′16″ N, 124°4′13″ W, 3.0 m elevation) on 6 July 2021. The trees were identified in the field by E. Ankney using the field guide by Turner and Kuhlmann [30] and confirmed
by comparison with samples from the C.V. Starr Virtual Herbarium, New York Botanical Garden (http://sweetgum.nybg.org/science/vh/, accessed on 14 January 2022). Leaves of *P. flexilis* were collected from a mature tree growing on the grounds of the Idaho Botanical Garden (43°36′04″ N, 116°09′35″ W, 862 m elevation) on 29 July 2021. The tree was identified by Daniel Murphy, Collections Curator of the Idaho Botanical Garden. Voucher specimens have been deposited in the University of Alabama in Huntsville herbarium.

The fresh leaves (needles) of each tree sample were hydrodistilled for 3 h using a Likens-Nickerson apparatus to give colorless essential oils (Table 6). The essential oils were stored under refrigeration (−20 °C) until analysis. Commercial *Pinus* essential oil samples from the collection from the Aromatic Plant Research Center (APRC) were analyzed as received.

### Table 6. Collection and hydrodistillation details of *Pinus* species.

| Tree Sample            | Voucher Number | Mass Leaves | Mass Essential Oil |
|------------------------|----------------|-------------|--------------------|
| *Pinus ponderosa* var. ponderosa #1 | EA-50553       | 33.25 g     | 106.6 mg           |
| *Pinus ponderosa* var. ponderosa #2 |               | 33.39 g     | 133.2 mg           |
| *Pinus ponderosa* var. ponderosa #3 |               | 67.72 g     | 313.8 mg           |
| *Pinus contorta* subsp. contorta | EA-50554       | 15.82 g     | 106.7 mg           |
| *Pinus flexilis*       | KS-58231       | 115.62 g    | 315.7 mg           |

### 3.2. Gas Chromatography–Mass Spectrometry

Gas chromatographic–mass spectral (GC-MS) analysis of the *Pinus* essential oils was carried as previously described [31]: Shimadzu GCMS-QP2010 Ultra, ZB-5ms fused silica capillary column (60 m length, 0.25 mm diameter, 0.25 µm film thickness), He carrier gas, 2.0 mL/min flow rate, injection and ion source temperatures 260 °C; GC oven program 50 °C to 260 °C at 2.0 °C/min; 0.1 µL of a 5% (w/v) sample of essential oil in CH₂Cl₂ injected, split mode, 24.5:1 split ratio. Retention index (RI) values were calculated using a linear equation by Van den Dool and Kratz [32]. Identification of the essential oil components was carried out by comparison of MS fragmentation and comparison of retention indices (RI) with those available in the databases [15–18]. Representative gas chromatograms of the *Pinus* species are shown in supplementary Figure S1.

### 3.3. Gas Chromatography–Flame Ionization Detection

The GC-FID analysis was carried out as previously described [33]: Shimadzu GC-2010 equipped with flame ionization detector, a split/splitless injector, and Shimadzu autosampler AOC-20i; ZB-5 capillary column (60 m × 0.25 mm i.d.; film thickness 0.25 µm); He carrier gas, 1.0 mL/min flow rate; GC oven program as above for GC-MS; injector and detector temperatures maintained at 260 °C; 0.1 µL of a 5% (w/v) solution in CH₂Cl₂ injected, split mode, 31:1 split ratio. The percent compositions of the essential oil components were determined from peak areas and standardized using external standards of representative compounds from each compound class (α-pinene, β-pinene, camphene, limonene, menthol, borneol, (E)-β-caryophyllene, eugenol, and methyl chavicol).

### 3.4. Chiral Gas Chromatography–Mass Spectrometry

Chiral GC-MS of the leaf essential oils was carried out, as reported previously [34]: Shimadzu GCMS-QP2010S, 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 (30 m length × 0.25 mm inside diameter × 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 CH₂Cl₂ 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.
4. Conclusions

The leaf essential oil compositions of _P. ponderosa_ var. _ponderosa_ and _P. contorta_ subsp. _contorta_ from Oregon, USA, have been determined. The enantiomeric distributions of these two _Pinus_ species are reported for the first time. The chemical composition as well as the enantiomeric distribution for _P. flexilis_ from Idaho, USA, are reported for the first time. Both α-pinene and limonene show considerable variation in enantiomeric distribution between and within _Pinus_ species, but (−)-β-pinene is consistently the more dominant enantiomer. This work adds to our knowledge of the essential oil compositions of the genus _Pinus_. Additional studies on chemical compositions as well as enantiomeric distributions of members of the Pinaceae are underway in our laboratories.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27175658/s1, Figure S1: Gas chromatograms of _Pinus ponderosa_ var. _ponderosa_ (A), _Pinus contorta_ subsp. _contorta_ (B), and _Pinus flexilis_ (C).

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Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Essential oil samples are no longer available.

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