**The Volatile Phytochemistry of Seven Native American Aromatic Medicinal Plants**

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**Abstract:** As part of our evaluation of essential oils derived from Native American medicinal plants, we have obtained the essential oils of *Agastache foeniculum* (Pursch) Kuntze (Lamiaceae), *Gaultheria procumbens* L. (Ericaceae), *Heliopsis helianthoides* (L.) Sweet (Asteraceae), *Liatris uvedalia* (L.) Mack. ex Mack. (Asteraceae), and *Verbena hastata* L. (Verbenaceae) by hydrodistillation. The essential oils were analyzed by gas chromatographic techniques. The essential oil of *A. foeniculum* was dominated by estragole (88–93%), while methyl salicylate (91%) dominated the *G. procumbens* essential oil. Germacrene D was the major component in *H. helianthoides* (42%) and *L. spicata* (24%). 1,8-Cineole (31%) and α-terpinel (17%) were the main compounds in *P. incanum* essential oil. The essential oil of *S. uvedalia* showed α-pinene (24%), perillene (15%), and β-caryophyllene (17%) as major components. *Verbena hastata* essential oil was rich in 1-octen-3-ol (up to 29%) and palmitic acid (up to 22%). Four of these essential oils, *H. helianthoides*, *L. spicata*, *P. incanum*, and *V. hastata*, are reported for the first time. Additionally, the enantiomeric distributions of several terpenoid components have been determined.

**Keywords:** *Agastache; Gaultheria; Heliopsis; Liatris; Pycnanthemum; Smallanthus; Verbena*; essential oil; Native American; ethnomedicine

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1. **Introduction**

Plants have been used in traditional medicine since prehistoric times. The therapeutic properties of medicinal plants are generally attributed to secondary metabolites produced by the plants as protection against pathogens and herbivory. As with many other aboriginal peoples, Native North Americans have used plants as medicines throughout their history. Although not as extensively documented as traditional Chinese medicine or Ayurvedic medicine, there are several sources of information regarding Native American ethnopharmacology [1–3]. As part of our ongoing investigations of the essential oil compositions of Native American medicinal plants, we have collected and examined seven aromatic medicinal plants growing in the southeastern United States.

*Agastache foeniculum* (Pursch) Kuntze (Lamiaceae) is native to north central United States and southern Canada, but has been recorded in southern Alabama [4]. The plant has been introduced to Europe, particularly the U.K., the Netherlands, and Germany, as an ornamental [5]. Cheyenne and Chippewa Native Americans used an infusion of the leaves of *A. foeniculum* as a cold medicine [2]. Essential oil compositions of *A. foeniculum* have been extensively studied, and the oils are typically dominated by methyl chavicol (estragole) with smaller amounts of (E)-anethole [6]. Nonvolatile phytochemicals from *A. foeniculum* include flavonoids (apigenin, quercetin), polyphenolics (rosmarinic acid, caffeic acid), pentacyclic triterpenoids (α-amyrin, β-amyrin), and sterols (campesterol, campestanol, sitosterol, stigmasterol, stigmastanol) [6].
**Gaultheria procumbens** L. (Ericaceae) naturally ranges in eastern North America from Canada, south through Alabama and Georgia [4]. Several native North American tribes used an infusion of *G. procumbens* to treat headaches, colds (Algonquin, Cherokee, Chippewa, Iroquois) or to treat arthritis, rheumatism, and lumbago (Iroquois, Menominee, Ojibwa, Potawatomi) [2]. The Cherokee were known to use a root infusion of *G. procumbens* along with the roots of *Epigaea repens* for chronic indigestion, and they also chewed the leaves as a substitute for chewing tobacco [7]. Much like its Asian relative, *Gaultheria fragrantissima* Wall., the essential oil of *G. procumbens* is dominated by methyl salicylate. Commercial *G. fragrantissima* essential oil (doTERRA International, Pleasant Grove, Utah) has 99.7% methyl salicylate, while methyl salicylate in *G. procumbens* essential oil typically ranges 96.6–99.8% [8–10].

*Heliopsis helianthoides* (L.) Sweet (Asteraceae) is native to North America from Saskatchewan, Canada east to the Atlantic coast of Newfoundland and south to the Gulf of Mexico, with the western range extending as far as New Mexico [4,11,12]. There are three subspecies of *H. helianthoides*, *ssp. helianthoides*, generally occurring east of the Mississippi River; *ssp. occidentalis*, found in the Great Plains region; and *ssp. scabra*, which is predominant in the Ozark region (Missouri, Arkansas, and Oklahoma) [11]. The Chippewa took a decoction of the roots of *H. helianthoides* as a stimulant [2]. The Cherokee used the roots in combination with *Scutellaria incana* “for young women”, presumably for menstruation-related discomforts, and sore feet were relieved by soaking in an infusion of what was called “swamp sunflower” [7]. Guaianolide sesquiterpenoids [13], *N*-alkylamides [14], and lignans [15] have been isolated and characterized from *H. helianthoides*.

The natural range of *Liatris spicata* (L.) Willd. (Asteraceae) is the eastern United States and Canada, east of the Mississippi River, from the south along the Gulf of Mexico including southern Alabama and northern Florida areas, north to Ontario and Quebec [4,16,17]. The Cherokee used the plant as an analgesic for backache and limb pains [2]. The guaianolide sesquiterpenoid spicatin has been isolated from the chloroform extract of *L. spicata* [18].

**Pycnanthemum incanum** (L.) Michx. (Lamiaceae) ranges naturally in the eastern United States from the Mississippi River east to the Atlantic coast and from southern Ontario, Canada south to the Gulf of Mexico, though it is primarily found from the Appalachian mountain region beginning in north Georgia north into Ontario, Canada [4,19]. The Cherokee and Choctaw people used the leaves of *P. incanum* externally to treat headaches [2]. Dein and Munafo have characterized the key odorants from *P. incanum* to be β-ionone, myrcene, linalool, and pulegone [20].

The natural range of *Smallanthus uvedalia* (L.) Mack. ex Mack. (Asteraceae) is the southeastern United States, from the Ohio river basin south to the Gulf of Mexico [4]. *Smallanthus uvedalia* was reportedly used internally by Native American Indians for laxative properties as well as a stimulant and also to treat swollen glands, especially mastitis [21]. The Cherokee used a salve of the roots to treat burns and cuts, while the Iroquois took an infusion of the plant for back pain and as an antiemetic [2]. Interestingly, the Cherokee were also reported to have used a tea made from this plant to induce vomiting, though it is unclear which portion was used [7]. A number of germacranolide sesquiterpenoids and ent-kaurane diterpenoids have been isolated and characterized from *S. uvedalia* [22]. The leaf essential oils of *S. uvedalia* from several locations in north Alabama have been analyzed previously [23,24].

**Verbena hastata** L. (Verbenaceae) ranges throughout North America [4]. The Cherokee used the plant to treat colds and coughs and to alleviate fevers [2]. The ethanol leaf extract of *V. hastata* has shown antiplasmodial [25], antinociceptive, anti-inflammatory, antipyretic [26], and anti-ulcer activities [27]. The iridoid glycoside hastatoside has been isolated from *V. hastata* [28].

The purpose of this study was to extend our understanding of the volatile phytochemistry of Native American aromatic medicinal plants by examination of the essential
oils of these seven plant species, to determine their chemical compositions as well as the enantiomeric distributions of terpenoid constituents.

2. Results and Discussion

The essential oils of each species were obtained by hydrodistillation of dried plant material (Table 1).

Table 1. Collection and hydrodistillation details of seven Native American medicinal plants.

| Plant Species          | Collection Site (Date)                  | Mass of Plant Material | Essential Oil Yield              |
|------------------------|----------------------------------------|------------------------|----------------------------------|
| Agastache foeniculum   | Cultivated, Kirkland Gardens, 31° 26' 27" N, 85° 21' 31' W (5 May 2020) | 24.78 g dried aerial parts | 367.1 mg (1.48%) pale yellow essential oil |
| Agastache foeniculum   | Cultivated, Kirkland Gardens, 31° 26' 27" N, 85° 21' 31' W (5 May 2020) | 28.22 g dried aerial parts | 587.7 mg (2.08%) pale yellow essential oil |
| Agastache foeniculum   | Cultivated, Kirkland Gardens, 31° 26' 27" N, 85° 21' 31' W (5 May 2020) | 13.77 g dried aerial parts | 316.6 mg (2.30%) pale yellow essential oil |
| Gaultheria procumbens  | Cultivated, Kirkland Gardens, 31° 26' 27" N, 85° 21' 31' W (10 June 2020) | 3.01 g dried leaves | 127.8 mg (4.25%) pale yellow essential oil |
| Heliopsis helianthoides| Cultivated, Kirkland Gardens, 31° 26' 27" N, 85° 21' 31' W (24 July 2020) | 27.70 g dried aerial parts | 263.6 mg (0.95%) pale yellow essential oil |
| Liatris spicata         | Cultivated, Kirkland Gardens, 31° 26' 27" N, 85° 21' 31' W (24 July 2020) | 31.90 g dried aerial parts | 133.1 mg (0.420%) pale yellow essential oil |
| Pycnanthemum incanum   | Wild-growing, South Carolina, 35° 06' 08.1" N, 82° 36' 44.4" W (31 August 2020) | 9.82 g dried aerial parts | 168.1 mg (1.71%) pale yellow essential oil |
| Sm Allenthus uvedalia  | Wild-growing, South Carolina, 35° 06' 08.1" N, 82° 36' 44.4" W (31 August 2020) | 90.77 g dried aerial parts | 369.7 mg (0.41%) yellow essential oil |
| Verbena hastata #1     | Wild-growing, Newville, Alabama, 31° 26' 27" N, 85° 21' 31' W (25 May 2020) | 24.61 g dried aerial parts | 134.2 mg (0.55%) pale yellow essential oil |
| Verbena hastata #2     | Wild-growing, Newville, Alabama, 31° 26' 27" N, 85° 21' 31' W (25 May 2020) | 28.50 g dried aerial parts | 62.2 mg (0.22%) pale yellow essential oil |
| Verbena hastata #3     | Wild-growing, Newville, Alabama, 31° 26' 27" N, 85° 21' 31' W (25 May 2020) | 36.22 g dried aerial parts | 214.2 mg (0.59%) pale yellow essential oil |

*The volatile materials reported in this research were obtained by hydrodistillation with continuous solvent extraction using a Likens–Nickerson apparatus. Many researchers consider these products not to be true “essential oils”, but rather “volatile fractions”.

2.1. Agastache foeniculum (Pursch) Kuntze (Lamiaceae)

The aerial parts of three different plant samples of *A. foeniculum* were collected from cultivated plants in Newville, Alabama. Hydrodistillation gave pale yellow essential oils in yields ranging from 1.48% to 2.30% yield. The essential oil compositions are compiled in Table 2.

The *A. foeniculum* essential oil was dominated by the phenylpropanoid methyl chavicol (=estragole). There are apparently five different chemotypes of *A. foeniculum* based on essential oil chemical profiles: (1) methyl chavicol, (2) spathulenol/bornyl acetate, (3) γ-cadinene/α-cadinol, (4) limonene, and (5) isomenthone [33,34]. Most *A. foeniculum* essential oils belong to the methyl chavicol chemotype, however [33,35–42].

Methyl chavicol contributes to the anise-like aroma of *A. foeniculum* and has shown anti-inflammatory and anti-edematogenic [43,44], cytotoxic [45], and antimicrobial activities against phytopathogens [46,47]. Unfortunately, however, methyl chavicol has also shown genotoxic and carcinogenic activities [48,49].
Table 2. Essential oil composition of three samples of anise fennel (*Agastache foeniculum*) cultivated in south Alabama.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound | Percent Composition |
|------------------|----------------|----------|---------------------|
|                  |                |          | #1  | #2  | #3  |
| 924              | 927            | α-Thujene | tr  | tr  |   |
| 932              | 933            | α-Pinene  | tr  | tr  | tr |
| 963              | 964            | Benzaldehyde | tr  | 0.1 | 0.1 |
| 971              | 972            | Sabinene  | tr  | tr  | tr |
| 971              | 974            | Hexanoic acid |   |   | tr |
| 975              | 974            | 1-Octen-3-ol | 0.3 | 0.7 | 0.6 |
| 983              | 984            | 3-Octanone | 0.1 | 0.2 | 0.2 |
| 987              | 989            | Myrcene  | 0.1 | 0.1 |   |
| 1016             | 1018           | α-Terpinene | 0.1 |   |   |
| 1024             | 1024           | p-Cymene  | 0.6 | tr  |   |
| 1028             | 1030           | Limonene  | 1.5 | 4.9 | 2.9 |
| 1030             | 1033           | Benzyl alcohol |   | 0.1 | 0.1 |
| 1030             | 1031           | β-Phellandrene | tr  | tr  | tr |
| 1032             | 1032           | 1,8-Cineole | tr  | —  | —  |
| 1057             | 1057           | γ-Terpinene | 0.1 |   |   |
| 1066             | 1068           | Acetophenone | tr  | —  |   |
| 1069             | 1069           | cis-Sabinene hydrate | tr  |   |   |
| 1097             | 1099           | Linalool  | 0.1 | tr  | tr |
| 1104             | 1107           | 1-Octen-3-yl acetate | 0.1 | 0.2 | 0.1 |
| 1198             | 1197           | Methyl chavicol (=Estragole) | 93.2 | 88.4 | 91.5 |
| 1213             | 1217           | Coumaran  |   | tr  | tr |
| 1248             | 1250           | Chavicol  | 0.1 | 0.2 | 0.3 |
| 1282             | 1285           | (E)-Anethole |   | tr  | tr |
| 1287             | 1289           | Thymol    | 0.9 | 0.1 | 0.1 |
| 1295             | 1296           | Carvacrol | 0.1 | tr  | tr |
| 1309             | 1309           | 4-Vinylguaiacol |   | tr  | tr |
| 1333             | 1334           | Bicycloelemene |   | tr  | tr |
| 1355             | 1356           | Eugenol   | 0.1 | 0.1 | 0.2 |
| 1362             | 1362           | Chavibetol | 0.7 | 2.3 | 0.7 |
| 1379             | 1379           | (E)-β-Damascenone |   | tr  | tr |
| 1384             | 1382           | β-Bourbonene |   | tr  | tr |
| 1390             | 1390           | trans-β-Elemene |   | tr  | tr |
| 1392             | 1392           | (Z)-Jasmone |   | —  | 0.1 |
| 1401             | 1403           | Methyl eugenol | tr  | 0.1 | tr |
| 1417             | 1417           | (E)-β-Caryophyllene | 1.2 | 1.6 | 1.9 |
| 1452             | 1453           | α-Humulene | 0.1 |   | 0.1 |
| 1475             | 1475           | γ-Muurolone |   | tr  | tr |
| 1478             | 1481           | (E)-β-Ironone |   | tr  | tr |
| 1481             | 1483           | Germacrene D | 0.2 | 0.3 | 0.2 |
| 1487             | 1487           | β-Selinene |   | tr  |   |
| 1491             | 1491           | Viridiflorene |   | —  | tr |
| 1496             | 1497           | Bicyclomacrorene | 0.4 | 0.4 | 0.6 |
| 1504             | 1503           | (E,E)-α-Farnesene |   | tr  | tr |
| 1513             | 1512           | γ-Cadinene |   | tr  | tr |
| 1518             | 1518           | δ-Cadinene | tr  | 0.1 | 0.1 |
| 1525             | 1574           | Germacrene D-4-ol | 0.1 | 0.1 | 0.2 |
| 1550             | 1577           | Caryophyllene oxide | tr  |   | tr |
| 1558             | 1590           | Globulol   |   | tr  | tr |
| 1593             | 1594           | Viridiflorol |   | tr  | tr |
| 1641             | 1643           | τ-Cadinol  |   | tr  | tr |
| 1641             | 1644           | α-Murolol (=δ-Cadinol) |   | —  | tr |
| 1643             | 1644           | τ-Murolol  |   | tr  | tr |
| 1656             | 1655           | α-Cadinol  | 0.1 | 0.1 | 0.1 |
### Table 2. Cont.

| RI_{\text{calc}} | RI_{\text{db}} | Compound                   | Percent Composition #1 | #2 | #3 |
|-----------------|----------------|----------------------------|-------------------------|----|----|
| 2.4             | 4.9            | Monoterpene hydrocarbons   |                         |    |    |
| 1.0             | 0.1            | Oxygenated monoterpenoids  |                         |    |    |
| 1.8             | 2.5            | Sesquiterpene hydrocarbons |                         |    |    |
| 0.2             | 0.2            | Oxygenated sesquiterpenoids |                        |    |    |
| 94.1            | 91.3           | Benzenoid aromatics        |                         |    |    |
| 0.5             | 1.0            | Others                     |                         |    |    |
| 100.0           | 100.0          | Total identified           |                         |    |    |

RI_{\text{calc}} = retention indices calculated with respect to a homologous series of n-alkanes on a ZB-5 column. 
RI_{\text{db}} = retention indices from the databases [29–32]. tr = trace (<0.05%).

#### 2.2. Gaultheria procumbens L. (Ericaceae)

The leaf essential oil of *G. procumbens* was obtained in 4.25% yield and the major component was methyl salicylate (91.1%) (Table 3). Methyl salicylate is the dominating component in *G. procumbens* essential oil regardless of geographical location of cultivation, ranging in concentration from 61.14% to 99.96% [8–10,50–52].

### Table 3. Essential oil composition of American wintergreen (*Gaultheria procumbens*) cultivated in southern Alabama.

| RI_{\text{calc}} | RI_{\text{db}} | Compound                               | %   |
|-----------------|----------------|----------------------------------------|-----|
| 1033            | 1033           | Benzyl alcohol                         | 0.2 |
| 1051            | 1051           | 2,3,6-Trimethylhepta-1,5-diene          | tr  |
| 1105            | 1104           | Nonanal                                | tr  |
| 1160            | 1158           | Menthone                               | 0.1 |
| 1193            | 1192           | Methyl salicylate                      | 91.1|
| 1215            | 1217           | Coumaran                               | tr  |
| 1237            | 1237           | Pulegone                               | 0.6 |
| 1262            | 1263           | (2E)-Decenal                           | tr  |
| 1271            | 1273           | (E)-Cinnamaldehyde                     | tr  |
| 1289            | 1289           | Thymol                                 | 0.3 |
| 1304            | 1304           | (E)-Cinnamyl alcohol                   | 0.8 |
| 1336            | 1339           | Piperitenone                           | tr  |
| 1388            | 1390           | trans-β-Elemene                        | tr  |
| 1417            | 1417           | (E)-β-Caryophyllene                    | tr  |
| 1431            | 1432           | trans-α-Bergamotene                    | tr  |
| 1445            | 1447           | Geranyl acetone                        | 0.1 |
| 1467            | 1463           | Tuberolactone                          | 5.3 |
| 1470            | 1471           | Massota lactone                        | 1.3 |
| 1479            | 1480           | Germacrene D                           | 0.1 |
| 1502            | 1503           | (E,E)-α-Farnesene                      | tr  |
| 1516            | 1518           | δ-Cadinene                             | tr  |
| 1579            | 1577           | Caryophyllene oxide                    | tr  |
| 1652            | 1655           | α-Cadinol                              | tr  |
Table 3. Cont.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                  | %      |
|-----------------|----------------|----------------------------|--------|
| 1679            | 1676           | 8-Hydroxyisobornyl isobutanoate | tr     |
| 1761            | 1762           | Benzyl benzoate             | tr     |
| 1863            | 1869           | Benzyl salicylate           | tr     |
|                 |                | Monoterpene hydrocarbons    | tr     |
|                 |                | Oxygenated monoterpenoids   | 1.1    |
|                 |                | Sesquiterpene hydrocarbons  | 0.1    |
|                 |                | Oxygenated sesquiterpenoids  | tr     |
|                 |                | Benzenoid aromatics         | 92.1   |
|                 |                | Others                      | 6.6    |
|                 |                | Total identified            | 99.9   |

Enantiomeric Distribution (+):(−)

Menthone 0:100
Pulegone 100:0

(E)-β-Caryophyllene 100:0
Germacrene D 100:0

RI<sub>calc</sub> = retention indices calculated with respect to a homologous series of n-alkanes on a ZB-5 column.
RI<sub>db</sub> = retention indices from the databases [29–32]. tr = trace (<0.05%).

The major component of *G. procumbens* essential oil, methyl salicylate, is well-known as an anti-inflammatory, antipyretic, analgesic agent [53], and accounts for the traditional use of the herb by Native Americans. Methyl salicylate is a common flavoring and fragrance ingredient in cosmetics, shampoos, toilet soaps, and other toiletries, however, it is also a potentially hazardous intoxicant [54–56].

2.3. *Heliopsis helianthoides* (L.) Sweet (Asteraceae)

The essential oil from the aerial parts of *H. helianthoides* was obtained in 0.95% yield. The major component in the essential oil was germacrene D (42.4%), with a lesser amount of 4-vinylguaicol (5.5%) (Table 4). As far as we are aware, this is the first report on the chemical composition of *H. helianthoides* essential oil.

Table 4. Essential oil composition of early sunflower (*Heliopsis helianthoides*) cultivated in southern Alabama.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                  | Percent Composition a |
|-----------------|----------------|----------------------------|-----------------------|
| 801             | 801            | Hexanal                    | 1.0 0.2               |
| 815             | 817            | 4-Hydroxy-2-pentanone      | 0.9 0.3               |
| 829             | 831            | Furfural                   | 0.3 0.1               |
| 848             | 850            | (2E)-Hexenal               | 1.0 0.2               |
| 879             | 876            | 5-Methyl-(3Z)-hexen-2-one  | 0.9 0.1               |
| 959             | 959            | Benzaldehyde               | 0.3 0.0               |
| 987             | 989            | 2-Pentyl furan             | 0.4 0.1               |
| 1102            | 1104           | Nonanal                    | 1.0 0.0               |
| 1290            | 1289           | Thymol                     | 1.8 0.6               |
| 1298            | 1300           | Carvacrol                  | 1.5 0.1               |
| 1309            | 1309           | 4-Vinylguaicol             | 5.5 0.6               |
| 1335            | 1335           | δ-Elemene                  | 0.5 0.1               |
| 1383            | 1382           | β-Bourbonene               | 2.7 0.1               |
| 1388            | 1390           | trans-β-Elemene            | 0.5 0.0               |
| 1417            | 1422           | β-Ylangene                 | 0.9 0.1               |
| 1418            | 1417           | (E)-β-Caryophyllene        | 2.7 0.0               |
| 1428            | 1430           | β-Copaene                  | 1.2 0.1               |
| 1443            | 1447           | iso-Germacrene D           | 0.4 0.0               |
| 1454            | 1453           | α-Humulene                 | 0.5 0.0               |
Table 4. Cont.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound | Percent Composition<sup>a</sup> | Average | St. dev. |
|------------------|----------------|----------|-------------------------------|---------|---------|
| 1477             | 1481           | (E)-β-Ionone | 0.5                           | 0.0     |         |
| 1480             | 1480           | Germacrene D | 42.4                          | 1.2     |         |
| 1494             | 1497           | Bicyclogermacrene | 0.8                        | 0.1     |         |
| 1497             | 1502           | ε-Amorphene | 0.3                           | 0.0     |         |
| 1503             | 1499           | (Z)-Dihydroapofarnesal | 0.3                    | 0.0     |         |
| 1509             | —              | Unidentified<sup>b</sup> | 1.1                           | 0.0     |         |
| 1516             | 1518           | δ-Cadinene | 0.4                           | 0.0     |         |
| 1523             | 1516           | (E)-Dihydroapofarnesal | 0.3                          | 0.1     |         |
| 1524             | 1524           | Dihydroactinidiolide | 0.7                             | 0.0     |         |
| 1537             | 1557           | Germacrene B | 0.7                           | 0.0     |         |
| 1560             | 1560           | (E)-Nerolidol | 0.8                           | 0.2     |         |
| 1566             | 1566           | 1,5-Epoxysalvia-4(14)-ene | 0.3                           | 0.0     |         |
| 1575             | 1576           | Spathulenol | 1.2                           | 0.0     |         |
| 1580             | 1577           | Caryophyllene oxide | 1.5                             | 0.0     |         |
| 1590             | 1593           | Salvial-4(14)-en-1-one | 0.6                          | 0.0     |         |
| 1626             | 1629           | iso-Spathulenol | 2.7                           | 0.0     |         |
| 1638             | 1644           | allo-Aromadendrene epoxide | 0.3                          | 0.1     |         |
| 1653             | 1655           | α-Cadinol | 1.0                           | 0.1     |         |
| 1683             | 1683           | Germacra-4(15),5,10(14)-tri-en-1α-ol | 1.4                      | 0.2     |         |
| 1685             | 1685           | Eudesma-4(15),7-dien-1β-ol | 0.5                          | 0.1     |         |
| 1689             | —              | Germacra-4(15),5,10(14)-tri-en-1β-ol | 1.1                      | 0.2     |         |
| 1735             | 1735           | Mint sulfide | 0.3                           | 0.1     |         |
| 1763             | —              | Unidentified<sup>c</sup> | 1.4                           | 0.0     |         |
| 1827             | —              | Unidentified<sup>d</sup> | 1.1                           | 0.0     |         |
| 1840             | 1841           | Phytone | 1.6                           | 0.0     |         |
| 2097             | 2098           | γ-Stearalactone | 2.1                             | 0.3     |         |
| 2106             | 2102           | Phytol | 2.8                           | 1.3     |         |
| 2273             | —              | Unidentified<sup>e</sup> | 2.3                           | 0.8     |         |

**RI<sub>calc</sub>** = retention indices calculated with respect to a homologous series of n-alkanes on a ZB-5 column. **RI<sub>db</sub>** = retention indices from the databases [29–32].<sup>a</sup> Average of three measurements. <sup>b</sup> MS(EI): 182(7%), 153(5%), 126(8%), 112(20%), 111(7%), 99(5%), 83(100%), 69(6%), 55(39%), 43(14%), 41(7%).<sup>c</sup> MS(EI): 236(2%), 193(20%), 180(10%), 173(19%), 163(48%), 151(71%), 147(35%), 137(26%), 123(36%), 121(24%), 109(25%), 105(26%), 95(50%), 93(38%), 81(100%), 79(28%), 69(31%), 55(38%), 43(30%), 41(41%).<sup>d</sup> MS(EI): 234(11%), 219(11%), 191(19%), 173(19%), 163(48%), 151(71%), 145(41%), 131(37%), 123(100%), 121(42%), 107(55%), 105(40%), 95(42%), 93(59%), 91(75%), 83(72%), 81(81%), 79(66%), 77(57%), 69(48%), 55(75%), 43(52%), 41(100%).<sup>e</sup> MS(EI): 161(4%), 147(15%), 133(10%), 119(14%), 105(23%), 95(47%), 93(51%), 91(45%), 80(51%), 79(100%), 67(66%), 55(32%), 43(10%), 41(44%).

Although not necessarily a phytochemical marker of the family, germacrene D has been found to be a major component in several members of the Asteraceae. For example, germacrene D is the dominant compound in the essential oils of *Centaurea hadimensis* Wagenitz,
K. Ertugrul & H. Dural (44.3%) [57], Centaurea pseudoscabiosa Boiss. & Buhse (36.0%) [57], Eupatorium cannabinum L. (33.5%) [58], Polymnia canadensis L. (63.6%) [23], Rudbeckia fulgida Aiton (30.1%) [59], Rudbeckia hirta L. (23.6%) [59], Solidago canadensis L. (64.1%) [60], Symphyotrichum novae-angliae (L.) G.L. Nesom (25.5%) [59], Verbesina macrophylla (Cass.) F.S. Blake (37.3%) [61], Verbesina turbacensis Kunth (36.9%) [62], and Liatris spicata (23.7%, this work, see below). Germacrene D has shown antimicrobial and cytotoxic activities [63,64].

2.4. Liatris spicata (L.) Willd. (Asteraceae)

The essential oil composition of L. spicata essential oil is presented in Table 5. The major components were germacrene D (23.7%), myrcene (13.7%), α-pinene (8.1%), and caryophyllene oxide (5.9%). Apparently, there have been no previous reports on the essential oil composition of L. spicata.

Table 5. Chemical composition of Liatris spicata aerial parts essential oil.

| Rl calc | Rl db | Compound                     | %   | ED, (+):(-) |
|---------|-------|------------------------------|-----|-------------|
| 905     | 902   | Santolinatriene              | 0.5 |             |
| 934     | 932   | α-Pinene                     | 8.1 | 17.1:82.9   |
| 950     | 950   | Camphene                     | 0.6 | 100:0       |
| 973     | 971   | Sabinene                     | 0.9 |             |
| 976     | 974   | Hexanoic acid                | 0.9 |             |
| 979     | 978   | β-Pinene                     | 3.1 | 52.3:47.7   |
| 990     | 989   | Myrcene                      | 13.7|             |
| 1030    | 1030  | Limonene                     | 2.1 | 33.4:66.6   |
| 1032    | 1031  | β-Phellandrene               | 0.4 |             |
| 1047    | 1045  | (E)-β-Ocimene                | 0.5 |             |
| 1100    | 1098  | Perillene                    | 0.3 |             |
| 1101    | 1099  | Linalool                     | 0.5 | 52.9:47.1   |
| 1106    | 1104  | Nonanal                      | 0.3 |             |
| 1115    | 1113  | (E)-4,8-Dimethylnona-1,3,7-triene | 0.3 |             |
| 1146    | 1145  | trans-Verbenol               | 0.7 |             |
| 1163    | 1164  | Pinocarvone                  | 0.3 |             |
| 1172    | 1170  | Borneol                      | 0.7 | 0:100       |
| 1181    | 1180  | Terpinen-4-ol                | 0.2 | 0:100       |
| 1196    | 1196  | Myrtenal                     | 0.6 |             |
| 1207    | 1205  | Verbenone                    | 0.7 | 0:100       |
| 1284    | 1282  | Bornyl acetate               | 3.0 | 0:100       |
| 1309    | 1309  | 4-Vinylgualicol              | 0.8 |             |
| 1319    | 1322  | (2E,4E)-Decadienal           | 0.4 |             |
| 1323    | 1319  | (3E)-Hexenyl tiglate         | 0.4 |             |
| 1330    | 1329  | Hexyl tiglate                | 0.3 |             |
| 1384    | 1382  | β-Bourbonene                 | 0.4 |             |
| 1388    | 1387  | β-Cubebeene                  | 0.2 |             |
| 1390    | 1390  | trans-β-Elemene              | 1.1 |             |
| 1416    | 1414  | α-Cedrene                    | 0.3 |             |
| 1418    | 1422  | β-Ylangene                   | 0.4 |             |
| 1419    | 1424  | (E)-β-Caryophyllene          | 4.4 | 100:0       |
| 1424    | 1423  | β-Cedrene                    | 0.4 |             |
| 1429    | 1427  | γ-Elemene                    | 0.7 |             |
| 1433    | 1432  | trans-α-Bergamotene          | 1.8 |             |
| 1447    | 1447  | Geranyl acetone              | 0.3 |             |
| 1453    | 1452  | (E)-β-Farnesene              | 0.3 |             |
| 1455    | 1454  | α-Humulene                   | 1.9 |             |
| 1475    | 1475  | γ-Murolene                   | 0.4 |             |
| 1478    | 1481  | (E)-β-Ionone                 | 0.2 |             |
| 1481    | 1480  | Germacrene D                 | 23.7| 100:0       |
| 1488    | 1489  | β-Selinene                   | 0.5 |             |
| 1495    | 1497  | Bicyclogermacrene            | 0.5 |             |
Table 5. Cont.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                | %   | ED<sub>r</sub> (+)(−) |
|------------------|----------------|--------------------------|-----|----------------------|
| 1498             | 1497           | α-Muurolene              | 0.3 |                      |
| 1518             | 1518           | δ-Cadinene               | 0.8 | 0:100                |
| 1524             | 1524           | Dihydroactinidiolide      | 0.4 |                      |
| 1558             | 1557           | Germacrene B             | 0.6 |                      |
| 1560             | 1561           | (E)-Nerolidol            | 0.5 | 0:100                |
| 1567             | 1566           | 1,5-Epoxyosalvial-4(14)-ene | 0.9 |                      |
| 1576             | 1576           | Spathulenol              | 2.5 |                      |
| 1581             | 1577           | Caryophyllene oxide      | 5.9 |                      |
| 1584             | −              | Unidentified<sup>a</sup> | 2.0 |                      |
| 1591             | 1593           | Salvial-4(14)-en-1-one   | 1.2 |                      |
| 1608             | 1611           | Humulene epoxide II      | 1.3 |                      |
| 1621             | 1620           | <i>epi</i>-Cedrol        | 1.8 |                      |
| 1627             | 1629           | <i>iso</i>-Spathulenol    | 1.6 |                      |
| 1654             | 1655           | α-Cadinol                | 1.6 |                      |

RI<sub>calc</sub> = retention indices calculated with respect to a homologous series of n-alkanes on a ZB-5 column. RI<sub>db</sub> = retention indices from the databases [29–32]. ED<sub>r</sub> = enantiomeric distribution (dextrorotatory enantiomer/levorotatory enantiomer). * MS(EI): 220(19%), 202(16%), 178(18%), 177(33%), 164(29%), 159(71%), 149(37%), 135(45%), 131(34%), 121(44%), 117(48%), 107(75%), 105(66%), 93(100%), 91(97%), 81(50%), 79(69%), 77(50%), 67(47%), 55(65%), 43(56%), 41(78%).

2.5. Pycnanthemum incanum (L.) Michx. (Lamiaceae)

Table 6 shows the chemical composition of the essential oil from the aerial parts of <i>P. incanum</i> growing wild in South Carolina. The essential oil was rich in oxygenated monoterpenoids, including 1,8-cineole (30.7%), α-terpineol (16.9%), borneol (8.2%), and <i>cis</i>-sabinene hydrate (5.6%). The sesquiterpene hydrocarbons (<i>E</i>-β-caryophyllene (11.0%), and germacrene D (5.0%) were also relatively abundant. To our knowledge, this is the first reported analysis of <i>P. incanum</i> essential oil. Volatiles obtained from a diethyl ether extract have been analyzed by gas chromatography-olfactometry to determine the key odorants [20]. Although the percentages of the volatiles were not reported, the enantiomeric distributions of several components were determined (Table 6). 1-Octen-3-ol, isomenthone, α-terpineol, and pulegone showed comparable enantiomeric distributions between <i>P. incanum</i> essential oil and the volatiles from the previously published diethyl ether extract [20]. Concentrations of α-pinene, linalool, and menthol were too low in this current study to obtain reliable enantiomeric distributions for comparison.

2.6. Smallanthus uvedalia (L.) Mack. ex Mack. (Asteraceae)

The essential oil composition of <i>S. uvedalia</i> from South Carolina is summarized in Table 7. The major components of <i>S. uvedalia</i> essential oil were α-pinene (23.9%), (<i>E</i>)-β-caryophyllene (16.9%), perillene (14.5%), germacrene D (12.2%), and limonene (6.1%). In comparison, <i>S. uvedalia</i> from northern Alabama (collected in September 2018) contained α-pinene (62.6%), limonene (11.4%), and β-pinene (6.0%), with lesser concentrations of (<i>E</i>)-β-caryophyllene (3.8%) [24]. Neither perillene nor germacrene D were observed in this northern Alabama sample. In contrast, two <i>S. uvedalia</i> samples collected in February, 2016, from northern Alabama were rich in (<i>E</i>)-β-caryophyllene (24.5% and 16.5%) and caryophyllene oxide (19.8% and 14.2%) [23]. α-Pinene concentrations were low (1.3% and 0.0%) and neither perillene nor germacrene D were observed. The differences in compositions in <i>S. uvedalia</i> may be attributed to geographical location and/or seasonal variation.
Table 6. Chemical composition of *Pycnanthemum incanum* aerial parts essential oil.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound | % | ED, (+):(--)[20] |
|-------------------|-----------------|-----------|---|-----------------|
| 933               | 933             | α-Pinene  | tr|                  |
| 972               | 971             | Sabinene  | 0.5| 0:100           |
| 978               | 978             | β-Pinene  | 0.1| 0:100           |
| 979               | 978             | 1-Octen-3-ol| 3.1| 0:100          |
| 989               | 989             | Myrcene   | 0.3|                |
| 1017              | 1017            | α-Terpinene| 0.1| 100:0          |
| 1024              | 1024            | p-Cymene  | 0.8|                |
| 1030              | 1030            | Limonene  | 1.2| 0:100           |
| 1032              | 1030            | 1,8-Cineole| 30.7|              |
| 1036              | 1034            | (Z)-β-Ocimene| 0.1|                |
| 1046              | 1046            | (E)-β-Ocimene| 0.2|                |
| 1058              | 1058            | γ-Terpinene| 0.6|                |
| 1069              | 1069            | cis-Sabinene hydrate| 5.6| 7.2:92.8 |
| 1086              | 1086            | Terpinolene| 0.2|                |
| 1100              | 1099            | Linalool   | 0.3| 95:5           |
| 1101              | 1099            | trans-Sabinene hydrate| 3.0| 36.5:63.5 |
| 1125              | 1124            | cis-p-Menth-2-en-1-ol| 0.2|                |
| 1142              | 1139            | trans-p-Menth-2-en-1-ol| 0.1|                |
| 1156              | 1156            | Menthone   | 0.2| 0:100          |
| 1164              | 1165            | Isomenthone| 1.0| 100:0          |
| 1170              | 1170            | δ-Terpinol| 2.6|                |
| 1171              | 1170            | Bornol     | 8.2| 0:100          |
| 1180              | 1180            | Terpinol-4-ol| 1.8| 33:66.9  |
| 1195              | 1195            | α-Terpinol| 16.9| 29:70.8   |
| 1237              | 1237            | Pulegone   | 1.8| 100:0         |
| 1283              | 1282            | Bornyl acetate| 0.2| 0:100        |
| 1289              | 1289            | Thymol     | 0.3|                |
| 1331              | 1331            | Bicycloelemene| 0.1|                |
| 1335              | 1335            | δ-Elemene  | 0.6| 0:100         |
| 1375              | 1375            | α-Copaene  | 0.2| 100:0         |
| 1383              | 1382            | β-Bourbonene| 0.2|                |
| 1389              | 1390            | trans-β-Elemene| 0.3| 47:53.0  |
| 1418              | 1417            | (E)-β-Caryophyllene| 11.0| 100:0    |
| 1429              | 1430            | β-Copaene  | 0.1|                |
| 1454              | 1453            | α-Humulene | 0.5|                |
| 1479              | 1480            | Germacrene D| 5.0| 90:9.9  |
| 1494              | 1497            | Bicyclgermacrene| 0.3|                |
| 1503              | 1504            | (E,E)-α-Farnesene| 0.2|                |
| 1517              | 1520            | δ-Cadinene | 0.3| 0:100         |
| 1557              | 1557            | Germacrene B| 0.1|                |
| 1559              | 1561            | (E)-Nerolidol| 0.1| 0:100        |
| 1575              | 1576            | Germacrene D-4-ol| 0.1|                |
| 1580              | 1577            | Caryophyllene oxide| 0.3|                |
| 1637              | 1639            | cis-Guaia-3,9-dien-11-ol| 0.3|                |

RI<sub>calc</sub> = retention indices calculated with respect to a homologous series of *n*-alkanes on a ZB-5 column. RI<sub>db</sub> = retention indices from the databases [29–32]. ED = enantiomeric distribution (dextrorotatory enantiomer/levorotatory enantiomer). tr = trace (<0.05%).

Monoterpene hydrocarbons 4.3
Oxygenated monoterpenoids 72.9
Sesquiterpene hydrocarbons 18.8
Oxygenated sesquiterpenoids 0.9
Others 3.1
Total identified 100.0
Table 7. Essential oil composition of *Smallanthus uvedalia* from South Carolina.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound | % ED, (+):(-) |
|------------------|----------------|----------|---------------|
| 801              | 801            | Hexanal  | 0.1           |
| 844              | 842            | Isovaleric acid | 1.7 |
| 849              | 850            | (2E)-Hexenal | 0.6 |
| 851              | 853            | (3Z)-Hexenol | 0.1 |
| 922              | 923            | Tricyclene | tr |
| 925              | 925            | α-Thujene | 0.1 19.1:80.9 |
| 935              | 933            | α-Pinene | 23.9 6.7:93.3 |
| 948              | 950            | Camphene | 0.4 100:0 |
| 952              | 953            | Thuja-2,4(10)-diene | tr |
| 960              | 960            | Benzaldehyde | 0.1 |
| 972              | 972            | Sabinene | 3.4 18.3:81.7 |
| 977              | 978            | β-Pinene | 0.9 30.7:69.3 |
| 988              | 989            | Myrcene | 1.0 |
| 1016             | 1017           | α-Terpine | 0.1 |
| 1024             | 1025           | p-Cymene | tr |
| 1030             | 1030           | Limonene | 6.1 95.2:4.8 |
| 1031             | 1031           | β-Phellandrene | 0.2 |
| 1032             | 1032           | 1,8-Cineole | tr |
| 1033             | 1033           | Benzyl alcohol | tr |
| 1034             | 1034           | (Z)-β-Ocimene | tr |
| 1042             | 1043           | Benzene acetaldehyde | 0.1 |
| 1045             | 1045           | (E)-β-Ocimene | 0.4 |
| 1057             | 1057           | γ-Terpinene | 0.2 |
| 1069             | 1069           | cis-Sabinene hydrate | 0.1 |
| 1084             | 1086           | Terpinolene | 0.1 |
| 1089             | 1091           | p-Cymene | tr |
| 1091             | 1091           | Rosefuran | 0.1 |
| 1101             | 1098           | Perillene | 14.5 |
| 1102             | 1101           | trans-Sabinene hydrate | 0.1 |
| 1105             | 1104           | Nonanal | tr |
| 1111             | 1111           | Phenethyl alcohol | 0.1 |
| 1112             | 1113           | (E)-1,4-Dimethylnona-1,3,7-triene | 0.2 |
| 1121             | 1121           | trans-p-Menth-2,8-dien-1-ol | tr |
| 1124             | 1124           | cis-p-Menth-2-en-1-ol | tr |
| 1126             | 1125           | α-Campholenal | 0.1 |
| 1139             | 1140           | trans-Pinocarveol | 0.1 |
| 1141             | 1141           | cis-Verbenol | 0.1 |
| 1145             | 1145           | trans-Verbenol | 0.4 |
| 1161             | 1164           | Pinocarvone | 0.1 |
| 1170             | 1171           | p-Menta-1,5-dien-8-ol | tr |
| 1179             | 1180           | Terpinen-4-ol | 0.4 28.8:71.2 |
| 1186             | 1186           | p-Cymen-8-ol | tr |
| 1194             | 1195           | α-Terpineol | 0.2 34.5:65.5 |
| 1205             | 1205           | Verbenone | 0.1 89.3:10.7 |
| 1217             | 1218           | trans-Carveol | 0.1 |
| 1288             | 1289           | Thymol | 0.1 |
| 1331             | 1334           | Bicycloelemene | 0.2 |
| 1335             | 1336           | δ-Eleme | 0.1 |
| 1351             | 1356           | Eugenol | 0.1 |
| 1359             | 1361           | Neryl acetate | 0.1 |
| 1375             | 1375           | α-Copaene | 0.1 100:0 |
| 1378             | 1379           | (E)-β-Damascenone | 0.1 |
| 1382             | 1383           | cis-β-Eleme | 0.1 |
| 1383             | 1382           | β-Bourbonene | 0.5 |
| 1386             | 1385           | α-Bourbonene | tr |
| 1387             | 1387           | β-Cubebene | tr |
| 1389             | 1390           | trans-β-Elemene | 1.0 17.1:82.9 |
Table 7. Cont.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound | %   | ED, (+):(-) |
|------------------|----------------|----------|-----|-------------|
| 1403             | 1405           | (Z)-β-Caryophyllene | tr  |             |
| 1415             | 1416           | cis-α-Bergamotene | tr  |             |
| 1423             | 1424           | (E)-β-Caryophyllene | 16.9| 100:0       |
| 1429             | 1427           | γ-Elemene | 1.3 |             |
| 1433             | 1432           | trans-α-Bergamotene | 0.1 |             |
| 1436             | 1438           | Aromadendrene | 0.1 |             |
| 1441             | 1444           | Guai-6,9-diene | 0.3 |             |
| 1443             | 1447           | iso-Germacrene D | 0.1 |             |
| 1448             | 1447           | Geranyl acetone | 0.1 |             |
| 1450             | 1453           | ε-Murolene | 0.1 |             |
| 1455             | 1454           | α-Humulene | 1.1 |             |
| 1467             | 1464           | 9-epi-(E)-Caryophyllene | tr  |             |
| 1476             | 1478           | γ-Murolene | 0.2 |             |
| 1483             | 1480           | Germacrene D | 12.2| 96.4:3.6    |
| 1489             | 1493           | Phenethyl isovalerate | 0.1 |             |
| 1492             | 1490           | γ-Amorphene | tr  |             |
| 1495             | 1497           | Bicyclogermacone | 1.9 |             |
| 1498             | 1497           | α-Murolene | 0.1 |             |
| 1502             | 1504           | Epizonarene | 0.1 |             |
| 1504             | 1505           | (E,E)-α-Farnesene | 0.2 |             |
| 1507             | 1508           | β-Bisabolene | 0.1 |             |
| 1512             | 1512           | γ-Cadinene | 0.1 |             |
| 1517             | 1518           | δ-Cadinene | 0.3 | 0:100       |
| 1526             | 1528           | (E)-γ-Bisabolene | 0.2 |             |
| 1536             | 1538           | α-Cadinene | 0.1 |             |
| 1536             | 1531           | (Z)-Nerolidol | 0.1 |             |
| 1548             | 1549           | α-Elemol | 0.1 |             |
| 1558             | 1557           | Germacrene B | 2.1 |             |
| 1561             | 1560           | (E)-Nerolidol | 0.3 | 34.1:65.9   |
| 1576             | 1576           | Spathulenol | 0.9 |             |
| 1581             | 1577           | Caryophyllene oxide | 1.3 |             |
| 1631             | 1630           | Caryophylla-4(12),8(13)-dien-5α-ol | 0.1 |             |
| 1636             | 1636           | Caryophylla-4(12),8(13)-dien-5β-ol | 0.2 |             |
| 1641             | 1640           | τ-Cadinol | 0.1 |             |
| 1643             | 1644           | τ-Murolol | 0.1 |             |
| 1654             | 1655           | α-Cadinol | 0.4 |             |
| 1657             | 1660           | Selin-11-en-4α-ol (=Kongol) | 0.1 |             |
| 1683             | 1683           | Germacra-4(15),5,10(14)-tri-en-1α-ol | 0.1 |             |
| 1715             | 1715           | Pentadecanal | 0.1 |             |
| 1841             | 1841           | Phytone | 0.2 |             |
| 2020             | 2022           | (E,E)-Geranyl linalool | 0.1 |             |

RI<sub>calc</sub> = retention indices calculated with respect to a homologous series of n-alkanes on a ZB-5 column.
RI<sub>db</sub> = retention indices from the databases [29–32]. ED = enantiomeric distribution (dextrorotatory enantiomer/levorotatory enantiomer). tr = trace (<0.05%).

There does not seem to be a trend in the major enantiomers for essential oils of the Asteraceae (see Supplementary Table S1). For example, (+)-α-pinene was the only
enantiomer observed in Erechtites hieracifolia (L.) Raf. [65], but (−)-α-pinene predominated in S. uvedalia (this work). Likewise, (+)-β-pinene was the only enantiomer in Coreopsis capillacea Kunth (syn. C. triloba S.F. Blake) [66], while (−)-β-pinene was the dominant enantiomer in Achillea ligustica All. [67]. (+)-Limonene was the dominant enantiomer in S. uvedalia (this work) and Solidago canadensis L. [68], whereas the (−)-enantiomer dominated E. hieracifolia [65] and C. capillacea [66].

2.7. Verbena hastata L. (Verbenaceae)

Three different specimens of V. hastata were collected and investigated (Table 8). Although collected from the same general location on the same day, the essential oils showed notable quantitative differences in their compositions. For example, the concentration of 1-octen-3-ol ranged from 2.4% to 29.1%, nonanal ranged from 1.8% to 11.1%, palmitic acid 8.5–21.6%, 1-octadecanol 2.8–14.0%, and phytol 5.2–12.6%. The enantiomeric distributions of linalool, α-terpineol, (E)-β-ionone, and (E)-nerolidol were the same for the three samples, however. As far as we know, this is the first report on the essential oil composition of V. hastata.

Table 8. Essential oil compositions of three samples of wild-growing Verbena hastata.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                        | Percent Composition |
|------------------|----------------|---------------------------------|---------------------|
|                  |                |                                 | #1    | #2    | #3    |
| 801              | 801            | Hexanal                         | 0.4   | 0.2   | —     |
| 850              | 853            | (3Z)-Hexenol                    | 0.8   | 0.6   | —     |
| 902              | 905            | Heptanal                        | 1.1   | 0.3   | —     |
| 960              | 960            | Benzaldehyde                    | 0.3   | 0.4   | —     |
| 974              | 973            | 1-Octen-3-one                   | 0.7   | 0.3   | —     |
| 977              | 978            | 1-Octen-3-ol                    | 29.1  | 22.5  | 2.4   |
| 983              | 984            | 3-Octanone                      | 0.2   | 0.2   | —     |
| 988              | 989            | 2-Pentylfuran                   | 0.3   | —     | —     |
| 991              | 995            | 6-Methyl-5-hepten-2-ol          | 0.3   | 0.2   | —     |
| 995              | 996            | 3-Octanol                       | 0.3   | 0.2   | —     |
| 1002             | 1005           | Octanal                         | 0.3   | 0.1   | —     |
| 1022             | 1025           | p-Cymene                        | —     | 0.5   | —     |
| 1027             | 1030           | Limonene                        | —     | 0.1   | —     |
| 1032             | 1033           | Benzyl alcohol                  | 0.3   | 0.9   | 0.3   |
| 1068             | 1069           | cis-Linalool oxide (furanoid)   | —     | 0.7   | —     |
| 1068             | 1076           | 1-Octanol                       | 1.0   | —     | 0.6   |
| 1083             | 1082           | Terpinolene                     | —     | 0.1   | —     |
| 1084             | 1086           | trans-Linalool oxide (furanoid) | —     | 0.3   | 0.1   |
| 1098             | 1101           | Linalool                        | 1.5   | 1.9   | 0.7   |
| 1103             | 1104           | Nonanal                         | 11.1  | 1.8   | 2.0   |
| 1110             | 1111           | Phenyl ethyl alcohol            | 1.7   | 2.3   | 1.2   |
| 1184             | 1186           | p-Cymen-8-ol                    | —     | 0.2   | 0.1   |
| 1189             | 1190           | Methyl salicylate               | 0.4   | 1.0   | 0.4   |
| 1193             | 1195           | α-Terpineol                     | —     | 0.3   | 0.3   |
| 1196             | 1197           | Methyl chavicol (=Estragole)    | 1.0   | 0.3   | 2.8   |
| 1204             | 1206           | Decanal                         | —     | 0.2   | 0.2   |
| 1214             | 1217           | Coumaran                        | —     | 0.2   | 0.5   |
| 1216             | 1219           | β-Cyclocitral                   | —     | 0.5   | 0.2   |
| 1263             | 1263           | (2E)-Decenal                   | 0.3   | 0.1   | 0.2   |
| 1267             | 1272           | Nonanoic acid                   | 0.8   | 1.0   | 2.6   |
| 1274             | 1271           | Decanol                         | 0.3   | —     | 0.6   |
| 1290             | 1293           | Thymol                          | 0.3   | 0.2   | 1.1   |
| 1298             | 1300           | Carvacrol                       | 0.3   | 0.1   | 0.4   |
| 1309             | 1309           | 4-Vinylguaiacol                 | —     | 0.2   | 0.6   |
Table 8. Cont.

| RI<sub>calc</sub> | RI<sub>db</sub> | Compound                                         | Percent Composition |
|-----------------|---------------|--------------------------------------------------|---------------------|
| 1351            | 1356          | Eugenol                                          | 0.3 0.3             |
| 1378            | 1380          | (E)-β-Damascenone                                 | 0.8 0.9             |
| 1408            | 1410          | Italicene                                        | — 0.4              |
| 1447            | 1447          | Geranyl acetone                                  | 0.3 0.6 0.6        |
| 1461            | 1461          | 4,6,8,10-Tetramethyltridecane                    | 0.8 0.3 0.7         |
| 1477            | 1481          | (E)-β-Ionone                                      | 0.6 0.8 0.8         |
| 1480            | 1480          | 5,6-Epoxo-β-ionone                               | 0.3 0.7 0.4         |
| 1524            | 1524          | Dihydroactinidiolide                              | 0.5 0.9 1.2         |
| 1560            | 1560          | (E)-Nerolidol                                     | — — 0.2             |
| 1596            | 1596          | Fokienol                                         | 0.3 1.0 1.1         |
| 1600            | 1600          | Hexadecane                                       | 0.3 — 0.2           |
| 1628            | 1627          | Eremoligenol                                     | 0.3 — 0.2           |
| 1630            | 1632          | γ-Eudesmol                                       | 1.0 — 1.1           |
| 1638            | 1640          | Hinesol                                          | 0.2 — —             |
| 1653            | 1656          | β-Eudesmol                                       | 2.1 0.9 1.8         |
| 1690            | 1694          | Germacrene                                       | — 0.4 —             |
| 1714            | 1715          | Pentadecanal                                     | 0.3 — 0.4           |
| 1758            | 1758          | Myristic acid                                    | — 0.8 —             |
| 1840            | 1841          | Phytone                                          | 4.4 3.1 7.3         |
| 1866            | 1869          | Benzyl salicylate                                | 1.1 2.0 1.8         |
| 1889            | 1891          | Hexadecatrienial                                 | — — 0.3             |
| 1904            | 1902          | (E,E)-6,10,14-Trimethyl-5,9,13-pentadecatrien-2-one | — — 0.3             |
| 1921            | 1921          | Methyl palmitate                                 | — — 0.3             |
| 1959            | 1958          | Palmitic acid                                    | 8.5 21.6 15.3       |
| 2019            | 2018          | Octadecanal                                      | 0.2 — 0.4           |
| 2082            | 2081          | 1-Octadecanol                                    | 9.6 2.8 14.0        |
| 2094            | 2098          | Methyl linolenate                                | — — 0.3             |
| 2106            | 2106          | Phytol                                           | 5.2 7.1 12.6        |
| 2128            | 2128          | Linoleic acid                                    | — 0.8 0.6           |
| 2132            | 2134          | α-Linolenic acid                                 | 1.1 4.4 3.2         |
| 2300            | 2300          | Tricosane                                        | 0.7 0.5 1.0         |
| 2500            | 2500          | Pentacosane                                      | 0.4 0.4 0.6         |
| 2700            | 2700          | Heptacosane                                      | 0.4 0.3 0.5         |
| 2700            | 2700          | Monoterpenoids                                   | 2.0 4.9 2.9         |
| 2700            | 2700          | Sesquiterpenoids                                 | 3.9 2.3 4.9         |
| 2700            | 2700          | Diterpenoids                                     | 5.2 7.1 12.6        |
| 2700            | 2700          | Benzenoids                                       | 4.9 7.5 7.9         |
| 2700            | 2700          | Others                                           | 75.7 66.3 58.1      |
|                 |               | Total identified                                 | 91.7 88.2 86.5      |

Enantiomeric distribution

|                  | (+):(-)       |
|------------------|---------------|
| 1-Octen-3-ol     | 0:100         |
| Linalool         | 22.9:77.1     |
| α-Terpineol      | 49.6:50.4     |
| (E)-β-Ionone     | 100:0         |
| (E)-Nerolidol    | 0:100         |

RI<sub>calc</sub> = retention indices calculated with respect to a homologous series of n-alkanes on a ZB-5 column. RI<sub>db</sub> = retention indices from the databases [29–32].

There are few Verbena essential oil compositions to compare. However, several Verbena officinalis L. essential oils have been reported, and these samples also show wide variation in composition. The major components in V. officinalis essential oil from Morocco were spathulenol (10.8%), limonene (7.5%), 1,8-cineole (7.5%), Caryophyllene oxide (7.3%), and α-curcumene (6.0%) [69]. In contrast, the essential oil of V. officinalis from Italy was rich in geranial (45.5%) and isobornyl formate (41.4%) [70]. Verbena officinalis from Algeria, on the
other hand, showed limonene (17.7%), geranial (14.8%), carvone (14.2%), and caryophyllene oxide (12.4%) as major components [71].

The (−)-enantiomer of 1-octen-3-ol was the only stereoisomer observed in V. hastata essential oils as it was in P. incanum essential oil (above). Notably, (−)-1-octen-3-ol is the major enantiomer, generally greater than 97%, in mushrooms [72], and is the stereoisomer responsible for mushroom odor [73]. Interestingly, although both enantiomers and the racemic mixture of 1-octen-3-ol attract mosquitoes, the (−)-enantiomer attracted more mosquito species [74].

A racemic mixture was observed for α-terpineol, but there was a higher concentration of (−)-linalool over (+)-linalool in V. hastata. (−)-Linalool also dominated in the essential oil of Lantana camara L. (Verbenaceae) from Madagascar [75]. In contrast, linalool in the essential oil of Lippia alba (Mill.) N.E. Brown (Verbenaceae) from Uruguay was dominated by the (+)-enantiomer [76].

3. Materials and Methods

3.1. Plant Material

The aerial parts of A. foeniculum, G. procumbens, and H. helianthoides were obtained from plants cultivated in at Kirkland Gardens, in Newville, Alabama (Table 1). The cultivated plants were started from commercially available seeds (A. foeniculum, Homegrown Seed Company, and H. helianthoides, Prairie Moon Nursery), tubers (L. spicata, Wal-Mart), or young plants (G. procumbens, The Home Depot). All the plants were grown in full sun, except the G. procumbens, which was located in a partially shaded location (4 h/day average sunlight), and all were watered at least once a week. The plants were cultivated directly in the ground, which was clayey-loamy sand, which was amended with composted chicken manure, worm castings, kelp meal, and bone meal at time of planting. Pycnanthemum incanum and S. uvedalia were collected in the wild from a fully shaded forest understory roadside location near a small waterfall in northern South Carolina. The plants were located beside highway 276 near the North Carolina–South Carolina border (see Table 1). The soil was a thick loam with a lot of leaf litter. Verbena hastata was collected in the wild near a disturbed fence-line area with full sun between a bovine field and a paved county road in rural Newville, Alabama (Table 1). Specimens of each plant were collected during the flowering phase (Table 1). Voucher specimens of P. incanum (SKL83120), S. uvedalia (SKL31820), and V. hastata (SKL51321) were deposited in the University of Alabama in Huntsville Herbarium (HALA); cultivated plants were not vouchered. For each species, the plant material was air-dried in the laboratory (around 23 °C) for 10 days. The dried plant materials of each species were chopped and hydrodistilled using a Likens–Nickerson apparatus with continuous extraction with dichloromethane for 4 h. The dichloromethane was evaporated using a stream of dry nitrogen to give the essential oils (Table 1).

3.2. Gas Chromatographic Analysis

The essential oils were analyzed by gas chromatography-mass spectrometry (GC-MS), gas chromatography-flame ionization detection (GC-FID), and chiral GC-MS as previously described [77].

GC-MS: Shimadzu GCMS-QP2010 Ultra, electron impact (EI) mode (electron energy = 70 eV), scan range = 40–400 atomic mass units, scan rate = 3.0 scans/s, and GC-MS solution software; ZB-5ms fused silica capillary column (30 m length × 0.25 mm inner diameter) with a (5% phenyl)-polymethylsiloxane stationary phase and a film thickness of 0.25 µm; He carrier gas with a column head pressure of 552 kPa and flow rate of 1.37 mL/min; injector temperature = 250 °C, ion source temperature = 200 °C; GC oven temperature 50–260 °C (2 °C/min), 1-µL injection of 5% solution of EO in dichloromethane (split mode, 30:1). The essential oil components were identified by MS fragmentation, and retention indices compared with those in the databases [29–32].
GC-FID: Shimadzu GC 2010 equipped with flame ionization detector, a split/splitless injector, and Shimadzu autosampler AOC-20i, with a ZB-5 capillary column (30 m length × 0.25 mm inner diameter) with a (5% phenyl)-polymethylsiloxane stationary phase and a film thickness of 0.25 µm; oven temperature was programmed the same as above for GC-MS; injector temperature = 250 °C, detector temperature = 280 °C, N₂ carrier gas, and flow rate = 1.0 mL/min. The composition percentages were calculated from raw peak areas without standardization. Chiral GC-MS: Shimadzu GCMS-QP2010S, EI mode (electron energy = 70 eV) with scan range of 40–400 amu and scan rate of 3.0 scans/s; Restek B-Dex 325 capillary column (30 m × 0.25 mm ID × 0.25 µm film); GC oven temperature program, 50–120 °C (1.5 °C/min), 120–200 °C (2 °C/min), and kept at 200 °C for 5 min; He carrier gas, flow rate = 1.8 mL/min; 0.1-µL injection of 3% solution of EO in dichloromethane (split mode, 1:45). The monoterpenoid enantiomers were identified by comparison of retention times with authentic samples obtained from Sigma-Aldrich (Milwaukee, WI, USA). Relative enantiomer percentages were determined based on peak areas. Chiral GC-MS chromatograms are available as Supplementary Figures S1–S7.

4. Conclusions

This report presented the essential oil compositions of seven aromatic medicinal plants used by Native Americans. Four of these essential oils, *Heliopsis helianthoides*, *Liatris spicata*, *Pycnanthemum incanum*, and *Verbena hastata*, were reported for the first time. Additionally, the enantiomeric distributions of several terpenoid components have been determined. The chemical compositions presented add to our knowledge of the phytochemistry of the medicinal plants.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/plants10061061/s1, Table S1: Enantiomeric distribution of terpenoids in Asteraceae species, Figure S1: Chiral gas chromatogram of *Agastache foeniculum* essential oil, Figure S2: Chiral gas chromatogram of *Gaultheria procumbens* essential oil, Figure S3: Chiral gas chromatogram of *Helianthus helianthoides* essential oil, Figure S4: Chiral gas chromatogram of *Liatris spicata* essential oil, Figure S5: Chiral gas chromatogram of *Pycnanthemum incanum* essential oil, Figure S6: Chiral gas chromatogram of *Smallanthus uvedalia* essential oil, Figure S7: Chiral gas chromatogram of *Verbena hastata* essential oil.

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