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The Essential Oils of *Wyethia* Species: *Wyethia Amplexicaulis* (Nutt.) Nutt. and *Wyethia Helianthoides* Nutt.

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Abstract

Background/Objective: *Wyethia amplexicaulis* (shiny mule's ears) and *Wyethia helianthoides* (white-head mule's ears) are conspicuous forbs growing in open hillsides and prairies at mid to upper elevations in the Intermountain West region of the United States. There have been no previous reports on the essential oil compositions of any *Wyethia* species, so the objective of this study is to examine the chemical compositions, including enantiomeric distribution of chiral terpenoids, of *W. amplexicaulis* and *W. helianthoides* from southern Idaho. **Methods:** Three individual samples of *W. amplexicaulis* and *W. helianthoides* were collected, and the essential oils were obtained by hydrodistillation using a Likens-Nickerson apparatus and analyzed by gas chromatography coupled with mass spectrometry (GC-MS), gas chromatography with flame ionization detection, and enantioselective GC-MS. **Results:** The essential oils were obtained in yields of 0.090% to 0.136% and 1.489% to 1.771% for *W. amplexicaulis* and *W. helianthoides*, respectively. The three *W. helianthoides* samples showed high similarity with (−)-germacrene D (16.5%-21.5%), (*E*)-β-ocimene (10.0%-14.3%), myrcene (8.6%-12.4%), α-pinene (6.3%-7.3%, ≥ 95% (+)-α-pinene), 15-copaenol (4.3%-6.0%), and carotol (3.5%-5.9%) as the major components. The *W. amplexicaulis* essential oils, on the other hand, showed variation. Two samples were rich in monoterpene hydrocarbons, mostly myrcene (22.4% and 32.2%), while the third sample was dominated by oxygenated sesquiterpenoids, 15-copaenol (11.4%), carotol (10.0%), silphiperolan-7β-ol (8.2%), and caryophyllene oxide (5.8%). This is the first investigation of *Wyethia* essential oils. **Conclusions:** There are 11 recognized *Wyethia* species, so additional research is needed to understand the volatile phytochemicals present in this genus.

Keywords
shiny mule's ears, white-head mule's ears, chemical composition, enantiomeric distribution, gas chromatography

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Introduction

The Asteraceae Bercht. & J. Presl is the largest plant family with around 33,000 accepted species.[1] *Wyethia* Nutt. belongs to the family Asteraceae, subfamily Asteroideae (Cass.) Lindl., tribe Heliantheae Cass., subtribe Engelmanniinae Stuessy.[1] Within the Engelmanniinae subtribe are ten genera, *Agnorhiza* (Jeps.) W.A. Weber, *Balsamorhiza* Hook., *Berlandiera* DC., *Borrichia* Adans., *Chrysogonum* L., *Engelmannia* A.Gray ex Nutt., *Lindheimera* A.Gray & Engelm., *Silphium* L., *Vigethia* W.A. Weber, and *Wyethia*.[1] There are 11 recognized species of *Wyethia*,[2] which are found only in western North America.[3] *Wyethia amplexicaulis* (Nutt.) Nutt. is a perennial forb found in eastern Washington and eastern Oregon, most of Idaho, western Montana, western Wyoming, and south into Nevada and Utah (Figure 1). The plant grows to 20 to 50 cm tall, with deep green leathery, glossy leaves. The heads are large with yellow ray flowers (Figure 2). *Wyethia helianthoides* Nutt. ranges from eastern Oregon, across southern Idaho, and into southwestern Montana, northwestern Wyoming, and northeastern Nevada (Figure 1). The plant is 30 to 50 cm tall, with dull gray-green leaves with a covering of soft hairs. The head is around 3 cm broad with cream-colored or white ray flowers (Figure 3).[3]

Wyethia species have proven to be a rich source of flavonoids.[4,5] However, there are apparently no previous reports on essential oils from *Wyethia* species. The purpose of this study is to examine the volatile chemicals present in *W. amplexicaulis* and *W. helianthoides* collected in the foothills near Boise, Idaho.

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Figure 1. Western United States showing the range of *Wyethia amplexicaulis* (▬), the range of *Wyethia helianthoides* (▬), based on Weber,[3] and the approximate location of the collection site (★).

Results and Discussion

Essential Oil Composition

Leaves of three individual *W. amplexicaulis* and three individual *W. helianthoides* were collected during the flowering stage from locations near Prairie, Idaho. The leaves were hydrodistilled to give pale yellow essential oils in yields of 0.090% to 0.136% and 1.49% to 1.77%, respectively. The essential oils were analyzed by gas chromatography with flame ionization detection (GC-FID) and gas chromatography coupled with mass spectrometry (GC-MS). A total of 125 compounds were identified in the leaf essential oils of *W. amplexicaulis* accounting for 89.6% to 95.6% of the compositions. The GC analysis of the essential oils of *W. helianthoides* allowed 76 compounds to be identified (89.3%-92.4% of the compositions). The essential oil components are compiled in Table 1.

There were several components in relatively high concentrations that were common to both *W. amplexicaulis* and *W. helianthoides*. These include α-pinene (2.4%-7.5% and 6.3%-7.3%, respectively), myrcene (0.3%-32.2% and 8.6%-12.4%), (*E*)-β-ocimene (0.2%-7.6% and 10.0%-14.3%), (*E*)-β-caryophyllene (3.7%-6.9% and 1.1%-4.1%), germacrene D (0.3%-6.4% and 16.5%-21.5%), 15-copaenol (5.3%-11.4% and 4.3%-6.0%), and carotol (2.8%-10.0% and 3.5%-5.9%). On the other hand, silphiperfolan-7β-ol was abundant in *W. amplexicaulis* (5.5%-10.2%) but was a minor constituent in *W. helianthoides*. Likewise, caryophyllene oxide showed 0.3% to 5.0% in *W. amplexicaulis* but was not observed in *W. helianthoides*.

Sample #3 of *W. amplexicaulis* seems to be a notable outlier in the *W. amplexicaulis* essential oils. Monoterpene hydrocarbons were very low (only 7.9%) compared to samples #1 (47.4%) and #2 (45.0%). Likewise, oxygenated sesquiterpenoids were

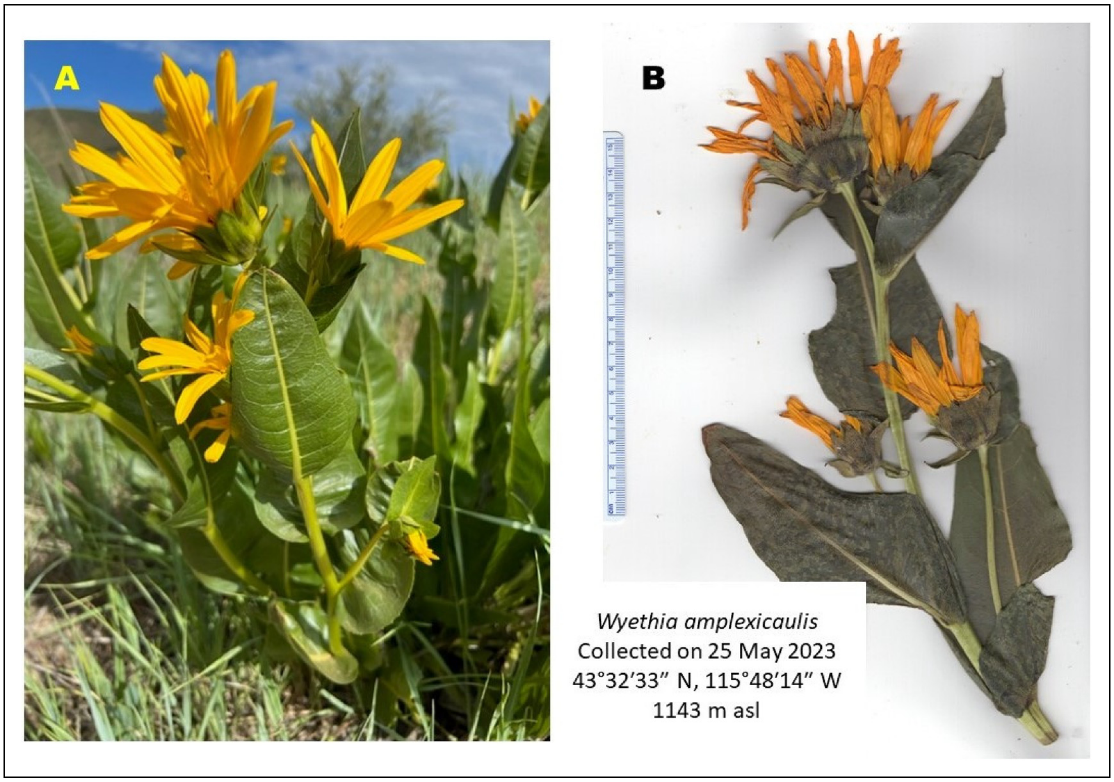

Figure 2. *Wyethia amplexicaulis* (Nutt.) Nutt. (A) Photograph of the plant (K. Swor). (B) Scan of pressed plant (W.N. Setzer).

high in sample #3 (64.1%) compared to samples #1 (27.9%) and #2 (29.0%). The reason for the large difference in compositions is not clear. The three samples were collected from the same location on the same day. The three *W. helianthoides* essential oils, on the other hand, are very similar to one another.

Multivariate analyses were carried out to reveal the similarities between the six essential oil samples. Hierarchical cluster analysis (HCA) showed three well-defined groups (Figure 4). *W. amplexicaulis* #1 and #2 form one group with > 90% similarity, *W. helianthoides* #1, #2, and #3 form another group with > 90% similarity, and *W. amplexicaulis* #3 is the outlier and is not similar to the other essential oil samples. Principal component analysis (PCA) verifies the groupings observed in the HCA (Figure 5). *W. amplexicaulis* samples #1 and #2 correlate strongly with myrcene; *W. helianthoides* #1, #2, and #3 correlate strongly with germacrene D and (*E*)-β-ocimene; and *W. amplexicaulis* #3 correlates strongly with caryophyllene oxide.

There have been no previous reports on essential oil compositions of *Wyethia* species for comparison. However, several members of the Engelmanniinae subtribe of the Asteraceae have been examined. *Silphium perfoliatum* L. leaf essential oil showed relatively high concentrations of α-pinene (5.9% and 5.4%), (*E*)-β-caryophyllene (4.8 and 4.0%), germacrene D (6.4 and 24.3%), and caryophyllene oxide (34.7 and 8.5%).[11] However, neither myrcene, (*E*)-β-ocimene, nor carotol were observed. Likewise, *Silphium integrifolium* Michx. and *Silphium trifoliatum* L. leaf essential oils were rich in α-pinene (7.3%-8.8% and 1.2%-6.0%), (*E*)-β-caryophyllene (2.8%-4.8% and 6.7%-14.9%), germacrene D (18.7%-28.4% and 8.3%-16.1%), and caryophyllene oxide (6.1%-12.4% and 25.4%-29.3%), but neither myrcene, (*E*)-β-ocimene, nor carotol were observed.[12] Another sample of *S. integrifolium* leaf essential oil, however, showed high concentrations of α-pinene (58.6%) and myrcene (9.7%), as well as (*E*)-β-caryophyllene (2.5%) and germacrene D (3.0%), but low concentrations of (*E*)-β-ocimene (0.4%) and caryophyllene oxide (0.5%).[13] *Borrichia frutescens* (L.) DC. leaf essential oil had high concentrations of α-pinene (3.8%-8.3%), myrcene (0.6%-7.8%), and germacrene D (0.7%-18.0%), but low concentrations of (*E*)-β-caryophyllene (0.2%-1.3%), carotol (0.0%-0.9%), and caryophyllene oxide (0.0%-0.1%), and (*E*)-β-ocimene was not observed.[14]

Enantiomeric Distribution

In order to more fully characterize the volatile phytochemistry of *Wyethia*, the essential oils were analyzed by chiral GC-MS. The enantiomeric distributions of chiral terpenoid components are listed in Table 2.

In the *Wyethia* essential oils, (+)-α-pinene, (−)-limonene, (+)-terpinen-4-ol, and (+)-α-terpineol were the major enantiomers; (−)-camphene was the dominant (> 99%) enantiomer, and (+)-δ-3-carene, (−)-(*E*)-β-caryophyllene, (−)-germacrene D, and (+)-δ-cadinene were the only enantiomers observed. (+)-Sabinene and (+)-(*E*)-nerolidol were the major enantiomers

Figure 3. *Wyethia helianthoides* Nutt. (A) Photograph of the plant (K. Swor). (B) Scan of pressed plant (W.N. Setzer).

in *W. amplexicaulis* essential oil, but neither sabinene nor (*E*)-nerolidol were observed in *W. helianthoides*. (+)-β-Pinene was the major enantiomer in *W. helianthoides*, but β-pinene was virtually racemic in *W. amplexicaulis*. Linalool was nearly racemic in the *Wyethia* essential oils with 52.8% to 60.6% (+)-linalool.

Consistent with these enantiomeric distributions, the leaf essential oil of a closely related species, *Balsamorhiza sagittata* (Pursh) Nutt.[3,15] showed comparable distributions with (−)-camphene, (−)-(*E*)-β-caryophyllene, (−)-germacrene D, (+)-δ-cadinene, and (+)-(*E*)-nerolidol as exclusive enantiomers; (+)-sabinene, (−)-limonene, and (+)-terpinen-4-ol as major enantiomers; while α-pinene and β-pinene were virtually racemic.[16] Interestingly, the enantiomeric distributions are reversed for several components identified in *Ericameria nauseosa* (Pursch) G.L. Nesom & G.I. Baird (Asteraceae).[17] The major enantiomers in this plant were (−)-α-pinene, (−)-sabinene, (−)-β-pinene, (−)-terpinen-4-ol, and (−)-α-terpineol.

Conclusions

This work reports, for the first time, the leaf essential oil compositions of 2 species of *Wyethia* collected from the foothills near Boise, Idaho. *W. amplexicaulis* essential oils are generally dominated by myrcene, while *W. helianthoides* shows germacrene D, and (*E*)-β-ocimene, as well as myrcene as major essential oil components. A limitation of this particular study is that only three individuals of each species were sampled from only one geographical location. Further research is needed to examine additional individuals from other locations. In addition, research on other *Wyethia* species is needed to help characterize the volatile components of this genus.

Materials and Methods

Plant Material

Leaves of *W. amplexicaulis* and *W. helianthoides*, three individuals each, were collected near Prairie, Idaho, on 25 May 2023. The plants were identified in the field by W.N. Setzer and confirmed by comparison with samples from the C.V. Starr Virtual Herbarium.[18] Voucher specimens (WNS-Wa-7104 and WNS-Wh-7114) have been deposited with the University of Alabama in Huntsville herbarium. The fresh leaves were stored frozen (–20 °C) until processing. For each plant sample, the fresh-frozen leaves were chopped and then added to a 500-mL flask and enough distilled water was added to cover the plant materials. The leaves were hydrodistilled, once per plant sample, for 4 h using a Likens-Nickerson apparatus[19–21] with continuous extraction of the distillate with dichloromethane to give pale-yellow essential oils (Table 3).

Gas Chromatographic Analyses

GC-MS was used to analyze the compositions of the *Wyethia* essential oils. A Shimadzu Model GC-MS-QP2010 Ultra

Table 1. Chemical Compositions (%) of the Leaf Essential Oils of *Wyethia amplexicaulis* and *Wyethia helianthoides* from Southwestern Idaho.

			Wyethia amplexicaulis			*Wyethia helianthoides*		
RI_{calc}	RI_{db}	Compound	#1	#2	#3	#1	#2	#3
802	801	Hexanal	-	-	-	0.3	0.2	0.1
850	849	(2*E*)-Hexenal	-	-	-	1.3	0.9	0.6
851	853	(3*Z*)-Hexenol	0.3	0.2	-	-	-	-
898	904	Angelic acid	0.4	0.4	0.8	-	-	-
923	923	Tricyclene	0.1	0.1	0.1	-	tr	tr
925	925	α-Thujene	0.2	tr	-	-	tr	0.1
933	932	α-Pinene	5.5	7.5	2.4	6.3	7.2	7.3
950	950	Camphene	2.2	2.7	2.6	0.9	1.3	0.9
963	960	Benzaldehyde	tr	0.1	0.1	-	-	-
972	971	Sabinene	0.4	0.2	0.2	0.1	0.3	0.5
978	978	β-Pinene	1.4	1.9	1.3	1.2	1.3	1.3
990	989	Myrcene	32.2	22.4	0.3	12.4	8.6	11.4
991	990	Dehydro-1,8-cineole	-	-	tr	-	-	-
1006	1008	(3Z)-Hexenyl acetate	0.1	tr	tr	-	-	-
1007	1007	α-Phellandrene	-	1.4	-	tr	0.1	tr
1009	1009	δ-3-Carene	-	0.2	-	1.1	0.8	0.6
1017	1018	α-Terpinene	0.2	tr	-	-	-	0.1
1026	1025	*p*-Cymene	0.7	0.1	0.4	-	-	-
1030	1030	Limonene	0.3	0.4	0.4	0.2	0.2	0.2
1031	1031	β-Phellandrene	0.1	0.2	tr	0.3	tr	0.1
1033	1032	1,8-Ocimene	tr	tr	tr	-	-	-
1035	1033	Benzyl alcohol	tr	tr	0.1	-	-	-
1035	1035	(*Z*)-β-Ocimene	tr	0.1	tr	0.3	0.3	0.3
1044	1045	Phenylacetaldehyde	tr	tr	-	0.7	0.4	0.2
1046	1046	(*E*)-β-Ocimene	1.9	7.6	0.2	14.0	10.0	14.3
1052	1051	23,6-Trimethylhepta-1,5-diene	tr	tr	-	-	-	-
1059	1058	γ-Terpinene	2.3	0.1	-	-	0.1	0.3
1067	1068	Acetophenone	tr	tr	tr	-	-	-
1071	1069	*cis*-Sabinene hydrate	tr	-	-	-	-	-
1071	1069	*cis*-Linalool oxide (furanoid)	-	0.1	0.1	-	-	-
1086	1086	Terpinolene	0.1	0.1	-	-	-	-
1087	1086	*trans*-Linalool oxide (furanoid)	tr	0.1	0.1	-	-	-
1091	1090	6,7-Epoxymyrcene	tr	tr	-	-	-	-
1091	1091	Rosefuran	-	-	0.1	-	-	-
1095	—	3,4-Decadiene (RI not available)	-	-	0.1	-	-	-
1097	1099	6-Camphenone	-	-	tr	-	-	-
1099	1101	(3Z)-Hexenyl propionate	tr	tr	tr	-	-	-
1101	1101	Linalool	0.1	0.2	0.2	0.6	0.8	0.6
1102	1101	*trans*-Sabinene hydrate	tr	tr	tr	-	-	-
1104	1102	6-Methylhepta-3,5-dien-2-one	tr	tr	0.1	-	-	-
1106	1107	Nonanal	tr	tr	tr	-	-	-
1113	1113	(*E*)-4,8-Dimethylnona-13,7-triene	0.1	0.1	0.1	0.1	0.1	-
1126	1124	*cis-p*-Menth-2-en-1-ol	tr	tr	tr	-	-	-
1139	1138	Benzeneacetonitrile	tr	0.1	tr	-	-	-
1139	1139	(*E*)-Myroxide	-	-	0.1	-	-	-
1142	1141	(3Z)-Hexenyl isobutanoate	tr	tr	-	-	-	-
1143	1142	*trans-p*-Menth-2-en-1-ol	tr	tr	tr	-	-	-
1148	1149	Camphor	-	-	tr	-	-	-
1156	1156	Camphene hydrate	-	-	0.1	-	-	-
1170	1169	Rosefuran epoxide	-	-	0.1	-	-	-
1173	1173	Borneol	tr	tr	0.5	-	-	-
1175	1174	*trans*-Linalool oxide (pyranoid)	-	-	0.1	-	-	-
1181	1180	Terpinen-4-ol	0.5	0.2	0.2	tr	0.2	0.5
1185	1187	(3Z)-Hexenyl butanoate	0.1	0.1	0.1	-	-	-
1188	1189	*p*-Cymen-8-ol	tr	tr	0.1	-	-	-
1195	1195	α-Terpineol	0.2	0.3	0.4	0.3	0.4	0.4

(Continued)

Table 1. Continued

			Wyethia amplexicaulis			*Wyethia helianthoides*		
RI_{calc}	RI_{db}	Compound	#1	#2	#3	#1	#2	#3
1231	1231	(3*Z*)-Hexenyl 2-methylbutanoate	0.3	0.2	0.2	-	-	-
1284	1285	Bornyl acetate	tr	tr	0.4	-	-	-
1309	1309	4-Vinylguaiacol	-	0.1	-	-	-	-
1325	1328	Silphiperfol-5-ene	0.2	0.3	0.3	-	-	-
1344	1349	7-*epi*-Silphiperfol-5-ene	0.2	0.4	0.1	-	-	-
1349	1348	α-Longipinene	0.1	0.1	0.5	0.3	0.4	0.5
1352	1356	Eugenol	tr	0.1	-	0.1	0.1	-
1357	1356	Benzylideneacetone	tr	0.1	0.1	-	-	-
1368	1367	Cyclosativene	tr	tr	0.1	tr	0.1	0.1
1369	1371	α-Ylangene	tr	tr	0.1	tr	0.1	0.1
1372	1372	Isoledene	tr	-	-	-	-	-
1373	1371	Silphiperfol-6-ene	0.2	0.5	0.5	-	-	-
1375	1375	α-Copaene	tr	tr	0.1	0.2	0.2	0.1
1378	1380	Daucene	0.1	0.1	0.3	-	-	-
1379	1382	(3*Z*)-Hexenyl hexanoate	0.1	tr	-	-	-	-
1381	—	Unidentified[a]	0.5	0.4	1.3	0.7	0.6	0.5
1387	1387	7-*epi*-Sesquithujene	tr	0.1	0.1	-	-	-
1389	1392	α-Isocomene	-	-	-	-	0.2	0.2
1392	1394	(*Z*)-Jasmone	0.1	0.3	0.1	-	-	-
1400	1403	Methyl eugenol	0.1	0.2	0.1	0.2	0.1	-
1412	1411	β-Isocomene	-	-	-	tr	0.1	0.1
1418	1422	β-Ylangene	-	-	-	0.2	0.2	0.2
1420	1424	(*E*)-β-Caryophyllene	6.9	6.1	3.7	1.1	2.0	4.1
1429	1427	γ-Elemene	-	-	-	-	0.1	-
1430	1430	β-Copaene	0.1	0.1	0.2	0.2	0.2	0.2
1432	1432	*trans*-α-Bergamotene	0.1	0.1	0.2	0.2	0.1	0.1
1440	1439	(*Z*)-β-Farnesene	0.4	0.9	1.8	1.1	0.6	0.2
1451	1449	α-Himachalene	-	-	-	0.1	0.1	0.1
1452	1452	(*E*)-β-Farnesene	0.2	0.2	0.4	0.4	0.3	0.2
1455	1454	α-Humulene	1.0	1.2	0.8	0.9	0.9	0.9
1471	1469	Dauca-5,8-diene	0.1	0.1	-	-	-	-
1475	1475	γ-Muurolene	0.2	0.3	0.6	0.4	0.5	0.3
1478	1480	γ-Curcumene	0.1	0.1	-	0.7	0.9	0.8
1480	1482	*ar*-Curcumene	-	-	0.5	-	-	-
1479	1479	α-Amorphene	-	-	0.2	tr	0.2	0.1
1481	1480	Germacrene D	5.9	6.4	0.3	21.5	19.7	16.5
1483	1479	β-Chamigrene	0.2	0.1	-	-	-	-
1483	1483	*trans*-β-Bergamotene	-	-	0.2	-	-	-
1483	1482	γ-Himachalene	-	-	-	0.5	0.5	0.3
1492	1492	*trans*-Muurola-4(14),5-diene	0.1	0.1	0.1	tr	0.2	0.1
1496	1497	Bicyclogermacrene	0.5	0.3	-	0.6	0.5	0.4
1499	1500	α-Muurolene	0.2	0.2	0.3	0.4	0.4	0.3
1500	1503	β-Himachalene	-	-	-	tr	0.2	0.2
1504	1504	(*E*,*E*)-α-Farnesene	-	-	-	0.6	0.6	0.7
1507	1508	β-Bisabolene	0.1	0.1	0.3	tr	0.1	0.1
1509	1509	β-Curcumene	0.1	0.2	-	-	-	-
1513	1512	γ-Cadinene	0.1	0.2	0.4	0.2	0.2	0.1
1518	1518	δ-Cadinene	0.5	0.6	0.3	1.0	1.3	0.8
1522	1522	7-*epi*-Silphiperfoln-6β-ol	0.2	0.4	-	-	-	-
1523	1523	Silphiperfolan-7β-ol	5.5	10.2	8.2	-	-	0.9
1524	1524	β-Sesquiphellandrene	-	-	-	0.4	0.5	-
1529	1533	Kessane	0.9	0.4	3.4	-	-	-
1535	1534	Phenylethyl tiglate	-	-	-	0.4	0.2	0.2
1537	1538	α-Cadinene	-	-	-	-	0.1	-
1543	1544	*cis*-Sesquisabinene hydrate	0.1	0.2	0.2	-	-	-
1560	1561	(*E*)-Nerolidol	1.3	1.2	1.3	tr	0.2	0.4

(Continued)

Table 1. Continued

RI$_{calc}$	RI$_{db}$	Compound	*Wyethia amplexicaulis*			*Wyethia helianthoides*		
			#1	#2	#3	#1	#2	#3
1565	1563	15-Copaenol	6.5	5.3	11.4	6.0	5.6	4.3
1570	1573	(3Z)-Hexenyl benzoate	-	0.1	0.1	-	-	-
1576	1576	Spathulenol	0.4	0.1	0.5	-	-	-
1579	1580	*trans*-Sesquisabinene hydrate	0.1	0.3	0.2	-	-	-
1582	1587	Caryophyllene oxide	0.5	0.3	5.8	-	-	-
1585	1590	Globulol	0.2	0.1	0.3	-	-	-
1596	1591	β-Copaen-4α-ol	0.2	0.2	0.6	-	-	-
1602	1601	Carotol	4.0	2.8	10.0	5.4	5.9	3.5
1610	1611	Humulene epoxide II	-	-	1.0	-	-	-
1622	1619	Junenol	-	-	-	0.2	0.2	0.3
1624	—	Unidentified[b]	0.9	0.7	1.0	0.8	0.7	0.7
1626	1624	Muurola-4,10(14)-dien-1α-ol	0.8	0.6	2.7	0.8	0.8	0.8
1632	1632	Muurola-4,10(14)-dien-1β-ol	2.9	1.8	2.4	2.5	2.5	2.8
1633	1631	Eremoligenol	0.3	0.3	1.2	-	-	-
1642	1643	τ-Cadinol	0.4	0.5	0.9	0.3	0.5	0.3
1644	1645	τ-Muurolol	0.5	0.6	1.1	0.6	0.9	0.5
1646	1651	α-Muurolol (= δ-Cadinol)	0.2	0.3	0.6	-	-	-
1654	1655	Himachalol	1.1	0.1	3.4	0.5	2.1	3.3
1655	1655	α-Cadinol	0.9	1.5	1.7	1.4	2.0	1.5
1664	1664	*cis*-Calamenen-10-ol	-	-	0.5	-	-	-
1668	1669	*epi*-β-Bisabolol	-	0.1	1.3	-	-	-
1670	1671	β-Bisabolol	-	0.8	-	tr	0.3	0.4
1672	1670	*trans*-Calamenen-10-ol	-	-	0.6	-	-	-
1672	—	Unidentified[c]	-	0.2	1.3	0.4	0.3	0.3
1684	1686	*epi*-α-Bisabolol	-	-	0.7	tr	0.2	0.2
1717	—	Unidentified[d]	0.4	0.2	1.2	0.4	0.3	0.4
1727	1730	*cis*-Ligustilide	-	-	-	1.0	0.6	0.4
1776	—	γ-Curcumen-15-al	-	-	0.3	-	-	-
1779	1778	14-Hydroxy-α-muurolene	0.9	1.0	3.3	1.1	1.7	1.0
1782	—	Unidentified[e]	1.8	2.3	2.1	2.4	3.3	3.0
1839	—	Unidentified[f]	-	-	-	1.0	2.1	1.3
1852	1856	Phenethyl benzoate	-	-	0.5	-	-	-
1861	1860	Platambin	-	-	0.3	-	-	-
1884	—	Unidentified[g]	-	-	-	0.6	1.5	1.0
1900	—	Unidentified[h]	-	-	1.2	-	-	-
1929	1932	Benzyl hydrocinnamate	-	-	0.5	-	-	-
2122	—	Unidentified[i]	1.0	0.5	1.2	0.5	0.3	0.4
2300	2300	Tricosane	-	-	-	0.3	0.2	0.3
2500	2500	Pentacosane	-	-	-	0.3	0.3	0.5
2529	2530	Methyl docosanoate	-	-	-	-	0.3	0.6
2700	2700	Heptacosane	-	-	-	-	0.2	0.3
		Monoterpene hydrocarbons	47.4	45.0	7.9	36.9	30.1	37.5
		Oxygenated monoterpenoids	0.9	0.8	2.3	0.9	1.4	1.5
		Sesquiterpene hydrocarbons	17.5	18.7	12.3	30.8	31.2	28.0
		Oxygenated sesquiterpenoids	27.9	29.0	64.1	18.7	22.9	20.2
		Benzenoid aromatics	0.1	0.8	1.5	1.4	0.8	0.4
		Others	1.4	1.2	1.4	3.3	2.6	2.9
		Total identified	95.2	95.6	89.6	92.0	89.0	90.4

RI$_{calc}$ is the retention index determined with respect to a homologous series of *n*-alkanes on a ZB-5 ms column using the linear equation of van den Dool and Kratz.[6] RI$_{db}$ is the reference retention index obtained from the databases.[7–10] tr = trace (< 0.05%).
aMS(EI): 220(5%), 205(7%), 177(69%), 159(100%), 149(35%), 135(38%), 121(46%), 107(80%), 93(94%), 91(59%), 81(50%), 55(40%), 43(57%), 41(48%).
bMS(EI): 220(7%), 205(5%), 202(8%), 177(38%), 159(100%), 135(36%), 107(35%), 105(36%), 93(65%), 91(59%), 79(34%), 55(30%), 43(32%), 41(42%).
cMS(EI): 207(8%), 204(10%), 189(5%), 163(7%), 149(19%), 107(19%), 95(40%), 81(22%), 67(15%), 59(100%), 43(114%), 41(14%).
dMS(EI): 220(2%), 105(8%), 204(11%), 177(41%), 159(100%), 135(33%), 121(44%), 119(38%), 107(50%), 93(73%), 91(47%), 81(49%), 55(56%), 43(98%), 41(58%).
eMS(EI): 220(36%), 189(16%), 150(24%), 135(100%), 133(46%), 107(55%), 105(81%), 91(95%), 79(59%), 67(34%), 55(44%), 41(54%).
fMS(EI): 121(11%), 120(100%), 107(10%), 83(12%), 77(8%), 55(27%).
gMS(EI): 121(12%), 120(100%), 107(8%), 83(35%), 77(8%), 55(16%).
hMS(EI): 236(13%), 221(14%), 167(55%), 126(29%), 109(30%), 107(35%), 98(86%), 95(62%), 91(43%), 79(54%), 69(99%), 55(85%), 43(100%), 41(76%).
iMS(EI): 202(12%), 177(10%), 159(34%), 132(18%), 83(100%), 55(55%), 43(16%), 41(15%).

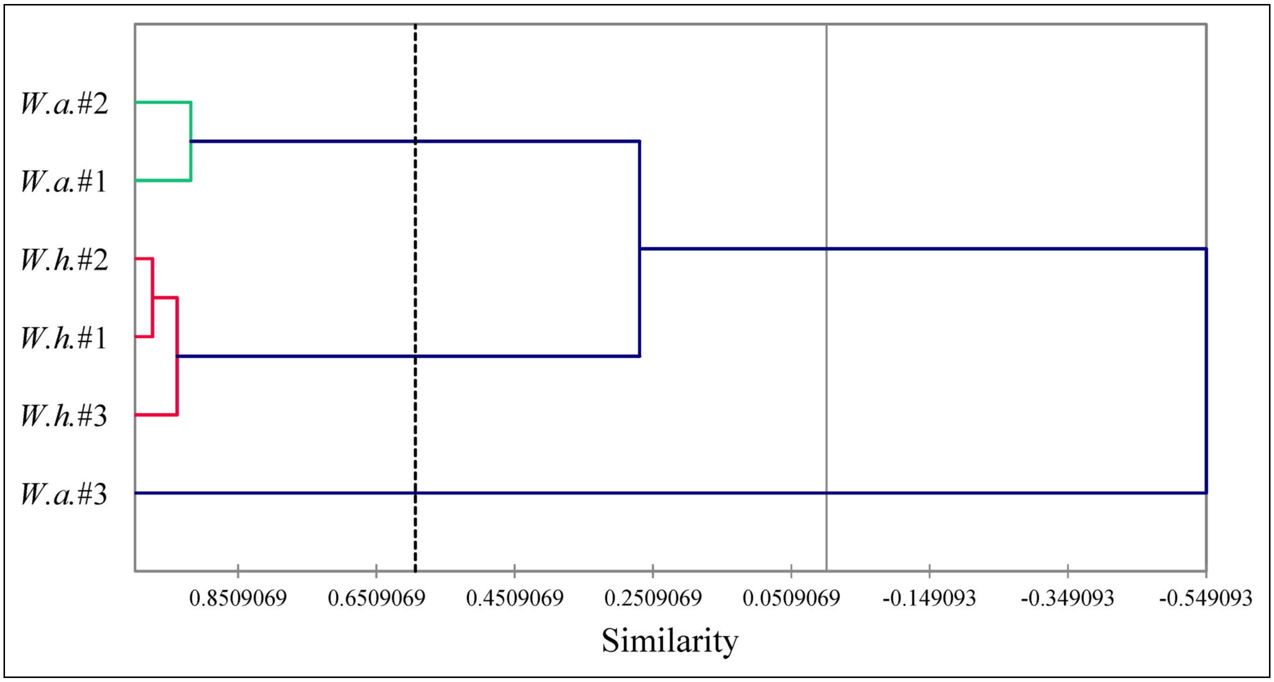

Figure 4. Dendrogram obtained by hierarchical cluster analysis (HCA) of *Wyethia amplexicaulis* (*W.a.*) and *Wyethia helianthoides* (*W.h.*) leaf essential oils.

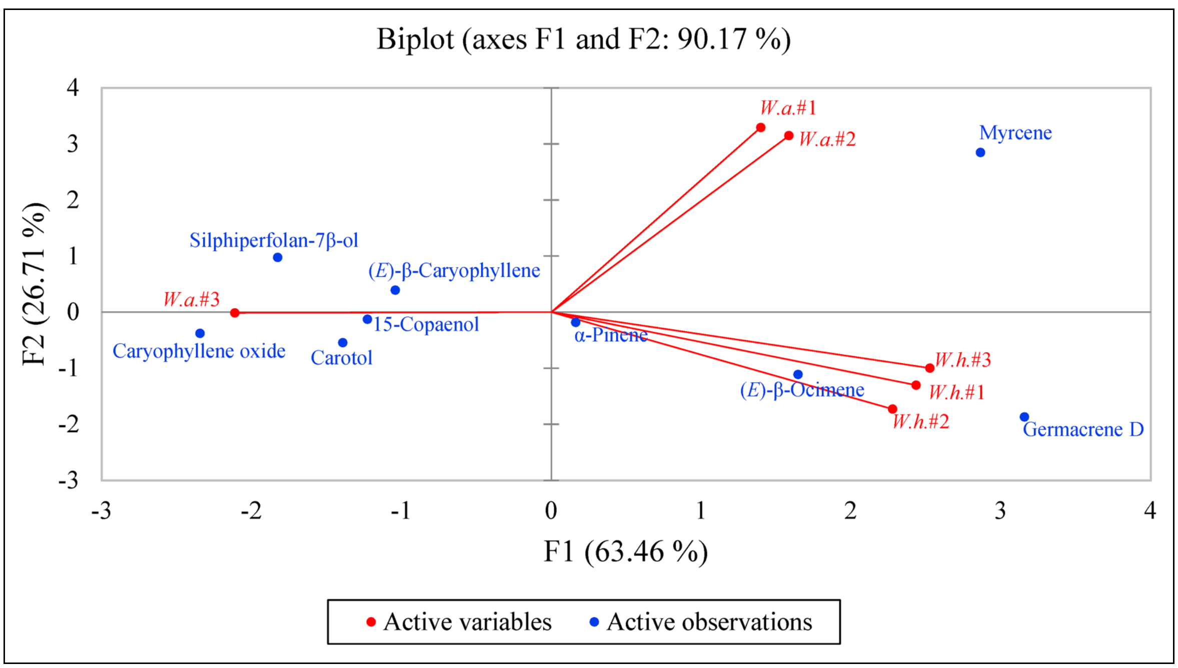

Figure 5. Principal component analysis (PCA) of *Wyethia amplexicaulis* (*W.a.*) and *Wyethia helianthoides* (*W.h.*) leaf essential oils.

(Shimadzu Scientific Instruments) equipped with a ZB-5 ms fused silica capillary column (60 m, 0.25 mm; 0.25 µm film thickness) as stationary phase was used (Phenomenex). The helium carrier gas was adjusted to 1.0 mL/min at 208.2 kPa head pressure. The injection of diluted essential oils in dichloromethane (5% w/v) were carried out in the split mode (1:24.5). The injector temperature was 260 °C. The programed oven temperature was 50 to 260 °C at a rate of 2 °C/min). The mass selective detector was operated in the EI mode with electron energy = 70 eV. The scan range was 40 to 400 amu, and

Table 2. Enantiomeric Distributions of Chiral Terpenoid Components in *Wyethia amplexicaulis* and *Wyethia helianthoides* Leaf Essential Oils.

			Wyethia amplexicaulis			*Wyethia helianthoides*		
Compound	RI_{db}	RI_{calc}	#1	#2	#3	#1	#2	#3
(+)-α-Thujene	950	950	81.1	-	-	-	-	-
(−)-α-Thujene	951	951	18.9	-	-	-	-	-
(−)-α-Pinene	976	976	10.3	10.6	20.2	4.6	5.0	4.8
(+)-α-Pinene	982	980	89.7	89.4	79.8	95.4	95.0	95.2
(−)-Camphene	998	999	99.3	99.2	99.4	100.0	100.0	100.0
(+)-Camphene	1005	1005	0.7	0.8	0.6	0.0	0.0	0.0
(+)-Sabinene	1021	1022	69.6	67.9	57.8	-	-	-
(−)-Sabinene	1030	1029	30.4	32.1	42.2	-	-	-
(+)-β-Pinene	1027	1027	55.2	60.8	41.2	82.3	77.3	82.7
(−)-β-Pinene	1031	1031	44.8	39.2	58.8	17.7	22.7	17.3
(+)-δ-3-Carene	1052	1053	-	100.0	-	100.0	100.0	100.0
(−)-δ-3-Carene	na	-	-	0.0	-	0.0	0.0	0.0
(−)-α-Phellandrene	1050	-	-	0.0	-	-	-	-
(+)-α-Phellandrene	1053	1053	-	100.0	-	-	-	-
(−)-Limonene	1073	1074	71.0	69.2	69.5	59.3	59.6	59.2
(+)-Limonene	1081	1081	29.0	30.9	30.5	40.7	40.4	40.8
(−)-β-Phellandrene	1083	1086	-	20.2	-	-	-	-
(+)-β-Phellandrene	1089	1089	-	79.8	-	100.0	-	-
(−)-Linalool	1228	1227	39.4	43.7	-	47.2	46.5	45.3
(+)-Linalool	1231	1230	60.6	56.3	-	52.8	53.5	54.7
(+)-Terpinen-4-ol	1297	1295	69.9	64.4	60.9	-	59.8	63.2
(−)-Terpinen-4-ol	1300	1300	30.1	35.6	39.1	-	40.2	36.8
(−)-Borneol	1335	1334	-	-	100.0	-	-	-
(+)-Borneol	1340	-	-	-	0.0	-	-	-
(−)-α-Terpineol	1347	1347	30.3	35.6	33.2	30.8	25.3	25.1
(+)-α-Terpineol	1356	1355	69.7	64.4	66.8	69.2	74.7	74.9
(−)-(*E*)-β-Caryophyllene	1461	1461	100.0	100.0	100.0	100.0	100.0	100.0
(+)-(*E*)-β-Caryophyllene	na	-	0.0	0.0	0.0	0.0	0.0	0.0
(+)-Germacrene D	1519	-	0.0	0.0	0.0	0.0	0.0	0.0
(−)-Germacrene D	1522	1522	100.0	100.0	100.0	100.0	100.0	100.0
(−)-δ-Cadinene	1563	-	0.0	0.0	0.0	0.0	0.0	0.0
(+)-δ-Cadinene	1576	1576	100.0	100.0	100.0	100.0	100.0	100.0
(−)-(*E*)-Nerolidol	1677	1676	4.9	4.1	10.2	-	-	-
(+)-(*E*)-Nerolidol	1680	1678	95.1	95.9	89.8	-	-	-

RI_{db} is the retention index from our database developed from reference compounds from Sigma-Aldrich. RI_{calc} is the retention index calculated with respect to a homologous series of *n*-alkanes on a Restek B-Dex 325 capillary column. Abbreviations: -, compound not detected; na, reference compound not available.

Table 3. Collection and Hydrodistillation Details for *Wyethia*.

Plant sample	Collection site	Mass of leaves (g)	Mass of essential oil (g)	Yield (%)
Wyethia amplexicaulis #1	43°32′33″ N, 115°48′14″ W, 1143 m asl	153.18	0.2079	0.136
Wyethia amplexicaulis #2	43°32′33″ N, 115°48′14″ W, 1143 m asl	124.13	0.1388	0.112
Wyethia amplexicaulis #3	43°32′33″ N, 115°48′14″ W, 1143 m asl	100.55	0.0901	0.090
Wyethia helianthoides #1	43°32′46″ N, 115°48′6″ W, 1148 m asl	124.61	1.8893	1.516
Wyethia helianthoides #2	43°32′46″ N, 115°48′6″ W, 1148 m asl	140.56	2.0934	1.489
Wyethia helianthoides #3	43°32′46″ N, 115°48′6″ W, 1148 m asl	86.25	1.5275	1.771

scan rate was 3.99 scans/s. the ion source and interface temperatures were 260 °C. Identification of the oil components was based on their retention indices, determined by reference to a homologous series of *n*-alkanes using the linear equation of van den Dool and Kratz,[6] and by comparison of their mass spectral fragmentation patterns with those reported in the Adams,[7] FFNSC 3,[8] NIST20,[9] and Satyal[10] libraries.

GC-FID, was carried out on each essential oil sample using a Shimadzu GC 2010 with FID detector (Shimadzu Scientific Instruments), ZB-5 GC column (60 m × 0.25 mm × 0.25 μm film thickness. (Phenomenex) using the same operating conditions as above for GC-MS. The percent compositions were determined from raw peak areas without standardization.

Enantioselective GC-MS were GC-FID analysis was carried out using a Shimadzu GC-MS-QP2010S instrument (Shimadzu Scientific Instruments) fitted with a Restek β-Dex 325 column, 30 m × 0.25 mm diameter × 0.25 μm film thickness, Restek Corp.). The injector and detector temperatures were 240 °C. Helium was the carrier gas with a flow rate of 1.00 mL/min and a column head pressure of 53.6 kPa. The GC oven temperature program was initial temperature of 50 °C, which was held for 5 min, then increased to 100 °C at a rate of 1.0 °C/min, then increased to 220 °C at a rate of 2 °C/min. Essential oil samples (0.3 μL of a 5% (w/v) essential oil solution in dichloromethane) were injected using a splitting mode of 1:24. The enantiomers were determined by comparison of calculated retention indices with those of authentic samples (Sigma-Aldrich). Enantiomeric ratios were calculated from GC-MS (TIC) peak areas.

Hierarchical Cluster Analysis and Principal Component Analysis

HCA was carried out to examine the similarity of oil samples based on the percentages of nine major components (myrcene, germacrene D, (*E*)-β-ocimene, 15-copaenol, α-pinene, carotol, silphiperfolan-7β-ol, (*E*)-β-caryophyllene, and caryophyllene oxide). The six essential oil samples were treated as operational taxonomic units. Pearson correlation was used to measure similarity, and the unweighted pair-group method with arithmetic average was used to define the clusters. Principal component analysis (PCA, type Pearson Correlation) was used to determine the interrelationship of essential oil components and to verify the previous HCA analysis. Both the HCA and PCA analyses were carried out using XLSTAT v. 2018.1.1.62926 (Addinsoft).

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Data Availability Statement

All the data for this study are available in the manuscript.

Declaration of Conflicting Interests

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