

# **Research** Article

# Essential oils of two Great Basin composites: Chaenactis douglasii and Dieteria canescens from southwestern Idaho

# Ambika Poudel<sup>1</sup>, Prabodh Satyal<sup>1</sup>, Kathy Swor<sup>2</sup>, and William N. Setzer<sup>1,3,\*</sup>

- 1. Aromatic Plant Research Center, 230 N 1200 E, Suite 100, Lehi, UT 84043, USA
- Independent Researcher, 1432 W. Heartland Dr, Kuna, ID 83634, USA 2.
- 3. Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35899, USA

# Abstract

Article Information Received: 01 August 2023 Revised: 02 September 2023 Accepted: 07 September 2023

Academic Editor Radosław Kowalski

**Corresponding Author** Prof. Dr. William N. Setzer E-mail: wsetzer@chemistry.uah.edu Tel.: +1-256-468-2862

#### Keywords

Douglas' dustymaiden, hoary tansyaster, Asteraceae. enantiomeric distribution, gas chromatography, chiral

Chaenactis douglasii and Dieteria canescens are two members of the Asteraceae found in western North America and utilized by Native Americans as herbal medicines. The purpose of this investigation was to examine previously unstudied/understudied volatile phytochemistry of members of the Asteraceae from southwestern Idaho as well as to extend our understanding of the properties of Native American aromatic medicinal plants. The essential oils from the fresh aerial parts were obtained by hydrodistillation and analyzed by gas chromatographic methods. The colorless essential oil of C. douglasii was obtained in 0.024% yield, while D. canescens gave a pale-yellow essential oil in 0.418% yield. Tiglic acid (35.9%) dominated the essential oil of C. douglasii, followed by thymol (8.4%),  $\delta$ -cadinene (5.0%), and  $8\alpha$ -acetoxyelemol (4.7%). There was also a large concentration of an unidentified component (RI = 1998, 8.7%). The major components in D. canescens essential oil were δ-cadinene (28.3%), epi-cubebol (24.4%), 1-epi-cubenol (10.9%), and cubenol (7.7%). (–)-β-Pinene, (–)-germacrene D, (+)-δ-cadinene, and (+) -(E)nerolidol were the exclusive enantiomers found in C. douglasii essential oil, while (+)- $\alpha$ pinene (75.7%) was the major enantiomer for  $\alpha$ -pinene. In *D. canescens* essential oil, the (–)-enantiomers were predominant for  $\alpha$ - and  $\beta$ -pinene (90.3% and 90.4%, respectively), *cis-* and *trans-*sabinene hydrate (86.9% and 85.0%, respectively), terpinen-4-ol (66.8%),  $\alpha$ terpineol (64.8%), and germacrene D (100%), while the (+)-enantiomer was the major for limonene (95.8%) and  $\delta$ -cadinene (100%). A perusal of the literature reveals there to be no obvious trends in enantiomeric distributions of terpenoids in the Asteraceae.

# 1. Introduction

CurrentScjence

Numerous members of the Asteraceae growing in desert regions of western North America have been used as traditional herbal medicines by Native American tribes [1]. Two members of the family, Chaenactis douglasii (Hook.) Hook. & Arn (Douglas' dustymaiden) and Dieteria canescens (Pursch) Nutt. (syn. Machaeranthera canescens (Pursch) A. Gray, hoary tansyaster) have been understudied in terms of their volatile phytochemicals.

Chaenactis douglasii occurs in western North America from British Columbia, south to southern California,

Publishing

northern Arizona and northern New Mexico, and east into Montana, Wyoming, and Colorado [2, 3]. Several Native North American tribes used C. douglasii as traditional medicines. For example, the Paiute took a decoction of the plant to treat coughs and colds, the Shoshoni used a poultice of crushed plants to treat swellings, and the Thompson people used a decoction of the plant on skin conditions and insect bites [1]. Guaianolide and germacranolide sesquiterpene lactones have been isolated and identified in the aerial parts of C. douglasii [4-6]. The crude methanol extract

(not phytochemically characterized) of *C. douglasii* from British Columbia, Canada, was screened for antibacterial [7] and antifungal [8] activity. The extract showed activity against *Bacillus subtilis*, *Escherichia coli*, *Mycobacter phlei*, both methicillin-susceptible and methicillin-resistant *Staphylococcus aureus*, *Salmonella typhimurium*, *Microsporum cookerii*, *Microsporum gypseum*, and *Trichophyton mentagrophytes*. Apparently there have been no previous reports on the essential oil composition of *C. douglasii*, however.

*Dieteria canescens* ranges throughout western North America from Canada, south through California, Arizona, and New Mexico, to Mexico [3, 9]. The Navajo used the dried, pulverized plant material as a snuff to treat throat problems, while a decoction of the plant was taken by parturient Hopi women for any disorder [1]. As far as we are aware, there are no previous studies on the phytochemistry of *D. canescens*.

Both C. douglasii and D. canescens are important native members of the plant communities of the Great Basin [10]. However, these native plant communities of the Great Basin are being lost or degraded at an alarming rate due to overgrazing, wildfires, drought, and invasive species; the sagebrush steppe is one of the most endangered ecosystems of North America [11,12]. Although relatively understudied, C. douglasii [13] and *D. canescens* [14] have been highlighted as priority species for restoration of degraded habitats in the Great Basin. However, neither plant has been investigated in terms of essential oil composition. As part of our continuing interest in essential oils of aromatic/medicinal plants of the Great Basin, the purpose of this study was to investigate the essential oil compositions of these two members of the Asteraceae, C. douglasii and D. canescens collected from Boise, Idaho.

# 2. Materials and methods

### 2.1 Plant material

Aerial parts of *C. douglasii* and *D. canescens* were collected from the Idaho Botanical Garden (43°36'04"N, 116°09'35"W, 862 m elevation) on 29 July 2021. The plants were identified by Daniel Murphy, Collections Curator, Idaho Botanical Garden. The fresh aerial parts of *C. douglasii* (17.34 g) were hydrodistilled using a Likens-Nickerson apparatus with continuous extraction with dichloromethane for

3 h to give a colorless residue (4.1 mg). The fresh aerial parts of *D. canescens* (48.19 g) were hydrodistilled for 3 h to give a pale-yellow essential oil (201.2 mg).

### 2.2 Gas chromatographic analyses

The aerial parts essential oils of C. douglasii and D. canescens were analyzed by GC-MS as previously reported [15]: Shimadzu GCMS-QP2010 Ultra (Shimadzu Scientific Instruments, Columbia, MD, USA), ZB-5ms capillary column (60 m × 0.25 mm, 0.25 µm film thickness, Phenomenex, Torrance, CA, USA); He carrier gas, head pressure = 208.3 kPa, flow rate = 2.00 mL/min, injector temperature = 260 °C, ion source temperature = 260 °C, interface temperature = 260 °C, GC oven program (50 °C initial temperature, ramp up to 260 °C at 2 °C/min, held at 260 °C for 5 min); 0.1 µL injection, 5% w/v essential oil/CH2Cl2, 24.5:1 split mode. A series of homologous n-alkanes was used to calculate the retention indices (RI) [16]. Chemical components were identified by comparing MS fragmentation and RI values with those in the Adams [17], FFNSC3 [18], NIST20 [19], and Satyal [20] databases. Gas chromatography - flame ionization detection (GC-FID) was carried out as previously described [15]: Shimadzu GC 2010 with FID detector (Shimadzu Scientific Instruments, Columbia, MD, USA), ZB-5 capillary column (60 m  $\times$  0.25 mm  $\times$  0.25 µm film thickness) (Phenomenex, Torrance, CA, USA), same operating conditions as above for GC-MS. The percent compositions were determined from raw peak areas without standardization. Chiral GC-MS was used to evaluate the enantiomeric distributions of chiral terpenoids as previously reported [15]: Shimadzu GCMS-QP2010S (Shimadzu Scientific Instruments, Columbia, MD, USA), Restek B-Dex 325 column (30 m  $\times$  0.25 mm diameter  $\times$  0.25 µm film thickness) (Restek Corp., Bellefonte, PA, USA); He carrier gas, head pressure = 53.6 kPa, flow rate = 1.00 mL/min, injector and detector temperatures = 240 °C, GC oven program (50 °C initial temperature held for 5 min, ramp up to 100 °C at 1.0 °C/min, then ramp to 220 °C at 2.0 °C/min); 0.3 µL injection, 5% w/v essential oil/CH2Cl2, 24.0:1 split mode. Retention indices (RI) determined with respect to a series (C8-C21) of *n*-alkanes. Enantiomers were determined by comparison of RI values with those in our in-house database. The enantiomer percentages were determined from raw peak areas.

# 3. Results and discussion

Hydrodistillation of the aerial parts of *C. douglasii* gave a colorless essential oil in very low (0.024%) yield while the aerial parts of *D. canescens* gave a pale-yellow essential oil in 0.418% yield. Gas chromatographic analyses (GC-MS and GC-FID) of the two essential oils are summarized in Table 1.

**Table 1.** Chemical composition (%) of the aerial parts essential oil of *Chaenactis douglasii* (CD) and *Dieteria canescens* (DC)

RIcalc	RIdb	Compound	CD	DC
933	933	α-Pinene	0.2	0.4
941	942	Tiglic acid	35.9	-
949	950	Camphene	-	0.1
971	971	Sabinene	-	tr
978	978	β-Pinene	1.6	1.3
979	979	Caproic acid	0.7	-
988	989	Myrcene	-	0.3
1007	1007	α-Phellandrene	-	tr
1017	1018	$\alpha$ -Terpinene	-	tr
1024	1024	<i>p</i> -Cymene	-	0.5
1026	1026	2-Acetyl-3-methylfuran	-	tr
1029	1030	Limonene	-	0.5
1030	1031	β-Phellandrene	-	tr
1031	1032	1,8-Cineole	-	tr
1035	1035	$(Z)$ - $\beta$ -Ocimene	-	tr
1045	1045	( <i>E</i> )-β-Ocimene	-	tr
1057	1057	γ-Terpinene	-	tr
1069	1069	<i>cis</i> -Sabinene hydrate	-	0.2
1085	1086	Terpinolene	-	tr
1100	1101	<i>trans</i> -Sabinene hydrate	-	0.1
1107	1106	$\alpha$ -Pinene oxide	-	tr
1121	1121	trans-p-Mentha-2,8-dien-1-	-	tr
		ol		
1124	1126	cis-p-Menth-2-en-1-ol	-	0.1
1137	1137	Nopinone	-	tr
1141	1142	trans-p-Menth-2-en-1-ol	-	0.1
1145	1145	trans-Verbenol	-	0.2
1149	1146	trans-Limonene oxide	-	tr
1161	1164	Pinocarvone	-	tr
1171	1170	Borneol	-	tr
1175	1176	cis-Pinocamphone	-	tr
1180	1180	Terpinen-4-ol	-	1.2
1186	1186	<i>p</i> -Cymen-8-ol	-	0.1
1195	1195	$\alpha$ -Terpineol	0.3	0.1
1196	1196	<i>cis</i> -Piperitol	-	tr
1206	1206	Verbenone	-	tr
1208	1208	trans-Piperitol	-	tr
1283	1282	Bornyl acetate	0.5	0.1
1289	1289	Thymol	8.4	-
1348	1348	$\alpha$ -Cubebene	_	0.7
1376	1375	$\alpha$ -Copaene	-	0.4
1384	1382	β-Bourbonene	-	0.1
1387	1385	α-Isocomene	0.2	_
1390	1392	β-Cubebene	-	0.9
1407	1406	$\alpha$ -Gurjunene	-	0.1

Table 1. (Continued)
----------------------

RIcalc	RIdb	Compound	CD	DC
1418	1422	β-Ylangene	-	tr
1419	1417	( <i>E</i> )-β-Caryophyllene	-	0.1
1446	1447	Geranyl acetone	0.3	-
1449	1448	cis-Muurola-3,5-diene	-	0.1
1454	1454	$\alpha$ -Humulene	0.2	tr
1465	1464	Ylangol	-	tr
1469	1463	cis-Cadina-1(6),4-diene	-	tr
1472	1472	trans-Cadina-1(6),4-diene	-	0.6
1475	1475	γ-Muurolene	-	0.1
1476	1481	(E)-β-Ionone	0.1	-
1482	1483	Germacrene D	0.7	0.2
1489	1489	β-Selinene	-	0.1
1492	1492	<i>trans</i> -Muurola-4(14),5-	0.7	1.9
		diene		
1496	1497	<i>epi</i> -Cubebol	2.3	24.4
1497	1497	$\dot{\alpha}$ -Muurolene	0.3	-
1511	1510	Tridecanal	0.5	-
1516	1515	Cubebol	0.9	2.9
1518	1518	δ-Cadinene	5.0	28.3
1520	1519	trans-Calamenene	0.6	-
1522	1521	Zonarene	0.3	-
1523	1524	Dihydroactinidiolide	0.3	-
1526	1527	trans-Calamenene	-	3.8
1533	1533	trans-Cadine-1.4-diene	0.4	0.6
1542	1541	$\alpha$ -Calacorene	_	0.4
1549	1549	$\alpha$ -Elemol	2.9	0.3
1560	1561	(E)-Nerolidol	0.3	_
1562	1564	β-Calacorene	_	0.3
1570	1568	Palustrol	-	0.2
1575	1576	Spathulenol	0.4	_
1584	1590	Globulol	0.3	-
1588	1590	Gleenol	-	1.4
1590	-	Unidentifiedª	-	1.8
1592	-	Unidentified <sup>b</sup>	-	2.7
1593	1594	Viridiflorol	0.2	-
1600	1600	Hexadecane	0.2	-
1613	1613	Tetradecanal	0.2	-
1622	1624	Selina-6-en-4β-ol	0.9	-
1629	1628	1- <i>epi</i> -Cubenol	3.2	10.0
1631	1632	γ-Eudesmol	0.9	0.1
1643	1643	Cubenol	2.3	7.7
1643	1644	τ-Muurolol	0.9	-
1646	1644	$\alpha$ -Muurolol (= $\delta$ -Cadinol)	0.7	1.9
1654	1655	α-Cadinol	3.8	-
1657	1663	cis-Calamenen-10-ol	-	0.5
1663	1665	Intermedeol	1.8	-
1664	1662	9-Methoxycalamenene	-	0.4
1714	1715	Pentadecanal	0.4	-
1757	1758	Myristic acid	0.3	-
1777	1775	8α-Acetoxyelemol	4.7	0.2
1792	1793	$\alpha$ -Phellandrene dimer A	0.5	-
1840	1841	Phytone	0.2	-
1889	1891	( <i>E</i> )-Hexadecantrienal	0.7	-
1957	1958	Palmitic acid	0.3	-
1998	-	Unidentified <sup>c</sup>	8.7	-
		Total identified	86.4	93.9

#### Table 1. (Continued)

Compound Classes	CD	DC
Monoterpene hydrocarbons	1.8	3.0
Oxygenated monoterpenoids	9.1	2.2
Sesquiterpene hydrocarbons	8.4	38.7
Oxygenated sesquiterpenoids	26.7	49.9
Diterpenoids	0.5	0.0
Others	39.9	traces

CD: *C. douglasii*, DC: *D. canescens*, RI<sub>calc</sub> = Retention index calculated with respect to a homologous series of *n*-alkanes on a ZB-5ms column. RI<sub>db</sub> = Reference retention index values from the databases [17–20]. tr = trace (< 0.05%), - = not detected. <sup>a</sup>MS(EI): 222(3%), 208(13%), 207(90%), 204(17%), 161(57%), 137(18%), 135(21%), 123(25%), 119(22%), 105(38%), 95(26%), 91(18%), 55(17%), 43(100%), 41(24%). <sup>b</sup> MS(EI): 222(2%), 208(14%), 207(100%), 179(9%), 161(37%), 135(19%), 123(23%), 119(22%), 105(35%), 95(26%), 91(21%), 81(27%), 55(18%), 43(88%), 41(26%). <sup>c</sup> MS(EI): 230(13%), 215(8%), 186(8%), 169(8%), 157(11%), 145(84%), 143(22%), 129(23%), 117(23%), 105(30%), 194(100%), 91(59%), 79(44%), 77(35%), 65(17%), 53(14%), 41(24%).

Tiglic acid (35.9%) dominated the essential oil of C. douglasii, followed by thymol (8.4%), δ-cadinene (5.0%), and  $8\alpha$ -acetoxyelemol (4.7%). There was also a large concentration of an unidentified component (RI = 1998, 8.7%). Although the essential oil yield and the terpenoid content were low, the enantiomeric distributions for the monoterpenoids  $\alpha$ -pinene,  $\beta$ pinene, and  $\alpha$ -terpineol, as well as the sesquiterpenoids germacrene D,  $\delta$ -cadinol, and (E)nerolidol, were determined (Table 2). (+)- $\alpha$ -Pinene

was the predominant enantiomer (enantiomeric excess, %ee, = 51.4%) and  $\alpha$ -terpineol was nearly racemic [52.4% (+), 47.6% (–)]; the (–) enantiomers were found exclusively for  $\beta$ -pinene and germacrene D, while the (+)-enantiomers were observed for  $\delta$ -cadinene, and (*E*)-nerolidol.

The major components in *D. canescens* essential oil were  $\delta$ -cadinene (28.3%), *epi*-cubebol (24.4%), 1-*epi*-cubenol (10.9%), and cubenol (7.7%). The levorotatory enantiomers were dominant for the monoterpenes  $\alpha$ -pinene (ee 80.6%),  $\beta$ -pinene (ee 80.8%), camphene (ee 84.2%), *cis*-sabinene hydrate (ee 73.8%) *trans*-sabinene hydrate (ee 70.0%), terpinen-4-ol (ee 33.6%), and  $\alpha$ -terpineol (ee 29.6%). On the other hand, (+)-limonene was the major limonene enantiomer (ee 91.6%). As observed in *C. douglasii*, the (–) enantiomer was the exclusive stereoisomer for the germacrene D, while (+)- $\delta$ -cadinene was the only enantiomer observed in *D. canescens*.

There have been no previous reports on the chemical compositions of either *C. douglasii* or *D. canescens* essential oils, so direct comparisons cannot be made. Nevertheless, comparisons with other members of the Asteraceae are possible.

Although tiglate esters occur in many essential oils, the occurrence of the free carboxylic acid is rare

Compound	Database	C. dougla	asii EO	D. canesce	ns EO
	RT (RI)	RT (RI)	ED (%)	RT (RI)	ED (%)
(–)-α-Pinene	15.92 (976)	16.34 (976)	24.3	16.36 (976)	90.3
(+)-α-Pinene	16.40 (982)	16.78 (981)	75.7	16.86 (983)	9.7
(+)-β-Pinene	20.27 (1027)	-	0.0	20.80 (1027)	9.6
(–)-β-Pinene	20.62 (1030)	21.36 (1032)	100.0	21.22 (1031)	90.4
(–)-Limonene	25.06 (1073)	-	-	25.73 (1074)	4.2
(+)-Limonene	25.99 (1081)	-	-	26.47 (1080)	95.8
(+)-cis-Sabinene hydrate	40.70 (1199)	-	-	41.48 (1198)	13.1
(–)- <i>cis</i> -Sabinene hydrate	41.25 (1202)	-	-	41.98 (1200)	86.9
(+)-trans-Sabinene hydrate	46.15 (1230)	-	-	46.96 (1231)	15.0
(-)-trans-Sabinene hydrate	46.84 (1235)	-	-	47.63 (1235)	85.0
(+)-Terpinen-4-ol	54.64 (1297)	-	-	55.40 (1299)	33.2
(–)-Terpinen-4-ol	54.93 (1299)	-	-	55.70 (1302)	66.8
(–)-α-Terpineol	59.73 (1347)	60.34 (1348)	47.6	60.45 (1349)	64.8
(+)- $\alpha$ -Terpineol	60.58 (1356)	61.14 (1356)	52.4	61.24 (1358)	35.2
(+)-Germacrene D	73.48 (1518)	-	0.0	-	0.0
(–)-Germacrene D	73.73 (1522)	74.01 (1521)	100.0	74.10 (1522)	100.0
(–)-δ-Cadinene	76.50 (1563)	-	0.0	-	0.0
(+)-δ-Cadinene	77.33 (1576)	77.67 (1576)	100.0	77.53 (1574)	100.0
(–)-(E)-Nerolidol	83.40 (1677)	-	0.0	-	-
(+)-(E)-Nerolidol	83.59 (1680)	83.96 (1681)	100.0	-	-

Table 2. Enantiomeric distributions of chiral terpenoids detected in Chaenactis douglasii and Dieteria canescens essential oils.

RT = Retention time (min). RI = Retention index calculated with respect to a homologous series of *n*-alkanes on a Restek B-Dex 325 column. EO = Essential oil. ED = Enantiomeric distribution. - = not observed.

e
Ge
ra
ste
A
the
of
$\mathbf{ls}$
io
tia
en
ess
Ē.
ds
.jo
Jer.
erl
of t
Ĕ
Itic
ibu
stri
di
ric
ne
lioi
an
Εn
ω.
ole
[ab

Matrix         Samme attant         Attant         Samme Attant         Attant         Samme Attant         Attant         Attantant         Attant         Attant	Pinen	e	β-Pin	ene	Limor	iene	cis-Sabii	nene	trans-	Ľ	erpinen-4	L	α-	Gen	nacrene	ô-Cad	linene	(E)-N	erolidol	Ref.
							hydra	tte	Sabinen	e	ol	Te	rpineol		D					
	(+) (-) (+) (-)	(+) (-) (+)	(+) (-)	Ð		Ĵ	(±	I	-) (+)	)÷		) ÷	1	£	Ĵ	£	I	£	1	
·         ·	41.0 2.0 98.0 -	2.0 98.0 -	- 0.86		1					- 56.	0 44.	- 0	1	·	•					[43]
100         ·	21.0- 0.0- 98.0- 97.0 2.0 100.0 <sup>-</sup>	0.0- 98.0- 2.0 100.0 <sup>-</sup>	98.0- 100.0 <sup>-</sup>	ï		ı	ı	ı		1	I	ı	,	I	ı	ı	ı	ı	ı	[44]
21         2.         2.         2.         4.3         5.6         0.0         0.0         0.0         1000         1000         16           1         1         2.         7.2         70.2	3.6- 0.0 100.0 0.0	0.0 100.0 0.0	100.0 0.0	0.0		100.0							'	1	1	1			·	[41]
	3.9 34.0 66.0 78.0	34.0 66.0 78.0	66.0 78.0	78.0		22.0	ı	ı			I	43.	4 56.6	0.0	100. 0	ı	ı	0.0	100.0	[45]
	0.0 100.0 0.0 -	- 0.0	- 0.0	ı		ı	ı	ı		- 25.	7 70.1 8 74.	3.2	ı	ı	ı	0.0	100. 0	7.9- 8.1	91.9-92.1	[46]
	55.6- $25.4$ - $56.2$ - $63.0$ 69.0 $43.8$ $74.6$ $_{80.5}^{-}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	56.2- 63.0 74.6	63.0 - 80.5		19.5- 37.0				35. 47	0 28. 65.	)- 51.( 0 68.(	0 32.( - 1	'		i.	,	,	I	[47]
338 $\cdot$ <td>63.4   41.7   50.1   70.2   66.9   49.9   58.3   -7.1   70.2</td> <td><math display="block">\begin{array}{cccccccccccccccccccccccccccccccccccc</math></td> <td>50.1- 70.2 58.3</td> <td>70.2</td> <td></td> <td>14.6- 29.8</td> <td></td> <td></td> <td></td> <td>- 30 - 30 - 30</td> <td>0 0 20.5</td> <td>-1 56.0</td> <td>0 19.0</td> <td>'</td> <td>1</td> <td>,</td> <td>,</td> <td></td> <td>ı</td> <td>[47]</td>	63.4   41.7   50.1   70.2   66.9   49.9   58.3   -7.1   70.2	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	50.1- 70.2 58.3	70.2		14.6- 29.8				- 30 - 30 - 30	0 0 20.5	-1 56.0	0 19.0	'	1	,	,		ı	[47]
7.7         86.1         1.3         90.5         9.5         7.1         8.7.4         47.6         0.0         0.0         0.0         0.0         0.0         100.           7.7         86.1         13.9         90.5         95.7         71.9         28.1         12.6         87.4         33.4         66.6         -         -         -         -         149           7.7         86.1         13.9         90.5         71.9         28.1         12.6         87.4         33.4         66.6         -         -         -         -         149           7.5         13.1         86.9         15.0         85.0         33.2         64.8         0.0         0.0         0.0         0.0         100.         100.         100.         100         100         140         149           10.0         10.1         86.9         33.2         64.8         0.0         0.0         0.0         0.0         100         140         140           40.2         13.4         65.8         33.2         64.8         0.0         0.0         0.0         0.0         100.         100.         140         140           40.2         13.4	85.4 96.0 73.0 27.0 66.2	85.4 73.0 27.0 66.2	85.4 27.0 66.2	85.4 66.2		33.8	,			- 38	۱	81.0	0 44.( -	'	ı	ı	·	ı	,	[48]
7.7         86.1         13.9         90.5         71.9 <th< td=""><td>24.3 0.0 100.0 -</td><td>0.0 100.0 -</td><td>- 100.0</td><td>,</td><td></td><td>ı</td><td>ı</td><td>ı</td><td></td><td>'</td><td>I</td><td>52.</td><td>4 47.6</td><td>0.0</td><td>100. 0</td><td>100. 0</td><td>0.0</td><td>100. 0</td><td>0.0</td><td>[This work]</td></th<>	24.3 0.0 100.0 -	0.0 100.0 -	- 100.0	,		ı	ı	ı		'	I	52.	4 47.6	0.0	100. 0	100. 0	0.0	100. 0	0.0	[This work]
7.5         .	94.5 0.2 99.8 92.3	0.2 99.8 92.3	99.8 92.3	92.3		7.7	86.1	13.9	90.5 9.	.5 71.	9 28.	1 12.0	6 87.4	33.4	9.99	,		ı	,	[15]
4.2         13.1         86.9         15.0         85.0         33.2         66.8         35.2         64.8         0.0         100.         0.0         2         c         This workl           7         2         2         2         7.1         28.4         2         7.7         92.3         2         2         5	81.6 100.0 0.0 2.5	100.0 0.0 2.5	0.0 2.5	2.5		97.5	ı	ı		'	I	ı	ı	0.0	100. 0	ı	ı	ı	·	[49]
.         .	90.3 9.6 90.4 95.8	9.6 90.4 95.8	90.4 95.8	95.8		4.2	13.1	86.9	15.0 85	5.0 33.	2 66.	8 35.2	2 64.8	0.0	100. 0	100. 0	0.0	ı	ı	[This work]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0 3.4 96.6 -	3.4 96.6 -		ī		ī	T	ī		- 71.	6 28.	4 -	1	7.7	92.3	I	ı	I	ı	[20]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0 10.3 89.7 0.0 1	10.3 89.7 0.0 1	89.7 0.0 1	0.0 1	-	0.00	ı	ı				'	1					ı	ı	[51]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	59.5- 0.4- 89.6- 4.2- <sup>4</sup> 90.6 10.4 99.6 59.8	0.4- 89.6- 4.2- <sup>(</sup> 10.4 99.6 59.8	89.6- 4.2- <sup>4</sup> 99.6 59.8	4.2- 59.8	4	40.2- 95.8	19.8-	80.2	20.9- 77, 22.1 79	7.9 31.  9.1 34.	4 65. 1 68.	8- 0.0 6 32.1	67.3 7 100 0		ı	ı	ı	ı.	·	[42]
-       -       -       -       -       4.5       95.5       -       -       -       53]         -       -       -       57.4       42.6       49.9       50.1       95.5       4.5       -       -       -       54]         2.3       -       -       -       72.4       27.6       -       -       -       54]	100.0 0.0 100.0 -	0.0 100.0 -	- 100.0	ï		ī	,	ï		- 0.0	0 100	- 0.	ı	ı	ī	ī	ï	ī	ı	[52]
57.4 42.6 49.9 50.1 95.5 4.5 [54] 2.3 72.4 27.6 [55]	99.1 44.1 55.9 -	44.1 55.9 -				ı					1	1	1	4.5	95.5	ī	ŀ	ī		[53]
2.3 72.4 27.6 [55]	62.9 100.0 0.0 -	- 0.0 -	- 0.0	,		ı	ı	ı	ı	- 57.	4 42.	6 49.9	9 50.1	95.5	4.5	ı	ı	ı	ı	[54]
	26.1 36.4 63.6 97.7	36.4 63.6 97.7	63.6 97.7	97.7		2.3	ı	ı		1	I	ı	ľ	72.4	27.6	ı	ı	,	ı	[55]

apparently [21]. Nevertheless, tiglic acid was found in relatively large concentration (18.9%) in the essential oil of *Ajuga orientalis* (Lamiaceae) from Jordan [22]. The Lamiaceae is known to be a rich source of thymol [23], especially *Thymus vulgaris* [24], *Monarda* spp. [25, 26], *Origanum tyttanthum* [27], and *Satureja intermedia* [28]. Although the distribution of thymol in the Asteraceae is limited [29], several members of the family have shown relatively high concentrations of thymol in their essential oils, including, for example, *Phagnalon sordidum* (1.3-11.0%) [30], *Tanacetum sinaicum* (17.0-18.7%) [31], *Tanacetum valteri* (22.5%) [32], and *Tridex procumbens* (20.9-68.9%) [33].

Numerous members of the Asteraceae have been shown to be rich sources of sesquiterpenoids such as (*E*)- $\beta$ -caryophyllene (*Eclipta prostrata*, 47.7% [34]; *Duhaldea cappa*, 27.5% [35]; and *Smallanthus uvedalia*, 16.5-24.5% [36]) and germacrene D (*Polymnia canadensis*, 44.5-63.6% [36]; *Verbesina turbacensis*, 29.1-36.9% [37]; and *Blumea lacera* 25.5% [38]). Additionally, comparable to *D. canescens* essential oil, *Calendula arvensis* essential oil, depending on the chemotype, has shown high concentrations of *epi*-cubebol (1.1-15.2%),  $\delta$ -cadinene (6.0-18.1%), 1-*epi*-cubenol (0.5-16.3%), and cubenol (0.3-9.2%) [39, 40].

Several essential oils of members of the Asteraceae have been analyzed by chiral GC-MS to evaluate their enantiomeric distributions (Table 3). There do not seem to be any obvious trends in enantiomeric distribution of monoterpene hydrocarbons in the family. (–)- $\alpha$ -Pinene seems to predominate in essential oils of Baccharis and Gnoxys essential oils, but is variable in Artemisia species. The distribution of  $\alpha$ pinene is not consistent within samples of Artemisia annua [41]. In the case of  $\beta$ -pinene, the enantiomeric distribution is inconsistent within the genera Artemisia, Baccharis, and Gnoxys. (+)-Limonene predominated in the essential oils of Baccharis species, but were not consistent in Ericameria nauseosa [42]. The oxygenated monoterpenoids terpenen-4-ol and  $\alpha$ terpineol also do not exhibit consistent enantiomeric distributions in the family. There are too few data available for the sesquiterpenes to draw any conclusive trends.

### 4. Conclusions

This is the first report on the volatile phytochemicals found in *Chaenactis douglasii* and *Dieteria canescens*.

The essential oil yield for C. douglasii was very low and the essential oil was dominated by tiglic acid and thymol. The presence of thymol may account for the reported antimicrobial effects of C. douglasii extracts. The essential oil of D. canescens, however, was rich in both sesquiterpene hydrocarbons and oxygenated sesquiterpenoids. The enantiomeric distributions of chiral monoterpenoids in these essential oils do not show trends consistent with other members of the Asteraceae. Several genotypes (ecotypes) have been described for C. douglasii and D. canescens, so it is likely that different chemotypes are also possible. Future research should be carried out on C. douglasii and D. canescens from other geographical locations and habitats to describe the phytochemical types of these species more completely.

# **Authors' contributions**

Conceptualization, W.N.S.; Methodology, P.S. and W.N.S.; Software, P.S.; Validation, W.N.S., Formal Analysis, P.S., A.P., and W.N.S.; Investigation, P.S., A.P., K.S., and W.N.S.; Resources, P.S. and W.N.S.; Data Curation, W.N.S.; Writing – Original Draft Preparation, W.N.S.; Writing – Review & Editing, P.S., A.P., K.S., and W.N.S.; Project Administration, W.N.S.

# Acknowledgements

This work was carried out as part of the activities of the Aromatic Plant Research Center (APRC, https://aromaticplant.org/). We are grateful to Daniel Murphy, Collections Curator, Idaho Botanical Garden, for identification of the plants in the Garden.

## Funding

This research received no specific grant from any funding agency.

# Availability of data and materials

All data will be made available on request according to the journal policy.

# **Conflicts of interest**

The authors declare no conflict of interest.

### References

- Moerman, D.E. Native American Ethnobotany; Timber Press, Inc.: Portland, OR, 1998; ISBN 978-0-88192-453-4.
- Tilley, D.; Ogle, D.; St. John, L. Plant guide for Douglas' dustymaiden: *Chaenactis douglasii* (Hook.) Hook. & Art.

United States Department of Agriculture, Natural Resources Conservation Service, Idaho Plant Materials Center. Aberdeen, ID, USA, 2010.

- Kartesz, J.T. The biota of North America program (BONAP) Available online: http://www.bonap.org/ (accessed on 19 February 2022).
- Geissman, T.A.; Atala, S. Distribution of eupatoriopicrin in Compositae. Phytochem. 1971, 10, 1075–1077.
- Stierle, D.B. Germacranolides from *Chaenactis douglasii*. Phytochem. 1986, 25, 743–745.
- Tanrisever, N.; Towers, G.H.N. Sesquiterpene lactones from *Chaenactis douglasii*. Phytochem. 1988, 27, 3893– 3895.
- McCutcheon, A.R.; Ellis, S.M.; Hancock, R.E.W.; Towers, G.H.N. Antibiotic screening of medicinal plants of British Columbian native peoples. J. Ethnopharmacol. 1992, 37, 213–223.
- McCutcheon, A.R.; Ellis, S.M.; Hancock, R.E.W.; Towers, G.H.N. Antifungal screening of medicinal plants of British Columbian native peoples. J. Ethnopharmacol. 1994, 44, 157–169, doi:10.1016/0378-8741(94)01183-4.
- Tilley, D.; Ogle, D.; St. John, L. Plant guide for hoary tansyaster: *Machaeranthera canescens* (Pursh) A. Gray. United States Department of Agriculture, Natural Resources Conservation Service, Idaho Plant Materials Center. Aberdeen, ID, USA, 2014.
- Bartz, T.A. How Predictable Are Evolutionary Responses to Environment? Comparing Trait-Environment Relationships Among Three Species of Asteraceae Forbs in the Great Basin, M.S. Thesis, University of Nevada, Reno, NV, USA, 2022.
- Baughman, O.W.; Kulpa, S.M.; Sheley, R.L. Four paths toward realizing the full potential of using native plants during ecosystem restoration in the Intermountain West. Rangelands. 2022, 44, 218–226, doi:10.1016/j.rala.2022.01.003.
- Meyer, M.D.; Slaton, M.; Wuenschel, A.; Merriam, K.E. Sagebrush steppe case study. In Postfire Restoration Framework for National Forests in California; Meyer, M.D., Long, J.W., Stafford, H.D., Eds.; United States Forest Service, Pacific Southwest Research Station: Albany, California, USA, 2021; pp. 123–149.
- Kildisheva, O.A.; Erickson, T.E.; Kramer, A.T.; Zeldin, J.; Merritt, D.J. Optimizing physiological dormancy break of understudied cold desert perennials to improve seed-based restoration. J. Arid Environ. 2019, 170, 104001, doi:10.1016/j.jaridenv.2019.104001.
- Zeldin, J.; Lichtenberger, T.M.; Foxx, A.J.; Webb Williams, E.; Kramer, A.T. Intraspecific functional trait structure of restoration-relevant species: Implications for restoration seed sourcing. J. Appl. Ecol. 2020, 57, 864–874, doi:10.1111/1365-2664.13603.

- Satyal, P.; Dosoky, N.S.; Poudel, A.; Swor, K.; Setzer, W.N. Chemical composition of the aerial parts essential oil of *Chrysothamnus viscidiflorus* from southwestern Idaho. J. Essent. Oil Plant Compos. 2023, 1, 115–121, doi:https://doi.org/10.58985/jeopc.2023.v01i02.16.
- van den Dool, H.; Kratz, P.D. A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography. J. Chromatogr. A 1963, 11, 463–471, doi:10.1016/S0021-9673(01)80947-X.
- Adams, R.P. Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry; 4th ed.; Allured Publishing: Carol Stream, IL, USA, 2007; ISBN 978-1-932633-21-4.
- Mondello, L. FFNSC 3; Shimadzu Scientific Instruments: Columbia, Maryland, USA, 2016.
- 19. NIST20; National Institute of Standards and Technology: Gaithersburg, Maryland, USA, 2020.
- Satyal, P. Development of GC-MS Database of Essential Oil Components by the Analysis of Natural Essential Oils and Synthetic Compounds and Discovery of Biologically Active Novel Chemotypes in Essential Oils, Ph.D. Dissertation, University of Alabama in Huntsville, Huntsville, AL, USA, 2015.
- 21. Buckles, R.E.; Mock, G. V.; Locatell, L. Tiglic and angelic acids. Chem. Rev. 1955, 55, 659–677, doi:10.1021/cr50004a002.
- 22. Al-Qudah, M.A.; Al-Smadi, Z.M.; Al-Jaber, H.I.; Tashtoush, H.I.; Alkhatib, R.Q.; Bataineh, T.T.; Al-Dalahmeh, Y.; Abu Orabi, S.T. GC/MS and LC-MS/MS phytochemical evaluation of the essential oil and selected secondary metabolites of *Ajuga orientalis* from Jordan and its antioxidant activity. Arab. J. Chem. 2023, 16, 104641, doi:10.1016/j.arabjc.2023.104641.
- Salehi, B.; Mishra, A.P.; Shukla, I.; Sharifi-Rad, M.; Contreras, M. del M.; Segura-Carretero, A.; Fathi, H.; Nasrabadi, N.N.; Kobarfard, F.; Sharifi-Rad, J. Thymol, thyme, and other plant sources: Health and potential uses. Phyther. Res. 2018, 32, 1688–1706, doi:10.1002/ptr.6109.
- Satyal, P.; Murray, B.L.; McFeeters, R.L.; Setzer, W.N. Essential oil characterization of *Thymus vulgaris* from various geographical locations. Foods. 2016, 5, 70, doi:10.3390/foods5040070.
- 25. Lawson, S.K.; Satyal, P.; Setzer, W.N. The volatile phytochemistry of *Monarda* species growing in south Alabama. Plants. 2021, 10, 1–13, doi:10.3390/plants10030482.
- Lawson, S.K.; Satyal, P.; Setzer, W.N. Leaf essential oil composition and terpenoid enantiomeric distribution of *Monarda bradburiana* Beck cultivated in south Alabama. Am. J. Essent. Oils Nat. Prod. 2021, 9, 10–13.
- 27. Sharopov, F.; Kukaniev, M.; Setzer, W.N. Composition of the essential oil of *Origanum tyttanthum* from

Tajikistan. Nat.Prod.Comm. 2011, 6, 1719-1722.

- 28. Ebadollahi, A.; Setzer, W.N. Evaluation of the toxicity of *Satureja intermedia* C. A. Mey essential oil to storage and greenhouse insect pests and a predator ladybird. Foods. 2020, *9*, 712, doi:10.3390/FOODS9060712.
- Başer, K.H.C.; Özek, G.; Hulley, I.M.; Özek, T.; Tilney, P.M.; Van Wyk, B.E. Essential oil composition and leaf trichomes of *Pegolettia baccharidifolia* and *Pegolettia retrofracta* (Asteraceae). South African J. Bot. 2017, 111, 275–282, doi:10.1016/j.sajb.2017.03.030.
- Chikhi, I.; Allali, H.; Costa, J. Chemical composition and biological activities of essential oils of *Phagnalon sordidum* (L.) Rchb. (Asteraceae) from Algeria. Agric. Conspec. Sci. 2019, 84, 271–281.
- 31. Elshamy, A.; Abd-ElGawad, A.; Mohamed, T.; El Gendy, A.E.-N.; Abd El Aty, A.A.; Saleh, I.; Moustafa, M.F.; Hussien, T.A.; Pare, P.W.; Hegazy, M.-E.F. Extraction development for antimicrobial and phytotoxic essential oils from Asteraceae species: *Achillea fragrantissima, Artemisia judaica* and *Tanacetum sinaicum*. Flavour Fragr. J. 2021, 36, 352–364, doi:10.1002/ffj.3647.
- Ghaderi, A.; Sonboli, A. Chemical composition and antimicrobial activity of the essential oil of *Tanacetum walteri* (Anthemideae-Asteraceae) from Iran. Nat. Prod. Res. 2019, 33, 1287–1790, doi:10.1080/14786419.2018.1434640.
- Coulibaly, A.; Soro, Y.; Siaka, S.; Nea, F.; Tonzibo, Z.F. Chemical variability of essential oils from the leaves of *Tridax procumbens* Linn (Asteraceae) from five cities of Côte d'Ivoire. Int. J. Biol. Chem. Sci. 2020, 14, 1843–1852, doi:10.4314/ijbcs.v14i5.27.
- Ogunbinu, A.O.; Flamini, G.; Cioni, P.L.; Ogunwande, I.A.; Okeniyi, S.O. Essential oil constituents of *Eclipta* prostrata (L.) L. and Vernonia amygdalina Delile. Nat. Prod. Commun. 2009, 4, 421–424.
- Priydarshi, R.; Melkani, A.B.; Mohan, L.; Pant, C.C. Terpenoid composition and antibacterial activity of the essential oil from *Inula cappa* (Buch-Ham. ex. D. Don) DC. J. Essent. Oil Res. 2016, 28, 172–176, doi:10.1080/10412905.2015.1090935.
- Craft, J.D.; Lawson, S.K.; Setzer, W.N. Leaf essential oil compositions of bear's foot, *Smallanthus uvedalia* and *Polymnia canadensis*. Am. J. Essent. Oils Nat. Prod. 2019, 7, 31–35.
- Ogungbe, I. V.; Crouch, R.A.; Haber, W.A.; Setzer, W.N. Phytochemical investigation of *Verbesina turbacensis* Kunth: Trypanosome cysteine protease inhibition by (–)-bornyl esters. Nat. Prod. Commun. 2010, 5, 1161– 1166.
- Hoi, T.M.; Hung, N.H.; Huong, L.T.; Hau, D.V.; Duyen, D.T.H.; Setzer, W.N.; Ogunwande, I.A. Chemical compositions of essential oils and antimicrobial activities of Asteraceae: The leaves of *Blumea lacera*

(Burm. f.) DC., *Tridax procumbens* (L.) L., and *Ageratum houstonianum* Mill., from Vietnam. J. Essent. Oil-Bearing Plants 2023, 26, 130–142, doi:10.1080/0972060X.2023.2165169.

- Paolini, J.; Barboni, T.; Desjobert, J.-M.; Djabou, N.; Muselli, A.; Costa, J. Chemical composition, intraspecies variation and seasonal variation in essential oils of *Calendula arvensis* L. Biochem. Syst. Ecol. 2010, 38, 865–874, doi:10.1016/j.bse.2010.07.009.
- Servi, H.; Vatansever, C.; Dogan, A.; Majeed, V.A. Antibacterial activity and essential oil composition of *Calendula arvensis* L. Int. J. Second. Metab. 2020, 7, 229– 236, doi:10.21448/ijsm.676985.
- Holm, Y.; Laakso, I.; Hiltunen, R.; Galambosi, B. Variation in the essential oil composition of *Artemisia annua* L. of different origin cultivated in Finland. Flavour Fragr. J. 1997, 12, 241–246, doi:10.1002/(SICI)1099-1026(199707)12:4<241::AID-FFJ641>3.0.CO;2-Z.
- Stirling, J.; Platt, B.G.; Satyal, P.; Swor, K.; Setzer, W.N. The essential oils of rubber rabbitbrush (*Ericameria nauseosa*) from north-central Utah and southwestern Idaho. Nat. Prod. Commun. 2023, 18, 1934578X231161186, doi:10.1177/1934578X231161186.
- Filippi, J.-J.; Lanfranchi, D.-A.; Prado, S.; Baldovini, N.; Meierhenrich, U.J. Composition, enantiomeric distribution, and antibacterial activity of the essential oil of *Achillea ligustica* All. from Corsica. J. Agric. Food Chem. 2006, 54, 6308–6313, doi:10.1021/jf060752y.
- Orth, M.; Czygan, F.C.; Dedkov, V.P. Variation in essential oil composition and chiral monoterpenes of *Achillea millefolium* s.1. from Kaliningrad. J. Essent. Oil Res. 1999, 11, 681–687, doi:10.1080/10412905.1999.9711995.
- Swor, K.; Poudel, A.; Satyal, P.; Setzer, W.N. The essential oil composition of *Artemisia dracunculus* growing wild in southwestern Idaho. Am. J. Essent. Oils Nat. Prod. 2022, 10, 16–19.
- Swor, K.; Satyal, P.; Poudel, A.; Setzer, W.N. Chemical characterization of three *Artemisia tridentata* essential oils and multivariate analyses: A preliminary investigation. Nat. Prod. Commun. 2023, 18, 1934578X231154965, doi:10.1177/1934578X231154965.
- Minteguiaga, M.; González, A.; Catalán, C.A.N.; Dellacassa, E. Relationship between *Baccharis dracunculifolia* DC. and *B. microdonta* DC. (Asteraceae) by their different seasonal volatile expression. Chem. Biodivers. 2021, 18, e2100064, doi:10.1002/cbdv.202100064.
- Minteguiaga, M.; Fariña, L.; Cassel, E.; Fiedler, S.; Catalán, C.A.N.; Dellacassa, E. Chemical compositions of essential oil from the aerial parts of male and female plants of *Baccharis tridentata* Vahl. (Asteraceae). J. Essent. Oil Res. 2021, 33, 299-307,

doi:10.1080/10412905.2020.1829720.

- Espinosa, S.; Bec, N.; Larroque, C.; Ramírez, J.; Sgorbini, B.; Bicchi, C.; Gilardoni, G. Chemical, enantioselective, and sensory analysis of a cholinesterase inhibitor essential oil from *Coreopsis triloba* S.F. Blake (Asteraceae). Plants 2019, 8, 448, doi:10.3390/plants8110448.
- Salinas, M.; Calva, J.; Cartuche, L.; Valarezo, E.; Armijos, C. Chemical composition, enantiomeric distribution and anticholinesterase and antioxidant activity of the essential oil of *Diplosthephium juniperinum*. Plants. 2022, 11, 1188, doi:10.3390/plants11091188.
- Lorenzo, D.; Saavedra, G.; Loayza, I.; Dellacassa, E. Composition of the essential oil of *Erechtites hieracifolia* from Bolivia. Flavour Fragr. J. 2001, 16, 353–355, doi:10.1002/ffj.1010.
- Cumbicus, C.; Malagón, O.; Cumbicus, N.; Gilardoni, G. The leaf essential oil of *Gynoxys buxifolia* (Kunth) Cass. (Asteraceae): A good source of furanoeremophilane and bakkenolide A. Plants. 2023, 12, 1323, doi:10.3390/plants12061323.

- Malagón, O.; Cartuche, P.; Montaño, A.; Cumbicus, N.; Gilardoni, G. A new essential oil from the leaves of the endemic Andean species *Gynoxys miniphylla* Cuatrec. (Asteraceae): Chemical and enantioselective analyses. Plants. 2022, 11, 398.
- Maldonado, Y.E.; Malagón, O.; Cumbicus, N.; Gilardoni, G. A new essential oil from the leaves of *Gynoxys rugulosa* Muschl. (Asteraceae) growing in southern Ecuador: Chemical and enantioselective analyses. Plants. 2023, 12, 849, doi:10.3390/plants12040849.
- 55. Chanotiya, C.S.; Yadav, A. Natural variability in enantiomeric composition of bioactive chiral terpenoids in the essential oil of *Solidago canadensis* L. from Uttarakhand, India. Nat. Prod. Commun. 2008, 3, 263–266.
- Lorenzo, D.; Loayza, I.; Dellacassa, E. Composition of the essential oil of *Tagetes maxima* Kuntze from Bolivia. Flavour Fragr. J. 2002, 17, 115–118, doi:10.1002/ffj.1062.