American Journal of Essential Oils and Natural Products
Available online at www.essencejournal.com
AJEONP American Journal of Essential Oils and Natural Products

ISSN: 2321-9114
AJEONP 2022; 10(1): 16-19

Received: 04-01-2022
Accepted: 11-02-2022

Kathy Swor
1432 W. Heartland Dr., Kuna, Idaho 83634, USA

Ambika Poudel
Aromatic Plant Research Center 230 N 1200 E, Suite 100, Lehi, Utah 84043, USA

Prabodh Satyal
Aromatic Plant Research Center 230 N 1200 E, Suite 100, Lehi, Utah 84043, USA

William N Setzer
A) Aromatic Plant Research Center 230 N 1200 E, Suite 100, Lehi, Utah 84043, USA
B) Department of Chemistry, University of Alabama in Huntsville Huntsville, Alabama 35899, USA

Corresponding Author:
William N Setzer
A) Aromatic Plant Research Center 230 N 1200 E, Suite 100, Lehi, Utah 84043, USA
B) Department of Chemistry, University of Alabama in Huntsville Huntsville, Alabama 35899, USA

The essential oil composition of *Artemisia dracunculus* growing wild in southwestern Idaho

Kathy Swor, Ambika Poudel, Prabodh Satyal and William N Setzer

Abstract
Artemisia dracunculus L. (tarragon) is an important herbal medicine and culinary herb. In this work, the essential oil of *A. dracunculus*, growing wild in southwestern Idaho, was obtained by hydrodistillation (0.768% yield) and analyzed by gas chromatographic techniques. The major components in the essential oil were terpinolene (20.0%), 5-phenyl-1, 3-pentadiyne (19.2%), capillene (13.8%), (*Z*)-β-ocimene (11.1%), methyl eugenol (8.7%), and β-phellandrene (5.8%). Chiral GC-MS showed the (+)-enantiomers of α-pinene, α-phellandrene, limonene, and β-phellandrene to be dominant, while (–)-β-pinene and (–)-linalool were the predominant enantiomers. The essential oil composition of *A. dracunculus* from southwestern Idaho was similar to those of several wild-growing samples from southern California and southeastern Oregon.

Keywords: Tarragon, gas chromatography, chemical composition, chiral, enantiomers

1. Introduction
Artemisia dracunculus L. (tarragon), Asteraceae, is native to south-eastern Russia, Central Asia, Turkey, Mongolia, and western North America [1]. The plant is widely cultivated as a culinary herb, but also has a long history of traditional medicinal uses, which have been reviewed [2–4]. French tarragon is widely favored for its spicy, anise-like flavor. The purpose of this work was to obtain the essential oil of *A. dracunculus* growing wild in southwestern Idaho and to analyze the essential oil using gas chromatographic methods.

2. Materials and Methods
2.1 Plant Material
Aerial parts of *A. dracunculus* var. *dracunculus* were collected on 28 June 2022 from a plant growing in southwestern Idaho (43°14′46″N, 116°22′46″W, 701 m elevation). The plant was identified in the field by W. N. Setzer and verified by comparison with samples from the New York Botanical Garden Virtual Herbarium (https://sweetgum.nybg.org/science/vh/, accessed on 30 June 2022). A voucher specimen (WNS-Add-5653) has been deposited in the University of Alabama in Huntsville Herbarium. The fresh-frozen (–20 °C) plant material (54.24 g) was hydrodistilled using a Likens-Nickerson apparatus for 4 h to give 416.6 mg yellow essential oil with a pungent aroma.

2.2 Gas Chromatographic Analysis
The essential oil of *A. dracunculus* var. *dracunculus* was analyzed by gas chromatographic techniques, including GC-MS, GC-FID, and chiral GC-MS as previously described [5]. Retention indices (RI) were determined based on a homologous series of *n*-alkanes on a ZB-5ms column [6]. The essential oil components were identified by comparison of the mass spectral fragmentation patters and by comparison of retention index values available in the Adams [7], FFNSC 3 [8], NIST20 [9], and our own in-house database [10]. The enantiomeric distributions were determined by comparison of retention times with authentic samples obtained from Sigma-Aldrich (Milwaukee, WI, USA).

3. Results and Discussion
The essential oil of *A. dracunculus* from southwestern Idaho was obtained in 0.768% yield. The essential oil was characterized using GC-MS and GC-FID (Table 1). A total of 79 compounds were identified in the essential oil accounting for 96.7% of the total composition. The essential oil was composed of 45.6% monoterpene hydrocarbons, including terpinolene

(20.0%), (*Z*)-β-ocimene (11.1%), and β-phellandrene (5.8%); 35.5% acetylenes, including 5-phenyl-1, 3-pentadiyne (19.2%) and capillene (13.8%); along with the phenylpropanoid methyl eugenol (8.7%).

Table 1: Chemical composition of *Artemisia dracunculus* essential oil from southwestern Idaho.

RI_{calc}	RI_{db}	Compound	% Composition
924	927[F]	α-Thujene	tr
932	933[F]	α-Pinene	0.5
947	948[F]	α-Fenchene	0.2
949	950[S]	Camphene	tr
962	959[S]	Benzaldehyde	tr
973	972[F]	Sabinene	tr
979	978[F]	β-Pinene	0.3
987	993[N]	Cyclohept-4-enone	0.1
990	989[S]	Myrcene	0.7
991	990[S]	2, 3-Dehydro-1,8-Cineole	0.1
1004	1005[S]	(3*Z*)-Hexenyl acetate	tr
1007	1007[F]	α-Phellandrene	0.8
1009	1008[S]	δ-3-Carene	0.1
1017	1017[S]	α-Terpinene	0.2
1025	1025[F]	*p*-Cymene	0.5
1030	1030[F]	Limonene	1.6
1032	1031[F]	β-Phellandrene	5.8
1037	1034[S]	(*Z*)-β-Ocimene	11.1
1047	1045[S]	(*E*)-β-Ocimene	3.5
1059	1057[S]	γ-Terpinene	0.3
1071	1069[F]	*cis*-Sabinene hydrate	tr
1088	1086[F]	Terpinolene	20.0
1092	1091[S]	*p*-Cymenene	0.1
1096	1097[N]	α-Pinene oxide	tr
1101	1101[F]	Linalool	0.2
1112	1113[F]	4,8-Dimethylnona-1,3,7-triene	0.1
1124	1124[F]	*cis*-*p*-Menth-2-en-1-ol	0.1
1127	1127[S]	(*E*,*Z*)-*allo*-Ocimene	0.5
1142	1142[S]	Epoxyterpinolene	1.0
1185	1188[F]	*p*-Methylacetophenone	tr
1188	1186[S]	*p*-Cymen-8-ol	1.2
1192	1192[F]	Methyl salicylate	0.1
1196	1195[F]	α-Terpineol	0.1
1198	1197[S]	Estragole (= Methyl chavicol)	0.1
1201	---	(3*Z*)-Octenyl acetate	0.1
1204	1203[S]	*p*-Cumenol	0.3
1209	1207[S]	(3*E*)-Octenyl acetate	0.1
1209	1209[F]	*trans*-Piperitol	tr
1225	1226[S]	Nerol	0.2
1227	1227[S]	Citronellol	0.1
1236	1235[F]	(3*Z*)-Hexenyl isovalerate	0.1
1251	1250[S]	Geraniol	tr
1257	1264[F]	*trans*-Mayol (= *trans* *p*-Menthan-7-ol)	0.2
1268	1273[F]	*cis*-Mayol (= *cis* *p*-Menthan-7-ol)	0.1
1274	1275[F]	Citronellyl formate	tr
1278	1276[S]	Neryl formate	0.1
1288	1286[N]	5-Phenyl-1,3-pentadiyne	19.2
1324	1325[F]	(3*Z*)-Hexenyl tiglate	0.1
1344	1343[N]	2-(2,5-Dimethylphenyl)propanal	0.3
1360	1361[F]	Neryl acetate	0.3
1404	1405[S]	Methyl eugenol	8.7
1424	1424[F]	(*E*)-β-Caryophyllene	tr
1479	1483[F]	Germacrene D	0.3
1481	1482[F]	γ-Curcumene	0.2
1500	1497[S]	Capillene	13.8
1513	1512[F]	γ-Cadinene	tr
1518	1518[F]	δ-Cadinene	0.1
1545	1548[S]	Elemicin	0.1
1548	1549[S]	α-Elemol	tr
1560	1562[F]	(*E*)-Nerolidol	0.4
1571	1573[F]	(3*Z*)-Hexenyl benzoate	0.1
1577	1576[F]	Spathulenol	tr
1579	1580[S]	*trans*-Sesquisabinene hydrate	tr

1583	1587[F]	Caryophyllene oxide	tr
1641	1639[F]	Capillin	0.4
1644	1640[F]	τ-Cadinol	tr
1646	1644[S]	τ-Muurolol	tr
1648	1644[S]	α-Muurolol (= δ-Cadinol)	tr
1650	1645[F]	Desmethoxyencecalin	0.1
1657	1655[S]	α-Cadinol	0.1
1668	1670[F]	(3*Z*)-Hexenyl salicylate	tr
1671	1670[A]	*epi*-β-Bisabolol	tr
1673	1674[A]	β-Bisabolol	tr
1688	1686[S]	*epi*-α-Bisabolol	0.1
1690	1688[F]	α-Bisabolol	tr
1749	1751[F]	(*E*)-Nuciferol	0.1
1769	1772[F]	Benzyl benzoate	tr
1880	1878[S]	Capillarin	2.2
2107	2109[S]	Phytol	tr
		Monoterpene hydrocarbons	45.6
		Oxygenated monoterpenoids	4.4
		Sesquiterpene hydrocarbons	0.5
		Oxygenated sesquiterpenoids	0.6
		Diterpenoids	tr
		Benzenoid aromatics	9.6
		Acetylenes	35.5
		Others	0.4
		Total identified	96.7
		Total compounds identified	79

RI_{calc} = Retention index determined with respect to a homologous series of *n*-alkanes on a ZB-5ms column. RI_{db} = Reference retention index obtained from the databases ([A] Adams [7], [F] FFNSC3 [8], [N] NIST20 [9], [S] Satyal [10]). tr = trace (< 0.05%).

Eisenman and co-authors have carried out an extensive study on North American wild tarragon from California, Nevada, Utah, Colorado, and Wyoming [11]. These workers were able to define six chemotypes based on the essential oil diversity:

1. Estragole (methyl chavicol)
2. Methyl eugenol
3. Terpinolene
4. Capillene
5. (5) 5-phenyl-1, 3-pentadiyne
6. β-ocimene

Interestingly, the chemical composition of *A. dracunculus* in this investigation belongs to the terpinolene chemotype, resembling most closely samples from San Bernardino County, Los Angeles County, and Inyo County, California in the report by Eisenman *et al.* [11] as well as a sample by Pappas and Sturtz from Malheur County, Oregon [12]. That is, the concentration of estragole was relatively low (0.1%), in marked contrast to cultivated "French tarragon", which is composed of 69.0-84.0% estragole [13]. The Idaho sample also differs from wild samples from Colorado (methyl eugenol and β-ocimene chemotypes) [11], Utah (5-phenyl-1,3-pentadiyne chemotype) [11], Nevada (estragole, capillene, and β-ocimene chemotypes) [11], northern California (estragole, capillene, and 5-phenyl-1,3-pentadiyne chemotypes), Wyoming (methyl eugenol chemotype) [11], or Central Alberta (methyl eugenol chemotype) [14]. The similarity between the Idaho sample and the Oregon sample is not surprising; the geographical locations are in close proximity.

The occurrence of cyclohept-4-enone in *A. dracunculus* essential oil is surprising. It is an uncommon phytochemical, but has been reported in the essential oil of *Tanacetum polycephalum* [15]. The compound is produced by several bacteria including *Saccharopolyspora erythraea* [16] and *Salinispora tropica* [17], so it may actually be a contaminant rather than an actual essential oil component.

Chiral GC-MS was carried out on the essential oil to determine the enantiomeric distributions of terpenoid components (Table 2). As far as we are aware, this is the first examination of *A. dracunculus* using chiral GC-MS. The dextrorotatory enantiomers were the exclusive isomers for δ-3-carene and β-phellandrene, while (+)-α-pinene (96.2%) and (+)-α-phellandrene (99.1%) also dominated. Germacrene D and (*E*)-nerolidol were exclusively the (–)-enantiomers.

Table 2: Enantiomeric distributions of chiral terpenoids in the essential oil of *Artemisia dracunculus* from southwestern Idaho.

Compound	Enantiomeric Distribution	
	% (+)	% (–)
α-Pinene	96.2	3.8
β-Pinene	34.0	66.0
α-Phellandrene	99.1	0.9
δ-3-Carene	100.0	0.0
Limonene	78.0	22.0
β-Phellandrene	100.0	0.0
Linalool	36.3	63.7
α-Terpineol	43.4	56.6
Germacrene D	0.0	100.0
(*E*)-Nerolidol	0.0	100.0

The terpenoid enantiomeric distributions are not consistent between *Artemisia* species. Thus, for example, *A. tridentata* subsp. *tridentata* showed 100% (+)-α-pinene and 100% (+)-β-pinene [5]. *Artemisia annua* cultivated in Finland showed 20.0-96.4% (+)-α-pinene, but only the (–)-enantiomers were detected for β-pinene and for limonene [18]. (–)-β-pinene (92.8-94.1%) was the major enantiomer in the essential oil of *A. arborescens* [19], while the (+)-enantiomer of linalool (95.4-99.3%) dominated *A. arborescens* essential oil [19, 20].

4. Conclusions

This work represents the first report of the essential oil of wild-growing *A. dracunculus* from Idaho and complements previous studies on *A. dracunculus* from other geographical locations in western North America. This is the first report on the enantiomeric distribution of terpenoids in *A. dracunculus*.

Acknowledgments
This work was carried out as part of the activities of the Aromatic Plant Research Center (APRC, https://aromaticplant.org/).

References

1. Flora of China Editorial Committee. Artemisia dracunculus Linnaeus. Flora of China, Vol. 20-21 (Asteraceae). http://www.efloras.org/florataxon.aspx?flora_id=2&taxon_id=200023201. Accessed January 15, 2023.
2. Aglarova AM, Zilfikarov IN, Severtseva OV. Biological characteristics and useful properties of tarragon (*Artemisia dracunculus* L.) (review). Pharm Chem J. 2008;42(2):81-86. Doi:10.1007/s11094-008-0064-3
3. Obolskiy D, Pischel I, Feistel B, Glotov N, Heinrich M. *Artemisia dracunculus* L. (tarragon): A critical review of its traditional use, chemical composition, pharmacology, and safety. J Agric Food Chem. 2011;59(21):11367-11384. Doi:10.1021/jf202277w
4. Ekiert H, Świątkowska J, Knut E, Klin P, Rzepiela A, Tomczyk M, *et al*. *Artemisia dracunculus* (Tarragon): A Review of its traditional uses, phytochemistry and pharmacology. Front Pharmacol. 2021;12:653993. doi:10.3389/fphar.2021.653993
5. Swor K, Satyal P, Timsina S, Setzer WN. Chemical composition and terpenoid enantiomeric distribution of the essential oil of *Artemisia tridentata* subsp. *tridentata* from southwestern Idaho. Nat Prod Commun. 2022;17(7):1934578X2211174. doi:10.1177/1934578x221117417
6. van den Dool H, Kratz PD. 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
7. Adams RP. Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry, 4th ed. Allured Publishing, Carol Stream, IL, USA; c2007.
8. Mondello L. *FFNSC 3*. Shimadzu Scientific Instruments, Columbia, Maryland, USA; c2016.
9. NIST20. National Institute of Standards and Technology, Gaithersburg, Maryland, USA; c2020.
10. 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; c2015.
11. Eisenman SW, Juliani HR, Struwe L, Simon JE. Essential oil diversity in North American wild tarragon (*Artemisia dracunculus* L.) with comparisons to French and Kyrgyz tarragon. Ind Crops Prod. 2013;49:220-232. doi:10.1016/j.indcrop.2013.04.037
12. Pappas RS, Sturtz G. Unusual alkynes found in the essential oil of *Artemisia dracunculus* L. var. *dracunculus* from the Pacific Northwest. J Essent Oil Res, 2001;13(3):187-188. doi:10.1080/10412905.2001.9699657
13. Technical Committee, International Organization for Standardization. ISO 10115: Essential oil of tarragon (*Artemisia dracunculus* L.); c2013.
14. Lopes-Lutz D, Alviano DS, Alviano CS, Kolodziejczyk PP. Screening of chemical composition, antimicrobial and antioxidant activities of *Artemisia* essential oils. Phytochemistry. 2008;69(8):1732-1738. doi:10.1016/j.phytochem.2008.02.014
15. Alamholo M. Antioxidant and antibacterial activity of *Tanacetum* spp. essential oil and chemical components. J Med Microbiol Infect Dis. 2022;10(1):24-29. doi:10.52547/jommid.10.1.24
16. Citron CA, Rabe P, Dickschat JS. The scent of bacteria: Headspace analysis for the discovery of natural products. J Nat Prod, 2012;75(10):1765-1776. doi:https://doi.org/10.1021/np300468h
17. Groenhagen U, Leandrini De Oliveira AL, Fielding E, Moore BS, Schulz S. Coupled biosynthesis of volatiles and salinosporamide A in *Salinispora tropica*. Chem Bio Chem. 2016;17(20):1978-1985. doi:10.1002/cbic.201600388
18. 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(4):241-246. doi:10.1002/(SICI)1099-1026(199707)12:4<241::AID-FFJ641>3.0.CO;2-Z
19. Lo Presti M, Crupi ML, Zellner B d'A, Dugo G, Mondello L, Dugo P, *et al*. Characterization of *Artemisia arborescens* L. (Asteraceae) leaf-derived essential oil from Southern Italy. J Essent Oil Res. 2007;19(3):218-224.
20. Said MEA, Militello M, Saia S, Settanni L, Aleo A, Mammina C, *et al*. *Artemisia arborescens* essential oil composition, enantiomeric distribution, and antimicrobial activity from different wild populations from the Mediterranean area. Chem Biodivers, 2016;13(8):1095-1102. doi:10.1002/cbdv.201500510