Journal of Essential Oil & Plant Composition

JEOPC, 1(1), 20-25, 2023
https://doi.org/10.00000/jeopc
ISSN:0000-0000

Research Article

Chemical Composition of the Wood Essential Oils of *Sequoia sempervirens* (California redwood)

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Article Information
Received: *12 December, 2022*
Revised: *19 January, 2023*
Accepted: *20 January, 2023*

Academic Editor
Radosław Kowalski

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Keywords:
Coast redwood, heartwood, sapwood, monoterpene enantiomers, α-pinene, fatty alcohol, diterpenoid.

Abstract

California redwood (*Sequoia sempervirens*) is a large tree that produces rot-resistant lumber. In this report, the sapwood and the heartwood essential oils of *S. sempervirens* have been obtained by hydrodistillation and analyzed by gas chromatographic methods. Both the sapwood and heartwood essential oils were dominated by α-pinene (27.4% and 21.0%), 1-dodecanol (6.6% and 6.8%), 1-tetradecanol (8.6% and 17.0%), abietadiene (10.0% and 9.6%), and *trans*-totarol (16.8% and 7.8%). The dextrorotatory enantiomers predominated for the monoterpenoids α-pinene, limonene, and α-terpineol. Wood chips, shavings, and millings of *S. sempervirens* from lumber mills may be a viable source of redwood essential oil.

1. Introduction

Sequoia sempervirens (D. Don) Endl. (Cupressaceae) is a large (up to 116 m high, 6.9 m diameter at breast height), long-living (> 2000 years), evergreen tree that ranges naturally along the coast of California, from the Oregon border south to San Luis Obispo County, California [1, 2] redwood is a valuable source of lumber and has been introduced to New Zealand [3], parts of Europe [4, 5], Great Britain [6], and China [7]. Unfortunately, in its native range, unregulated intensive logging has drastically reduced the extent of old-growth redwood forests; approximately 95% of redwood forests in California have been logged [2, 8]. Furthermore, climate change threatens redwood forests in their native range and could results in decline and loss of genetic diversity [9]. Although *S. sempervirens* is resilient to forest fires, climate change-driven high severity fires may lead to vegetation type conversion of redwood forests [2, 10].

The heartwood of *S. sempervirens* is resistant to decay [11–13]. Extracts of *S. sempervirens* wood has yielded several nor-lignan phenolics (the sequirins and sequosempervirins) [7, 14, 15], and these compounds may be responsible for the antifungal properties of the heartwood [13]. The leaf essential oil of *S. sempervirens* has been reported [16–19]. Monoterpenes generally dominate the foliar essential oils of *S. sempervirens*; the major components in the essential oils were sabinene (8.5-16.5%), limonene (8.7-10.4%), β-phellandrene (3.1-13.7%), α-pinene (6.3-10.4%), and myrcene (3.5-7.0%) [17,18]. As far as we are aware, however, the wood essential oil has not been investigated. As part of our ongoing interest in wood essential oils [20–23], we have obtained and analyzed the heartwood and sapwood essential oils of *S. sempervirens*.

2. Materials and methods

2.1 *Plant Material*

Milled heartwood and chipped sapwood of *S. sempervirens* were generously provided by Mr. Paul Bialkowsky (Mendocino Forest Products Co., 850 Kunzler Ranch Road, Ukiah, CA 95482) on 1 October 2022. The wood samples were stored at –20 °C until distillation. The milled heartwood (659.70 g) was steam distilled for 6 h using a Likens-Nickerson apparatus to give 5.1337 g yellow essential oil. The chipped sapwood (334.04 g) was hydrodistilled for 6 h using a Likens-Nickerson apparatus to give 4.8076 g pale yellow essential oil.

2.2 Gas Chromatographic Analysis

The essential oils were analyzed by gas chromatography with flame ionization detection (GC-FID), gas chromatography – mass spectrometry (GC-MS) and chiral GC-MS as previously described [24]. Retention index values were determined using a homologous series of *n*-alkanes on a ZB-5ms column using the linear formula of van den Dool and Kratz [25]. The essential oil components were identified by comparison of the mass spectral fragmentation patters and by comparison of retention index (RI) values available in the Adams [26], FFNSC 3 [27], NIST20 [28], and our own in-house database [29]. The identification of enantiomers was determined by comparison of retention times with authentic samples obtained from Sigma-Aldrich (Milwaukee, WI, USA).

3. Results and discussion

3.1 Essential Oil Composition

The yellow heartwood essential oil of *S. sempervirens* was obtained in 0.778% yield, while the pale-yellow sapwood was obtained in 1.439% yield. The essential oils were analyzed by GC-MS and GC-FID and the compositions are presented in Table 1. The major components in the sapwood and heartwood essential oils were the monoterpene α-pinene (27.4% and 21.0%, respectively), the diterpenoids abietadiene (10.0% and 9.6%) and *trans*-totarol (16.8% and 7.8%), and the fatty alcohols 1-dodecanol (6.6% and 6.8%) and 1-tetradecanol (8.6% and 17.0%). Thus, although there are quantitative differences, the heartwood and sapwood essential oils are very similar in composition. There are some notable differences between the heartwood and sapwood essential oils however. Diterpenoid concentrations were higher in the sapwood (40.0%) than the heartwood (26.5%), attributed mainly to the 6,7-dehydroferruginol (4.3% vs. 1.4%) and *trans*-totarol (16.8% vs. 7.8%) concentrations in the sapwood essential oil. On the other hand, two long-chain fatty alcohols were more abundant in the heartwood than the sapwood (1-tetradecanol, 17.0% and 8.6%, respectively; 1-hexadecanol, 1.8% and 0.3%, respectively). The concentrations of 1-decanol, 1-dodecanol, and 1-tridecanol were comparable in the heartwood and sapwood, however.

Not surprisingly, the wood essential oils show very different volatile chemical profiles compared to the foliar essential oils. The α-pinene concentration in the foliar essential oil from California ranged from 5.8% to 29.5%, depending on the season and age of needles [16]. Neither fatty alcohols nor diterpenoids were reported, however. The foliar essential oil from *S. sempervirens* grown in Egypt showed 8.7% α-pinene, no fatty alcohols, and phytol (1.5%) as the only diterpenoid [19]. Interestingly, lichens are relatively resistant to habitation on redwoods compared to other coniferous trees, and it has been suggested that phytochemicals in the foliage or bark may serve to deter lichen establishment and growth [30]. The aqueous foliar leachate of *S. sempervirens* was found to significantly decrease lichen population. A chemical analysis of the leachate was not done, however.

Curie-point pyrolysis GC–MS of *S. sempervirens* wood showed 4-methylguaiacol, 4-vinylguaiacol, and 4-methylsyringol as the major components [31]. Guaiacol was also detected as a minor component and this compound was found in the wood essential oils of *S. sempervirens* in this study (0.2% and 1.5% for the sapwood and heartwood, respectively).

3.2 Enantiomeric Distribution

The enantiomeric distributions for the monoterpenoids α-pinene, limonene, and α-terpineol were determined using chiral GC-MS (Table 2). The dextrorotatory enantiomers were the major enantiomers for α-pinene, limonene, and α-terpineol. Limonene, in particular, was dominated by (+)-limonene. Interestingly, many conifer species show (–)-limonene to be the dominant enantiomer in their

Table 1. Chemical composition of *Sequoia sempervirens* wood essential oils.

RT (min)	RI_{calc}	RI_{db}	Compound	Sapwood	Heartwood
11.528	924	923	Tricyclene	0.1	0.1
12.071	934	932	α-Pinene	27.4	21.0
12.939	950	950	Camphene	0.2	0.1
14.317	975	977	Phenol	tr	0.3
14.456	978	978	β-Pinene	0.2	0.2
15.086	989	989	Myrcene	tr	0.1
17.225	1025	1024	*p*-Cymene	0.1	0.1
17.514	1030	1030	Limonene	1.1	2.6
21.041	1084	1086	*o*-Guaiacol	0.2	1.5
21.122	1085	1086	Terpinolene	0.2	0.1
21.340	1089	1090	Fenchone	0.1	tr
23.383	1119	1119	*endo*-Fenchol	0.2	0.2
23.906	1127	1126	α-Campholenal	0.4	0.3
24.844	1141	1140	*trans*-Pinocarveol	0.3	0.3
25.273	1147	1145	Camphor	0.4	0.2
25.829	1155	1156	Camphene hydrate	---	0.1
26.311	1162	1164	Pinocarvone	0.1	tr
26.390	1163	1163	4-Ethylphenol	---	0.2
26.971	1172	1170	Borneol	0.5	0.5
27.578	1180	1180	Terpinen-4-ol	0.2	0.2
28.023	1187	1186	*p*-Cymen-8-ol	0.1	0.1
28.581	1195	1195	α-Terpineol	2.0	2.2
29.374	1207	1205	Verbenone	0.5	0.2
32.785	1257	1258	(4*Z*)-Decen-1-ol	0.5	0.4
33.854	1272	1271	1-Decanol	1.4	1.2
34.617	1284	1285	Bornyl acetate	0.2	0.1
35.258	1293	1293	2-Methylnaphthalene	---	0.1
36.932	1322	1325	Whiskey lactone	0.2	0.2
38.716	1349	1253	2-Nonyl isobutyrate	---	2.0
38.725	1350	1349	α-Terpinyl acetate	0.2	---
39.019	1354	1357	Eugenol	0.1	0.2
40.316	1374	---	3-Hydroxy-2,2,4-trimethylpentyl isobutyrate	0.1	2.9
42.737	1411	1411	Longifolene	0.1	0.1
42.851	1413	1410	Dodecanal	0.1	0.1
43.366	1421	1424	(*E*)-β-Caryophyllene	0.1	0.1
46.894	1478	1476	1-Dodecanol	6.6	6.8
47.234	1483	1480	*ar*-Curcumene	0.2	0.1
48.884	1510	1510	β-Bisabolene	0.1	0.1
49.170	1515	1516	γ-Cadinene	0.2	0.1
49.487	1520	1520	δ-Cadinene	0.1	0.1
52.042	1563	1560	(*E*)-Nerolidol	0.2	0.6
52.995	1579	1580	1-Tridecanol	0.2	0.2
53.220	1583	1587	Caryophyllene oxide	0.2	0.3
54.758	1609	1610	Cedrol	0.2	0.1
54.847	1611	1610	Dodecyl acetate	---	0.1
55.137	1616	1614	Tetradecanal	---	0.2
56.096	1633	1633	γ-Eudesmol	0.2	0.1
56.680	1643	1643	τ-Cadinol	---	0.1
56.790	1645	1645	τ-Muurolol	---	0.1
57.378	1656	1656	β-Eudesmol	1.6	2.1
57.769	1663	1665	Tetradec-(9*Z*)-en-1-ol	0.7	1.1
58.604	1677	1681	γ-Dodecalactone	0.1	0.1
58.723	1680	1680	1-Tetradecanol	8.6	17.0
68.520	1864	1864	14-Methylhexadec-(8*Z*)-enal	0.4	0.8

Table 1 (*continued*)

RT (min)	RIcalc	RIdb	Compound	Sapwood	Heartwood
69.502	1883	1884	1-Hexadecanol	0.3	1.8
70.751	1908	1908	Isopimara-9(11),15-diene	0.1	0.1
72.405	1942	1942	2,4b-Dimethyl-8-methylene-2-vinyl-1,2,3,4,4a, 4b,5,6,7,8,8a,9-odecahydrophenanthrene	0.3	0.4
73.270	1960	1958	Palmitic acid	0.6	1.7
74.984	1995	1997	Isopimara-7,15-diene	0.2	0.2
76.009	2017	2019	Levopimaradiene [38]	0.3	0.2
77.589	2051	2049	Abietatriene	1.6	1.3
79.068	2083	1086	Abietadiene	10.0	9.6
81.175	2129	2127	Nezukol	1.3	1.7
81.795	2143	2140	Neoabietadiene [38]	0.8	0.7
83.392	2179	2180	Sandaracopimarinal	0.2	0.3
85.124	2218	2222	Isopimarinal [37]	0.4	0.6
85.629	2230	c	Copalol	0.7	0.8
87.286	2269	2270	Sandaracopimarinol	1.0	0.6
88.998	2309	2311	Isopimarinol	0.7	0.4
89.125	2312	2315	6,7-Dehydroferruginol	4.3	1.4
89.272	2316	2315	*trans*-Totarol	16.8	7.8
94.635	2448	2454	6-Ketoferruginol	1.3	0.7
			Monoterpene hydrocarbons	29.2	24.2
			Oxygenated monoterpenoids	5.4	4.3
			Sesquiterpene hydrocarbons	0.8	0.7
			Oxygenated sesquiterpenoids	2.4	3.3
			Diterpenoids	40.0	26.5
			Benzenoid aromatics	0.3	2.2
			Others	19.9	36.5
			Total identified	**98.0**	**97.8**

RT = Retention time in minutes. RIcalc = Retention index determined using a homologous series of *n*-alkanes on a ZB-5ms column [25]. RIdb = Reference retention index from the databases [26–29].
[c] MS match (92%), but RI not available in the literature.

Table 2. Enantiomeric distribution of monoterpenoid constituents of *Sequoia sempervirens* wood essential oils.

Compound	RT (min)	Enantiomeric Distribution (%)	
		Sapwood	Heartwood
(−)-α-Pinene	15.92	29.9	26.7
(+)-α-Pinene	16.40	70.1	73.3
(−)-Limonene	25.06	10.0	2.7
(+)-Limonene	25.99	90.0	97.3
(−)-α-Terpineol	59.73	25.3	27.8
(+)-α-Terpineol	60.58	74.7	72.2

RT = Retention time in minutes.

foliar essential oils, including Abies spp. [32–34], Picea spp. [35, 36], and Pinus spp. [37]. The enantiomeric distribution of α-pinene, however, seems to be variable in these foliar essential oils. On the other hand, (−)-α-terpineol was the major enantiomer in foliar essential oils of Pinus [37] and Abies [34] species.

4. Conclusions

The sapwood and heartwood essential oils of California redwood are qualitatively very similar. Therefore, the wood chips and sawdust from redwood lumber mills may be a viable source of an interesting essential oil. Conservation efforts within the native range of California redwoods in addition to cultivation in suitable alternative habitats may serve to provide additional sources of redwood for the lumber and essential oil industries.

Authors' contributions

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

Funding

This research received no specific grant from any funding agency.

Conflicts of interest

The authors declare no conflict of interest.

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