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Chemical composition and enantiomeric distribution of *Picea pungens* essential oil

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Abstract

The essential oils from the leaves and twigs of *Picea pungens* (blue spruce) were obtained from trees growing in Kuna, Idaho, and analyzed by GC-MS, GC-FID, and chiral GC-MS. The essential oils were dominated by monoterpenoids, including limonene (24.5-32.2%), α-pinene (9.7-12.9%), camphor (4.9-10.1%), camphene (7.3-8.1%), bornyl acetate (5.4-10.2%), myrcene (5.3-8.0%), and δ-3-carene (3.2-7.6%). The (–)-enantiomers dominated distributions for camphene, β-pinene, limonene, β-phellandrene, camphor, borneol, and bornyl acetate, while the (+)-enantiomers dominated sabinene, δ-3-carene, and fenchone α-Pinene, terpinen-4-ol, α-terpineol, and citronellol showed considerable variation in enantiomeric distribution.

Keywords: Blue spruce, Pinaceae, gas chromatography, chiral, enantiomers

1. Introduction

Picea pungens Engelm. (blue spruce, Pinaceae) is a tree, up to 40 m tall, with scaly grey or brown bark and blue or green foliage [1] (Figure 1). The natural range of *P. pungens* is the western United States, from Idaho and Wyoming, south through Utah and Colorado, and into Arizona and New Mexico [2], but this tree is a popular ornamental and has been introduced to Canada, Europe, and elsewhere where the cool, humid climate is suitable. Previous investigations on the essential oil of *P. pungens* include the leaf essential oil from Westmount, Quebec, Canada [3], the aerial parts essential oil from Minsk, Belarus [4], and the seed and cone essential oils from Łódź, Poland [5]. The purpose of this investigation was to compare and contrast the essential oil of *P. pungens* from southwestern Idaho with previous samples and to examine the enantiomeric distribution of the monoterpenoid components in *P. pungens* essential oil.

Fig 1: *Picea pungens* (Blue spruce). A: tree, B: foliage, C: bark.

2. Materials and Methods

2.1 Plant Material

Leaves and twigs of *P. pungens* were collected from three individual mature trees growing in Kuna, Idaho (43°30′11″N, 116°25′34″W, 823% m elevation) on 26 July 2021. The fresh plant materials (75.12 g, 95.57 g, and 136.88 g) were chopped and hydrodistilled using a Likens-Nickerson apparatus with continuous extraction with dichloromethane to give colorless essential oils (595.8 mg, 918.4 mg, and 469.7 mg, respectively).

2.2 Gas Chromatographic Analysis

Gas chromatography – mass spectrometry (GC-MS) was carried out as previously described

[6]: Shimadzu GCMS-QP2010 Ultra, ZB-5ms GC column (60 m × 0.25 mm × 0.25 µm film thickness), injector and detector temperatures 260 °C; He carrier gas, column head pressure 208 kPa, flow rate 2.00 mL/min; GC oven temperature program 50 °C – 260 °C (2 °C/min), 1.0 µL injection, 5% solution of each essential oil in dichloromethane (split mode, 24:1).The retention index (RI) values were determined by using a series of homologous *n*-alkanes. The compounds listed in Table 1 were identified by comparing the mass spectrum fragmentation data and calculated retention indices with those in the databases [7–10].

Gas chromatography – flame ionization detection (GC-FID) was carried out as previously described [11]. Shimadzu GC 2010 with FID detector, ZB-5 GC column, same operating conditions as above for GC-MS. The percent compositions were determined from raw peak areas without standardization. Chiral GC-MS was carried out as previously described [11]: Shimadzu GCMS-QP2010S, Restek B-Dex 325 column (30 m × 0.25 mm × 0.25 µm film thickness), injector and detector temperatures 240 °C; He carrier gas, column head pressure 53.8 kPa, flow rate 1.00 mL/min; GC oven temperature program 50 °C, held for 5 min, increased 1.0 °C/min to 100 °C, then increased 2.0 °C/min to 220 °C; 0.3µL injection of each essential oil in dichloromethane (split mode, 24:1).

3. Results and Discussion

The essential oils from leaves and twigs of *P.pungens* from three individual mature trees were obtained by hydrodistillation in 0.793%, 0.961%, and 0.343% yield, respectively, for trees #1, #2, and #3. Gas chromatographic analysis of the essential oils indicated a total of 107 components identified accounting for 99.8%, 99.4%, and 99.9% of the compositions, which are compiled in Table 1.

Table 1: Essential oil composition of *Picea pungens*.

RI$_{calc}$	RI$_{db}$	Compound	Percent Composition		
			#1	#2	#3
798	797	(3*Z*)-Hexenal	tr	0.1	tr
801	801	Hexanal	0.4	0.5	0.3
848	849	(2*E*)-Hexenal	1.6	2.9	1.1
849	953	(3*Z*)-Hexenol	---	---	0.2
859	863	(2*E*)-Hexenol	---	0.1	tr
863	860	1-Hexanol	---	0.4	0.1
880	880	Santene	0.2	0.1	tr
922	923	Tricyclene	0.9	0.8	0.7
924	925	α-Thujene	tr	0.1	0.1
933	932	α-Pinene	9.7	10.0	12.9
947	948	α-Fenchene	tr	tr	tr
949	950	Camphene	8.1	8.0	7.3
971	971	Sabinene	0.3	0.7	0.9
977	978	β-Pinene	4.9	2.8	3.0
989	989	Myrcene	8.0	5.3	6.5
1006	1006	α-Phellandrene	0.1	0.1	0.1
1009	1008	δ-3-Carene	3.2	6.7	7.6
1011	1012	Isoamyl isobutyrate	tr	tr	tr
1016	1017	α-Terpinene	0.1	0.1	0.1
1021	1022	Ethyl 3-methylbut-3-enyl carbonate	0.1	0.1	0.1
1024	1024	*p*-Cymene	tr	0.1	0.2
1030	1030	Limonene	32.2	28.2	24.5
1031	1031	β-Phellandrene	0.6	0.5	tr
1032	1032	1,8-Cineole	tr	3.2	4.8
1034	1034	(*Z*)-β-Ocimene	0.1	0.1	0.1
1045	1045	(*E*)-β-Ocimene	0.7	1.1	0.3
1056	1057	γ-Terpinene	0.1	0.2	0.3
1063	1064	3-Methyl-2-butenyl butyrate	tr	tr	tr
1082	1082	*p*-Mentha-2,4(8)-diene	tr	tr	tr
1086	1086	Terpinolene	0.8	1.3	1.2
1089	1090	Fenchone	0.1	0.1	0.2
1097	1099	6-Camphenone	0.1	0.1	tr
1101	1101	Linalool	0.2	0.4	0.2
1107	1109	Isoamyl isovalerate (= Solusterol)	tr	tr	tr
1112	1109	Pent-4-en-1-yl 3-methylbutanoate	0.2	0.2	0.1
1117	1115	3-Methyl-3-butenyl 3-methylbutanoate	0.3	0.2	0.1
1120	1120	*endo*-Fenchol	0.1	tr	---
1125	1125	Methyl octanoate	tr	tr	---
1125	1124	*cis*-*p*-Menth-2-en-1-ol	tr	tr	tr
1127	1126	α-Campholenal	0.2	0.2	0.1
1139	1140	3-Methyl-2-butenyl 2-methylbutanoate	tr	0.1	tr
1141	1140	*trans*-Pinocarveol	0.1	0.1	tr
1144	1142	*trans*-*p*-Menth-2-en-1-ol	tr	tr	tr
1148	1145	Camphor	4.9	8.8	10.1
1153	1151	Citronellal	tr	tr	tr
1156	1156	Camphene hydrate	3.3	2.9	3.4

1161	1160	*trans*-Pinocamphone	tr	tr	---
1163	1164	Pinocarvone	tr	tr	tr
1164	1165	*iso*-Borneol	0.1	tr	tr
1169	1167	*exo*-Acetoxycamphene	tr	0.1	---
1171	1170	Ethyl benzoate	---	---	tr
1174	1173	Borneol	5.1	1.0	1.9
1177	1176	*iso*-Pinocamphone	tr	tr	---
1181	1180	Terpinen-4-ol	0.2	0.5	0.8
1187	1186	*p*-Cymen-8-ol	tr	tr	0.1
1192	1190	2-Methyl-2-butenyl angelate	tr	---	---
1196	1195	α-Terpineol	0.7	2.0	2.2
1198	1197	Estragole (= Methyl chavicol)	0.1	0.1	tr
1207	1205	Verbenone	tr	0.1	tr
1209	1209	*trans*-Piperitol	0.1	0.1	---
1219	1218	*trans*-Carveol	tr	0.1	tr
1225	1226	Nerol	---	0.1	---
1227	1227	Citronellol	0.5	1.4	0.8
1238	1238	Neral	---	0.2	tr
1244	1246	Carvone	---	---	tr
1251	1249	Geraniol	tr	0.2	---
1254	1254	Piperitone	0.4	tr	tr
1268	1268	Geranial	---	0.2	tr
1286	1285	Bornyl acetate	10.2	5.4	6.7
1287	1287	*iso*-Bornyl acetate	tr	---	---
1290	1289	Thymol	tr	tr	tr
1308	1307	Methyl (4*Z*)-decenoate	0.1	tr	---
1324	1322	Methyl decanoate	tr	---	---
1350	2349	Citronellyl acetate	tr	tr	tr
1378	1378	Geranyl acetate	tr	---	---
1389	1390	*trans*-β-Elemene	tr	tr	tr
1419	1417	(*E*)-β-Caryophyllene	tr	---	tr
1437	1439	Isoamyl benzoate	---	---	tr
1444	1451	Prenyl benzoate	tr	0.2	0.2
1453	1452	(*E*)-β-Farnesene	tr	tr	tr
1475	1475	Dodecanol	tr	0.1	---
1497	1497	α-Muurolene	tr	tr	tr
1510	1511	(*Z*)-γ-Bisabolene	tr	---	---
1512	1512	γ-Cadinene	tr	tr	tr
1517	1518	δ-Cadinene	0.1	0.1	0.1
1540	1541	(*E*)-α-Bisabolene	0.1	tr	0.1
1559	1559	Dodecanoic acid	---	tr	---
1560	1561	(*E*)-Nerolidol	---	tr	tr
1575	1575	Germacra-1(10),5-dien-4β-ol	0.1	0.1	tr
1601	1600	α-Oplopenone	---	---	tr
1607	1611	β-Atlantol	tr	---	---
1630	1632	γ-Eudesmol	---	---	tr
1640	1640	τ-Cadinol	tr	0.1	tr
1642	1644	τ-Muurolol	tr	0.1	tr
1645	1646	Himachal-2-en-7β-ol	0.1	tr	tr
1654	1655	α-Cadinol	0.1	0.2	0.1
1663	1665	Intermedeol	---	---	tr
1714	1716	(2*Z*,6*Z*)-Farnesol	---	0.1	---
1735	1735	(2*E*,6*E*)-Farnesal	---	tr	---
1741	1742	(6*S*,7*R*)-Bisabolone	tr	---	---
1746	1746	Isoamyl (*E*)-cinnamate	---	---	tr
1961	1968	Sandaracopimara-8(14),15-diene	tr	tr	tr
1990	1989	Manoyl oxide	0.1	0.1	0.1
1994	2000	9β-Isopimara-7,15-diene	0.2	0.2	0.1
2081	2086	Abietadiene	tr	tr	tr
2141	2147	*cis*-Abienol	0.1	0.2	0.1
2225	2245	Palustral	0.1	0.1	tr
		Monoterpene hydrocarbons	70.0	66.2	65.9
		Oxygenated monoterpenoids	26.1	27.1	31.3
		Sesquiterpene hydrocarbons	0.2	0.1	0.2
		Oxygenated sesquiterpenoids	0.3	0.4	0.1
		Diterpenoids	0.4	0.7	0.2
		Esters	0.8	0.5	0.3
		Benzenoid aromatics	0.1	0.3	0.2
		Others	1.9	4.1	1.7

		Total identified	99.8	99.4	99.9

RI_{calc} = Calculated retention index based on a homologous series of *n*-alkanes on a ZB-5ms column. RI_{db} = Reference retention index from the databases [7–10]. tr = trace (< 0.05%).

The major components in the essential oils were limonene (32.2%, 28.2%, and 24.5%), α-pinene (9.7%, 10.0%, and 12.9%), camphor (4.9%, 8.8%, and 10.1%), camphene (8.1%, 8.0%, and 7.3%), bornyl acetate (10.2%, 5.4%, and 6.7%), myrcene (8.0%, 5.3%, and 6.5%), δ-3-carene (3.2%, 6.7%, and 7.6%), β-pinene (4.9%, 2.8%, and 3.0%), camphene hydrate (3.3%, 2.9%, and 3.4%), borneol (5.1%, 1.0%, and 1.9%), and 1,8-cineole (trace, 3.2%, and 4.8%).Based on the major components (Table 2), the chemical composition of *P. pungens* from Idaho in this work is qualitatively similar to *P. pungens* cultivated in Belarus [4] and from *P. pungens* from Canada [3], but it is also similar to *Picea glauca* (Moench) Voss. from Canada [12] and *Picea engelmannii* Parry ex Engelm. cultivated in Poland [13].

Table 2: Major components in essential oils of *Picea* species.

Compound	***P. pungens*** [a]	***P. pungens*** [b]	***P. pungens*** [c]	***P. glauca*** [d]	***P. engelmannii*** [e]
α-Pinene	10.9	10.0	4.1	12.1	12.8
Camphene	7.8	16.2	7.0	7.7	2.6
β-Pinene	3.6	1.4	0.0	20.5	15.5
Myrcene	6.6	6.9	7.5	4.3	8.9
δ-3-Carene	5.9	0.8	0.0	2.2	4.8
Limonene	28.3	12.2	0.0	8.0	3.5
1,8-Cineole	2.7	19.8	0.5	1.0	1.0
Camphor	7.9	10.2	26.4	20.2	8.0
Camphene hydrate	3.2	0.0	0.0	0.9	2.7
Borneol	2.7	1.8	3.6	2.7	2.8
Bornyl acetate	7.4	8.5	29.4	11.8	2.1

[a] Average of three samples from this work. [b] Average of two samples from Vladykina *et al.* (2013) [4]. [c] From Koçak and Kılıç (2014) [3].[d] From Garneau *et al.* (2012) [12]. [e] Average of juvenile and old foliage from Mardarawicz *et al.* (2004) [13].

The enantiomeric distribution of chiral monoterpenoid components has been determined from the three *P. pungens* samples in this work using chiral gas chromatography – mass spectrometry (Table 3).

Table 3: Enantiomeric distribution, %(+): %(–), for chiral monoterpenoid components of *Picea pungens* essential oils.

Compound	**Tree #1**		**Tree #2**		**Tree #3**	
	(+)	**(–)**	**(+)**	**(–)**	**(+)**	**(–)**
α-Pinene	25.6	74.4	20.2	79.8	62.5	37.4
Camphene	7.4	92.6	7.0	93.0	7.4	92.6
Sabinene	---		100.0	0.0	100.0	0.0
β-Pinene	1.8	98.2	3.6	96.4	4.0	96.0
δ-3-Carene	100.0	0.0	100.0	0.0	100.0	0.0
Limonene	3.3	96.7	3.6	96.4	5.5	94.5
β-Phellandrene	2.8	97.2	6.4	93.6	10.9	89.1
Fenchone	100.0	0.0	100.0	0.0	100.0	0.0
Linalool	21.1	78.9	23.7	76.3	31.9	68.1
Camphor	4.4	95.6	2.5	97.5	2.0	98.0
Borneol	0.0	100.0	0.0	100.0	0.0	100.0
Terpinen-4-ol	29.0	71.0	41.0	59.0	55.8	44.2
α-Terpineol	12.3	87.7	61.2	38.8	70.4	29.6
Citronellol	32.6	67.4	63.0	37.0	75.4	24.6
Piperitone	4.3	95.7	---		---	
Bornyl acetate	0.0	100.0	0.0	100.0	0.0	100.0

The levorotatory enantiomers predominated in *P. picea* essential oil for camphene, β-pinene, limonene, β-phellandrene, linalool, camphor, borneol, and bornyl acetate, while the dextrorotatory enantiomers dominated sabinene, δ-3-carene, and fenchone α-Pinene, terpinen-4-ol, α-terpineol, and citronellol showed considerable variation in enantiomeric distribution. The enantiomeric distributions for limonene, α-pinene, β-pinene, and camphene are consistent with those found in the seed and cone essential oils of *P. pungens* [5], as well as the leaf [14] and bark [15] essential oils of *Piceaabies* (L.) Karst from Sweden.

4. Conclusions

The chemical composition and the enantiomeric distribution of monoterpenoids have been determined for *P. pungens* growing in Idaho, USA. The composition and the enantiomeric distribution are qualitatively similar to those found for *P. pungens* from other geographical locations. Thus, the volatile phytochemistry of this species seems to be relatively consistent.

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6. References

1. Van Buren R, Coope JG, Shultz LM, Harper KT. Woody Plants of Utah. Utah State University Press, Logan, Utah, USA, ISBN: 978-0-87421-824-4, 2011.
2. Kartesz JT. The biota of North America program (BONAP). http://bonap.net/napa 10 February, 2022.
3. Koçak A, Kılıç Ö. Identification of essential oil composition of four *Picea* Mill. (Pinaceae) species from Canada. J Agric. Sci. Technol. B. 2014;4(3):209-214.
4. Vladykina DS, Lamotkin SA, Litvinova EV, Vyglazov OG. Influence of the constituent composition on antimicrobial and perfume properties of fir essential oils. Proc. Belarusian State Technol. Univ, 2013, 178-181.
5. Wajs Bonikowska A, Szoka Ł, Karna E, Wiktorowska Owczarek A, Sienkiewicz M. Composition and biological activity of *Picea pungens* and *Picea orientalis* seed and cone essential oils. Chem. Biodivers. 2017;14(3):e1600264.
6. DeCarlo A, Johnson S, Okeke Agulu KI, Dosoky NS, Wax SJ, Owolabi MS, *et al*. Compositional analysis of the essential oil of *Boswellia dalzielii* frankincense from West Africa reveals two major chemotypes. Phytochemistry. 2019;164:24-32.
7. Adams RP. Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry, 4th ed. Allured Publishing, Carol Stream, Illinois, USA, ISBN: 978-1-932633-21-4, 2007.
8. Mondello L. FFNSC 3. Shimadzu Scientific Instruments, Columbia, Maryland, USA, 2016.
9. National Institute of Standards and Technology.NIST17. National Institute of Standards and Technology, Gaithersburg, Maryland, USA, 2017.
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, University of Alabama in Huntsville, Huntsville, Alabama, USA, 2015.
11. Lawson SK, Satyal P, Setzer WN. Phytochemical analysis of the essential oils from aerial parts of four *Scutellaria* Skullcap species cultivated in south Alabama: *Scutellaria baicalensis* Georgi, *S. barbata* D. Don, *S. incana* Biehler, and *S. lateriflora* L. Nat. Prod. Commun. 2021;16(8):1934578x211025930.
12. Garneau FX, Collin G, Gagnon H, Pichette A. Chemical composition of the hydrosol and the essential oil of three different species of the Pinaceae family: *Picea glauca* (Moench) Voss., *Picea mariana* (Mill.) B.S.P., and *Abies balsamea* (L.) Mill. J Essent. Oil Bear. Plants, 2012;15(2):227-236.
13. Mardarowicz M, Wianowska D, Dawidowicz AL, Sawicki R. Comparison of terpene composition in Engelmann spruce (*Picea engelmannii*) using hydrodistillation, SPME and PLE. Z. Naturforsch. - Sect. C. 2004;59(9/10):641-648.
14. Persson M, Borg Karlson AK, Norin T. Enantiomeric composition of six chiral monoterpene hydrocarbons in different tissues of *Picea abies*. Phytochemistry. 1993;33(2):303-307.
15. Zhao T, Krokene P, Björklund N, Långström B, Solheim H, Christiansen E, *et al*. The influence of *Ceratocystis polonica* inoculation and methyl jasmonate application on terpene chemistry of Norway spruce, *Picea abies*. Phytochemistry. 2010;71(11-12):1332-1341.