

Supporting information

**Chemical Fingerprinting of Conifer Needle Essential Oils and Solvent
Extracts by Ultrahigh-Resolution Fourier Transform Ion Cyclotron
Resonance Mass Spectrometry**

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Table S1. Compounds identified with (–) ESI from conifer needle essential oils.

Calculated <i>m/z</i> [M–H] [–]	Observed <i>m/z</i> [M–H] [–]	Error (ppm)	DBE	Elemental formula	Relative intensity (%)				Putative compound(s)
					Pine	Spruce	Larch	Juniper	
101.060803	101.060787	0.1583	1	C ₅ H ₁₀ O ₂	0.2434	N.D.	N.D.	N.D.	3-Methylbutanoic acid
121.029503	121.029504	0.0103	5	C ₇ H ₆ O ₂	1.1166	0.2880	0.6484	0.1846	Benzoic acid
133.065888	133.065877	0.0827	5	C ₉ H ₁₀ O ₁	0.0398	N.D.	N.D.	N.D.	Cinnamyl alcohol
137.024418	137.024414	0.0292	5	C ₇ H ₆ O ₃	0.0332	0.0327	N.D.	N.D.	Salicylic acid
143.107753	143.107756	0.0192	1	C ₈ H ₁₆ O ₂	1.2584	0.8338	0.7156	1.2582	Octanoic acid
147.045153	147.045165	0.0816	6	C ₉ H ₈ O ₂	0.0212	0.0220	N.D.	N.D.	Cinnamic acid
149.097189	149.097200	0.0740	4	C ₁₀ H ₁₄ O ₁	0.0909	0.0422	0.1290	0.8362	Verbenone
151.040068	151.040067	0.0588	5	C ₈ H ₈ O ₃	0.1205	0.7678	0.0091	N.D.	4-hydroxyphenyl acetic acid
153.128489	153.128504	0.0980	2	C ₁₀ H ₁₈ O ₁	N.D.	N.D.	0.0115	N.D.	Terpinen-4-ol
163.076453	163.076463	0.0598	5	C ₁₀ H ₁₂ O ₂	0.2556	0.1549	0.0173	0.1059	Eugenol
165.055718	165.055718	0.0000	5	C ₉ H ₁₀ O ₃	0.0504	0.0968	N.D.	0.0063	Dihydro-p-coumaryl acid
167.034982	167.035005	0.1377	5	C ₈ H ₈ O ₄	0.0262	0.0339	N.D.	0.0078	Vanillin
167.107753	167.107764	0.0643	3	C ₁₀ H ₁₆ O ₂	4.7921	5.8765	0.0333	3.0039	Geranic acid
169.123403	169.123408	0.0296	2	C ₁₀ H ₁₈ O ₂	21.6252	25.5989	0.0371	9.2987	Citronellic acid
171.139053	171.139069	0.0920	1	C ₁₀ H ₂₀ O ₂	1.9039	1.9187	0.5046	1.4933	Decanoic acid
177.092103	177.092092	0.0635	5	C ₁₁ H ₁₄ O ₂	0.0188	0.0263	0.0122	0.0305	Methyl eugenol
181.123403	181.123410	0.0400	3	C ₁₁ H ₁₈ O ₂	0.0623	0.1167	0.0116	0.0304	Terpinyl formate
183.102668	183.102680	0.0065	3	C ₁₀ H ₁₆ O ₃	0.1679	0.1296	0.0489	0.0867	Pinonic acid
183.139053	183.139072	0.1065	2	C ₁₁ H ₂₀ O ₂	0.4203	0.5523	0.1860	0.2925	Z-3-Hexenyl isovalerate
185.081932	185.081953	0.1121	3	C ₉ H ₁₄ O ₄	0.1602	0.0686	0.0647	0.1472	Pinic acid
191.056112	191.056153	0.2146	2	C ₇ H ₁₂ O ₆	0.0308	0.0761	0.0110	0.0324	Quinic acid
193.050632	193.050629	0.0173	6	C ₁₀ H ₁₀ O ₄	0.0193	0.0417	N.D.	0.0075	Ferulic acid
193.123403	193.123431	0.1450	4	C ₁₂ H ₁₈ O ₂	0.0485	0.0757	0.0731	0.0548	Myrtenyl acetate
195.139053	195.139064	0.0577	3	C ₁₂ H ₂₀ O ₂	0.1248	0.1848	0.0486	4.5168	Terpinyl acetate
205.123403	205.123430	0.1292	5	C ₁₃ H ₁₈ O ₂	0.0539	0.2114	0.0103	N.D.	Phenylethyl-3-methyl butanoate
205.159789	205.159796	0.0341	4	C ₁₄ H ₂₂ O ₁	0.0633	N.D.	0.0755	0.2079	α -Irene
209.081932	209.081942	0.0454	5	C ₁₁ H ₁₄ O ₄	0.0317	0.0364	0.0263	N.D.	Sinapyl alcohol
209.154703	209.154714	0.0526	3	C ₁₃ H ₂₂ O ₂	0.1467	0.1999	0.2829	0.1291	Isobornyl propionate
215.165268	215.165286	0.0837	1	C ₁₂ H ₂₄ O ₃	N.D.	N.D.	0.1071	0.0374	Sabinic acid
215.165268	217.159825	0.1658	5	C ₁₅ H ₂₂ O ₁	0.0194	N.D.	0.0106	0.0448	Nootkatone
219.175439	219.175448	0.0395	4	C ₁₅ H ₂₄ O ₁	0.1145	0.0235	0.0116	0.1006	Caryophyllene oxide
221.081932	221.081946	0.0645	6	C ₁₂ H ₁₄ O ₄	0.0466	0.0233	0.1101	0.0280	Dillapiole
221.191089	221.191093	0.0158	3	C ₁₅ H ₂₆ O ₁	0.0545	N.D.	0.3763	0.0570	Germacrene D-4-ol
227.071368	227.071389	0.0910	9	C ₁₄ H ₁₂ O ₃	0.5709	0.0669	N.D.	0.0246	Benzyl salicylate
227.201654	227.201674	0.0866	1	C ₁₄ H ₂₈ O ₂	5.8457	7.8471	6.7531	11.5091	Ethyl laurate
237.186004	237.186029	0.1043	3	C ₁₅ H ₂₆ O ₂	0.4452	0.2997	0.0469	0.2204	Geranyl isovalerate
239.201654	239.201685	0.1275	2	C ₁₅ H ₂₈ O ₂	0.3200	0.6206	0.5442	0.2858	Methyl isovalerate
253.217304	253.217330	0.1007	2	C ₁₆ H ₃₀ O ₂	1.0361	1.5414	2.8826	1.1305	Cyclohexadecanolide
255.232954	255.232940	0.0539	1	C ₁₆ H ₃₂ O ₂	25.0550	19.8753	46.7484	28.3596	Palmitic acid
269.248604	269.248597	0.0269	1	C ₁₇ H ₃₄ O ₂	0.9011	0.9374	1.3521	0.5864	Methyl palmitate
271.227868	271.227879	0.0396	1	C ₁₆ H ₃₂ O ₃	0.4615	0.6611	0.5226	0.2946	Hydroxypalmitic acid

281.248604	281.248591	0.0471	2	C ₁₈ H ₃₄ O ₂	3.7514	4.6453	4.5079	2.5868	Oleic acid
283.264254	283.264240	0.0512	1	C ₁₈ H ₃₆ O ₂	12.8553	2.5077	3.8847	9.3023	Steric acid
289.253689	289.253636	0.1832	4	C ₂₀ H ₃₄ O ₁	0.0440	N.D.	0.0065	N.D.	Isoabienol
291.232954	291.232952	0.0069	4	C ₁₉ H ₃₂ O ₂	N.D.	N.D.	0.0147	N.D.	15-Norpinifolic acid
299.201654	299.201635	0.0652	7	C ₂₀ H ₂₈ O ₂	1.0363	0.8936	0.4583	0.4346	Dehydroabiatic acid
301.217304	301.217305	0.0026	6	C ₂₀ H ₃₀ O ₂	4.3814	2.6722	14.0433	14.8488	Pimaric acid
301.238433	301.238412	0.0705	1	C ₁₇ H ₃₄ O ₄	0.8371	1.1883	0.6341	1.2170	2,3-Dihydroxypropyl tetradecanoate
303.232954	303.232931	0.0750	5	C ₂₀ H ₃₂ O ₂	0.2245	0.1072	0.3229	0.1827	Anticopalic acid
305.248604	305.248576	0.0925	4	C ₂₀ H ₃₄ O ₂	0.1440	0.2366	0.8551	0.5622	3- α -Hydroxymanool
315.196568	315.196533	0.1102	7	C ₂₀ H ₂₈ O ₃	0.0637	0.1222	3.0093	0.0101	Lambertianic acid
317.212218	317.212202	0.1497	6	C ₂₀ H ₃₀ O ₃	0.1522	0.4172	0.0387	0.5830	12-Hydroxyabiatic acid
319.227868	319.227845	0.0713	5	C ₂₀ H ₃₂ O ₃	0.2574	0.6459	N.D.	0.0108	Isocupressic acid
321.243519	321.243501	0.0553	4	C ₂₀ H ₃₄ O ₃	0.0636	0.1171	0.2147	0.0256	Imbricatolic acid (dihydroisocupressic acid)
329.269733	329.269719	0.0440	1	C ₁₉ H ₃₈ O ₄	1.0562	1.5550	0.4619	0.3422	2,3-Dihydroxypropyl hexadecanoate
331.191483	331.191487	0.0128	7	C ₂₀ H ₂₈ O ₄	0.0292	0.1459	0.0088	0.1054	Pinusolic acid
335.222783	335.222770	0.0380	5	C ₂₀ H ₃₂ O ₄	0.8810	4.0941	0.0551	0.3944	Pinifolic acid
349.202048	349.202037	0.0315	6	C ₂₀ H ₃₀ O ₅	0.1645	0.2953	0.1547	0.1180	Andrographolide
357.301033	357.301034	0.0028	1	C ₂₁ H ₄₂ O ₄	1.5215	2.6635	4.2769	N.D.	2,3-Dihydroxypropyl octadecanoate
361.238433	361.238401	0.0879	6	C ₂₂ H ₃₄ O ₄	0.2844	0.1568	0.9465	0.6259	Acetylisocupressic acid
385.332334	385.332326	0.0210	1	C ₂₃ H ₄₆ O ₄	2.0682	4.3174	1.5368	1.2646	2,3-dihydroxypropyl eicosanoate
413.363634	413.363651	0.0417	1	C ₂₅ H ₅₀ O ₄	2.3874	3.9363	2.1463	2.9763	2,3-dihydroxypropyl docosanoate

N.D. –Not detected

Table S2. Compounds identified with (–) ESI from conifer needle solvent extracts.

Calculated m/z [M–H] [–]	Observed m/z [M–H] [–]	Error (ppm)	DBE	Elemental formula	Relative intensity (%)		Putative compound(s)
					Hexane	Toluene	
121.029503	121.029503	0.0000	5	C ₇ H ₆ O ₂	0.0090	0.0275	Benzoic acid
137.024418	137.024422	0.0292	5	C ₇ H ₆ O ₃	0.0056	0.0933	Salicylic acid
143.107753	143.107757	0.0280	1	C ₈ H ₁₆ O ₂	0.0140	0.0190	Octanoic acid
145.087018	145.087027	0.0586	1	C ₇ H ₁₄ O ₃	0.0107	0.0492	2-Hydroxyheptanoic acid
149.045547	149.045556	0.0604	1	C ₅ H ₁₀ O ₅	0.0573	N.D.	Arabinose
151.040068	151.040074	0.0397	5	C ₈ H ₈ O ₃	0.0066	0.0229	4-hydroxyphenyl acetic acid
163.061197	163.060648	0.0552	1	C ₆ H ₁₂ O ₅	0.0126	N.D.	Rhamnose
167.107753	167.107770	0.1017	3	C ₁₀ H ₁₆ O ₂	0.0107	0.2334	Geranic acid
171.139053	171.139068	0.0819	1	C ₁₀ H ₂₀ O ₂	0.0056	N.D.	Decanoic acid
179.056112	179.056124	0.0540	1	C ₆ H ₁₂ O ₆	0.2072	0.0153	Fructose
183.102668	183.102689	0.0942	3	C ₁₀ H ₁₆ O ₃	N.D.	0.0219	Pinonic acid
183.139053	183.139068	0.0518	2	C ₁₁ H ₂₀ O ₂	0.0513	N.D.	Z-3-Hexenyl isovalerate
185.081932	185.081942	0.0906	3	C ₉ H ₁₄ O ₄	0.0075	0.0286	Pinic acid
191.056112	191.056094	0.0276	2	C ₇ H ₁₂ O ₆	3.4664	0.3052	Quinic acid
193.050632	193.050642	0.0536	6	C ₁₀ H ₁₀ O ₄	N.D.	0.0473	Ferulic acid
193.071762	193.071780	0.0047	1	C ₇ H ₁₄ O ₆	0.0523	0.0637	Pinitol

199.170354	199.170360	0.0813	1	C ₁₂ H ₂₄ O ₂	0.0281	0.0309	Lauric acid
205.159789	205.159778	0.0023	4	C ₁₄ H ₂₂ O ₁	0.0169	N.D.	Alpha irone
213.186004	213.186005	0.1155	1	C ₁₃ H ₂₆ O ₂	0.0063	N.D.	Tridecanoic acid
215.165268	215.165286	0.1285	1	C ₁₂ H ₂₄ O ₃	0.0185	0.0297	Sabincic acid (hydroxylauric acid)
221.081932	221.081933	0.1501	6	C ₁₂ H ₁₄ O ₄	0.0052	0.0159	Dillapiole
225.092103	225.092129	0.1155	9	C ₁₅ H ₁₄ O ₂	0.0337	N.D.	Flavon-3-ol
227.201654	227.201683	0.1276	1	C ₁₄ H ₂₈ O ₂	N.D.	0.0280	Myristic acid
239.201654	239.201709	0.2299	2	C ₁₅ H ₂₈ O ₂	0.0059	N.D.	Methyl isovalerate
241.217304	241.217335	0.1285	1	C ₁₅ H ₃₀ O ₂	0.0121	N.D.	Pentadecanoic acid
253.217304	253.217335	0.1501	2	C ₁₆ H ₃₀ O ₂	0.0165	0.0165	Palmitoleic acid
255.232954	255.232951	0.0137	1	C ₁₆ H ₃₂ O ₂	0.2940	0.1350	Palmitic acid
269.248604	269.248559	0.1671	1	C ₁₇ H ₃₄ O ₂	0.0153	N.D.	Methyl palmitate
271.227868	271.227872	0.0129	1	C ₁₆ H ₃₂ O ₃	0.1633	0.2314	Hydroxypalmitic acid
277.217304	277.217325	0.0739	4	C ₁₈ H ₃₀ O ₂	0.3064	0.0501	Linolenic acid
279.232954	279.232967	0.0448	3	C ₁₈ H ₃₂ O ₂	0.0727	0.0281	Linoleic acid
281.248604	281.248559	0.0181	2	C ₁₈ H ₃₄ O ₂	0.0357	N.D.	Oleic acid
283.264254	283.264232	0.0777	1	C ₁₈ H ₃₆ O ₂	0.2192	0.0757	Stearic acid
285.040462	285.040469	0.0246	11	C ₁₅ H ₁₀ O ₆	N.D.	0.0334	Kaempferol
291.232954	291.232955	0.0034	4	C ₁₉ H ₃₂ O ₂	0.0092	N.D.	15-Norpinifolic acid
297.279904	297.279948	0.1480	1	C ₁₉ H ₃₈ O ₂	0.0064	N.D.	Nonadecanoic acid
299.165268	299.165246	0.0735	8	C ₁₉ H ₂₄ O ₃	0.0174	0.0191	Z-Bornyl-p-coumarate
299.201654	299.201619	0.1170	7	C ₂₀ H ₂₈ O ₂	0.8487	0.6294	Dehydroabietic acid
301.035376	301.035324	0.1727	11	C ₁₅ H ₁₀ O ₇	N.D.	0.0175	Quercetin
301.217304	301.217288	0.0548	6	C ₂₀ H ₃₀ O ₂	6.7897	3.5646	Abietic acid
301.238433	301.238377	0.1859	1	C ₁₇ H ₃₄ O ₄	0.0877	N.D.	2,3-Dihydroxypropyl tetradecanoate
303.051026	303.051083	0.1881	10	C ₁₅ H ₁₂ O ₇	N.D.	0.0209	Taxifolin
303.232954	303.232900	0.1797	5	C ₂₀ H ₃₂ O ₂	0.0347	0.0191	Anticopalic acid
305.248604	305.248533	0.2326	4	C ₂₀ H ₃₄ O ₂	0.0273	N.D.	3- α -Hydroxy manool
311.295554	311.295523	0.0996	1	C ₂₀ H ₄₀ O ₂	0.0661	0.0258	Arachidic acid
313.180918	313.180901	0.0559	8	C ₂₀ H ₂₆ O ₃	0.0071	0.0251	7-Oxodehydroabietic acid
315.051026	315.051018	0.0254	11	C ₁₆ H ₁₂ O ₇	N.D.	0.0502	Isorhamnetin
315.196568	315.196534	0.1079	7	C ₂₀ H ₂₈ O ₃	0.0886	0.1914	Lambertianic acid
317.212218	317.212208	0.0315	6	C ₂₀ H ₃₀ O ₃	0.4904	1.1300	12-Hydroxyabietic acid
319.227868	319.227841	0.0846	5	C ₂₀ H ₃₂ O ₃	1.3126	2.8905	Isocupressic acid
321.243519	321.243482	0.1167	4	C ₂₀ H ₃₄ O ₃	0.1606	0.4492	Imbricatolic acid (dihydroisocupressic acid)
329.269733	329.269684	0.1488	1	C ₁₉ H ₃₈ O ₄	0.0118	0.2700	2,3-Dihydroxypropyl hexadecanoate
331.191483	331.191442	0.1238	7	C ₂₀ H ₂₈ O ₄	0.0465	N.D.	Pinusolic acid
333.207133	333.207094	0.1185	6	C ₂₀ H ₃₀ O ₄	9.5100	10.8080	Dehydropinifolic acid
335.222783	335.222739	0.1313	5	C ₂₀ H ₃₂ O ₄	8.4787	27.8598	Pinifolic acid
339.326854	339.326797	0.1695	1	C ₂₂ H ₄₄ O ₂	0.0516	0.0178	Behenic acid
341.108935	341.108914	0.0616	2	C ₁₂ H ₂₂ O ₁₁	0.1491	0.0586	Sucrose
345.207133	345.207115	0.0521	7	C ₂₁ H ₃₀ O ₄	0.0358	0.0442	Pinusolide
349.202048	349.202019	0.0845	6	C ₂₀ H ₃₀ O ₅	0.1486	0.4292	Andrographolide

349.238433	349.238396	0.1059	5	C ₂₁ H ₃₄ O ₄	33.1969	44.5993	Methyl pinifolate
353.342504	353.342436	0.1924	1	C ₂₃ H ₄₆ O ₂	0.0067	N.D.	Tricosanoic acid
355.321769	355.321733	0.1027	1	C ₂₂ H ₄₄ O ₃	0.0238	0.0494	Hydroxydocosanoic acid
357.134362	357.134358	0.0112	10	C ₂₀ H ₂₂ O ₆	N.D.	0.0440	Matairesinol
357.301033	357.300986	0.1315	1	C ₂₁ H ₄₂ O ₄	0.0049	0.0193	2,3-Dihydroxypropyl octadecanoate
361.238433	361.238406	0.0747	6	C ₂₂ H ₃₄ O ₄	2.3195	1.6923	Acetylisocupressic acid
363.254083	363.254057	0.0730	5	C ₂₂ H ₃₆ O ₄	0.7503	1.1065	Dimethyl pinifolate
365.196962	365.196957	0.0137	6	C ₂₀ H ₃₀ O ₆	1.0325	N.D.	7-Oxo-12 α ,13 β ,15-trihydroxyabiet-8(14)-en-18-oic acid
371.11950	371.119478	0.0593	2	C ₁₃ H ₂₄ O ₁₂	4.9789	N.D.	6-O-Heptopyranosyl-d-glucopyranose
373.129277	373.129310	0.0643	10	C ₂₀ H ₂₂ O ₇	N.D.	0.0244	Hydroxymatairesinol
381.373804	381.373829	0.0656	1	C ₂₅ H ₅₀ O ₂	0.0063	N.D.	Pentacosanoic acid
385.332334	385.332301	0.0830	1	C ₂₃ H ₄₆ O ₄	0.0719	0.2834	2,3-Dihydroxypropyl eicosanoate
395.389454	395.389407	0.1189	1	C ₂₆ H ₅₂ O ₂	0.0175	N.D.	Hexacosanoic acid
409.259562	409.259559	0.0073	5	C ₂₃ H ₃₈ O ₆	23.8423	1.6595	Vitetrifolin D
413.363634	413.363648	0.0339	1	C ₂₅ H ₅₀ O ₄	0.0327	0.1216	2,3-Dihydroxypropyl docosanoate
419.243912	419.243883	0.0704	7	C ₂₄ H ₃₆ O ₆	0.0841	0.2778	Succinylisocupressic acid
423.420755	423.420773	0.0425	1	C ₂₈ H ₅₆ O ₂	0.0287	N.D.	Octacosanoic acid
451.452055	451.452026	0.0642	1	C ₃₀ H ₆₀ O ₂	0.0320	N.D.	Triacosanoic acid
463.08820	463.088170	0.0648	12	C ₂₁ H ₂₀ O ₁₂	0.0071	N.D.	Isoquercetin
479.483355	479.483310	0.0939	1	C ₃₂ H ₆₄ O ₂	0.0103	N.D.	Dotriacontanoic acid
503.161758	503.161703	0.1093	3	C ₁₈ H ₃₂ O ₁₆	0.0087	N.D.	Raffinose

N.D. –Not detected

Table S3. Compounds identified with (+) APPI from conifer needle essential oils

Calculated <i>m/z</i> [M+H] ⁺	Observed <i>m/z</i> [M+H] ⁺	Error (ppm)	DBE	Elemental formula	Relative intensity (%)				Putative compound(s)
					Pine	Spruce	Larch	Juniper	
121.101177	121.101168	0.0716	4	C ₉ H ₁₂	0.9168	1.0286	0.4138	1.0538	1,2,4-Trimethylbenzene
133.101177	133.101175	0.0175	5	C ₁₀ H ₁₂	0.1279	0.1079	0.2609	0.1249	3,5-Dimethylstyrene
135.080441	135.080446	0.0370	5	C ₉ H ₁₀ O ₁	0.0348	0.0289	0.1455	0.0129	Chavicol
135.116827	135.116826	0.0074	4	C ₁₀ H ₁₄	0.4837	2.0141	0.4364	0.9049	Verbenene
137.132477	137.132464	0.0972	3	C ₁₀ H ₁₆	5.9086	21.0899	0.5062	11.0749	Pinene
139.111742	139.111740	0.0144	3	C ₉ H ₁₄ O ₁	0.0640	3.5497	0.1218	0.0714	Sebina Ketone
149.096091	149.096079	0.0827	5	C ₁₀ H ₁₂ O ₁	0.0973	0.0693	0.1944	0.0694	Methyl chavicol
151.111742	151.111719	0.1522	4	C ₁₀ H ₁₄ O ₁	1.6385	0.8118	1.1858	0.3063	Verbenone
153.127392	153.127376	0.1023	3	C ₁₀ H ₁₆ O ₁	0.2257	4.7042	0.2309	0.4604	Methyl thymol, Thujone, Piperitone
155.143042	155.143032	0.0677	2	C ₁₀ H ₁₈ O ₁	N.D.	0.1961	N.D.	0.0114	Borneol, Citronellal, Eucalyptol, linalool, Caraneol
161.132477	161.132444	0.2027	5	C ₁₂ H ₁₆	2.2558	1.1657	9.6802	6.1491	3-Methyl-2-phenyl-2-pentene
163.075356	163.075350	0.0399	6	C ₁₀ H ₁₀ O ₂	N.D.	0.0605	0.0460	0.0107	Safole
165.091006	165.091005	0.0081	5	C ₁₀ H ₁₂ O ₂	0.0955	0.0486	0.2249	0.0408	2-Phenylethyl acetate
165.127392	165.127384	0.0515	4	C ₁₁ H ₁₆ O ₁	0.0620	0.0647	0.0956	0.0679	Thymol methyl ether
167.106656	167.106653	0.0160	4	C ₁₀ H ₁₄ O ₂	0.2318	0.1488	0.6396	0.0608	Perillic acid
169.122306	169.122300	0.0335	3	C ₁₀ H ₁₆ O ₂	0.0606	0.2716	0.3167	0.0847	Geranic acid
171.137956	171.137952	0.0263	2	C ₁₀ H ₁₈ O ₂	N.D.	0.0453	0.0090	0.0374	Citronellic acid

179.106656	179.106657	0.0037	5	C ₁₁ H ₁₄ O ₂	0.0159	0.0351	0.0825	0.0208	Methyl eugenol
181.085921	181.085915	0.0331	5	C ₁₀ H ₁₂ O ₃	N.D.	0.0096	0.0670	N.D.	Coniferyl alcohol
183.137956	183.137943	0.0710	3	C ₁₁ H ₁₈ O ₂	0.0345	0.0890	0.0523	0.0565	Geranyl formate
193.085921	193.085900	0.1088	6	C ₁₁ H ₁₂ O ₃	N.D.	N.D.	0.0129	N.D.	Myristicin
193.122306	193.122302	0.0207	5	C ₁₂ H ₁₆ O ₂	0.0670	0.1862	0.3605	0.0532	β -Phenylethyl isobutyrate
197.153606	197.153568	0.1927	3	C ₁₂ H ₂₀ O ₂	N.D.	0.0062	0.0080	N.D.	Geranyl acetate
201.163777	201.163745	0.1591	6	C ₁₅ H ₂₀	0.6235	0.2380	0.7323	0.1514	Calorene
203.179427	203.179378	0.2428	5	C ₁₅ H ₂₂	2.7711	4.2812	2.1884	1.8958	Calamenene
205.158692	205.158671	0.1024	5	C ₁₄ H ₂₀ O ₁	2.7894	0.8269	1.9393	0.0915	Khusimone
205.195077	205.195005	0.3509	4	C ₁₅ H ₂₄	56.4577	32.5175	56.6424	58.6900	Germacrene D, Caryophyllene
207.137956	207.137956	0.0016	5	C ₁₃ H ₁₈ O ₂	0.1590	0.1029	0.2404	0.0416	3-Methyl-2-phenylethyl ester
207.174342	207.174319	0.1110	4	C ₁₄ H ₂₂ O	2.4766	0.4495	3.9191	2.2276	Alpha iron
209.117221	209.117204	0.0829	5	C ₁₂ H ₁₆ O ₃	N.D.	0.0538	0.1549	0.0299	Pinchotene acetate
211.169256	211.169248	0.0395	3	C ₁₃ H ₂₂ O ₂	0.0245	0.0905	0.0486	0.0191	Isobornyl propanoate
217.158692	217.158686	0.0299	6	C ₁₅ H ₂₀ O ₁	1.3740	0.5028	1.6941	0.2251	Hexyl cinnamaldehyde
217.195077	217.195069	0.0353	5	C ₁₆ H ₂₄	1.5713	3.1080	0.1362	5.4005	Vulgraon B
219.174342	219.174303	0.1779	5	C ₁₅ H ₂₂ O ₁	7.0388	2.8140	8.1671	1.1068	Nootkatone
221.153606	221.153593	0.0573	5	C ₁₄ H ₂₀ O ₂	1.1009	0.1587	1.5341	0.0915	Phenylethyl hexanoate
221.189992	221.189962	0.1341	4	C ₁₅ H ₂₄ O ₁	3.0924	5.9276	2.5463	2.1145	Caryophyllene oxide, Farnasal, Spathulenol
223.075356	223.075371	0.0672	11	C ₁₅ H ₁₀ O ₂	N.D.	0.0062	N.D.	N.D.	Aurone, Flavone
223.096485	223.096450	0.1569	6	C ₁₂ H ₁₄ O ₄	N.D.	0.0082	0.0254	N.D.	Apiole
223.205642	223.205644	0.0105	3	C ₁₅ H ₂₆ O ₁	0.0408	0.0958	0.2454	0.0931	Germacrene D-4-ol
225.184906	225.184889	0.0755	3	C ₁₄ H ₂₄ O ₂	0.0206	0.0467	0.0517	0.0226	Bornyl isobutyrate
237.184906	237.184902	0.0169	4	C ₁₅ H ₂₄ O ₂	1.6275	0.6122	1.7964	0.4036	Myrtenyl isovalerate
239.164171	239.164157	0.0599	4	C ₁₄ H ₂₂ O ₃	0.0939	0.0273	0.3354	0.0297	Pinchotene acetate
239.200557	239.200565	0.0334	3	C ₁₅ H ₂₆ O ₂	0.0261	0.0883	0.0389	0.0397	Bornyl-2-methylbutyrate
255.210727	255.210745	0.0705	7	C ₁₉ H ₂₆	N.D.	0.2620	0.1356	0.2895	Norabieta-4(18),8,11,13-tetraene
257.226377	257.226391	0.0557	6	C ₁₉ H ₂₈	N.D.	1.3167	0.1103	0.3278	Norabietatriene
271.242027	271.241958	0.2532	6	C ₂₀ H ₃₀	0.9916	2.1543	0.2152	2.0669	Abieta-8,11,13-triene
273.257677	273.257649	0.1025	5	C ₂₀ H ₃₂	2.8188	4.9122	0.1459	1.3402	Abietadiene
285.221292	285.221284	0.0269	7	C ₂₀ H ₂₈ O ₁	0.3728	0.3426	0.2719	0.2837	Dehydroabietal
287.236942	287.236908	0.1184	6	C ₂₀ H ₃₀ O ₁	0.7638	1.2838	0.3542	0.9583	Ferruginol
289.252592	289.252589	0.0104	5	C ₂₀ H ₃₂ O ₁	0.2117	0.6814	0.0950	0.3281	Isopimarol
291.268242	291.268250	0.0257	4	C ₂₀ H ₃₄ O ₁	N.D.	0.0314	0.0132	0.0310	Isoabienal
293.247507	293.247523	0.0529	4	C ₁₉ H ₃₂ O ₂	N.D.	0.0111	0.0088	0.0084	15-Norpinifolic acid
301.179821	301.179831	0.0321	8	C ₁₉ H ₂₄ O ₃	0.0305	0.0261	0.0085	0.0653	Z-Bornyl-p-coumarate
303.231857	303.231830	0.0890	6	C ₂₀ H ₃₀ O ₂	0.4327	0.3394	0.3379	0.2148	Abietic acid
305.247507	305.247468	0.1278	5	C ₂₀ H ₃₂ O ₂	0.0579	0.3791	0.2433	0.1525	Anticypalic acid
315.231857	315.231865	0.0254	7	C ₂₁ H ₃₀ O ₂	0.0935	0.1261	0.1918	0.0381	Methyl dehydroabietate
317.211121	317.211118	0.0095	7	C ₂₀ H ₂₈ O ₃	0.1307	0.0626	0.0367	0.1696	Lambertianic acid
319.226771	319.226527	0.0052	6	C ₂₀ H ₃₀ O ₃	0.1944	0.0907	0.0353	0.1792	3-Oxoanticypalic acid
317.247507	319.263769	0.0620	6	C ₂₁ H ₃₂ O ₂	0.0326	0.0618	0.0761	0.0298	Methyl sandaracopimarate
319.263157	319.263165	0.0261	5	C ₂₁ H ₃₄ O ₂	0.0326	0.0334	0.0227	0.0427	Methyl arachidonate
321.242421	321.242394	0.0830	5	C ₂₀ H ₃₂ O ₃	0.0876	0.0685	0.0238	N.D.	Isocupressic acid
323.258071	323.258082	0.0340	4	C ₂₀ H ₃₄ O ₃	N.D.	0.0247	N.D.	0.0249	Imbricatolic acid (dihydroisocupressic acid)
331.226771	331.226784	0.0392	7	C ₂₁ H ₃₀ O ₃	0.0431	0.0315	0.0914	0.0099	Methyl daniellate
333.206036	333.206998	0.1150	7	C ₂₀ H ₂₈ O ₄	0.0542	0.0194	0.0088	0.0733	Pinosolide

337.237336	337.237326	0.0297	5	C ₂₀ H ₃₂ O ₄	0.0222	0.0279	0.0241	N.D.	Pinifolic acid
351.216601	351.216617	0.0456	6	C ₂₀ H ₃₀ O ₅	0.0207	0.0076	0.0224	N.D.	Andrographolide
363.252986	363.252934	0.1432	6	C ₂₂ H ₃₄ O ₄	N.D.	0.0177	N.D.	0.0194	Acetyliscupressic acid

N.D. –Not detected

Table S4. Compounds identified with (+) APPI from conifer needle solvent extracts

Calculated <i>m/z</i> [M] ⁺⁺	Observed <i>m/z</i> [M] ⁺⁺	Error (ppm)	DBE	Elemental formula	Relative intensity (%)		Putative compound(s)
					Hexane	Toluene	
134.072616	134.072608	0.0597	5	C ₉ H ₁₀ O ₁	0.0219	N.D.	Chavicol
134.109002	134.109005	0.0186	4	C ₁₀ H ₁₄	0.2152	0.1316	Verbenene
136.124652	136.124654	0.0110	3	C ₁₀ H ₁₆	0.3829	0.1208	Pinene
138.103916	138.103922	0.0434	3	C ₉ H ₁₄ O ₁	N.D.	0.0137	Sabina ketone
148.088266	148.088252	0.0945	5	C ₁₀ H ₁₂ O ₁	0.0423	0.0242	Methyl chavicol
150.103916	150.103912	0.0266	4	C ₁₀ H ₁₄ O ₁	0.0469	0.0363	Verbenone
152.119567	152.119559	0.0559	3	C ₁₀ H ₁₆ O ₁	0.0235	0.0244	Methyl thymol, Thujone, Piperitone,
162.067531	162.067537	0.0370	6	C ₁₀ H ₁₀ O ₂	0.0239	0.0137	Safrole
164.083181	164.083170	0.0701	5	C ₁₀ H ₁₂ O ₂	0.0280	0.0152	2-Phenylethyl acetate
164.119567	164.119580	0.0792	4	C ₁₁ H ₁₆ O ₁	0.0387	0.0251	Thymol methyl ether
166.098831	166.098834	0.0151	4	C ₁₀ H ₁₄ O ₂	0.0940	0.0675	Perillic acid
168.114481	168.114484	0.0149	3	C ₁₀ H ₁₆ O ₂	0.0625	0.0465	Geranic acid
178.098831	178.098832	0.0028	5	C ₁₁ H ₁₄ O ₂	0.0440	0.0257	Methyl eugenol
180.078096	180.078100	0.0222	5	C ₁₀ H ₁₂ O ₃	0.0362	0.0272	Coniferyl alcohol
182.130131	182.130140	0.0467	3	C ₁₁ H ₁₈ O ₂	0.0474	0.0360	Geranyl formate
192.114481	192.114489	0.0390	5	C ₁₂ H ₁₆ O ₂	0.0413	0.0300	β-Phenylethyl isobutyrate
200.155952	200.155948	0.0200	6	C ₁₅ H ₂₀	0.0973	0.0687	Calorene
202.171602	202.171604	0.0099	5	C ₁₅ H ₂₂	0.2410	0.1885	Calamenene
204.150867	204.150861	0.0294	5	C ₁₄ H ₂₀ O ₁	0.0846	0.0549	Khusimone
204.187252	204.187263	0.0514	4	C ₁₅ H ₂₄	3.9589	3.0658	Germacrene D, Caryophyllene
206.130131	206.130141	0.0485	5	C ₁₃ H ₁₈ O ₂	0.1365	0.1051	Phenylethyl isovalerate
206.166517	206.166508	0.0437	4	C ₁₄ H ₂₂ O ₁	0.1094	0.0560	Alpha iron
208.109396	208.109415	0.0913	5	C ₁₂ H ₁₆ O ₃	N.D.	0.0452	Pinchotene acetate
216.150867	216.150872	0.0231	6	C ₁₅ H ₂₀ O ₁	0.1767	0.1206	Hexyl cinnamaldehyde
218.166517	218.166504	0.0596	5	C ₁₅ H ₂₂ O ₁	0.0790	0.0487	Nootkatone
220.145781	220.145782	0.0045	5	C ₁₄ H ₂₀ O ₂	0.2837	0.2432	Phenylethyl hexanoate
220.182167	220.182167	0.0000	4	C ₁₅ H ₂₄ O ₁	0.1338	0.0899	Caryophlene oxide, Farnasal, Spathulenol
222.067531	222.067501	0.1373	6	C ₁₅ H ₁₀ O ₂	0.0367	0.0268	Aurone, Flavone
222.197817	222.197810	0.0315	3	C ₁₅ H ₂₆ O ₁	0.1482	0.0515	Germacrene D-4-ol
224.177081	224.177137	0.2498	3	C ₁₄ H ₂₄ O ₂	0.0249	0.0000	Bornyl isobutyrate
234.161431	234.161425	0.0256	5	C ₁₅ H ₂₂ O ₂	0.2303	0.1844	Polygodial
236.177081	236.177079	0.0106	4	C ₁₅ H ₂₄ O ₂	0.2438	0.2002	Myrtenyl isovalerate
238.156346	238.156319	0.1155	4	C ₁₄ H ₂₂ O ₃	0.0226	0.0135	Pinchotene acetate
254.202902	254.202904	0.0079	7	C ₁₉ H ₂₆	1.1065	0.9565	Norabieta-4(18),8,11,13-tetraene

256.218552	256.218563	0.0429	6	C ₁₉ H ₂₈	0.4677	1.7426	Norabietatriene
270.234202	270.234212	0.0370	6	C ₂₀ H ₃₀	0.1482	0.1128	Abieta-8,11,13-triene
272.249852	272.249865	0.0478	5	C ₂₀ H ₃₂	5.3297	4.0430	Abietadiene
284.213467	284.213473	0.0194	7	C ₂₀ H ₂₈ O ₁	0.6454	0.5597	Dehydroabietal
286.229117	286.229121	0.0122	6	C ₂₀ H ₃₀ O ₁	0.5142	0.3811	Ferruginol
288.244767	288.244751	0.0572	5	C ₂₀ H ₃₂ O ₁	0.4556	0.3226	Isopimarol
290.260417	290.260411	0.0207	4	C ₂₀ H ₃₄ O ₁	2.2275	1.6607	Isoabienol
292.239682	292.239679	0.0120	4	C ₁₉ H ₃₂ O ₂	0.4933	0.5583	15-Norpinifolic acid
300.171996	300.171965	0.1033	8	C ₁₉ H ₂₄ O ₃	0.1481	0.0998	Z-Bornyl-p-coumarate
300.208382	300.208370	0.0416	7	C ₂₀ H ₂₈ O ₂	4.8995	5.5528	Dehydroabietic acid
302.224032	302.223991	0.1373	6	C ₂₀ H ₃₀ O ₂	40.8471	45.5916	Abietic acid
304.239682	304.239697	0.0493	5	C ₂₀ H ₃₂ O ₂	1.3418	1.0819	Anticopalic acid
314.187646	314.187635	0.0366	8	C ₂₀ H ₂₆ O ₃	0.2962	0.2178	7-Oxodehydroabietic acid
314.224032	314.224027	0.0159	7	C ₂₁ H ₃₀ O ₂	2.6948	2.3663	Methyl dehydroabietate
316.203296	316.203295	0.0032	7	C ₂₀ H ₂₈ O ₃	3.0338	2.0948	Lambertianic acid
316.239682	316.239666	0.0522	6	C ₂₁ H ₃₂ O ₂	0.2248	0.2072	Methyl sandaracopimarate
318.218946	318.218948	0.0047	6	C ₂₀ H ₃₀ O ₃	2.6830	2.6527	3-Oxoanticopalic acid
318.255332	318.255347	0.0471	5	C ₂₁ H ₃₄ O ₂	0.0560	0.0827	Methyl arachidonate
320.234596	320.234612	0.0500	5	C ₂₀ H ₃₂ O ₃	1.6867	1.5772	Isocupressic acid
322.250246	322.250263	0.0528	4	C ₂₀ H ₃₄ O ₃	0.0688	0.0504	Imbricatolic acid (dihydroisocupressic acid)
330.218946	330.218919	0.0818	7	C ₂₁ H ₃₀ O ₃	0.1521	0.1060	Methyl daniellate
332.198211	332.198188	0.0707	7	C ₂₀ H ₂₈ O ₄	0.3339	0.2482	Pinusolic acid
332.234596	332.234598	0.0045	6	C ₂₁ H ₃₂ O ₃	5.5126	5.9585	12-Methoxy-6 α ,11-dihydroxyabieta-8,11,13-triene
334.213861	334.213891	0.0883	6	C ₂₀ H ₃₀ O ₄	2.6595	1.7846	Dehydropinifolic acid
336.229511	336.229518	0.0193	5	C ₂₀ H ₃₂ O ₄	1.4024	1.7652	Pinifolic acid
346.213861	346.213891	0.1126	7	C ₂₁ H ₃₀ O ₄	0.1044	0.0957	Pinusolide
350.208775	350.208760	0.0428	6	C ₂₀ H ₃₀ O ₅	0.0554	0.0499	Andrographolide
350.245161	350.245133	0.0785	5	C ₂₁ H ₃₄ O ₄	12.8697	12.5939	Methyl pinifolate
362.245161	362.245159	0.0055	6	C ₂₂ H ₃₄ O ₄	0.2316	0.2039	Acetylisocupressic acid
414.385618	414.385526	0.2232	5	C ₂₉ H ₅₀ O ₁	0.0558	0.0372	β -Sitosterol
430.380532	430.380463	0.1615	5	C ₂₉ H ₅₀ O ₂	0.0555	0.0181	Tocopherol
446.339061	446.339044	0.0381	6	C ₂₈ H ₄₆ O ₄	0.0422	0.0249	Didecyl phthalate

N.D. –Not detected

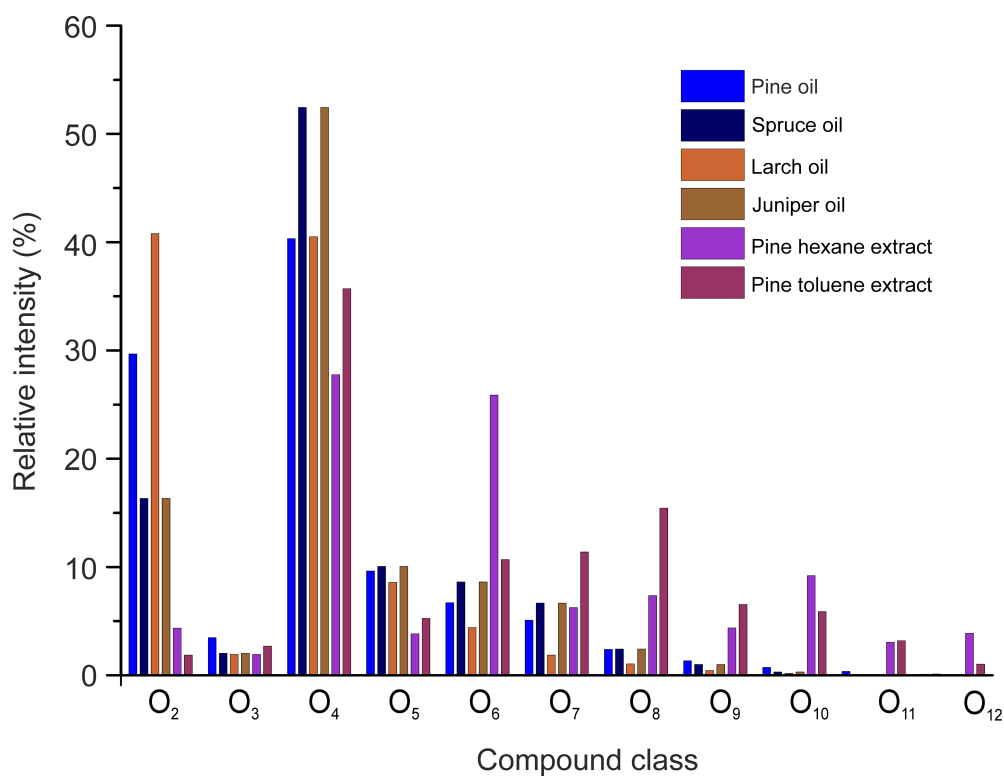


Figure S1. Negative-ion ESI compound class distributions of conifer needle essential oils and solvent extracts.

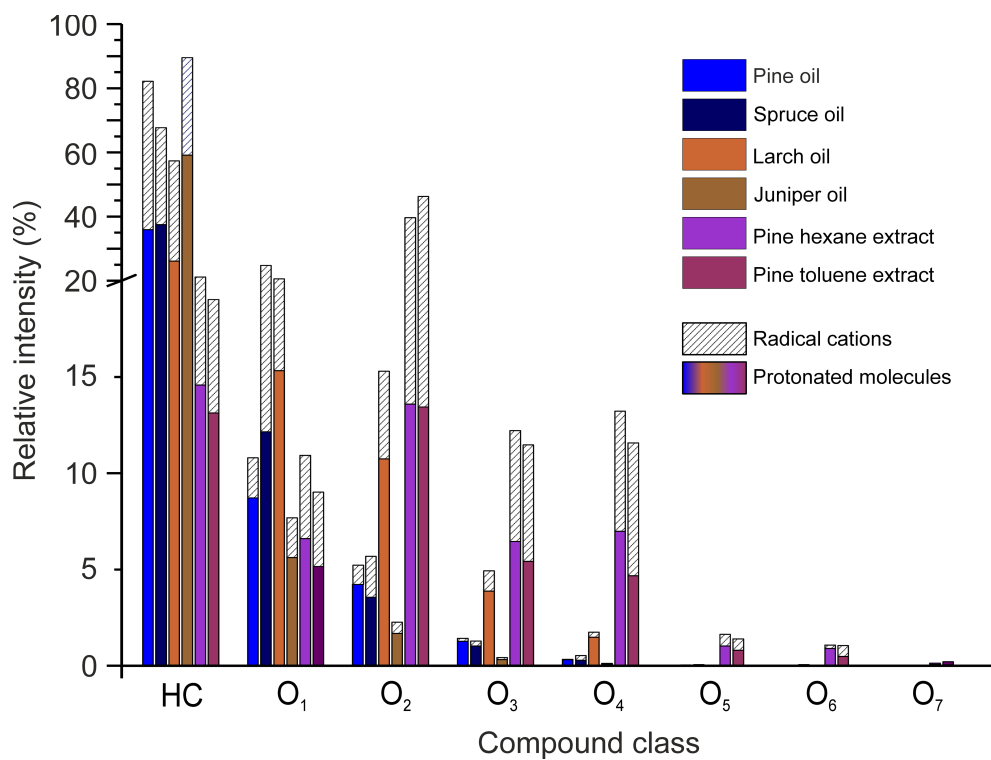


Figure S2. Positive-ion APPI compound class distributions of conifer needle essential oils and solvent extracts.