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Alexis St-Gelais
Laboratoire Phytochemia, 628, boulevard du Saguenay Ouest, Saguenay (Chicoutimi), QC, Canada

Guy Collin
Département des sciences fondamentales, Université du Québec à Chicoutimi, 555 boul. de l'Université, Saguenay (Chicoutimi), QC, Canada

Johanna Helbig
Coastal First Nations / Great Bear Initiative, Granville Street, Vancouver, BC, Canada

Hélène Gagnon
Département des sciences fondamentales, Université du Québec à Chicoutimi, 555 boul. de l'Université, Saguenay (Chicoutimi), QC, Canada

Correspondence
Guy Collin
Département des sciences fondamentales, Université du Québec à Chicoutimi, 555 boul. de l'Université, Saguenay (Chicoutimi), QC, Canada

Essential oils from the foliage of *Picea sitchensis* from British Columbia

Alexis St-Gelais, Guy Collin, Johanna Helbig and Hélène Gagnon

Abstract
Several essential oil samples of *Picea sitchensis*, Sitka spruce, needles were obtained from local producers in three different regions of British Columbia. They were analyzed by capillary GC and GC / MS techniques. These samples mainly contain monoterpenes (70 ± 10%) including Myrcene (12 - 33%) and β-phellandrene (16 - 35%). They also contain a variety of aliphatic and aromatic esters of saturated and unsaturated alcohols. It should be noted in particular the presence of isoamyl (0.8 - 6.4%) and 3-methyl-3-buten-1-yl (0 - 5.3%) isovalerates. These two esters make it possible to verify whether certain Sitka spruce populations have been "contaminated" byintrogression with white spruce populations. This seems to be the case for one of the samples collected in the Bella Coola Valley area, unlike those harvested in the Kitimaat area or on Graham Island.

Keywords: *Picea sitchensis*, *Pinaceae*, Sitka spruce, needle oil, monoterpenes, myrcene, β-phellandrene, aliphatic esters, Isovalerates

1. Introduction
Picea sitchensis (Bong.) Carr. Sitka spruce, a member of the Pinaceae family, is a large tree found mainly along the Pacific coast of Canada and the US from Northwestern California to the South coast of Alaska [1]. It is a very large tree; some "*may commonly reach a heigh of 70 m and diameter of 300 cm*" [2]. β-Phellandrene and β-pinene were identified as major compounds of the oil, many years ago [3]. Oils from10 populations of this tree species were collected in British Columbia and studied a long time ago by von Rudloff [4-5].The main identified compounds in the leaves were hydrogenated as well oxygenated monoterpenes and some C_5isovalerates and monoterpenyl esters.
We recently had the opportunity to get several samples of this oil from local producers. The dual goal of the present study were to: i) check the composition of the oil with available analytical modern devices and ii) see if, as mentioned by von Rudloff, there was "*possible introgression of Sitka and white spruce*" [5].

2. Material and methods
2.1 Isolation of the essential oil
Foliage was collected in several places. First, near the village of Old Massetton Graham Island, Haida Gwaii, (decimal latitude: 54.04°and longitude: -132.19°).Two samples come from Kitamaat Village (53.98° and longitude: -128.64°),close to the town of Kitimat and two more samples, D and E, Table 2, from the Bella Coola valley (latitude: 52.37° and longitude: -126.76°), in coastal British Columbia (Figure1). Typical quantities of 100 kg of foliage were steam-distilled with vapor for 90 minutes, 24 hours after or sooner after their collection. In a typical run, the measured essential oilyield appeared to be 0.053% (vol/weight) in agreement with a reported value [3]: 0.059%, but smaller than that reported elsewhere [4]: 0.36%.

2.2 GC/FID and GC/MS analyses
GC/FID and GC/MS analyses were carried out on a Hewlett-Packard 5890 gas chromatograph fitted with a non-polar DB-5 capillary column and a polar Supelcowax 10 column (30 m × 0.25 mm; film thickness 0.25 µm). GC/MS analyses were performed on HP 5972 mass spectrometer at 70 eV coupled to an HP 5890 GC, equipped either with a non-polar DB-5 column or a polar Supelcowax-10 column (same as above). Temperature programming for both the GC and GC/MS is 40 °C for 2 min, then 2 °C/min to 210 °C and held constant for 33 min. Identification of the components was done by comparison to their retention indices,

with available standards and by a comparison of their mass spectra with literature values[6-9]. Quantitative data were obtained electronically from GC/FID peak area percentages.

In order to discriminate between the 3-methyl-3-buten-1-yl and 4-penten-1-yl hexanoate and octanoate the synthesis of these four moleculeswas undertaken. About 10 mg of DMAP (dimethylaminopyridine) and 15 mg of EDC (*N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride) were dissolved in 500 µL of ACS dichloromethane, to which was added a drop of the alcohol and the respective acid. After one night, the solution was injected onto GC-MS without further treatment.

3. Results and Discussion

3.1 Composition of the essential oil

The composition of the *Picea sitchensis* oil is characterized by a high percentage of monoterpenes. Table 1 gives the main compounds with percentages higher than 1%. These values are compared with the same obtained by Von Rudloff [4,5].Myrcene and β-phellandrene are by far the main compounds of the essential oil although the percentages present large variations from one sample to another: ~34 ± 7%. In the Von Rudloff's papers, Piperitone is the second more important compound: 19.3 to 23.2%. In the present study, Piperitone accounts for 12.5 ± 3.5%. The situation is the reverse for camphor. Our value shows an important difference: 3.5 ± 2.3% against 11 -17%. Isopentyl and 3-methyl-3-buten-1-yl isovalerates, two uncommon compounds in essential oils, are noteworthy. They have similar percentages, at least when looking at our maximum values: around 6 and 5%, respectively. The essential oil composition obtained in the different regions of British Colombia [5] as well as the location of the needles on the trees and the seasonal variations [10] show large variations in concentration. The myrcene percentage decreases significantly between April and October, from 93 to 35% [5]. Those of β-phellandrene and Piperitone do the reverse: from 1 to 15% and 0 to 18%, respectively, much less than what we observe. Thus, at first glance, the percentages observed in the present study are roughly in line with other published values. The two samples from Kitimaat Village have compositions within the described limits shown in Table 1.

A more detailed analysis appears in Table 2 and Figure 2. More than 100 compounds are identified. Monoterpene molecules are the main constituents: between 68 and 80%. Myrcene and β-phellandrene form almost 50% of the oil.α-Pinene (7 - 11%), β-pinene (4 - 7%) and limonene (4 - 5%) are important compounds. In the oxygenated monoterpenes, one has to mention the presence of camphor (1 -2%) and more particularly Piperitone (3 - 9%).Thirty compounds accounting for *ca* 84 ± 5% of the total were previously detected (Table 2) by Von Rudl off [4, 5]. The main sesquiterpene is δ-cadinene and the main diterpene is 13-epi-manool (Table 2). As such, they do not need more discussion.

3.2 Discussion

More interesting is the presence of a several saturated and unsaturated aliphatic, as well as aromatic, esters. The two most important are isoamyl isovalerate (2.3 - 3.7%) and 3-methyl-3-buten-1-y isovalerate (1.6 - 3.3%). Both compounds were observed by Von Rudl off [4, 5]. The first one is rather common, but not the second one. Both molecules are reported in the oil of two Cupressaceae: *Chamaecyparis nootkatensis* [11] and *Juniperus communis* [12]. Isobutyl 2-methylbutyrate, Isopentyl butyrate, isovalerate, hexanoate, and octanoate are well known esters. However, to the knowledge of the authors they have not yet been associated with any member of the *Picea* family. Some others are relatively uncommon.3-Methyl-2-buten-1-yl valerateis observed either in the berries or the needles of *Juniperus communis* growing in Estonia and in Kosovo [13].Isopentyl 3-methyl-2-butenoate (senecioate) is observed in a few natural extracts extract [14]. The oil from the fruits of *Morinda citrifolia* contains 3-methyl-2-buten-1-yl (prenyl) hexanoate and octanoate; both of which are rather uncommon compounds [15]. Apart from Isopentyl benzoate, several uncommon aromatic esters are also observed in the *P. sitchensis* oil. For example, 3-methyl-3-buten-1-yl benzoate was observed in the needle extract of *Picea orientalis* [16], and the ylang-ylang [17] and Anibarosa eodora [18] essential oils. Isopentyl dihydro cinnamate (benzenepropanoate) is observed in the essential oil of *Achillea eriophora* from Iran [19] and 3-methyl-2-buten-1-yl dihydro cinnamate was synthesized [20]. To our knowledge, this is the first report of the latter in a natural extract.(*E*)-Isoamyl cinnamate is observed in the essential oils of the Douglas fir headspace samples (*Pseudotsuga menziesii*- 1.14%)[21]and in the rhizomes of *Alpiniasmithiae* (7.2%)[22]. (*E*)-3-Methyl-3-buten-1-yl cinnamate has only one reference in the Sci Finder database: it contains its mass spectrum. It is observed in the ripe fruit *Pandanus tectorius* [23]. Dihydrocinnamyl isovalerate was observed in the volatiles of *Pleurospermumaustriacum* [24]. Finally, dihydrocinnamyl (phenylpropyl) pentanoate is identified in the peel of jackfruit (*Artocarpus heterophyllus*) and in the leaves of *Vernonia arborea*. Unfortunately, in both cases, the given relative orders of elution (the relative retention times on the non-polar DB-5 column) have no rational values in the retention index system and do not correspond to the RI values given in ref. [6a].The peak (RI (DB-5) = 1615) gives a poor fit (724/1000) for cyclopentyl dihydro cinnamate, a compound not yet reported as a natural product. The spectrum shows a parent peak at 218 (Figure 4). Moreover, it shows the main three peaks (*m/z* = 91, 104, and 150) in the mass spectrum of dihydro cinnamic acid. The synthetic 3-methyl-3-buten-1-yl ester has the same mass spectrum observed in the oil (Figure 4). This would be the first mention of this compound as a natural compound.

A few compounds are not identified at all. They appear with measured RI (DB-5) values of 1335, 1603, 1604, and 1610. The only reliable information is the observed MS fit of 842/1000 for the dihydrocinnamyl isovalerate (Figure 5). Its RI (DB-5) value is in agreement with the one reported in literature [25, 26].

Finally, from the oil composition, the concentration of isopentyl and 3-methyl-3-buten-1-yl isovalerates, there is an apparent introgression of the tested populations with white spruce [5]. From the known spatial distribution, there is no white spruce on Graham Island. Kitimaat village also seems out of the white spruce, *Picea Glauca*, habitat range, which reaches from the Atlantic coast to the East of the Rocky Mountains in Western Canada. Apparently, the situation seems different for the sample appearing in the last column of Table 1. A possible introgression of Sitka and white spruce cannot be excluded for this sample [5].

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Declaration of interest

No potential conflict of interest was reported by the authors.

Table 1: The main compounds (percentage higher than 1%) observed in 13 samples[a] of the leaf essential oil of *P. sitchensis*.

1		**Mean**	**Min.**	**Max.**	**Std. Dev.**	**Ref. [4]** [b]	**Ref. [5]** [b]
2	**Refractive index**	1.4725	1.4715	1.4845	0.0030	1.4735	-
3	**Compound**						
4	α-Pinene	7.4	2.9	11.5	2.6	1.5	1.6
5	Camphene	1.0	0.0	1.6	0.9	1.7	2.1
6	β-Pinene	5.6	2.9	9.8	2.1	0.8	0.7
7	Myrcene	23.1	12.1	33.3	5.8	23.5	27.3
8	δ-3-Carene	2.9	0.0	5.9	2.1	0.6	0.6
9	Limonene	4.5	1.3	9.9	2.4	0.9	3.6
10	β-Phellandrene	a21.1[c]	15.5	35.6[c]	7.1	4.1	4.7
11	1,8-Cineole (N= 6 samples)	1.3	1.2	1.8	0.4	3.0	3.2
12	Isoamyl isovalerate	3.4	0.8	6.4	1.5	5.5	7.7
	Terpinolene	0.9_5	0.0	1.7	0.4		0.5z
13	3-Methyl-3-buten-1-yl isovalerate	2.3_5	0.0	5.3	1.3	5.3[d]	4.7[d]
14	Camphor	2.2_5	0.0	3.5	1.0	17.2	11.4
15	Borneol	0.7	0.0	1.8	0.5	1.1	1.7
16	α-Terpineol	0.63	0.0	1.0	0.26		2.4
17	Piperitone	7.0	0.5	12.5	3.3	23.2	19.3
18	δ-Cadinene	1.3	0.3	4.2	1.0	-	-
19	(13-epi-?)Manool	1.7	0.3	3.3	1.0	-	-

[a]: The last sample E in Table 2 is included in this Table; [b]: these samples also contains bornyl acetate (1.8% and 0.7%, respectively); [c]: This higher value includes 1,8-cineole.Both compounds have very similar RI values on both columns and, at high percentages, they are not properly separated; [d]: identified as isopentenyl isovalerate in ref [5].

Table 2: Composition (%) of the essential oil of *P. sitchensis*

	Compounds	**RI**[1]	**RI**[2] (ref. [7], ref. [8])	**RIp**[3] Swax-10	**Samples**				
					A	**B**	**C**	**D**	**E**
1	Hexanal	796	801, 801	1092				tr	tr
2	Octane	800	800, -	800				tr	tr
3	(*E*)-2-Hexenal *	839	855, 851	1224	tr				
4	(*Z*)-3-Hexen-1-ol	841	859, 851	1352	0.0_5				
5	Santene *	870	888, 884	1002	0.0_5	0.1	0.0_5	0.1	0.05
6	Styrene #	874	885 ± 20 [6a]	1214	tr			0.3	0.3
7	Heptanal	883	902, 902	1140	tr			tr	tr
8	Tricyclene *	906	926, 921	1006	0.1	0.4	0.0_5	0.1	0.0_5
9	α-Thujene	913	930, 926	1001	0.0_5	0.1	0.2	0.3	0.6
10	α-Pinene *	919	939, 932	1016	7.1	10.8	6.3	10.5	18.6
11	α-Fenchene	933	952, 945	1022	tr			tr	tr
12	Camphene*	935	954, 947	1045	1.6	0.7	0.7	1.0	0.4
13	Thuja-2,4(10)-diene	941	960, 943	1107				tr	tr
14	Benzaldehyde	946	960, 958	1494	tr			0.2	
15	Sabinene *	965	975, 973	1097	0.4	1.3	0.8	0.9	1.8
16	β–Pinene *	967	979, 975	1081	4.1	7.2	4.8	7.2	14.9
17	Myrcene *	990	990, 991	1151	32.2	18.7	23.4	21.0	10.2
18	α-Phellandrene*	1002	1002, 1004	1144	0.8	0.7	0.9	0.8	0.2
19	Isobutyl 2-methylbutyrate	1002	1008 ± 6 [6a]	1149	1.0				
20	δ-3-Carene *	1007	1011, 1010	1126	0.1	5.8	5.8	4.6	5.9
21	α-Terpinene *	1013	1017, 1017	1162	0.3	0.5	0.4	0.5	0.6
22	*p*-Cymene	1021	1024, 1024	1246	0.8	0.8	1.1	0.6	0.8
23	Limonene *	1025	1029, 1028	1184	3.7	4.8	3.3	4.0	3.7
24	β-Phellandrene *	1031	1029, 1028	1190	16.4	26.1	19.0	23.1	29.0
25	1,8-Cineole *	1027	1031, 1031	1188	1.2	tr	0.5		
26	*cis*-β-Ocimene *	1037	1037, 1038	1220	tr		tr	tr	
27	*trans*-β-Ocimene *	1047	1050, 1048	1234	0.0_5		0.0_5	tr	
28	γ-Terpinene *	1055	1059, 1058	1223	0.2	0.7	0.5	0.6	1.0
29	Isopentylbutyrate	1055	1058, 1057 ± 3 [6a]	1248	0.3	0.1	0.2		
30	3-Methyl-3-buten-1-yl butanoate	1065	1067[15]	1319[15]	0.1	tr	tr		

31	Isoterpinolene	1083	1088, 1086	1256					tr
32	Terpinolene*	1084	1088, 1088	1256	0.5	1.7	1.7	1.6	2.5
33	Fenchone	1086	1086, 1088	1371				0.1	
34	*p*-Cymenene	1088	1091, 1089	1393	tr	tr	0.1	0.1	0.1
35	Linalool *	1099	1096, 1100	1543	0.1	0.2	0.3	0.5	0.2
36	α-Thujone	1101	1102, 1106	1400	0.5	0.4		0.1	0.7
37	Nonanal	1102	1100, 1105	1391	0.1	tr	0.0_5		
38	Isoamyl isovalerate *	1105	1103, 1106	1277	3.7	2.3	3.3	2.3	0.2
39	Fenchol (endo/exo)	1109	1116/1121	1569	0.2	0.3	0.1	0.4	
40	β-Thujone	1112	1114, 1117	1417					0.1
41	3-Methyl-3-buten-1-yl isovalerate *	1116	1114, 1118 and [12]	1422[12]	3.3	1.6	1.8	1.5	
42	*trans*-*p*-Mentha-2,8-dien-1-ol	1116	1122, 1121	1608					0.1
43	*cis*-*p*-Menth-2-en-1-ol	1117	1118, 1121	1549	tr		tr	0.4	
44	*trans*-Pinocarveol	1134	1139, 1138	1637				0.0_5	0.1
45	*trans*-*p*-Menth-2-en-1-ol	1135	1140, 1141	1612	0.2			0.2	
46	Camphor *	1137	1146, 1144	1478	2.1	0.7	2.2		0.4
47	Prenyl pentanoate	1149	1132 [12], 1134 [13]	1450 [12]	0.4	0.1	0.2		
48	Camphene hydrate	1151	1149, 1148	1571				0.2	0.0_5
49	6-Hydroxymyrcene	1155	1146, 1161 [28]		tr		tr		
50	Borneol *	1161	1169, 1166	1670	0.8	0.1	0.3	0.6	0.5
51	Terpinen-4-ol *	1173	1177, 1177	1581	0.2	0.1	0.4	0.6	1.1
52	Cryptone	1179	1185, 1187	1650	0.1	0.6	0.2	0.0_5	0.1
53	*p*-Cymen-8-ol	1183	1182, 1186	1830	0.1	tr	0.1	0.1	
54	Isopentyl 3-methyl-2-butenoate	1183	1184 [14], 1185	1462	tr		0.1		
55	α-Terpineol *	1188	1188, 1191	1678	0.5	0.2	0.5	0.7	0.3
56	Myrtenal	1190	1195, 1195	1593					0.1
57	*cis*-Piperitol *	1192	1196, 1195		0.1	0.1	0.1		
58	*trans*-Piperitol	1205	1208, 1207	1711	0.1	0.0_5	0.1	0.1	
59	Citronellol *	1230	1225, 1229	1749	0.2	0.1	0.1	0.2	
60	Methyl thymol	1234	1235, 1236	1576	tr	0.3	0.3	0.1	0.1
61	Cuminaldehyde	1234	1241, 1241	1750	0.1	0.2	tr		
62	Piperitone *	1249	1252, 1255	1662	8.8	2.9	7.9	4.4	0.5
63	Isopentyl hexanoate	1252	1249, 1251	1456	0.3	0.2	0.4_5	0.2	
64	3-Methyl-3-buten-1-yl hexanoate	1263	1241 [18], 1239[30]1261[16]	1511[16]	0.3	0.2	0.3		
65	*p*-Menth-1-en-7-al	1269	1275, 1276	1700 10 [6a]	0.1	0.2			
66	Bornylacetate *	1283	1285, 1287	1549	0.2	0.2	0.6	0.3	0.1_5
67	*p*-Cymen-7-ol = cuminol	1289	1290, 1293	2056	tr				
68	2-Undecanone	1294	1293, -	1602	tr		tr		
69	Thymol	1296	1290, 1292	2170	tr		tr		
70	Prenyl hexanoate	1298	1292, 1296 [16]	2205	0.1				
71	Carvacrol	1305	1299, 1302	2205	tr		0.0_5		
72	Methyl geranate	1328	1324, -	1692			0.1		
73	Methyl decanoate	1328	1325, -	1578			0.1		
74	Unidentified	1335					0.1		
75	α-Cubebene	1348	1351, 1351	1441			0.0_5	0.0_5	0.1
76	α-Longipinene	1352	1352, 1352	1447	0.1		tr		0.1
77	Nerylacetate	1364	1361, 1366	1711	0.1		0.1		
78	Dihydrocinnamylacetate	1370	1368, -				tr		
79	α-Copaene	1373	1374, 1378	1472			0.1	0.2	0.2
80	Geranylacetate*	1383	1381, 1385	1738	tr	tr	0.3		
81	Longifolene	1398	1407, 1408	1540	0.1	0.1	0.4	0.1	
82	β-Caryophyllene	1414	1419, 1422	1568	0.1	tr	tr	tr	0.0_5
83	*cis*-Muurola-3,5-diene		1450, 1448					tr	0.1
84	3-Methylbutyl benzoate	1437	1435, 1438	1891	0.3	0.1		0.0_5	
85	3-Methyl-3-buten-1-yl benzoate	1442	1449 [17], -	1969	0.2	tr			
86	α-Humulene	1449	1454, 1456	1642	tr				0.0_5
87	Isoamyl octanoate	1452	1445, 1447±2 [6a]	1651	0.2	0.1	0.5	0.0_5	
88	(*E*)-β-Farnesene	1458	1456, 1458	1658	tr	tr	0.1_5		
89	3-Methyl-3-buten-1-yl octanoate	1464	1442 [29], 1451[15]	1726	0.1		tr		
90	*cis*-Muurola-4(14),5-diene	1466	1466, 1465						0.1
91	*trans*-Cadina-1(6),4-diene	1471	1475, 1476	1639			0.1		0.0_5
92	γ-Muurolene	1474	1479, 1480	1654		0.2	0.1	0.1	0.1
93	Germacrene D	1478	1481, 1484	1681		0.1	0.1	0.0_5	tr
94	β-Selinene	1482	1490, 1488	1692		0.1	0.1		
95	α-Selinene	1492	1498, 1496	1698					0.0_5
96	(*Z*,*E*)-α-Farnesene	1497	1505, 1510	1706	0.1	tr			
97	3-Methyl-2-buten-1-yl octanoate	1499	1480 [15]	1763 [15]	0.1	0.2			
98	α-Muurolene	1499	1500, 1502	1711	0.1	0.2	0.3	0.2	0.2

99	2-Tridecanone	1499	1496, -	1796	0.1		0.1		
100	γ-Cadinene	1511	1513, 1517	1724	0.2	0.9	0.5	0.5_5	0.5
101	(*E*)-Calamenene	1522	1522, 1524	1797		tr	tr	tr	tr
102	δ-Cadinene	1522	1523, 1527	1724	0.5	1.9	1.1	1.3	1.3
103	*trans*-Cadina-1,4-diene	1530	1534, 1536	1771	tr		tr	0.0_5	
104	(*E*)-γ-Bisabolene	1531	1531, 1534	1756	0.1	0.0_5			
105	α-Cadinene	1534	1538, 1541	1726			0.0_5	0.0_5	tr
106	(*E*)-α-Bisabolene	1543	1540±4 [6a], 1545	1754	tr	tr	tr		
107	*trans*-Nerolidol	1563	1563, 1535	2022	0.1	0.1	0.2		
108	3-Hexenyl benzoate-(Z)	1574	1566, 1572	2110	tr	0.5			
109	Isoamyldihydrocinnamate	1598	1593 [19]	2074	0.1	tr	0.1		
110	Phenylpropyl isovalerate : see Fig. 4	1604	1613 [24]	2080	tr		0.1		
111	3-Methyl-3-buten-1-yl dihydrocinnamate: see Fig. 5	1615			0.1		tr		
112	τ-Cadinol	1637	1640, 1643	2131	tr	0.1	0.0_5	0.0_5	tr
113	τ-Muurolol	1637	1642, 1644	2147	tr	0.1	0.0_5	0.0_5	
114	α-Muurolol	1642	1646, -						tr
115	α-Cadinol	1650	1654, 1658	2181	0.1	0.2	0.1	0.1	0.0_5
116	Prenyldihydrocinnamate	1651			tr				
117	α-Bisabolol	1681	1685, 1688	2199	tr	0.1			
118	(Z)-5-Tetradecen-14-olide	1716		2143	0.1	0.1	0.05		
119	(*E*)-Isoamyl cinnamate	1736	1740, 1736 [22]	2310 ±20	0.1	tr	tr		
120	3-Methyl-3-buten-1-yl cinnamate	1744	1758 [6a],1747[23]	2400 ± 20	0.1	tr	tr		
121	Cembrene	1921	1938, 1937	2125	0.2	0.2	0.2	0.4	0.2
122	*m*-Camphorene	1948	1947 [9], 1953	2179	0.1		0.1		
123	Manooloxide	1976	1987, 1992	2436	0.2	tr			
124	*p*-Camphorene	1981	1980 [9], 1988	2241	tr				
125	13-epi-Manool oxide (isomer)	**1996**	2010, 2014	2296	0.2				
126	8,13-Abietadiene	2035	2035 [6a], -	2239		0.2			tr
127	Unidentified	2037			0.1	0.1		0.1	
128	Manool	2042	2057, 2057					0.5	0.05
129	13-epi-Manool	2042	2060, -	2620	2.4	0.3	1.3		
130	7,13-Abietadiene	2080	2087, 2083	2345		0.1	0.0_5		
131	Phytol	2108	2115 [6a], 2113	2606			0.0_5		
	Monoterpenes				68.5	80.4	69.1	77.2	90.4
	Oxygenatedmonoterpenes				14.6	6.8	14.4	9.1	4.5
	Aliphatic and aromatic esters				10.9	5.4	7.0	6.9	0.2
	Sesquiterpenes				1.3	3.6	3.1	2.9	2.9
	Total (%)				99.9	97.6	96.0	94.6	98.6

*: Compounds previously reported in ref [3] and[4]; tr : trace of compound identified by MS only, < 0.05%; #: probably an artefact;
[1]: RI calculated on the a-polar DB-5 column; [2]: RI from ref [7] and [8] unless otherwise indicated; [3]: R.I. calculated on the polar Swax-10.

Fig 1: Locations of collected samples

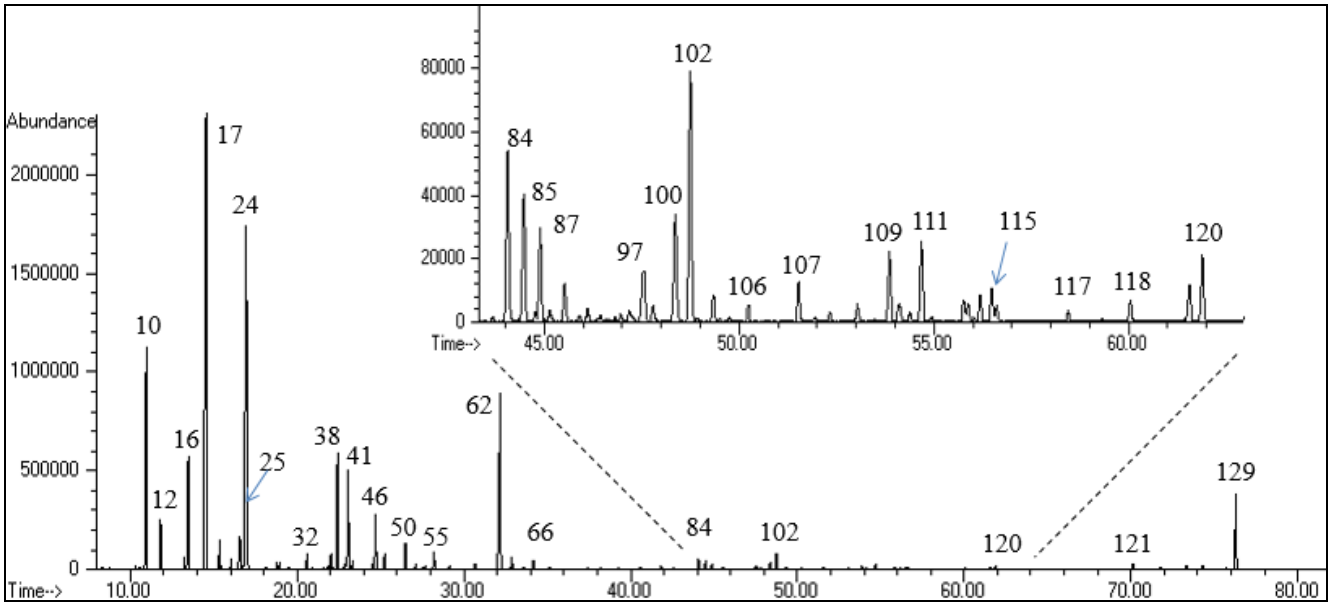

Fig 2: Total ion current of the MS of the *P. sitchensis* essential oil. Sample Ain Table 2. Numbers: see first column of Table 2.

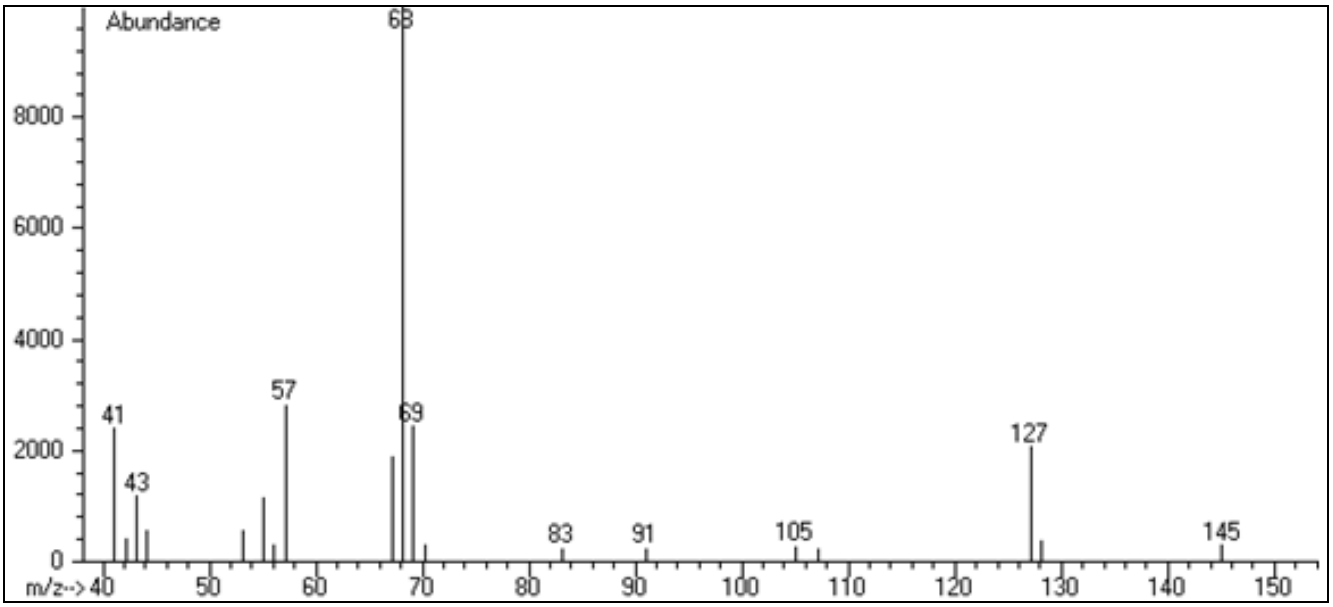

Fig 3: Mass spectrum of3-methyl-3-buten-1-yl octanoate: RI(DB-5) = 1464 in Table 2.

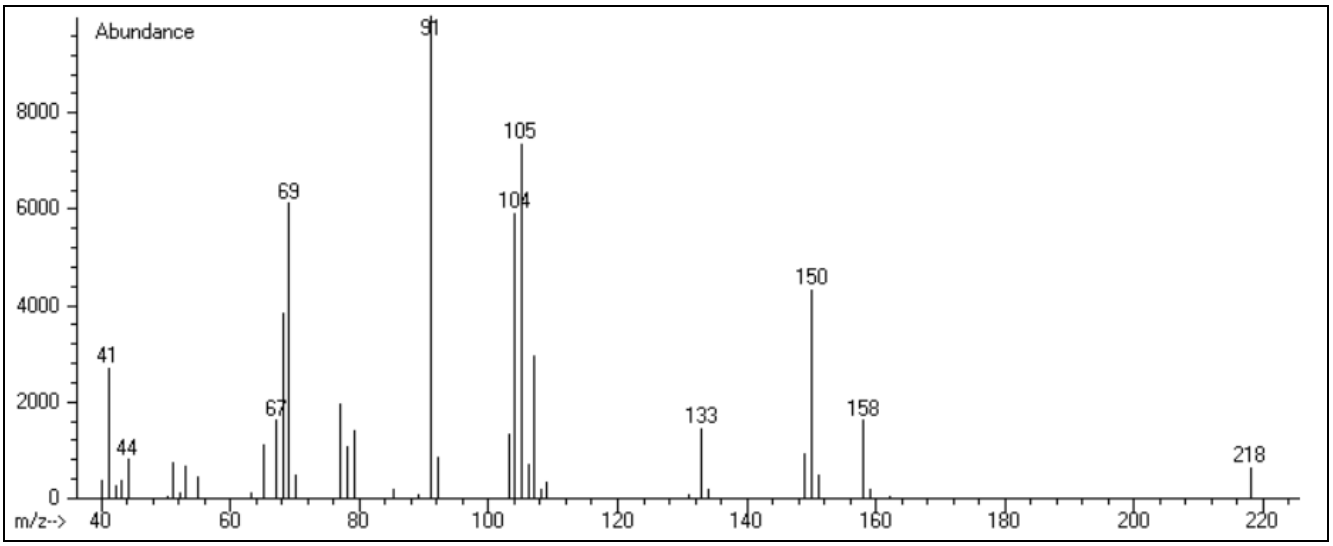

Fig 4: Unidentified compound: RI (DB-5) = 1615 in Table 2.

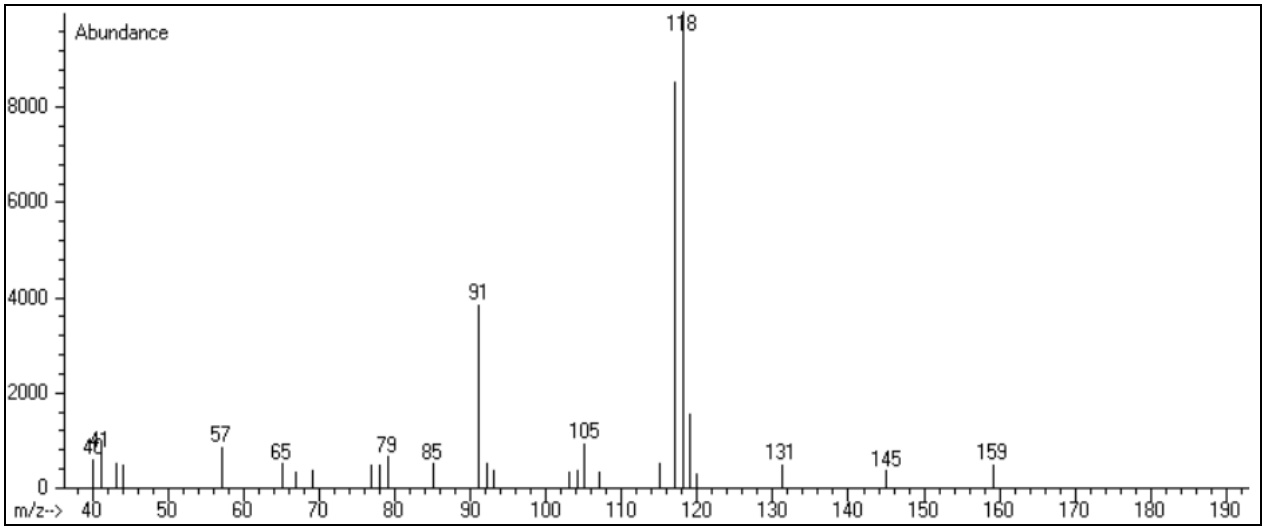

Fig 5: Proposed hydrocinnamyl isovalerate mass spectrum RI (DB-5) = 1604 in Table 2: see text.

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