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Aromas from Quebec. IV. Chemical composition of the essential oil of *Ledum groenlandicum*: A review

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Abstract

Limonene and β -selinene are the most important compounds of the essential oil of the aerial parts of *Ledum groenlandicum*. However there are important variations either in the composition or in the relative percentages between the twelve analyzed commercial samples. Uncommon or rare compounds such as hydroperoxides and *p*-mentha-1,8(10)-dien-9-yl esters are observed in one and two samples, respectively. Germacrone, a reputed compound of this oil, is not ever present in the samples. Germacrone epoxides observed in a sample containing almost 30% of germacrone could be the results of an oxidation process. Short comparison with the composition of the *Ledumpalustre* oil is made. In both cases, equally large variation in composition is observed.

Keywords: *Ledum groenlandicum*, *Rhododendron groenlandicum*, essential oil composition, limonene, β -selinene, germacrone

1. Introduction

Rhododendron groenlandicum (Oeder) Kron and Judd (old: *Ledum groenlandicum* Retzius, Labrador tea), Ericaceae, is present on a large northern part of the North American continent from Greenland to Alaska. It is found in most parts of the territory of Canada and in several states in the north of the United States. It is a subshrub to erect port top tens of centimeters but can, in good growing conditions, form bushes up to 1.50 m in height. This plant is so strongly impregnated of resinous molecules that it is practically rot-proof^[1]. The plant is used in different forms in the Native American pharmacopoeia, for example, in the treatment of respiratory diseases^[2]. Dried leaves are used in several recipes and their infusion is commonly used in this Province.

Three years ago, B. Lawrence produced a review on the composition of the Labrador tea oil^[3]. The analyzed samples have different origin: Finland, Ontario and Quebec Provinces from Canada and a commercial sample from unknown geographical origin. The results show important variations in the composition. Very recently, a review appears on Labrador tea. This paper discusses the ethno medicinal application of *Rhododendron tomentosum*, *R. groenlandicum* and *R. neoglandulosum* and identifies commercial Labrador tea products available in the market (essentially from the Province of Quebec)^[4].

Since our first papers dealing with this subject^[5, 6], this laboratory analyzed numerous samples of the oil available on the market. We observed large variations in the composition of these samples. The main goal of this review is to shed light on the observed compositions of commercial samples.

2. Materials and methods

Essential oil samples: All the analyzed samples were obtained from various producers of this Province. They are the results of the hydrodiffusion process of the aerial parts of the plant.

GC-FID and GC-MS analysis: Samples were analyzed by gas chromatography on a HP 5890, equipped with a flame ionisation detector (GC-FID) and two capillary columns: a Supelcowax 10 and a DB-5 column (30 m \times 0.25 mm \times 0.25 μ m). Samples were also analyzed by gas chromatography, HP 5890, coupled with an HP 5972 mass spectrometer at 70 eV (GC/MS) and equipped either with a DB-5 or a Supelcowax column (same as above). Injection port and detector temperature are 220 and 260 $^{\circ}$ C, respectively. The temperature program for both GC-FID and GC/MS is 40 $^{\circ}$ C for 2 min, then 2 $^{\circ}$ C/min until 210 $^{\circ}$ C and

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held under constant temperature for 33 min. Identification of the components is done by comparison of their retention indices (RI) with standards, by comparison of their mass spectra with literature data [7, 8, 9] and with our own data bases. Quantitative data are obtained electronically from GC-FID area percentages. The FID response factors for compounds relative to tetradecane are taken as one.

3. Results & Discussion

The composition of the various essential oil samples appears in Table 1. From this table, more than one hundred and sixty compounds are unequally distributed among twelve samples. Several monoterpenes are common to all samples. They are sabinene, particularly in sample **E** (0.05-35%), β -pinene (0.05-8.4%), *p*-cymene (0.2-3.4%), and limonene, see sample **J** (0.3-67%). This last compound is by far the most important: five samples contain more than 10%. Camphene (max. 1.3%), α -terpinene (max. 2.3%), terpinolene (max. 1.5 %) are present in eleven over twelve samples.

There is a long list of oxygenated monoterpenes. Terpinen-4-ol (0.5-5.1%), myrtenal (0.3-3.8%), and bornyl acetate (0.3-8.4%) are common to all samples. *trans*-Pinocarveol (max. 2.3%) is missing in one sample. Two relatively uncommon compounds, isopiperitenol A and B are present in samples **B** and **C**. In this group of molecules, one should mention the presence of five menthadienhydroperoxides only in sample **F**, a sample rich in limonene and β -selinene. Their identification is based upon their mass spectra available in literature. These compounds were synthesized through the photosensitized oxidation of limonene [10, 11]. Not only the MS are very similar to those observed, the relative retention times as well as the relative quantities are also very similar. A sixth and minor compound may be imbedded in the last (*2S,4R*)-*p*-mentha-6,8-diene-2-hydroperoxide it was observed in the photosensitized oxidation synthesis [11]. The origin of these hydroperoxides must be addressed. These products were never present in any way in the lab. There is no indication of the presence of a photosensitized device in the factory. In a rose Bengal sensitized oxidation study, it was suggested that these hydroperoxides are involved in the formation *cis*- and *trans*-1,2-epoxylimonene as it is only observed in the sample **F** [12]. To our knowledge, these hydroperoxides with natural origin were reported only once in the diethyl ether extract of the aerial part of *Chenopodium ambrosoides* [13]. One of the six hydroperoxides, *p*-mentha-2,8-diene-1-hydroperoxide-(*1R,4R*), was observed in the essential oil of the fresh seeds of *Illicium wardii* collected in China. Unfortunately, the RI value measured for this compound on the DB-5 column does not agree with our value [14]. It was suggested that these hydroperoxides were formed through the singlet-oxygen oxidation of limonene. Such a mechanism would imply the presence in the plant molecules acting as photosensitizer [11, 12]. Finally, the formation of similar hydroperoxides could be active with other unsaturated compounds such as β -selinene, the main compound of sample **F** (see below). β -Costol, a compound observed in sample **F**, has been identified as the result of the photooxydation of β -selinene in the presence of rose Bengal [15].

A second group of uncommon esters, namely *p*-mentha-1,8(10)-dien-9-yl esters, appears in samples **I** and **L** (Table 1). Propanoate, 2- and 3-methylbutanoate were observed in dichloromethane extract of the fruits of *Citrus australasica* collected in Australia [16]. On the basis of the observed MS and the measured retention index values, the esters observed in this study could be isobutanoate, butanoate and 2- or 3-methylbutanoate.

Finally, 3,9-epoxy-*p*-mentha-1,8(10)-diene, is a very rare compounds compound reported in the oil of *Cymbopogon giganteus* [17]. It was well documented in the *L. palustre* oil [18, 19, 20, 21, 22]. To our knowledge, this is the first observation of this compound in *L. groenlandicum*.

Among the sesquiterpene hydrocarbon family, β -selinene (2.3-35.4%) particularly in sample **D** and α -selinene (0.3-9.9%) are the main compounds. β -Caryophyllene is also present in all samples from traces to 3.1%. β -Elemene (max. 1.6%) and δ -cadinene (max. 2.2%) are missing in one sample. β -Bisabolene (0-10.8%) and germacrene B (0-9.4%) are noticeable.

In the oxygenated sesquiterpene group, the only common compound to all samples is eudesma-3,11-dien-2-one (0.2-8.9%). However, germacrone, present in five samples over twelve, has a high percentage in sample **A**: 29.3%. The instability of germacrone in gas chromatographic analysis is well documented [23]. Under the effect of temperature, through Cope rearrangement, germacrone isomerize to *trans*-elemenone. The presence of 1,10- and 4,5-germacrone epoxides is interesting. These compounds were recently isolated from the oil of the aerial parts of *Geranium macrorrhizum* [23]. They are possibly the result of an oxidation process of germacrone [24, 25]. Finally, a MS very similar to that of (*E,E*)-germacrone is tentatively identified as a germacrone isomer. A similar peak was observed in another (*E,E*)-germacrone rich essential oil with very close RI on the a-polar column [26].

These last papers indicate several similarities and several differences between the oil compositions of *L. groenlandicum* and *L. palustre* (see Table 1). Among the similarities, great variability is observed in the percentages of several compounds such as limonene, *p*-cymene, sabinene, *cis*- and *trans*-*p*-mentha-1,7(8)-diene. 3-Thujen-10-al, a minor compound in the *L. groenlandicum* oil, has percentages between 0 and 17.1 % in the oil extracted from *L. palustre* [18]. Until new different observations are made, palustrol and ledol are among the very minor compounds (< 1%) in this Province in opposition to what is observed, for example in Lithuania (30 \pm 10% for each compound). Belousova *et al.* recognized three chemotypes among *L. palustre*: limonene, sabinene and *p*-cymene in various regions of Siberia [18]. From the results appearing in Table 1, one may infer the presence of at least four chemotypes: limonene, sabinene, β -selinene, β -bisabolene, probably also a limonene + β -selinene combination in the *L. groenlandicum* population of the Province of Quebec.

Table 1: Composition (%) of the essential of *L. groenlandicum* from the Quebec Province

	Compound	RI¹	RI²	A	B	C	D	E	F	G	H	I	J	K	L
1	Tricyclene*	928	1001	0.1	0.1		0.2	0.1			0.1	0.1		0.1	
2	α -Thujene*	935	1026	0.2	0.1	0.3	0.1	0.3		0.3	0.3	0.4	0.1	0.8	
3	α -Pinene*	940	1019	2.6	2.4		1.5	7.5		3.7	3.2	5.4	0.7	8.0	1.0
4	Thuja-2(4),10-diene	949	1135					0.1							
5	Camphene*	953	1057	0.5	0.5	0.7	1.3	1.4		0.8	0.7 ₅	1.3	0.2	1.1	0.5
6	Sabinene*	976	1122	2.6	3.1	7.3	2.1	35.0	0.1	8.3	4.3	17.4	1.9	22.5	0.8
7	β -Pinene*	977	1107	2.0	1.8	1.3	1.6	6.1	0.1	3.8	3.7	6.1	1.0	8.4	2.6
8	Myrcene*	992	1169	0.4			0.1	0.1	0.1	0.3	0.2	0.2	0.5	0.6	0.1
9	<i>p</i> -Mentha-1,5,8-triene	1000	1212	t ³	2.2	1.4	0.1	t		0.6	0.2	t	1.0	0.1	
10	α -Phellandrene*	1001	1164	t			0.2	0.1	t	0.1	0.2	0.2		0.3	0.1
11	α -Terpinene*	1017	1177	0.6	0.5	1.0	0.2	0.8		0.8	1.3	1.2	0.1	2.3	0.4
12	<i>p</i> -Cymene*	1026	1276	0.8	0.6	1.2	0.8	3.1	0.4	1.7	1.6	1.8	0.2	3.4	0.6
13	Menthatriene	1026	1208	0.1	4.0	2.4	0.2		0.2	1.3	0.3	0.1	1.9	0.1	
14	Limonene*	1031	1194	5.5	23.0	19.7	1.6	1.3	11.5	11.8	2.1	1.1	67.2	1.8	0.3
15	β -Phellandrene*	1031	1201	0.2	0.2	0.4	0.1	0.6	0.1	0.4	0.5	0.6		1.3	0.2
16	<i>cis</i> - β -Ocimene*	1046	1242	0.1	0.1		0.1	0.1		0.1	0.1	0.2	0.0 ₅	0.2	0.2
17	<i>trans</i> - β -Ocimene*	1058	1261	t			0.1			t	0.0 ₅				0.1
18	γ -Terpinene*	1067	1248		1.2	2.9	1.5	4.2		2.5	3.3	4.3	0.2	12.2	1.1
19	<i>cis</i> -Sabinene hydrate	1075	1466					0.1							
20	C ₁₀ H ₁₄	1076	1249	0.1			0.1								
21	Terpinolene*	1098	1288	0.3	0.3	0.5	0.2	0.4	-	0.4	0.7	0.6	0.1	1.5	0.2
22	<i>p</i> -Cymenene*	1098	1430	t	0.8	0.4	0.1	t	0.2	0.3	0.1		0.3		0.2
23	<i>trans</i> -Sabinene hydrate*	1109	1532					0.1							
24	Linalool*	1112	1557	t							0.1				0.1
25	Nonanal*	1117	1382	t			0.1	0.1							
26	Fenchol	1125	1592								0.4				
27	Dehydrosabina ketone*	1128	1593	t			0.1	0.7		0.7	t	0.3		0.2	0.2
28	<i>cis-p</i> -Menth-2-en-1-ol*	1128	1547					0.2			t				
29	<i>trans-p</i> -Mentha-2,8-dien-1-ol*	1128	1608		1.5	1.0	0.3	0.4	4.6		t		1.0	0.1	
30	<i>trans</i> -Sabinol	1139	1641					1.9							
31	<i>cis</i> -Limonene oxide	1140	1438						0.1						
32	α -Campholenal*	1142	1485				0.2								
33	<i>cis-p</i> -Mentha-2,8-dien-1-ol*	1142	1671	t	1.2	0.9	0.2	0.1	2.9	0.5			0.9		
34	<i>trans</i> -Limonene oxide	1143	1445						0.3						
35	<i>trans</i> -Pinocarveol*	1145	1648	0.6	1.1	0.8	2.3			1.1	1.2	1.0	0.2	0.6	1.1
36	Sabina ketone*	1151	1596	0.1			0.4	0.9		0.2	0.4	0.4	0.8	0.3	0.1
37	Pinocarvone*	1165	1556	0.1	0.4		1.9	1.3	0.2	0.3	0.3	0.5		0.4	0.4
38	Borneol*	1169	1698	0.1	0.3		0.2	t		0.1	0.1		0.2		0.1
39	Isopinocampone	1174	1515								0.1				
40	Terpinen-4-ol*	1179	1593	1.4	1.4	2.3	0.5	2.2	0.1	2.3	3.4	2.1	0.4	5.1	0.9
41	<i>p</i> -Methylacetophenone	1182	1767						0.1						
42	Thuj-3-en-10-al*	1182	1596	t	0.4		0.3	1.2		0.5	0.3	0.9	0.2	0.2	0.2
43	<i>p</i> -Cymen-8-ol*	1184	1821							0.1					
44	3,9-Epoxy- <i>p</i> -mentha-1,8(10)-diene*	1185	1543						0.2						
45	<i>trans-p</i> -Mentha-1(7),8-dien-2-ol*	1186	1800	0.1	6.4	3.5	0.8	0.1	7.0	2.3	0.5		2.7		
46	α -Terpineol*	1190	1698	0.1	0.2		t	0.1		0.2	0.3	0.1	0.1	0.3	0.2
47	Myrtenal*	1192	1594	0.5	1.5	1.3	3.8	1.7	0.3	1.9	2.0	2.5	0.3	1.1	4.3
48	Myrtenol*	1194	1770	t			0.5	0.5		0.5	0.4	0.4	0.1	0.3	0.3
49	<i>trans</i> -4-Caranone	1194	1599				0.3		1.0	0.1	0.1				
50	<i>cis</i> -4-Caranone	1196	1625				0.2	0.6	0.4		0.1				
51	IsopiperitenolA	1195	1745		1.4	1.7			3.1	0.9	0.1		1.5		
52	Dihydrocarveol ?	1196	1775		1.3	0.6									
53	IsopiperitenolB	1215	1745		1.9	0.2			1.2	0.2					
54	<i>trans</i> -Carveol*	1216	1832			0.6			1.4	0.4	0.1		0.6		
55	<i>cis-p</i> -Mentha-1(7),8-dien-2 ol*	1226	1887	0.1	6.2	3.1	0.7	0.1	6.9	2.1	0.4				
56	<i>cis</i> -Carveol	1230	1864						0.4	0.2	0.5				
57	Cumin aldehyde*	1229	1766	0.1	0.2		0.5	0.5	0.1	0.4		0.5		0.3	t
58	Carvotanacetone	1246	1649			1.0									
59	Carvone*	1230	1701	t	1.9		0.1	0.1	1.8	0.7	0.2		1.0		
60	Thymol methyl ether	1237	1592												0.2
61	Unidentified A	1239	1783	0.2											

62	<i>trans</i> -2-Decenal	1263	1665				0.1								
63	Perillaldehyde*	1276	1784		0.4		0.2		0.2	0.2	0.1				
64	Bornyl acetate*	1293	1573	1.2	1.1	1.4	8.4	2.5	0.4	1.6	1.8	2.4	0.3	1.9	1.9
65	<i>p</i> -Cymen-7-ol	1297	2066								0.1				
66	Carvacrol*	1310	2205				0.2	0.1							
67	(1 <i>S</i> ,4 <i>R</i>)- <i>p</i> -Mentha-2,8-diene-1-hydroperoxide	1317							1.5						
68	(1 <i>R</i> ,4 <i>R</i>)- <i>p</i> -Mentha-2,8-diene-1-hydroperoxide	1329							0.4						
69	Myrtenyl acetate	1331		t			0.2	0.3	0.1						
70	<i>p</i> -Mentha-1,4-dien-7-ol	1333	2041				0.1	0.4			0.2				
71	(2 <i>R</i> ,4 <i>R</i>)- <i>p</i> -Mentha-1(7),8-diene-2-hydroperoxide	1341							0.7						
72	δ -Elemene	1352	1458	0.1							0.2				0.3
73	α -Cubebene	1353	1444	t			0.1	0.1							0.1
74	Citronellyl acetate*	1360	1679	0.1			0.1				0.1				t
75	(2 <i>R</i> ,4 <i>R</i>)- <i>p</i> -Mentha-6,8-diene-2-hydroperoxide	1368							0.2						
76	cyclosativene	1368	1452												0.2
77	α -Copaene	1376	1489	0.2			0.1	0.4		0.2	0.5	0.3	0.0 ₅	0.3	0.8
78	(2 <i>S</i> ,4 <i>R</i>)- <i>p</i> -Mentha-1,7(8)-diene-2-hydroperoxide	1379							0.3						
79	β -Bourbonene	1382	1506				0.1								0.1
80	β -Cubebene	1387	1528	t			0.2	0.1							
81	Geranyl acetate*	1389	1768	0.1											0.1
82	β -Elemene	1390	1582	1.6	0.4	0.5			0.3	0.7	1.2	0.4	0.1	0.5	1.4
83	α -Gurjunene*	1403	1510	0.3		0.6		0.1		0.6	0.3	0.1	0.7	0.5	
84	β -Caryophyllene*	1415	1582	0.1	0.2	0.2	0.1		t	0.6	1.7	0.6	0.1	0.5	3.1
85	<i>cis</i> - α -Bergamotene	1415	1558								0.1				t
86	Unidentified B	1429									0.1				
87	γ -Elemene*	1433	1630	0.4							0.5				0.3
88	<i>trans</i> - α -Bergamotene	1439	1583								0.5				0.4
89	<i>cis</i> - β -Farnesene	1443													0.3
90	<i>trans</i> -Muurolo-3,5-diene	1449	1622				0.2		0.1						0.3
91	α -Humulene*	1453	1656	0.3	0.8	0.8				2.1	6.8		0.3	1.5	12.1
92	<i>allo</i> -Aromadendrene*	1462	1622	0.3			0.4	0.3	0.1	0.3	0.4	0.3	0.1	0.2	0.7
93	(<i>E</i>)- β -Farnesene	1462	1660	t	0.3					0.4	1.3	0.7			1.2
94	<i>trans</i> -Cadina-1(6),4-diene	1475	1639						0.3						0.5
95	Selina-4,7-diene	1476	1618		0.3					0.1	0.3				
96	Eudesma-2,4,11-triene	1476	1725	0.3			0.6	0.5	0.1	0.4	0.4	0.3			
97	γ -Muurolole*	1478	1661	0.3											0.5
98	Germacrene D	1483	1698	1.4	0.2	0.4	0.3		t	0.4	0.8	0.5	0.1	0.3	1.5
99	β -Selinene	1488	1706	7.4	11.1	11.4	35.4	3.9	20.3	11.5	7.1	10.6	2.3	8.1	2.8
100	<i>trans</i> -Muurolo-4(14),5-diene	1488	1740						0.2						
101	Bisabola-1,3,5,7(11)-tetraene	1490													0.2
102	Bicyclosesquiphellandrene	1492	1678				0.3	0.3			0.2				0.3
103	α -Selinene	1498	1712	9.9	3.1	4.3	0.3	1.1	2.2	4.4	4.6	3.7	1.3	4.5	2.5
104	<i>epi</i> -Cubebol	1498	1878				0.3								
105	Curzerene	1501	1861	0.7						0.2	0.2	0.2			2.8
106	α -Muurolole	1505	1714	t				t		0.3	0.4	0.1		0.4	0.2
107	Eudesma-2,4(15),11-triene	1504	1863	0.1					0.4						
108	Germacrene A	1507	1726	0.9					0.4	0.3	1.0	0.4			0.6
109	7- <i>epi</i> -Eremophila-1(10),8,11-triene	1507	1772				0.3	0.1	0.4		0.2	0.3	0.1	0.2	
110	β -Bisabolene	1513	1725	1.8		1.1			0.1	4.5	12.6	6.6	0.3	1.3	10.8
111	Cubebol	1516	1929				0.3	0.2							
112	7- <i>epi</i> - α -Selinene	1519	1734						0.1		0.2	0.2	0.1	0.2	0.2
113	γ -Cadinene*	1517	1748	0.2		0.5	0.3	0.1						0.1	0.1
114	δ -Cadinene*	1527	1749	1.1	0.3		1.7	0.9	0.1	0.9	1.6	1.3	0.3	0.7	2.2
115	<i>trans</i> -Calamenene*	1529	1816	t			0.1	t	t	0.1	0.2				0.4
116	Zonarene	1535	1745								0.4				0.5
117	<i>trans</i> -Cadina-1,4-diene	1535	1793				0.1	0.1				0.2			
118	<i>cis</i> -Calamenene*	1535	1829				0.1								
119	Selina-4(15),7(11)-diene	1538		0.3											0.6

120	α -Calacorene*	1543	1900	t				0.1				0.1		0.2		0.2
121	(E)- α -Bisabolene	1545	1723													0.9
122	Selina-3,7(11)-diene	1548	1762	0.3								0.3				0.6
123	Isozierene	1551	1830	0.5								0.5				
124	Germacrene B	1556	1805	8.9	1.0	1.3			0.1	1.8	4.9	1.8		0.3	9.4	
125	Palustrol*	1563	1906	t		0.6	0.4	0.6						0.3		
126	trans-Nerolidol	1565	2023									0.1				
127	Caryophyllene oxide*	1576	1943							0.1	0.1					0.3
128	p-Mentha-1,8(10)-dien-9-yl ester 1 ⁴	1578	1978										0.3			0.6
129	β -Copaen-4 α -ol	1579	2041	0.4				0.7				0.2				
130	p-Mentha-1,8(10)-dien-9-yl ester 2 ⁴	1588	1978										0.4			0.7
131	Viridiflorol*	1588	2067	0.4												
132	Ledol*	1597	1995	t				0.3								
133	trans-Elementone*	1599	2073	0.9												
134	Rosifoliol	1601	2106	1.3				0.5	4.3	0.3	0.8	0.5	1.0		0.7	0.3
135	Humulene epoxide II	1601	1982									0.3		0.1		0.7
136	β -Oplopenone*	1603						1.0					0.2			
137	UnidentifiedC	1605								0.3						
138	p-Mentha-1,8(10)-dien-9-yl ester 3 ⁴	1619	2027											0.3		0.6
139	1- <i>epi</i> -Cubenol*	1622	2048	t				0.1	0.1					0.4		
140	α -Corocalene	1627	1820					0.3	0.1							
141	γ -Eudesmol	1629	2138	0.2												
142	Cubenol	1637	2044	t				0.3	0.1							
143	S-Cadinol	1639	2144									0.1				
144	τ -Muurolool*	1639	2161									0.2				
145	β -Eudesmol	1644	2199					0.4	0.1							
146	α -Cadinol*	1650	2204	0.2								0.2				
147	α -Eudesmol	1650	2194					0.1	0.1							
148	Selin-11-en-4 α -ol	1652	2229	0.1												
149	UnidentifiedD	1663								0.8						
150	Germacrene-(Z,Z) ?	1667	2131	0.6												
151	Germacrene-4(15),5,10(14)-trien-1- ol?	1678	2185					1.7	0.1					0.7		
152	Unidentified E	1678	2195							1.2						
153	Unidentified F	1678	2360							1.2						
154	Atractylone ?	1688	2126	t				0.2						0.2		0.4
155	<i>epi</i> -Nootkatol?	1691	2188					1.0	0.1	1.4						
156	Juniper camphor	1692	2266	0.1												
157	(E,E)-Germacrene*	1694	2197	29.3							1.8	3.4	2.2	0.4	0.3	5.2
158	Nootkatol	1719	2249	t				2.1	0.5	2.0	0.3	0.2	0.4	0.1		
159	Cyclocolorenone*	1740	2255	0.2	1.9			0.2			1.0	0.2	2.2	0.8	0.3	
160	Cyclocolorenone(<i>epi</i> ?)*	1751	2325			1.0		3.0	0.2							
161	β -Costol	1761						t		0.6						
162	Eudesma-3,11-dien-2-one	1779	2469	0.8	0.9	1.0	3.5	0.3	8.9	1.3	0.4	1.7	0.1	0.7	0.2	
163	1,10-Germacrene epoxide ⁵	1824	2505	t												
164	4,5- Germacreneepoxide ⁵	1851	2569	0.1												
165	Unidentified G	2157	2577							1.8						
166	UnidentifiedH	2251	2711							1.0						
	Monoterpene hydrocarbons			16.1	40.9	39.5	12.2	61.2	12.7	37.2	23.0	41.0	75.4	64.7	8.5	
	Oxygenated monoterpenes			4.6	28.8	18.4	22.6	16.2	36.1	11.7	13.3	11.1	10.3	10.8	10.5	
	Sesquiterpene hydrocarbons			37.1	17.7	21.1	40.0	8.4	23.7	33.8	49.6	28.9	6.3	19.6	59.6	
	Oxygenated sesquiterpenes			34.6	2.8	2.0	12.8	9.8	15.7	5.2	5.7	8.7	1.5	2.0	8.1	
	Others (unidentified)			0.5		0.6	1.2	0.4	4.9	1.9	0.2	1.0				
	Total (%)			92.9	90.2	81.6	88.8	96.0	93.1	89.8	91.8	90.7	93.6	97.1	86.6	

¹: retention index on DB-5; ²: retention index on S-wax 10; ³: traces, < 0.05%; ⁴: **1**, **2** et **3**: these compounds could be esters of p-mentha-1,8(10)-dien-9-ol. **1**: isobutanoate, **2**: butanoate and **3**: 2- or 3-methylbutanoate; see text; ⁵: this compound was observed only between 30 and 60 min of the extraction time; *: compounds observed in the *L. palustre* oil, see ref. [18, 20, 21]; ?: need to be ascertained; Unidentified compounds (RI on DB-5; *m/e*(intensity): **A**: 1239; 93(100), **192**(96), 177(60), 121(46), 136(44)...; **B**: 1429; 93(100), 91(40), 119(36), 134(34), 105(32), 77(24), 41(18)...; **C**: 1605; 204(100), 207(77), 189(69), 135(59), 81(59), 43(47), 95(42)... **222**(4); **D**: 1663; 205(100), 43(26), 206(21), 107(20), 91(20), 93(18)... **220**(12); **E**: 1678; 107(100), 91(94), 93(87), 79(85), 105(76), 95(61)... **220**(37); **F**: 1678; 91(100); 121(92), 79(83), 93(81), 77(62), 105(61)... 218(53); **G**: 2157: **300**(100),107(38), 301(22), 91(20), 79(20)...; **H**: 2251; **300**(100), 107(44),301(24), 79(22),91(20)...

4. Conclusions

Thus, great variations appear in the composition of the essential oil of *L. groenlandicum*. For example, more than 20 years ago, this lab reported the drastic decrease of germacrone during the vegetative period, from 62.6% early in June to less than 1% after the beginning of July [3]. A similar study made on the oil of *L. palustre*, an oil containing palustrol + ledol (50 – 70%), shows lesser variations between April and October [22]. From what we know from the local producers, one can anticipate geographical effects and differences between in the used hydro diffusion processes. Finally, as far as the sample F is concerned, a note was indicated on the sample: oil was obtained from the “head” of the plant. Thus, one may infer that differences may also become from different parts of the plant as it was observed in Estonia [20].

Because several of chemicals identified in some samples have phytochemical properties a systematic research involving the above mentioned parameters is badly needed.

5. Disclosure Statement

The authors declare no competing conflict of interest.

6. Acknowledgment

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