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ESSENTIAL OILS OF *BACCHARIS SALICIFOLIA*, *B. LATIFOLIA* AND *B. DRACUNCULIFOLIA*

INGRID LOAYZA, DAVID ABUJDER, ROSEMARY ARANDA, JASMIN JAKUPOVIC,* GUY COLLIN,†‡ HÉLÈNE DESLAURIERS‡ and FRANCE-IDA JEAN‡

Programa Agroquimico "CORDECO-UMSS", Universidad Mayor de San Simón, Casilla 992, Cochabamba, Bolivia; * Institut für Organische Chemie, Technische Universität Berlin, D-1000, Berlin 12, Germany; ‡ Laboratoire d'Analyse et de Séparation des Essences Végétales, Université du Québec à Chicoutimi, Chicoutmi (Quebec), G7H 2B1 Canada

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Key Word Index—*Baccharis salicifolia*; *B. latifolia*; *B. dracunculifolia*; Compositae; verboccidentafuran; chromolaenin; germacrone.

Abstract—Samples of the essential oil from *Baccharis salicifolia*, four samples from *B. latifolia*, and one sample from *B. dracunculifolia* collected in the high valleys of Bolivia in the province of Cochabamba were analysed by a combination of gas chromatography and mass spectrometry. The identified products may be divided into four different groups: monoterpenes, oxygenated monoterpenes, sesquiterpenes, and various oxygenated sesquiterpenes such as germacrone and ledol. The latter compounds are characteristic constituents of the essential oils of *Ledum groenlanicum*. Rather unusual monooxygenated compounds with a cadinane structure were also detected, including verboccidentafuran, chromoleanin and related compounds.

INTRODUCTION

Baccharis (Compositae–Asteraceae) is a large genus of plants widely distributed from Mexico to Argentina. In Bolivia, *B. salicifolia* Pers. (local name: Chilca) can be found in the very high valleys at 2400–2800 m of altitude [1A]. *B. latifolia* (R. & P.) Pers. (local name: Yana chilka, Chilca negra) grows in the same region but at higher altitudes: > 3000 m [1B]. *B. dracunculifolia* (local name: Thola) grows also in the same region at 3280 m. These plants are used by local people for traditional medicinal uses [1, 2]. Bohlmann and co-workers have characterized several classes of compounds [3–11]. Among them are germacrene derivatives [4], diterpenes [5–7, 11], clerodanes and labdanes [8–10]. On the other hand, the essential oils from these species have not been studied. This paper reports the first systematic study of the essential oils of *Baccharis salicifolia*, *B. latifolia* and *B. dracunculifolia* collected in central Bolivia.

RESULTS AND DISCUSSION

B. salicifolia

Table 1 gives a complete analysis of the essential oil obtained from *B. salicifolia*. The constituents can be divided into three main groups of compounds: (1) monoterpenes with α-phellandrene as the main component, (2) sesquitepenes with germacrene D, bicyclogermacrene, and δ-cadinene as the main products, and (3) numerous monooxygenated sesquiterpenes such as *cis*-α-copaen-8-ol, (*E*)-nerolidol, the cadinols, and 5-guaien-4-ol (**9**). The solvent extract of the same plant collected in Texas and Mexico showed the presence of bisabolene, bisabolol, β-eudesmol, and cadinol [11]. Unfortunately, the lack of pure reference samples makes it difficult to have complete confidence in the proposed identifications. One example of this difficulty lies in the identification of the product appearing in the # 61 peak. The data included in the Chicoutimi data bank indicates cubenol (4-cadinen-1-ol) (**1**) (see Scheme 1), whereas the Berlin data bank shows a different structure for the same peak: 4-cadinen-10-ol (**2**).

Several uncommon monooxygenated cadinanes, with a furan structure, were also found. For example, verboccidentafuran (**3**) which was previously described as a major compound extracted from *Verbesina occidentalis* [12]. This compound was also observed as an important product in the solvent extract of *B. salicifolia* [11]. The fragment peaks at m/z 201 and 216 are the main peaks in the mass spectrum of this compound. Both in Chicoutimi and in Berlin, the intensity of the m/z 119 peak is much smaller than previously published [12] m/z (rel. int.) 216 $[M]^+$ (60), 201 (100), 91 (41), 41 (39), 43 (37), 145 (26).

Chromolaenin (**4**) has a similar structure to that of verboccidentafuran (**3**), with a deficit of four hydrogen atoms. This compound was identified in *Chromolaena laevigata* [13] and again in *B. salicifolia* [11]. The mass spectrum is in agreement with what was published [13] m/z (rel. int.): 212 $[M]^+$ (90), 197 (100), 152 (40), 153 (38), 182 (37).

†Author to whom correspondence should be addressed.

Table 1. Essential oils of *Baccharis salicifolia*

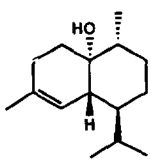
No.	Identification	DB-5 column R.T.	DB-5 column K.I.	DB-5 column %	Supelcowax 10 R.T.	Supelcowax 10 K.I.	Supelcowax 10 %
2	α-Thujene	11.13	934	0.10	7.79	1028	0.10
3	α-Pinene	11.44	938	0.17	7.55	1021	0.18
4	Camphene	12.13	951	0.42	9.22	1066	0.33
5	Sabinene	13.68	972	0.06	11.89	1124	0.07
6	β-Pinene	13.95	976	0.62	11.08	1108	0.50
7	Myrcene	15.17	992	0.35			Traces
8	**α-Phellandrene**	15.82	1000	**8.54**	14.27	1165	**7.98**
9	*p*-Cymene	17.16	1022	1.00	20.71	1277	0.92
10	Limonene	17.46*	1030	0.29	16.23	1195	0.20
	+ β-Phellandrene				16.72	1202	0.03
	γ-Terpinene			Traces	19.11	1249	0.04
	trans-β-Ocimene			Traces	19.77	1261	0.04
11	Terpinolene	21.66	1098	0.09	21.43	1289	0.05
12	Menthone?	26.09	1155	0.08			Traces
13	Menthol	27.65	1174	0.17	44.42	1642	0.19
14	Lavandulyl acetate?	36.40	1301	0.17	42.62	1609	0.12
15	Isomer of δ-elemene	39.33	1326	0.03			
	δ-Elemene	38.98	1342	Traces	36.55	1472	0.03
16	α-Cubebene	40.14	1353	0.29	32.72	1458	0.20
17	α-Copaene	41.82	1375	0.16	34.79	1492	0.21
18	β-Cubebene	42.82	1387	0.45	37.61	1539	0.43
19	β-Elemene	42.97	1389	0.19	in β-caryophyllene peak		
20	α-Gurjunene	44.02	1403	0.51	37.08	1528	0.47
21	β-Caryophyllene	44.59	1413	2.07	41.27	1588	2.03*
22	β-Bourbonene?	45.25	1425	0.17	36.55	1519	0.13
23	6,9-Guaiadiene	46.62	1445	1.05	43.50	1625	1.02
24	Humulene	46.78	1447	0.69	45.69	1665	0.67
25	(*Z*)-β-Farnesene	47.39	1457	0.76	45.99	1670	0.74
27	γ-Muurolene	48.18	1471	1.05	in valencene peak		
29	**Germacrene D**	48.58*	1475	**6.90**	48.14	1707	**6.08**
	+ α-Amorphene				37.84	1539	0.43
30	β-Selinene	48.87	1479	0.40	48.64	1715	0.31
31	ar-Curcumene?	48.98	1481	0.35	52.17	1772	0.34
32	M_r 204	49.22	1484	3.11*	45.40	1657	1.01
	+ *m/z*: 43, 161, 41, 105, 119, 207				58.24?	1888	2.27
33	Valencene	49.47	1488	2.20	48.40	1711	3.05*
34	**Bicyclogermacrene**	49.57	1490	**5.19**	49.56	1731	**5.46**
37	α-Selinene	50.07	1497	0.35	48.82	1718	0.33
38	M_r 204	50.33	1501	0.21			
40	γ-Cadinene	50.73	1508	1.63	49.13	1724	1.51
41	δ-Cadinene	51.35	1519	4.86*	51.03	1754	4.55
	+ β-Sesquiphellandrene				51.90	1768	0.28
	+ Eudesmadiene?				55.90	1835	0.53
42	(*E*)-β-Farnesene	51.89	1528	0.82			
44	α-Calacorene	52.40	1537	1.08	59.89	1914	1.01
45	(*E*)-Calamenene	52.72	1542	0.51	55.32	1826	0.63
47	γ-Elemene	53.21	1554	0.19	54.69	1819	0.33
48	*cis*-α-Copaen-8-ol	53.60	1557	3.18	68.82	2085	2.92
49	*trans*-Nerolidol	53.92	1562	3.34	66.79	2043	3.52
50	Spathulenol	54.43	1570	1.19	70.66	2120	1.08
51	Caryophyllene oxide	54.73	1575	0.49	63.27	2005	0.38
53	M_r 220??	55.28	1584	0.22			
55	*m/z*: 41, 43†, 95†, 109, 55, 161	56.01	1595	1.27	3.22	2172	0.89
	Cadinol: M_r 222 (mixture?)						
59	5-Guaien-4-ol?	57.34	1619	3.56	in verboccidentafuran peak		
61	Cubenol? M_r222	57.84	1628	4.55	69.41	2097	5.20
	m/z: 43, 119, 161, 105, 41, 81						
62	T-Cadinol	58.34*	1637	0.80	72.93	2166	0.32
	+ T.Muurolol				73.48	2181	0.33
64	α-Cadinol	59.03	1649	0.26	in # 71 peak		

Continued overleaf

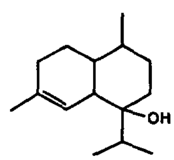
Table 1. *Continued*

No.	Identification	DB-5 column R.T.	K.I.	%	Supelcowax 10 R.T.	K.I.	%
65	**Verboccidentafuran**	59.81	1662	**7.69**	71.79	2144	**11.68***
67	*m/z*: 159, 132, 41, 105; M_r220	60.44	1673	0.96	74.45	2192	0.93
70	epi-α-Bisabolol	60.97	1682	0.96	75.51	2219	0.96
71	3,4,10,11-Tetradehydrocadinan-8-one	61.57	1692	4.67	75.79	2224	6.37*
72	M_r 220?	62.46	1709	0.13			
73	M_r 220	62.74	1713	0.56			
74	Chromolaenin	63.42	1726	1.22	82.68	2374	1.15
76	*m/z*: 199, 214, 115, 128	64.25	1741	6.05	80.66	2336	5.42
77	Dihydroisochromolaenin	65.50	1763	2.35	?		
	1,6-Dihydrochromolaenin			?	83.12	2383	1.22
80	4,6-Eudesmadiene-3,8-dione	69.29	1833	0.42	88.20?	2492	0.15
81	*m/z*: 43†, 68†, 41, 55, 57, 67, 82	69.61	1839	0.71	60.84	1931	0.74
82	*m/z*: 81, 109, 95, 69; M_r 262	71.32	1872	0.33			
83	*m/z*: 210, 209, 165	72.82	1900	0.11	94.50?	2613	0.14
84	*m/z*: 119, 69, 132, 105; M_r 772?	74.47	1934	0.17			
85	*m/z*: 119, 91, 132, M_r 216	75.28	1950	0.25			
87	*m/z*: 119, 132, 91; M_r 228?	76.50		Traces			
87	*m/z*: 228, 213; M_r 228?	76.80		Traces			
	Total			97.38			88.47

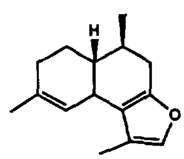
Date of collection: 89-11-07, sample No. 02.
*Multiple peak.
†Peaks were of the same relative abundance. Missing peaks in left column indicate unidentified compounds.



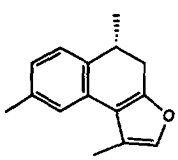
1 Cubenol
(4-Cadinen-1-ol)



2
4-Cadinen-10-ol



3
Verboccidentafuran



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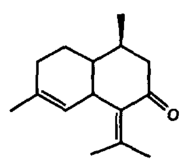
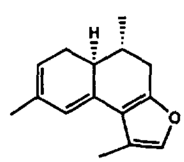
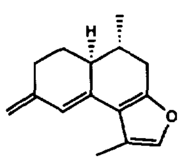
Chromolaenin



5
3,4,10,11-Tetradehydrocadinan-8-one



6
Dihydroisochromolaenin



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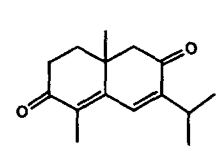
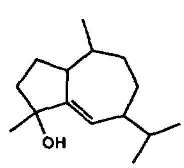
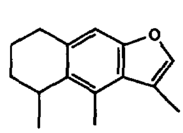
1,6-Dihydrochromolaenin



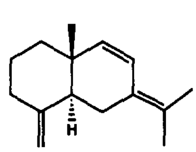
8
4,6-Eudesmadiene-3,8-dione



9
5-Guaien-4-ol



10



11
Selina-4(15),7(11),8(9)-triene

Scheme 1.

One peak on the apolar column (DB-5) gave a mass spectrum very similar to that of dihydroisochromolaenin (**6**) m/z (rel. int.): 214 $[M]^+$ (100), 91 (35), 115 (34), 128 (33), 77 (30), . . . 212 (22), 197 (22). However, on the polar column, the corresponding mass spectrum is rather similar to that of 1,6-dihydrochromolaenin (**7**) [14] m/z (rel. int.): 214 $[M]^+$ (100), 128 (36), 41 (32), 115 (30). We were unable to find a mass spectrum corresponding to **7** during analysis on the apolar column. Both products were identified in *Chromolaena* species.

3,4,10,11-Tetradihydrocadinan-8-one (**5**) was isolated from *B. boliviensis* (Wedd.) Cuatr. [15] and *B. viminea* [16]. Both mass spectra from Berlin and from Chicoutimi are in agreement with the previously published spectrum m/z (rel. int.): 218 $[M]^+$ (63), 161 (95), 133 (95), 105 (75), 91 (100), 77 (79). Moreover, in the same paper, it was suggested that oxidation products from this compound are structurally related to verboccidentafuran [16].

Sesquiterpenes of elemane, eudesmane (selinane), and guaiane types are closely related in that ionic cyclization and ionic isomerization are processes relatively easily transforming one structure to another. Thus, isomerization from germacrene-D into δ- and γ-cadinenes, δ-elemene, β-bourbonene, and γ-muurolene is known [19].

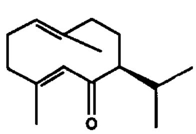
B. latifolia

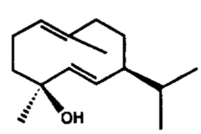
Table 2 gives the composition of the essential oils from 4 samples of *B. latifolia* collected in three localities of the Province of Cochabamba. For example, the composition of the essential oil from Colomi (Table 2, sample # 03) is simpler than the one just described above. Limonene is the main monoterpene. There are also several sesquiterpenes such as β-cubebene, germacrene D, and δ-cadinene. Several monooxygenated sesquiterpenes are also present such as verboccidentalol, epi-α-bisabolol, and dihydroisochromolaenin. Ledol is also a major compound. It may also be added that there exists a strong correlation between the structure of bicyclogermacrene and those of ledene and guaiene (ledol and guaiol) [17].

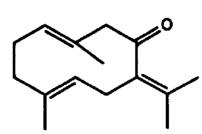
The essential oil from Montepunco has a different composition in that germacrone is a major compound (40%) (Table 2). In some cases, the germacrone percentage is so high that crystallization occurs during the steam distillation process. Note that the analysis on both columns are quantitatively different. This is partly due to the fact that germacrone is thermally sensitive. Since its residence time on the polar column is longer than that on the apolar column (the temperature at the exit of germacrone is higher than that on the apolar column: $T = 157°$), the germacrone peak is preceded by a large shoulder indicating a high rate of conversion of the molecule. A Cope rearrangement, isomerization of germacrone to β-elemenone, is a facile process at temperatures higher than 165° [18]. We have observed the same behaviour in the analysis of the essential oil obtained from *Ledum groenlandicum* [19]. It is also valuable to recall that it is known that *L. groenlandicum* gives rise to different sub-varieties: one well-known for its ledol (**16**) content (mainly the European sub-variety) and the North American sub-variety for its high germacrone (**15**) content [19]. It should be mentioned that one of the unknown spectra is similar to that of eudesm-11-en-4-ol (neointermedol) [20]. An important product with a M_r of 202 appears in this analysis. Its mass spectrum is similar to that of selina-4(15),7(11),8(9)-triene (**11**) [20] (Scheme 2).

The essential oil from *B. lalifolia* collected in Kayarani (Table 2) may be described as a mixture of those from Colomi and Montepunco. Verboccidentafuran, chromolaenin as well as germacrone are present in high amounts. The second sample of the essential oil from Colomi (Table 2, sample # 06) is rather different. This sample contains a high fraction of α-pinene and other monoterpenes and a variety of monooxygenated monoterpenes such as α-pinene oxide, β-thujone, pinocarveol, verbenol, myrtenol, myrtenal, and carvone. Among the sesquiterpenes, ledol (**16**) is again an important product. This composition again is similar to the composition of the essential oil obtained from *L. groenlandicum*.

A solvent extract from this plant collected in Bolivia showed the presence of bacchascandon (**12**), 4-hydroxygermacra-1(10),5-diene (**13**), and 7-hydroxybisabola-3,10-dien-15-al (**15**) [10] (Scheme 2).


12
Bacchascandon


13
4ß-Hydroxygermacra-1(10),5*E*-diene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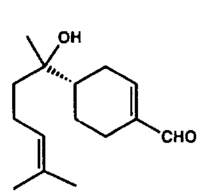
Germacrone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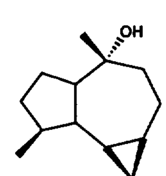
7α-Hydroxybisabola-3,10-dien-15-al


16
Ledol

Scheme 2.

Table 2. Essential oils of *Baccharis latifolia*

Origin of sample:		Colomi			Colomi			Montrepunco	Kayarani	Colomi
Date of collection: 92-03-12-No.		03			03			04	05	06
		DB-5 column			Supelcowax 10					
No.	Identification	R.T.	K.I.	%	R.T.	K.I.	%	%	%	%
1	**α-Thujene**	10.88	933	**10.89**	7.69	1020	**12.88**	0.25	1.92	**7.86**
2	**α-Pinene**	11.18	938	**6.28**	7.45	1012	**7.39**	1.15	1.74	**23.04**
3	Camphene	11.97	950		9.00	1057		0.27		
4	Sabinene	13.55	974	3.47	11.48	1115	4.03	1.32	3.12	4.52
5	β-Pinene	13.75	975	3.76	10.71	1099	4.20	0.82	8.06	6.83
6	Myrcene	14.87	992	2.31	13.97	1162	2.97	0.60	0.62	0.51
7	α-Phellandrene	15.50	999	2.81	13.75	1158	2.95	0.49	**12.63**	
8	*p*-Cymene	16.82	1024	1.70	19.93	1268	2.01	0.22	3.41	2.19
9	*m/z*: 43, 91, 109, 41	16.92	1026							0.74
10	**Limonene** +	17.13	1030	**23.63***	15.64	1189	**22.15**	3.31	1.06	**17.50**
11	β-Phellandrene				16.09	1196	1.48	Tr	6.98	Tr
12	*trans*-β-Ocimene	18.71	1057	0.65	19.05	1252	0.75	1.71	1.45	
13	γ-Terpinene	19.25	1066	0.44	18.39	1240	0.46	0.15	0.29	
14	Terpinolene	21.29	1097	0.74	20.63	1280	0.69	0.13	0.12	0.11
15	α-Pinene oxide	21.74	1103							0.28
16	*m/z*: 43, 41, 91, 69	22.31	1111		39.52?	1570				1.03
17	β-Thujone	23.11	1122							0.38
18	*cis*-Pinene hydrate?	23.46	1127							0.36
19	Nojigiku alcohol	23.81	1131							0.30
20	Pinocarveol	24.58	1141		43.97	1642				1.18
21	*trans*-Verbenol	25.14	1148							0.51
22	Terpinen-4-ol	27.49	1175	0.52	41.06	1591	0.41	0.27	0.43	0.53
23	para-Cymen-8-ol	28.08	1183		55.45	1841				0.28
24	Myrtenal	28.64	1189		42.33	1612				0.26
25	Myrtenol + ?	28.84	1191		42.69	1618				0.37
26	Verbenone	29.54	1198		47.07	1697				0.31
27	*trans*-Carveol	30.51	1214		54.70	1826				0.35
28	Carvone	32.11	1241		49.01	1730				0.44
29	Sabinyl acetate?	36.04	1302							0.30
30	2-Carene epoxyde??	37.77	1326							0.24
31	δ-Elemene	38.91	1342		32.67	1464		0.20		1.23
32	α-Cubebene?	39.71	1353	0.11			Traces			
33	Neryl acetate	40.91	1368	0.27						
34	α-Ylangene	41.08	1370					0.22		
35	α-Copaene	41.38	1374	0.40	33.91	1485	0.36			
37	Geranyl acetate	42.19	1385	1.43	50.37	1751	1.26			
38	β-Cubebene	42.38	1387	0.13	36.88	1531	0.13			

Continued overleaf

Table 2. *Continued*

Origin of sample:		Colomi 03 DB-5 column			Colomi 03 Supelcowax 10			Montrepunco 04	Kayarani 05	Colomi 06
Date of collection: 92-03-12-No.										
No.	Identification	R.T.	K.I.	%	R.T.	K.I.	%	%	%	%
39	β-Elemene	42.53	1389		40.14*	1578		2.98	0.22	1.25
40	α-Gurjunene	43.57	1402	0.34	36.08	1518	0.28			
41	β-Caryophyllene	44.11	1412	2.17	40.20	1579	2.01	1.82		0.29
42	**Selina-4(15),7(11),8(9)-triene**	45.31	1433		46.10?	1681		**9.92**	0.37	0.10?
43	Humulene	46.31	1451		44.55	1652		0.85		0.19
45	*cis*-β-Farnesene	46.88	1461	0.64	45.12	1663	0.60		0.36	
46	γ-Gurjunene	47.57	1472	0.41	45.83?	1675	0.40			0.31
48	Germacrene-D	48.13	1480	4.74*	47.01	1696	1.64	2.83	0.11	0.80
49	(+)δ-Cadinene?				44.54?	1653		0.82		
50	(+)Longipinene				44.86	1658	1.95		0.88	
51	+ Isomer of α-muurolene	48.12	1480							0.80
52	β-Selinene???	48.38	1486	0.35	47.26?	1700	0.34	0.66		
54	α-Selinene + ?	49.00	1495		47.48	1704		1.27*		0.44
55	Bicyclogermacrene	49.09	1497	1.98	48.39	1719	1.74		0.87	
56	α-Muurolene	49.44	1502	0.50						0.22
56	Isomer of β-elemene	49.59	1505					3.76		
58	δ-Cadinene	49.85	1509					1.64		
59	Geranyl isobutyrate? + ?	50.09	1513	0.78				0.39	0.32	
60	γ-Cadinene	50.23	1515	0.59	48.07	1714	0.36		0.21	0.41
61	δ-Cadinene	50.87	1515	2.58	49.86	1743	2.26	0.77	0.59	
62	Selinatriene? M_r 202	51.40	1534	0.68					0.82	
63	α-Calacorene	51.90	1541	0.32	58.66	1901	0.28			
64	m/z: 146, 41; M_r 202	52.39	1549	0.38*					0.54	
65	β-Vetiven? (+)Elemol?				66.39	2049	0.11	0.39		0.32
66	**γ-Elemene**	52.72	1554		53.71?	1805		**10.29**	0.55	
68	**Ledol**	53.35	1563	**4.29**	59.33?	1914	**3.48**			**6.12**
69	*trans*-Nerolidol	53.47	1564		67.74	2076		0.36	0.33	
70	Spathulenol	53.92	1571	0.84	69.43	2110	0.50			0.55
71	Caryophyllene oxide	54.21	1577	0.36	62.02	1963	0.21			2.66
72	m/z: 41, 55, 126 . . . M_r 220	54.51	1580					0.31		
73	Globulol?	54.87	1585		67.53	2073				0.33
74	m/z: 43, 41, 69, 55	55.46	1594	0.64						0.84
75	m/z: 107, 41, 67, 121, 135	55.63	1596					0.64	0.34	
76	m/z: 43, 41, 67, 55, 109	55.76	1598							0.75
77	m/z: 41, 43, 79, 55, 91	56.12	1604					0.25		

78	*m/z*: 43, 81, 41, 55; M_r 222	56.55	1612					0.88†		
79	*m/z*: 43, 41, 59, 91; M_r 220?	56.80	1617	0.86					1.21	
80	*m/z*: 43, 93, 95, 41; M_r 220	56.85	1618		67.76?	2076		0.59		
81	*m/z*: 43, 41, 119, 91	57.04	1622	0.33				0.33		1.58
82	Cubenol	57.33	1628	4.11	68.14?	2084	3.83		7.67	0.25
83	β-Eudesmol	58.15	1643							1.32
84	T-Muurolol	58.35	1647		72.20	2165		0.70		0.41
85	α-Cadinol	58.53	1650	0.34	in epi-α-Bisabolol peak		0.32			
86	**Verboccidentafuran**	59.29	1665	**5.78**	70.44	2130	**5.39**		**7.89**	
87	epi-α-Bisabolol	60.34	1683	0.64	74.69*	2210	1.35		1.31	
89	**Germacrone**	60.76	1691		74.41	2209		**41.85**	**18.19**	0.34
90	3,4,10,11-Tetradehydro cadinan-8-one	61.04	1696	0.80	73.02	2181	0.82		2.52	
91	*m/z*: 199, 214; M_r 214	62.21	1716						0.59	
92	Chromolaenin	62.88	1728	0.75	81.35	2362	0.77		2.41	
93	Oplapanone?	63.06	1731						0.43	0.34
94	*m/z*: 199 = 214; M_r 214	63.71	1742	0.35					5.25	
95	*m/z*: 41, 43, 55, 67, 81; M_r 220	64.31	1753					2.52	0.20	
96	Dihydroisochromolaenin	64.95	1763	0.62	81.89	2373	0.20		2.14	
97	*m/z*: 43, 41, 79, 55	65.61	1774							0.33
98	*m/z*: 41, 43, 55, 91	68.34	1824							0.54
99	*m/z*: 43, 41, 57, 55, 68	69.16	1841	0.28						
100	*m/z*: 212, 197; M_r 212	71.02	1879						0.24	
101					75.74	2241				2.42
	Total			99.04			92.64	97.50	98.69	95.15

*Multiple peak.
†*m/z* (rel. int.): 202 $[M]^+$ (< 2), 81 (70), 161 (26), 105 (26), 55 (27), 43 (100), 41 (50).

B. dracunculifolia

The extract from *B. dracunculifolia* showed the presence of germacrene-D, bicyclogermacrene, and 4β-hydroxygermacra-1(10),5*E*-diene (**13**) as well as prenylated coumarinic acid derivatives [10]. Germacrene-D and bicyclogermacrene (1–4%) are among the main products of the essential oil together with δ-cadinene (13%) and germacrone (**14**) (5%) (Table 3). The analysis of the essential oils fom these three *Baccharis* species and parti-

Table 3. Essential oils of *Baccharis dracunculifolia*

No.	Identification	DB-5 column R.T.	K.I.	%	Supelcowax 10 R.T.	K.I.	%
1	α-Thujene	10.91	933	0.50	7.71	1021	0.73
2	α-Pinene	11.21	938	3.23	7.49	1014	4.22
3	**β-Pinene**	13.67	976	**17.23***	10.75	1100	**19.56**
	(+)Sabinene				11.51	1116	0.69
4	Myrcene	14.89	992	1.52	14.00	1163	1.69
5	α-Terpinene	16.36	1016	0.15	14.58?	1172	0.16
6	*p*-Cymene	16.86	1025	0.26	19.97	1269	0.30
7	Limonene	17.15	1030	4.17	15.67	1189	4.16
	(+)β-Phellandrene				16.03	1195	0.82
8	*trans*-β-Ocimene	18.74	1058	0.46	19.11	1254	0.52
9	γ-Terpinene	19.26	1066	0.41	18.43	1241	0.43
10	Terpinolene	21.32	1097	0.67	20.66	1281	0.66
11	Linalool	22.32	1112	0.12	38.08	1549	0.21
13	Terpinen-4-ol	27.52	1176	0.22	40.91	1589	0.38
14	α,β-Terpineol	28.54	1188	0.09		in germacrene-D peak	
16	α-Cubebene	39.73	1353	0.51	31.91	1451	0.41
17	α-Copaene	41.39	1374	1.07	33.93	1485	1.04
18	β-Elemene	42.54	1389	0.16	39.99	1576	0.15
19	α-Gurjunene	43.58	1402	0.31	36.10	1519	0.34
20	β-Caryophyllene	44.44	1412	3.23	40.23	1579	3.21
21	β-Bourbonene?	44.82	1425	0.30	36.90?	1531	0.20
22	Aromadendrene	45.40	1435	0.45	40.91	1589	0.38
23	6,9-Guaiadiene	45.95	1444	0.36	43.13	1626	0.38
25	α-Humulene	46.32	1451	0.68	44.60	1653	0.52
27	Alloaromadendrene	46.96	1462	1.10	44.17	1645	0.91
28	γ-Gurjunene?	47.73	1475	0.98	47.28?	1700	1.12
29	γ-Muurolene?	47.93	1478	1.89	45.86	1676	2.10
30	Germacrene-D	48.15	1481	7.29*	47.04	1696	3.42
	(+)α-Longipinene				44.89	1658	3.70
31	β-Selinene	48.40	1486	0.46		in germacrene-D peak	
33	Bicyclogermacrene	49.09	1497	1.81*	48.42	1720	0.89
	(+)α-Selinene				47.53	1705	0.56
34	α-Muurolene	49.46	1503	3.16	48.11	1714	3.02
35	γ-Cadinene??	50.23	1515	4.80	54.61?	1823	4.32
36	**δ-Cadinene**	50.90	1526	**12.97**	49.91	1744	**15.93***
37	Selinatriene??	51.43	1534	5.10	54.61?	1823	4.32
39	Elemol? (+)β-Vetiven?	52.41	1549	1.21*	66.44	2049	0.43
40	(*E*)-Nerolidol	53.48	1565	2.11	65.69	2033	1.78
41	Spathulenol	53.94	1572	0.86	69.48	2110	0.76
42	Caryophyllene oxide	54.23	1576	0.16	62.06	1963	0.28
43	Cubenol?	55.47	1594	0.42	72.22	2165	0.37
46	Cubenol	57.34	1628	1.77	68.14	2085	1.73
47	T-Cadinol	57.77	1636	3.86*	71.72	2155	2.84
	(+)T-Muurolol				72.56	2171	0.86
48	β-Eudesmol	58.09	1642	0.25		in germacrone peak	
49	α-Cadinol	58.54	1650	1.61		in germacrone peak	
50	epi-α-Bisabolol	60.30	1682	0.15		in germacrone peak	
53	**Germacrone?**	61.06	1696	**4.96**	74.54	2212	**7.10***
	Total			99.85			98.77

Date of collection: 92-10-03, sample No. 06.
*Multiple peak. Missing peaks in left column indicate unidentified compounds.

cularly the occurrence of germacrone do not indicate a high specificity in the composition of its essential oils [10].

EXPERIMENTAL

Material. B. salicifolia can be found from Colombia to Chile and Argentina. It mainly grows along the rivers, in humid places with a temperate climate. This is a very frequent perennial plant that can be found in the high valleys of the Province of Cochabamba. We have collected *ca* 10 plants in the region of Queru-Queru (city of Cochabamba) at 2258 m of altitude. *B. latifolia* grows in the Andean region of South America, from Venezuela to Argentina. This is a perennial plant that prefers a cold climate. Altogether 4 samples were collected, 2 (*ca* 10 plants) in Colomi (3100 m), one (*ca* 50 plants) in Montepunco (2850 m), and one (*ca* 10 plants) in Kayarani (3460 m). A sample of *B. dracunculifolia* (10 plants) was collected in Waca Huasi (3280 m). The botanical classification of the 3 species has been performed by the Botany Dept at The Smithsonian Institute, Washington, DC. Also, these voucher specimens can be found at the National Herbarium in La Paz, Bolivia, with the respective keys: *B. salicifolia* (R & P) Pers.: Beck 8160 (LPB, SI); *B. latifolia* (R & P) Pers.: Beck y Seidel 14459 (LPB); *B. dracunculifolia* D.C.: Hensen 2497 (LPB).

Isolation of volatile compounds. 1 kg of fresh aerial parts was extracted ($\times 3$) by steam distillation (at 564 mm Hg) until exhaustion (5–6 hr). The yield of a pale yellow essential oil measured from *B. salicifolia* was 0.16 to 0.30% (v/w), *B. dracunculifolia* 0.16 to 0.32% (v/w), and *B. latifolia* 0.18 to 0.45% (v/w).

Analysis. The essential oils were analysed by GC and GC/MS. We used 2 chromatographs equipped with either a split–splitless injector and a DB-5 column (30 m), or an "on column" injector and a Supelcowax 10 column (30 m). The GC/MS system is a VG 1250 equipped with an "on column" injector. Both columns were used with this apparatus and were temp. programmed as follows: 2 min at 40°, 2°C min^{-1} up to 210°, and maintained at this temp. up to 120 min. The identity of each compound was, first, determined by Kovats indices [21], using either our own data bank or data from the literature. In a second step, the mass spectrum of each compound was compared to those available from the literature [21, 22].

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REFERENCES

1. Correa, J. E. and Hernal, H. Y. (1990) in *Especies vegetales promisorias del convenio Andres Bello*, pp. 200–209. SECAB, Tomo V, Bogotá, DC Colombia.
2. Girault, L. (1984) in *Kallawaya, Guérisseurs itinérants des Andes*, Ed. ORSTOM, Paris.
3. Bohlmann, F., Knauf, W., King, R. M. and Robinson, H. (1979) *Phytochemistry* **18**, 1011.
4. Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1979) *Phytochemistry* **18**, 1993.
5. Bohlmann, F., Zdero, C., Grenz, M., Dhar, A. K., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 281.
6. Bohlmann, F., Kramp, W., Grenz, M., Robinson, H and King, R. M. (1981) *Phytochemistry* **20**, 1907.
7. Bohlmann, F., Kramp, W., Jakupovic, J., Robinson, H. and King, R. M. (1982) *Phytochemistry* **21**, 399.
8. Bohlmann, F., Banerjee, S., Jakupovic, J., Grenz, M., Misra, L. M., Schmeda-Hirschmann, G., King, R. M. and Robinson, H. (1985) *Phytochemistry* **24**, 511.
9. Zdero, C., Bohlmann, F., King, R. M. and Robinson, H. (1986) *Phytochemistry* **25**, 2841.
10. Zdero, C., Bohlmann, F., Solomon, J. C., King, R. M. and Robinson, H. (1989) *Phytochemistry* **28**, 531.
11. Jakupovic, J., Schuster, A., Ganzer, U., Bohlmann, F. and Boldt, P. E. (1990) *Phytochemistry* **29**, 2217.
12. Bohlmann, F. and Lonitz, M. (1978) *Phytochemistry* **17**, 453.
13. Bohlmann, F. and Zdero, C. (1977) *Chem. Ber.* **110**, 487.
14. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1979) *Phytochemistry* **18**, 1177.
15. Cuatrecasas, J. (1975) *Phytologia* **31**, 317.
16. Bohlmann, F., Banerjee, S., Jakupovic, J., King, R. M. and Robinson, H. (1984) *Rev. Latinoamer. Quím.* **15**, 71.
17. Tesseire, P. J. (1991) in *Chimie des substances odorantes.* TEC-DOC, Lavoisier, Paris.
18. Kubezka, K.-H., Bohn, I. and Formacek, V. (1986) in *Progress in Essential Oil Research*, p. 279. Proc. Inter. Symp. Essent. Oils, Holzminden, September 1985, Walter de Gruyter, Berlin.
19. Belleau, F. and Collin, G. J. (1993) *Phytochemistry* **33**, 117.
20. Kesselmans, R. P. W., Wijnberg, J. B. P. A., de Groot, A. and van Beek, T. A. (1992) *J. Ess. Oils Res.* **4**, 201.
21. Jennings, W. and Shibamoto, T. (1990) in *Qualitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography*, Academic Press, New York.
22. Adams, R. P. (1989) in *Identification of Essential Oils by Ion Trap Mass Spectrometry*, Academic Press, New York.