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COMPARATIVE CHARACTERIZING ANALYSIS OF ESSENTIAL OILS OF FIVE SPECIES OF THE GENUS *BACCHARIS*, COLLECTED IN THREE COUNTIES AT LA PAZ, BOLIVIA

ANÁLISIS COMPARATIVO DE CARACTERIZACIÓN DE ACEITES ESENCIALES DE CINCO ESPECIES DEL GÉNERO *BACCHARIS*, COLECTADAS EN TRES CONDADOS DE LA PAZ, BOLIVIA

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Full original article *Peer-reviewed*

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Palabras clave: *Monoterpenos, Sesquiterpenos, Aceite esencial, Baccharis, B. boliviensis, B. densiflora, B. latifolia, B. papilllosa, B. tola.*

ABSTRACT

The essential oils from the leaves of five species of the genus *Baccharis*, namely *Baccharis boliviensis*, *B. densiflora*, *B. latifolia*, *B. papilllosa* and *B. tola* collected in three counties, Cota-Cota, Mecapaca and Carpani at La Paz, Bolivia, were extracted using hydrodistillation procedures and subsequently analyzed by GC/MS. Four of the species were collected in two places of the La Paz valley, in order to establish the changes in composition in function of the place of origin. *B. densiflora* was collected only in one place because of the scarcely availability of the plant material in the other collecting sites. The essential oils obtained from the five species are composed mainly by monoterpenes, and a less percentage of sesquiterpenes, in addition, few non terpenic components were detected. The only exception was *B. latifolia* that showed almost the same amount of sesquiterpenes and monoterpenes. The samples of a same species collected at two different sites showed, as a rule, similar GC/MS profiles with the exception of *B. tola* that showed higher amounts of hydrocarbon sesquiterpenes and lower quantities of cyclic monoterpenes from Carpani to Cota Cota. The analysis of the identified compounds showed that some of them were present in good quantities in all the samples of essential oils examined, like for instance, β-myrcene, D-limonene, α-thujene, D-α-pinene, sabinene, L-β-pinene and α-muurolene.

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RESUMEN

Los aceites esenciales de las hojas de cinco especies del género *Baccharis*, a saber, *Baccharis boliviensis*, *B. densiflora*, *B. latifolia*, *B. papilllosa* y *B. tola*, recogidas en tres condados, Cota-Cota, Mecapaca y Carpani en La Paz, Bolivia, se extrajeron mediante procedimientos de hidrodestilación y posteriormente se analizaron por GC/MS. Cuatro de las especies fueron recolectadas en dos lugares del valle de La Paz, a fin de establecer los cambios en la composición en función del lugar de origen. *B. densiflora* se recolectó solo en un lugar debido a la escasa disponibilidad del material vegetal en los otros sitios de recolección. El aceite esencial obtenido de las cinco especies está compuesto principalmente por monoterpenos, y un menor porcentaje de sesquiterpenos, además, se detectaron pocos componentes no terpénicos. La única excepción fue *B. latifolia* que mostró casi la misma cantidad de sesquiterpenos y monoterpenos. Las muestras de una misma especie recolectadas en dos sitios diferentes mostraron, por regla general, perfiles GC/MS similares con la excepción de *B. tola* que mostró mayores cantidades de sesquiterpenos hidrocarbonados y menor cantidad de monoterpenos cíclicos de Carpani a Cota Cota. El análisis de los compuestos identificados mostró que algunos de ellos estaban presentes en buenas cantidades en todas las muestras de aceites esenciales examinadas, como por ejemplo, β-mirceno, D-limoneno, α-tujeno, D-α-pineno, sabineno, L-β-pineno y α-muuroleno.

INTRODUCTION

Baccharis is the largest genus in the Asteraceae family, with more than 500 species distributed in all Americas [1], with wider incidence in Brazil, Bolivia, Argentina, Colombia, Chile and Mexico [2]. The five species employed in the present investigation proceeded form the valley of La Paz, Bolivia: *Baccharis latifolia*, *B. densiflora*, *B. boliviensis*, *B. tola* and *B. papillosa*, all of them are well-reputed in folk Bolivian medicine for the treatment of rheumatism, liver diseases, infectious problems, wounds and ulcers [1,3,4]; they were previously reported by our research group for their flavonoid contents [5-9]. The first four were collected in two places of the La Paz valley at different dates, to see the changes in composition due of the change of environment. *B. densiflora* was collected only in one place because of the scarcely availability of the plant material in the other collecting sites

The essential oils are the odoriferous principles found in several parts of the plant, they have the function of adapting the plant organism to the environment, chemically they are complex and highly variable mixtures of constituents that belong, almost exclusively, to two groups characterized by different biogenetic origins: the group of terpenoids and the group of aromatic compounds derived from phenylpropane, much less frequent [10]. Biologically, these compounds act in the defense of the plant against the attack of predators, attraction of pollination agents, protection against water loss and as inhibitors of germination [11,12]. Economically, they're in food, cosmetic and cleaning products industries, also in medicine thanks to their many therapeutic properties. However, despite of their many beneficial characteristics, toxic effects of those substances can't be discarded [13].

Their presence depends of several different factors, such as: soil conditions, geographic location, vegetative cycle and the process of obtaining [10,14,15].

There are several studies of essential oils from *Baccharis* species, reporting more than one hundred constituents in some Latin American species [16-18]. The compounds that appear most frequently in these species are: sabinene, α- and β-pinene, myrcene, limonene, δ-cadinene, nerolidol, terpinen-4-ol, α-tujeno, α-fellandreno, β-Cimeno and elemol. In particular, Bolivian researchers identified about 100 compounds in the essential oil of *B. latifolia*, from specimens collected in three locations in Cochabamba, where the major monoterpenes were α-pinene, limonene, β-tujeno, pinocarvenol, verbenol, mirtenol, mirtenal and carvone, in addition to important sesquiterpenes such as germacrene D and ledol [19], among others.

RESULTS AND DISCUSSION

The essential oils of five *Baccharis* species of high bioavailability in the Valley of La Paz-Bolivia, were obtained. The oils were extracted by hydrodistillation technique, with yields among 0.08 and 0.18% (Table 1). From the first four species the oils were obtained from two collection sites with different environmental characteristics. The collections were done in the same phenological stage and the same period of the year to have data about the effect of the environmental change on the production of essential oils. From *Baccharis densiflora*, the study could not be carried out at two collection sites because there were not two sites with a significant presence of this species among the collection sites.

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Table 1. *Details of the studied Baccharis species from La Paz, Bolivia*

N°	Species	Collecting site	Height masl	Collecting date	Period	Phenological Stage	Oil Yield%
1	*B. papillosa*	Cota Cota	3422	15/01/19	Wet	Flowering	0.14
2	*B. papillosa*	Carpani	4012	15/11/18	Wet	Flowering	0.16
3	*B. tola*	Cota Cota	3427	07/06/18	Dry	Maturation	0.11
4	*B. tola*	Carpani	4011	04/06/18	Dry	Maturation	0.12
5	*B. latifolia*	Cota Cota	3415	15/05/18	Dry	Maturation	0.18
6	*B. latifolia*	Carpani	3361	04/06/18	Dry	Maturation	0.15
7	*B. boliviensis*	Cota Cota	3423	15/01/19	Wet	Flowering	0.13
8	*B. boliviensis*	Mecapaca	2986	15/11/18	Wet	Flowering	0.10
9	*B. densiflora*	Carpani	3365	15/11/18	Wet	Flowering	0.08

Below are the tables with the results of the analyses obtained in the GC/MS equipment of each oil, divided into types of compounds and by species

Table 2. *Percentage composition of the essential oils of Baccharis papillosa from two collecting sites*

Nº	Compound	Area % Cota Cota	Area % Carpani	Nº	Compound	Area % Cota Cota	Area % Carpani
	Acyclic monoterpenes				**Hydrocarbon sesquiterpenes**		
1	β -Myrcene	4,46	4,10	**18**	Copaene	0,78	0,85
2	β –Cis-Ocimene	1,30	0,53	**19**	Caryophyllene	0,17	Nd
3	Cis-Geranyl acetate	0,29	Nd	**20**	α -Caryophyllene	0,37	0,19
4	Geranyl acetate	0,54	0,85	**21**	α -Cubebene	0,80	12,45
5	Neryl acetate	Nd	0,35	**22**	Guaia 6,9-diene	1,23	1,02
	Monocyclic monoterpenes			**23**	γ-Muurolene	1,17	4,16
6	Pesudolimenene	0,14	0,24	**24**	D-Germacrene	0,36	0,67
7	α - Phellandrene	1,45	1,64	**25**	α - Guaiene	1,08	Nd
8	1,3,5 cyclopentatriene, 3,7,7 trimethyl	0,61	1,18	**26**	γ-Elemene	2,97	1,21
9	γ -Terpinene	1,43	0,84	**27**	α -Muurolene	3,26	4,14
10	Terpinen-4-Ol	0,56	0,52	**28**	γ-Amorphene	9,57	0,98
11	Isopropyl Benzoate	Nd	0,21	**29**	α -Copaene	0,31	Nd
	Bicyclic monoterpenes			**30**	Cubebene	0,72	0,49
12	α -Thujene	10,30	7,40	**31**	Germacrene B	0,49	Nd
13	D- α- Pinene	23,62	20,37	**32**	α -Ylangene	Nd	1,44
14	Sabinene	4,13	2,92	**33**	β -Eudesmane	Nd	0,50
15	L-β-Pinene	5,85	5,39		**Oxygenated sesquiterpenes**		
16	(+) 4 Carene	0,82	0,48	**34**	(+/-) Trans Nerolidol	0,66	Nd
17	(+) 2 Carene	0,45	0,35	**35**	Di-epi-1, 10 cubenol	1,86	0,28
	Total percentage monoterpenes	**55,95**	**47,37**	**36**	Tau muurolol	1,61	Nd
	Others			**37**	α -Cadinol	Nd	1,85
38	1,3,7, Nonatriene 4, 8 dimethyl (E)	0,21	0,22		**Total percentage sesquiterpenes**	**27,41**	**30,23**
39	Benzyl isobutanoate	Nd	0,36				
40	Cinnamyl Butyrate	Nd	0,63		**Not Identified**	**16,41**	**21,17**
	Total percentage others	**0,21**	**1,21**				

The essential oil of *Baccharis papillosa* was obtained in two collecting sites of La Paz: University campus of Cota Cota, a metropolitan region, and Carpani a rural community near of La Paz city. Both samples were taken in wet station and flowering phenological stage (Table 1), giving a yield of 0,14% (Cota Cota) and 0,16% (Carpani). The GC/MS analysis (Table 2) show a similar profile for both with monoterpenes as major components 55,95% (Cota Cota) and 47,37% (Carpani), followed by sesquiterpenes 27,41% (Cota Cota) and 30,23% (Carpani). A total

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of 40 compounds were identified, constituting 83,57% of total essential oil obtained in Cota Cota and 78,81% in Carpani. The main compounds of the essential oils of both samples were the monoterpenes: β-myrcene, α-thujene, D α-pinene, sabinene and L-β-pinene. The major difference between both samples was in the sesquiterpenes where we can see the α-cubebene as the main component in the sample from Carpani (12,45%) but not in Cota Cota (0,80%), and the γ-amorphene as the main component in the sample from Cota Cota (9,57%) but not in Carpani (0,98%). Therefore, the difference in the environmental conditions of both places affect mainly the biosynthesis of hydrocarbon sesquiterpenoids.

Table 3. *Percentage composition of the essential oils of Baccharis tola from two collecting sites*

Nº	Compound	Area % Cota Cota	Area % Carpani	Nº	Compound	Area % Cota Cota	Area % Carpani
	Acyclic monoterpenes				**Hydrocarbon sesquiterpenes**		
1	β -Myrcene	3,62	3,79	25	Bycyclo [5.2.0] nonane, 2 Methylene 4,8,8 trimethyl-4-vinyl	0,42	Nd
	Cis-Geranyl Actetate	0,30	Nd	26	β- Humelene	0,20	0,74
2	Geranyl Acetate	2,30	1,34	27	α -Muurolene	1,23	3,56
3	2 Methylbutyl 2-methylbutanoate	Nd	0,29	28	γ-Muurolene	1,49	4,50
4	Neryl Acetate	Nd	0,33	29	Isoledene	0,38	4,09
	Monocyclic monoterpenes			30	Cis -Calamene	0,40	Nd
5	Pseudolimonene	0,44	Nd	31	α -Cubebene	Nd	1,17
6	β-Cymene	2,50	2,53	32	Caryophyllene	Nd	0,32
7	D-Limonene	18,52	12,55	33	1,5,9,9-Tetramethyl 1,4,7, cycloundecatriene	Nd	0,40
8	Cryptone L	1,53	0,64	34	Copaene	Nd	1,70
9	P-cumic-Aldehyde	0,24	Nd	35	α -Amorphene	Nd	0,56
10	D-Carvone	0,35	Nd	36	Guaia 6,9 diene	Nd	0,57
11	1,2 Diisopropenyl Cyclobutanote.	Nd	0,82	37	α -Guaiene	Nd	0,38
	Bicyclic monoterpenes			38	Trans-Calamene	Nd	1,04
12	α -Thujene	3,36	3,90	39	Neophytadiene	Nd	0,28
13	D - α - Pinene	22,01	15,02		**Oxygenated sesquiterpenes**		
14	Camphene	0,22	Nd	40	(+/-) Trans Nerolidol	1,77	0,56
15	Sabinene	4,34	1,97	41	Spathulenol	4,06	1,96
16	L-β-Pinene	21,91	18,41	42	Isoshyobunone	0,41	1,35
17	α -Pinene Epoxide	0,72	Nd	43	α -Humelene epoxi	0,37	Nd
18	Trans-Verbenol	0,49	Nd	44	β- Phenylethyl benzoate	0,25	Nd
19	Tran-Pinocarveol	0,60	Nd		**Total percentage sesquiterpenes**	**10,98**	**23,18**
20	Pinocarvone	0,35	Nd		**Others**		
21	Myrtenal	0,73	Nd	45	Hexyl 2 methylbutyrate	0,41	3,78
22	Levoverbenone	0,20	Nd	46	Chrysantenyl acetate	0,31	Nd
23	Myrtenol	0,30	Nd	47	β-Phenylethyl isovalerate	0,19	Nd
24	(+) 3 Carene	Nd	0,95	48	Cinnamyl butyrate	Nd	0,26
	Total percentage monoterpenes	**85,03**	**62,54**	49	Methanol (1,4 dihydriphenyl)	Nd	1,54
					Total percentage others	**0,91**	**5, 58**
	Not Identified	**3,20**	**8,67**				

The essential oil of *Baccahris tola* was obtained in the same collecting sites than *B. papillosa*: Cota Cota and Carpani, but in the dry season, when the plants are in maturation phenological stage (Table 1). The oil yields were very similar 0,11% (Cota Cota) and 0,12% (Carpani) but the GC/MS analysis (Table 3) shows bigger differences than in *B. papillosa*. Both oils have monoterpenes as main components and sesquiterpenes as second major metabolites, but the sample collected in Cota Cota has 85,03% of monoterpenes and 10,98% of sesquiterpenes, while the sample from Carpani has 62,54% of monoterpenes and 23,19% of sesquiterpenes. So, the environmental conditions in Carpani seems to stimulate the production of sesquiterpenes instead of some monoterpenes. The main monoterpenes in both samples were: β-myrcene, D-limonene, α-thujene, D-α-pinene and L-β-pinene, in general with

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bigger concentration in the oil obtained of the sample from Cota Cota. Respect of sesquiterpenes the main components were: α-muurolene, γ-muurolene, isoledene and spathulenol, in the first three there were major production in Carpani than in Cota Cota, and in the last one there was major production in Cota Cota. In total 49 compounds were identified representing more than 90% of the analyzed oils from *B. tola*.

Table 4. *Percentage composition of the essential oils of Baccharis latifolia from two collecting sites*

Nº	Compound	Area % Cota Cota	Area % Carpani	Nº	Compound	Area % Cota Cota	Area % Carpani
	Acyclic monoterpenes				**Hydrocarbon sesquiterpenes**		
1	β-Myrcene	3,81	3,37	**25**	α -Cubebene	0,29	Nd
2	β-Cis -Ocimene	2,05	1,88	**26**	Caryophyllene	0,79	0,78
3	Geranyl acetate	0,54	0,38	**27**	Humelene	0,53	0,65
	Monocyclic monoterpenes			**28**	Cadina 3,5 diene	0,39	0,45
4	β -Cymene	2,27	2,50	**29**	γ- Muurolene	1,88	2,03
5	D-Limonene	2,53	2,01	**30**	β -Copaene	0,41	Nd
6	γ- terpinene	0,86	0,97	**31**	D-Germacrene	0,49	0,44
7	Para Cymen 8 Ol	0,30	0,36	**32**	α - Muurolene	4,44	4,56
	Bicyclic monoterpenes			**33**	γ- Cadinene	5,91	5,31
8	α - Thujene	7,99	6,18	**34**	1 (10) Aromadendrene	12,05	Nd
9	D- α -Pinene	8,57	6,27	**35**	α - Cadinene	1,13	1,18
10	(+) Sabinene	4,31	3,35	**36**	(-)β-Cadinene	1,27	10,23
11	L- β -Pinene	5,18	4,30	**37**	Copaene	Nd	1,10
12	(+) 4 Carene	3,19	3,47		**Oxygenated sesquiterpenes**		
13	Eucalyptol	Nd	0,77	**38**	6 -Epishyobunone	1,99	2,43
	Total percentage monoterpenes	**41,6**	**35,81**	**39**	Cubebol	0,72	0,86
				40	Germacrene D-4-Ol	3,46	3,54
	Not Identified	**17,43**	**23,23**	**41**	Caryophyllene oxide	0,57	0,45
				42	α - Cadinol	3,55	4,56
				43	(-) - Oplopanone	1,12	0,82
				44	α - Bisabolol	Nd	1,57
					Total percentage sesquiterpenes	**40,99**	**40,96**

The samples of *Baccharis latifolia* also were collected in the same sites: Cota Cota and Carpani in dry season. The oil yields were a little bigger than those of the other *Baccharis* studied, 0,18% (Cota Cota) and 0,15% (Carpani). The GC/MS analysis (Table 4) showed a different profile than those of the other *Baccharis*, with a similar percentage of monoterpenes and sesquiterpenes (Cota Cota, monoterpenes 41,6% and sesquiterpenes 40,99%; Carpani, monoterpenes 35,81% and sesquiterpenes 40,96%). So, this was the species with major production of sesquiterpenes. The composition of the essential oils from both sites was very similar with the exception of sesquiterpenes 1(10)-aromadendrene which represents 12,05% in the oil from Cota Cota and it was not identified in the oil from Carpani, and (-) β-cadinene which represents 1,27% in the oil from Cota Cota and 10,23% in the oil from Carpani. The major identified components were: β-myrcene, α-thujene, D-α-pinene, (+) sabinene, L-β-pinene, (+) 4-carene, α-muurolene, γ-cadinene, 1 (10)-aromadendrene, β-cadinene and germacrene D-4-ol, among 44 compounds identified in the oil from *B. latifolia*, which represents 82,49% of the essential oil obtained from Cota Cota and 76,77% from Carpani.

The samples of *B. boliviensis* were collected in the University Campus of Cota Cota (3300 m.a.s.l.) and in Mecapaca (3000 m.a.s.l.), a different site wetter and at lower meters above sea level than the other two sites. The oil yield of the sample from Cota Cota (0,13%) was higger than that of Mecapaca (0,10%). The GC/MS profile of the essential oil from both species were very similar with a clear predominance of monoterpenes: 88,32% (Cota Cota) and 91,12% (Mecapaca). A total of 46 compounds were identified representing more than 95% of the analyzed oil from *B. boliviensis.* The main components in both samples were: β-myrcene, geranyl acetate, β-cymene, D-limonene, α-thujene, D-α- pinene, sabinene and L-β-pinene, showing some quantitative differences especially in geranyl acetate, D-limonene and sabinene.

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Finally, *Baccharis densiflora* (Syn *B. pentlandii*) was collected only in Carpani. Its essential oil yield was the lowest (0,08%) and its GC/MS profile was the simplest, with a total of 17 compounds identified.

Table 5. *Percentage composition of the essential oils of Baccharis boliviensis from two collecting sites*

Nº	Compound	Area % Cota Cota	Area % Mecapaca	Nº	Compound	Area % Cota Cota	Area % Mecapaca
	Acyclic monoterpenes				**Hydrocarbon sesquiterpenes**		
1	β- Myrcene	5,81	4,59	**28**	α - Cubebene	0,30	0,76
2	Trans- β- Ocimene	3,28	0,79	**29**	Aromandrene	0,20	Nd
3	β -Cis Ocimene	0,96	Nd	**30**	α -Ylangene	0,33	Nd
4	n-Hexyl butanoate	0,61	0,37	**31**	α - Guaiene	0,32	Nd
5	Cis Geranyl acetate	3,26	0,89	**32**	α - Muurolene	0,28	0,47
6	Geranyl acetate	5,07	2,43	**33**	γ- Amorphene	0,27	Nd
	Monocyclic monoterpenes			**34**	α - Copaene	Nd	0,46
7	α -Phellandrene	1,37	Nd	**35**	γ- Muurolene	Nd	0,91
8	β -Cymene	10,38	8,63	**36**			
9	D-Limonene	17,37	29,57				
10	Terpinen-4-Ol	0,46	0,20		**Oxygenated sesquiterpenes**		
11	Cryptone L	0,60	0,85	**37**	D-Viridiflorol	0,41	Nd
12	P-Cymen-8-Ol	0,31	0,25	**38**	Butanoic Acid, 2-Methyl-, 3,7-Dimethyl-2,6-Octadienyl Esther, (E)	2,01	Nd
13	Cyclohexanone, 2-(1-methyl-2-oxopropyl)	1,11	Nd	**39**	Tau Muurolol	0,28	Nd
14	(-) Carvone	Nd	0,24	**40**	α - Cadinol	0,37	0,18
	Bicyclic monoterpenes			**41**	Trans-Sesquisabinene Hydrate	Nd	0,35
15	α -Thujene	3,83	4,19	**42**	(E)-3,7-Dimethylocta 2,6-dien-1yl 3 methylbutanoate	Nd	0,18
16	D Alpha Pinene	14,72	11,93	**43**	(+/-) Trans Nerolidol	2,02	Nd
17	Camphene	0,51	0,20		**Total percentage sesquiterpenes**	**6,79**	**3,31**
18	Sabinene	7,24	12,11		**Others**		
19	L –β- Pinene	10,00	10,36	**44**	4 Methylpentyl 2-Methylbutanoate	0,32	Nd
20	3 Carene	0,72	3,11	**45**	α - Limonene diepoxide	1,77	1,86
21	2 Carene	0,71	Nd	**46**	Hexanoic Acid Hexyl Esther	0,25	Nd
22	Limonene Oxide Trans	Nd	0,20		**Total percentage others**	**2,34**	**1,86**
23	Car 3 en 5 one	Nd	0,21				
	Total percentage monoterpenes	**88,32**	**91,12**		**Not Identified**	**2,56**	**3,71**

Table 6. *Percentage composition of the essential oil of B. densiflora from Carpani*

N	Monoterpenes		N	Sesquiterpenes	
	Compound	Area %		Compound	Area %
	Acyclic monoterpenes			Hydrocarbon sesquiterpenes	
1	β -Myrcene	5.64	9	Caryophyllene	0.57
2	trans-Ocimene	5.85	10	Germacrene D	0.50
3	cis-Ocimene	2.38	11	Elixene	1.16
4	α -Muurolene	1.20	12	γ-Cadinene	1.61
	Monocyclic monoterpenes		13	β -Cadinene	4.60
5	D-Limonene	46.15		Oxygenated sesquiterpenes	
	Bicyclic monoterpenes		14	6-Epishyobunone	0.99
6	α -Pinene	16.44	15	Shyobunone	3.00
7	Thujene	0.78	16	tau-Muurolol	0.88
8	β -Pinene	7.19	17	α -Cadinol	1.08
	Total percentage	**85.63**		**Total percentage**	**14.39**

Thus, in *Baccharis densiflora*, there was a predominance of monoterpenes, like in the major part of the species analyzed, representing 85,63% of the essential oil. In this case all compounds were identified, the main

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monoterpenes were: β-myrcene, trans-ocimene, D-limonene, and α- pinene, among them it was remarkable the presence of D-limonene which represents almost half of the essential oil (46,15%). On the other hand, there was 14,39% of sesquiterpenes and the main were β-cadinene and shyobunone.

Making a global analysis of all *Baccharis* species under study, we conclude that their oils were composed mainly by monoterpenes, and the only exception was *B. latifolia* that had almost the same amount of sesquiterpenes. It was also observed that there were few compounds that are not terpenoids (Figure 1) with the exception *B. tola* from Carpani which contained 5.58% of non-terpenic compounds.

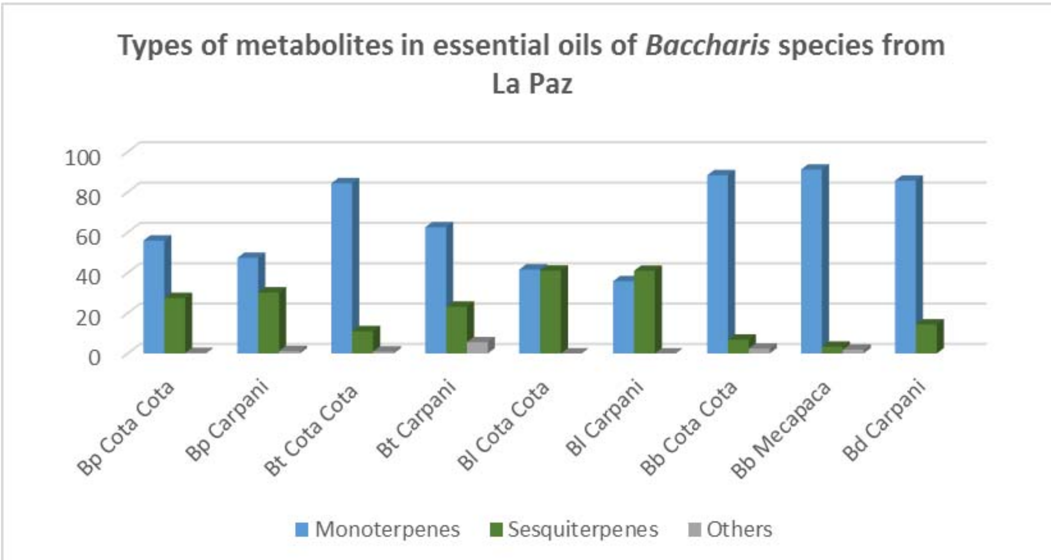

Figure 1*. Types of metabolites in essential oils of Baccharis species from La Paz.*

Figure 2 shows the types of monoterpenes and sesquiterpenes identified in the essential oils. In this graphic we can see similar profiles for the same species collected in two sites, but with some exceptions: *Baccharis tola* which clearly showed bigger quantities of hydrocarbon sesquiterpenes and lower quantities of monocyclic and bicyclic monoterpenes in Carpani than in Cota Cota. So, the environmental conditions in Carpani seem to stimulate the production of hydrocarbon sesquiterpenes instead of some cyclic monoterpenes in this species. There were also some differences in the production of sesquiterpenes in the samples of *B. boliviensis*, the sample from Cota Cota had more quantity of oxygenated sesquiterpenes than hydrocarbon sesquiterpenes, and the sample from Mecapaca had less oxygenated sesquiterpenes and more hydrocarbon sesquiterpenes.

Among the essential oils of the *Baccharis* studied, only that of *B. latifolia* has been previously studied (Loayza, 1995). In such previous study, the samples were collected in three localities of Cochabamba, Bolivia. The GC/MS profiles were similar with large quantities of sesquiterpenes and monoterpenes. They showed some similar major components, like α-thujene and α-pinene, but also there were some components very different in percentage, like germacrone (41,85%), γ-elemene (10,29%) and D-limonene (22,15%) in the essential oil from Montepunco (2850 m.a.s.l.), probably due to very different environmental conditions compared to the collecting sites of La Paz.

The analysis of the identified compounds in all five species studied, shows that there were some of them present in good quantities in almost all the essential oils studied, like the monoterpenes: β-myrcene, D-limonene, α-thujene, D-α-pinene, sabinene and L-β-pinene. Those compounds and others identified were isolated in other species and showed good pharmacological activities like β-myrcene, which showed anti-inflammatory, antiseptic, antispasmodic and analgesic properties [20-22] or D-limonene, which presented immunostimulant activity, apoptotic of breast cancer cells, and effectiveness against the bacteria that cause acne [23]. There are several studies about the antimicrobial activities of essential oils, showing that specific compounds cannot explain these properties due to complex mixtures of terpenes, mainly those with aromatic rings and phenolic hydroxyl groups [24]. Nevertheless, some of them have strong antibacterial activity proven like α-pinene, β-pinene and D-limonene [25-27]. In addition, some others like α-pinene, 3-carene and β-cymene can inhibit acetylcholinesterase (AChE) showing a potential

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against Alzheimer [28]. Regarding sesquiterpenes, they were present in lower quantities but some of them were remarkable like α-cubebene, which stimulates the production of chemokines (CXCL8 or IL-8) in human neutrophils [29], or trans-nerolidol, which was identified as antiulcer constituent from the essential oil of *Baccharis dracunculifolia* [30].

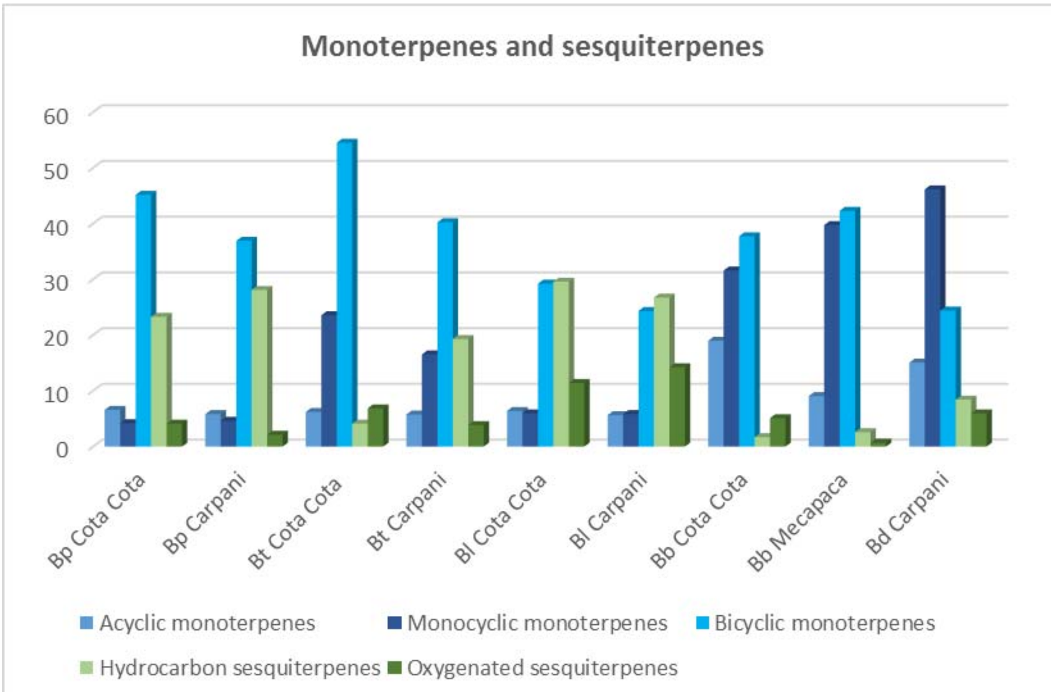

Figure 2. *Types of monoterpenes and sesquiterpenes of essential oils of Baccharis species from La Paz*

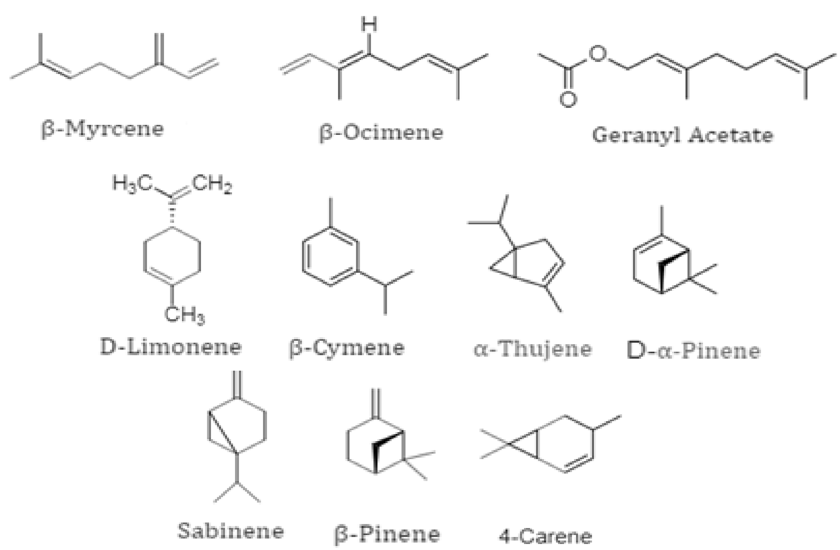

Figure 3. *Major monoterpenes identified in the essential oils of Baccharis species from La Paz*

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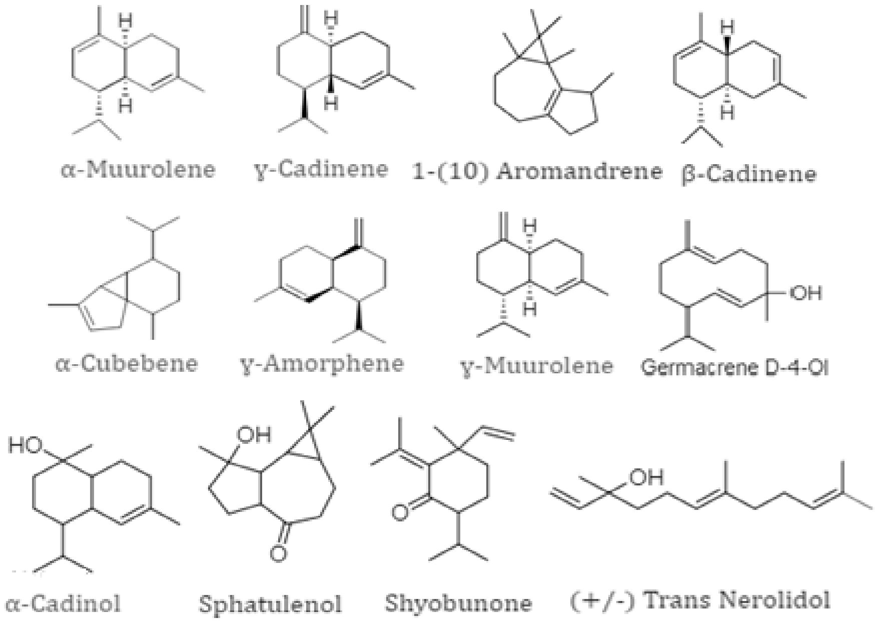

Figure 4. *Major sesquiterpenes identified in the essential oils of Baccharis species from La Paz*

EXPERIMENTAL

Plant material.

The plant material was collected around the city of La Paz according to the details shown in table 1, so *Baccharis boliviensis* was collected from the community of Mecapaca (K 0606505 UTM 8157314) and University Campus of Cota Cota (K 0599543 UTM 8171528), *B. densiflora* of the Community of Carpani (K 0602947, UTM 8181212) and Cota Cota University Campus, *B. latifolia* of the Community of Carpani (K 0603029, UTM 8182407) and University Campus of Cota Cota, *B. papillosa* of the Community of Carpani and University Campus of Cota Cota, *B. tola* of the Community of Carpani and Cota Cota University Campus and finally *B. densiflora* of the Community of Carpani. The collected material was identified by Esther Valenzuela from JBLP (Botanic Garden of the National Herbarium of Bolivia), where samples of the collected specimens are deposited.

Essential oils extraction

The essential oil was extracted from 5 Kg of fresh leaves of each species by hydrodistillation, the extraction was carried out for 3 hours, and the oil obtained was separated, dried with anhydrous magnesium sulphate and stored at 4 ° C for further analysis by GC MS [31]

GC/MS conditions for analysis

1 uL of each oil was dissolved in 98% N-Hexane up to 2 mL, then filtered with 0.2 µm PTFE and subsequently analyzed in the GC-MS.

The composition of the oils was determined in a GC 2010 PLUS gas chromatograph coupled to a QP 2020 mass spectrometric detector, both SHIMADZU. The compounds separation was performed by a column of Sil MS RESTEK with 5% diphenyl and 95% dimethyl polysiloxane (30 m x 0.25 mm and 0.25 µm film thickness). The injection volume was 1 µL at a total flow of 15.6 mL/min, and the column flow was of 0.60 mL/min. The temperature of the injector was 280 ° C, the initial temperature was 40 °C, maintained for 2 min, subsequently the temperature was increased up to 210 °C with a speed of 2 °C/min, for 5 min, the ionization temperature used was of 230 ° C and the interface temperature was of 280 °C.

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The identification of the compounds was achieved by comparison of their mass spectra with a library data base (NIST14). Also mass spectra of the peaks were compared with published spectrometric data. Spectra were considered coincident if the similarity index was higher than 95%. The percentage of compounds was calculated from the peak areas of the chromatograms [32].

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