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REVISTA STRICTO SENSU

Análise comparativa de óleos essenciais de *Baccharis L*.: uma revisão

Comparative analysis of essential oils of *Baccharis* L.: a review

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Resumo
Baccharis pertence à família Asteraceae e é fonte de biomoléculas que têm sido utilizadas como novos medicamentos. *Baccharis* é rico em óleos essenciais e contém vários compostos como α-pineno, β-pineno, limoneno, β-cariofileno, germacreno-D e espatulenol. Este trabalho avaliou vários artigos científicos e comparou a quantidade e a composição química dos óleos essenciais de 33 amostras de 22 espécies de *Baccharis*. Variações foram observadas nos constituintes terpênicos bem como na quantidade de monoterpenos e sesquiterpenos.
Palavras-chave: Asteraceae, monoterpenos, sesquiterpenos, óleos essenciais

Abstract
Baccharis belongs to Asteraceae and has provided valuable biomolecules in the discovery of new natural medicinal products. *Baccharis* is a rich source of essential oils and many compounds have been identified as α-pinene, β-pinene, limonene, β-caryophyllene, germacrene-D, and spathulenol. This work brought together several papers and compared the essential oil content and chemical constituents of 33 samples of 22 species of

Baccharis. Variations can be observed both in the terpene constituents as well as the content of monoterpenes and sesquiterpenes.
Keywords: Asteraceae, monoterpenes, sesquiterpenes, volatile oil.

1. Introduction

Asteraceae is the largest family of Magnoliophyta and several species of this family has been studied for their chemical constituents and biological activities, contributing to the development of drugs and insecticides. They are economically important, because many members of the family produce essential oil, being used therapeutically and in the perfume and food industries (CRAVEIRO et al., 1981; VERDI et al., 2005; BUDEL et al., 2008; BOBEK et al., 2016a; CAMPOS et al., 2016).

Baccharis L. belongs to Asteraceae and includes over 400 species, distributed throughout the American continent, predominantly in South America (BARROSO; BUENO, 2002). In Brazil, 178 species were described, mainly in Southern and Southeastern (FLORA DO BRASIL 2020 [201-]). Paraná State is considered one of the major centers of occurrence of this genus covering 83 species (HEIDEN; RIBAS, 2012; HEIDEN; SCHNEIDER, 2013; HEIDEN et al., 2014). They are woody shrubs or subshrubs with high morphological variety presenting from 0.5 to 4.0 m tall. They are dioecious, having male and female inflorescences on separate plants (BUDEL et al., 2008). Among them, species popularly known as “carquejas” and “vassouras” are used in traditional medicine as diuretic, stomachic, anti-inflammatory and detoxifying to the organism (KORBES, 1995; VERDI et al., 2005; SIMÕES-PIRES et al., 2005; ABAD; BERMEJO, 2007; BUDEL et al., 2008; BUDEL et al., 2015).

Concerning the chemical composition of *Baccharis*, approximately 120 species have been analyzed (VERDI et al., 2005) and more than 150 compounds have been isolated and identified (ABAD; BERMEJO, 2007). Diterpenoids, flavonoids and phenolic acids represent the largest groups of compounds isolated from the extracts in *Baccharis* (CAMPOS et al., 2016). Diterpenes, kauranes and labdanes can be found (GIANELLO et al., 2000; HIKAWCZUK et al., 2002; AKAIKE et al., 2003; VERDI et al., 2005; HAYASHI et al., 2005; PETENATTI et al., 2007; GARCIA et al., 2014; CAMPOS et al., 2016). Flavonoids are mainly represented by flavones (SHARP et al., 2001; VERDI et al., 2004; VERDI et al., 2005; ABAD; BERMEJO, 2007; GRECCO et al., 2012; CAMPOS et al., 2016).

Baccharis also is a rich source of essential oils and many papers focus on the identification of its constituents, such as α-cadinene, spathulenol β-caryophyllene, germacrene-D (ABAD; BERMEJO, 2007; LAGO et al., 2008a, b; SCHOSSLER et al., 2009; BUDEL et al., 2012). There are several reports about the biological activity of essential oils from *Baccharis* as fungicide, anti-bactericidal (GIANELLO et al., 2000; COBOS et al., 2001; DEMO et al., 2005), antiulcerogenic (KLOPELL et al., 2007) and insect repellent (ABAD, BERMEJO, 2007; GARCIA et al., 2005). A research showed that the triterpenes from *Baccharis* species can be explored as a new therapeutic agent for use against American Tegumentar Leishmaniasis (YAMAMOTO et al., 2014). Schistosomicidal activity was demonstrated for essential oil of *B. trimera* (Less.) DC. (OLIVEIRA et al., 2012). *Baccharis* articulata (Lam.) Pers., *B. genistelloides* subsp. *crispa* (Spreng.) Joch. Müll., *B. dracunculifolia* DC. and *B. gaudichaudiana* DC. showed anti-inflammatory potential (FLORÃO et al., 2012).

In the last years, our group has extensively worked on the morpho-anatomical analysis the secretory elements related to the oil production and essential oil composition of different *Baccharis* species, leading to provide similarities and differences among them (BUDEL, DUARTE, 2010; SOUZA et al., 2011; OLIVEIRA et al., 2011; JASINSKI et al., 2014; PEREIRA et al., 2014; BUDEL et al., 2015; BARRETO et al., 2015; BOBEK et al., 2015; BOBEK et al., 2016b). Regarding the importance of the oil components of *Baccharis* the goal of this paper is to gather data on the composition of the terpene constituents of several species of *Baccharis*, as well as compare the main components from these essential oils.

2. Material and Methods

The data collected for the composition of this review were conducted by research in the Chemical Abstract, PubMed, Web of Science, Google Scholar and Science Direct. The key words used in the research, in many combinations, were: *Baccharis*, essential oils, essence, terpenes, monoterpenes and sesquiterpenes. The relevant references were analyzed and used to compose the tables of this review. The considered data were only from papers, books, and theses. Communications in congresses and symposia were not considered.

This study presents information on the essential oils of 22 species, with a total of 33 samples. The studied species are native to many parts of Brazil and Argentina, and were collected in different months of year. The procedures used in the development of the researches were extraction by hydrodistillation and identification by GC/MS (Gas Chromatography - Mass Spectrometry).

3. Results and Discussion

According to Table 1, the volatile oils content ranged between 0.08% and 1.25%. The species with the highest yield was *B. tandilensis*, while the lowest content were achieved for *B. crispa* collected in Argentina and *B. schultzii* from Brazil.

Table 1. Data obtained for *Baccharis* species from the reviewed literature.

Species	Place of collection	Month	Oil content	[ ]%	Terpenes	Ref.
				Mono	Sesqui	
B. articulata	Córdoba, Argentina	Feb	0.15	1.30	94.0	Zunino et al. (1998a)
B. articulata	Campestre da Serra - RS, Brasil	Nov	0.20	63.00	15.2	Agostini et al. (2005)
B. articulata	Campo Magro – PR, Brasil	Sep	0.5	12.36	77.78	Budel (2003)
B. articulata	Guaíba - RS, Brasil	Jul	0.3	44.10	49.5	Simões-Pires et al. (2005)
B. cognata	Caxias do sul - RS, Brasil	Sep	0.1	47.50	33.7	Agostini et al. (2005)
B. crispa	Castro - PR, Brasil	Aug	0.2	-	92.7	Simões-Pires et al. (2005)
B. crispa	Guaíba - RS, Brasil	Jul	0.2	7.80	68.8	Simões-Pires et al. (2005)
B. crispa	Córdoba, Argentina	Feb	0.08	-	92.6	Zunino et al. (1998b)
B. cylindrica	Campo Largo – PR, Brasil	Feb	0.6	6.50	85.45	Budel (2003)
B. darwinii	Comodoro Rivadavia, Argentina	Oct	0.32	94.3	2.9	Kurdelas et al. (2012)
B. dracunculifolia	Ponta Grossa – PR, Brasil	Feb	0.8	16.60	77.05	Budel (2003)
B. dracunculifolia	Campos do Jordão - SP, Brasil	Jul	0.21	0.30	71.97	Lago et al. (2008a)
B. dracunculifolia	Viçosa - MG, Brasil	Aug	0.8	20.1	52.2	Lage et al. (2015)

B. gaudichaudiana	Inácio Martins – PR, Brasil	Oct	0.1	13.08	86.96	Budel (2003)
B. microcephala	Guaíba - RS, Brasil	Jul	0.2	-	85.6	Simões-Pires et al. (2005)
B. microdonta	Campos do Jordão - SP, Brasil	Jul	0.09	9.23	66.70	Lago et al. (2008a)
B. milleflora	São Francisco de Paula - RS, Brasil	Nov	0.1	38.40	29.5	Agostini et al. (2005)
B. myriocephala	São Francisco de Paula - RS, Brasil	Aug	0.2	8.20	90.2	Simões-Pires et al. (2005)
B. myrtilloides	Córdoba, Argentina	Feb	0.10	16.90	77.5	Zunino et al. (1998a)
B. oxyodonta	Caxias do Sul - RS, Brasil	Jul	0.30	69.20	14.9	Agostini et al. (2005)
B. regnelli	Campos do Jordão - SP, Brasil	Jul	0.12	35.79	44.34	Lago et al. (2008a)
B. rufescens	Córdoba, Argentina	Feb	0.14	24.40	73.1	Zunino et al. (1998a)
B. salicifolia	Córdoba, Argentina	Feb	0.23	8.59	89.4	Zunino et al. (1998b)
B. schultzii	Campos do Jordão - SP, Brasil	Jul	0.08	34.93	57.63	Lago et al. (2008a)
B. semisserata	Caxias do sul - RS, Brasil	Jul	0.10	36.60	29.2	Agostini et al. (2005)
B. tandilensis	Buenos Aires, Argentina	Sep	1.25	48.21	40.93	Prado et al. (2003)
B. tridentata	Itumirim – MG, Brasil	Oct	0.091	78.64	14.54	Souza et al. (2011b)
B. trimera	Campos do Jordão - SP, Brasil	Jul	0.15	7.20	68.07	Lago et al. (2008a)
B. trimera	São Francisco de Paula - RS, Brasil	Aug	0.9	43.10	50.8	Simões-Pires et al. (2005)
B. uncinella	São Francisco de Paula - RS, Brasil	Nov	0.2	44.80	34.8	Agostini et al. (2005)
B. uncinella	Campos do Jordão - SP, Brasil	Jul	0.17	21.34	48.61	Lago et al. (2008a)
B. uncinella	Ponta Grossa - PR, Brasil	Nov	0.27	2.19	80.56	Ascari et al. (2009)
B. uncinella	Vacas Gordas - PR, Brasil	Jul	0.47	36.41	52.34	Ascari et al. (2009)

[ ] = Concentration, mono = monoterpenes, sesqui = sesquiterpenes, Ref = References

Source: own authors' compilation (2016).

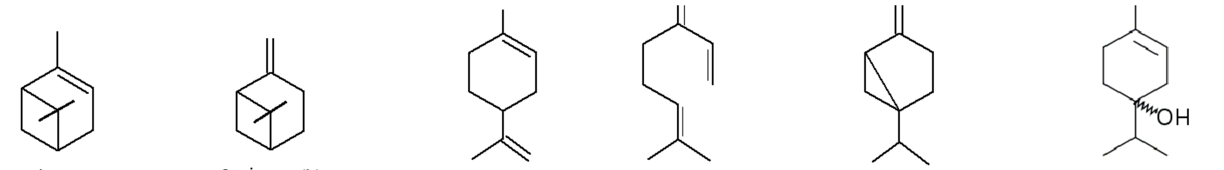
Table 2 shows the terpene components that were reported to the investigated species. Among the monoterpenes, the highlights were α-pinene, β-pinene, limonene, myrcene, sabinene and terpinen-4-ol (Figure 1). Regarding the sesquiterpenes, the main compounds were *β*-caryophyllene, germacrene-D, spathulenol, nerolidol, bicyclogermacrene and caryophyllene oxide (Figure 2).

Table 2. Chemical constituents of essential oils of *Baccharis* from the reviewed literature.

	Species																															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
Contents	[.] % of chemical constituents																															
Monoterpenes																																
α-pinene (a)	-	2.6	0.6	3.1	5.7	-	0.4	-	0.2	4.6	1.4	-	2.6	-	-	8.1	2.9	0.3	-	-	1.1	-	0.1	1	7.8	7.4	0.6	1.1	-	13	14	-	13
β-pinene (b)	0.1	47	5.6	30	27	-	6.4	-	-	-	6.6	0.5	6.7	-	-	1.1	34	4.8	0.1	9.3	-	2	0.4	0.4	5.8	33	20.3	-	2.4	9.8	6.7	-	5.3
α-thujene	-	-	-	-	1.2	-	-	-	-	-	0	-	-	-	-	-	-	-	0.1	-	-	3.2	0.1	-	-	0.1	-	-	-	2.4	-	-	1.4
limonene (c)	0.1	16	3.3	7.1	10	-	-	-	3.3	47.1	6.7	-	6.9	2	-	-	2.4	0.7	0.8	24	-	14	1	34	12	3.7	1.3	-	0.8	14	-	-	9.9
myrcene	0.1	-	0.2	1.2	1.4	-	-	-	-	3.6	0.6	-	1.3	-	-	-	0.1	-	0.3	5	2.4	0.1	-	-	2.6	1.4	6.08	6.1	-	1.3	-	-	-
sabinene (d)	-	-	-	-	1.8	-	-	-	-	5.7	-	-	-	-	-	-	-	-	0.1	21	2.3	1.3	-	-	0.4	0.4	-	-	-	1.1	0.3	-	-
α-terpinene (e)	-	-	0.6	-	-	-	-	-	-	0.1	-	-	0.1	-	-	-	-	-	0.3	-	-	0.1	-	-	-	0.1	-	-	-	0.6	-	-	0.9
terpinen-4-ol (f)	0.1	-	0.1	-	-	-	-	-	-	6.4	0.1	-	0.4	0.7	-	-	-	0.5	8.2	1.2	-	1.6	-	-	7.4	0.2	3.53	-	-	2.1	-	0.4	2.8
carquejol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.7	-	-	-	-
carquejyl acetate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	36	-	-	-	-
Sesquiterpenes																																
β-elemene	0.4	-	0.3	-	-	-	-	1.3	1	-	0.3	53	0.5	-	1.7	-	-	-	1.2	-	11	0.1	0.1	-	-	0.4	0.26	1.7	0.4	-	3.1	-	1.6
β-caryophyllene (g)	17	1.5	14	4.4	2.7	2.5	5.3	10	1.5	-	6.3	-	2.4	3.9	5.2	-	0.9	-	4.7	1.6	-	4.5	6	8.3	6.7	1.7	4.24	-	-	1.5	3.6	11	0.5
germacrene D (h)	9.3	2.9	14	-	1.1	17	-	19	12	-	5.4	4	7.2	0.7	-	-	2	-	9.5	2.8	-	8.3	8.8	-	0.6	1.5	4.44	8.9	-	2.1	3.3	6.3	0.3
α-himachalene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.9	-	-	-	-	-	-	-	-	-	-	0.3	-	-	-	-	-	-	4.2
viridiflorol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.6	-	-	-	-	-	-	-	-	-	16	-	-	-	-	-	-	3.5
γ-cadinene	2.6	-	-	-	-	-	-	3.3	-	0.6	-	-	-	-	-	-	-	-	4.2	-	-	7.5	4.8	-	-	0.2	0.34	-	-	-	-	-	5.4
δ-cadinene	1.1	0.7	7.2	4.2	-	-	1.8	0.6	3.5	-	3	-	3.8	5.6	3.6	2.4	4.9	-	0.1	-	13	1.7	3.1	2.7	-	1.5	0.81	0.6	-	0.6	13	-	0.3
spathulenol (i)	2	7.4	4.8	9.7	21	24	14	3.1	1.9	0.4	14	-	5.3	21	8.6	0.8	11	5.6	3.5	6.7	-	0.1	1.6	17	16	6.9	0.19	-	1.2	23	-	17	16
globulol	-	-	2.8	4.1	-	30	3	-	0.6	-	3.9	-	-	18		-			-	-	-	-	-	-		1.1	-	1.7		-	-	-	-
nerolidol (j)	16	-	0.1	-	-	-	2	27	-	-	12	2.3	22.3	-	1.9	-	-	2.5	8.8	-	3.6	15	2.1	-	-	-	-	-	20	-	-	-	0.4
α-eudesmol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.5	1.9
β-eudesmol	-	-	0.1	-	-	-	-	-	0.1	-	0.2	-	-	-	-	-	-	9.8	-	-	-	-	-	-	0.9	-	-	-	14	-	-	-	-
humulene oxide	-	-	-	-	-	-	1.5	-	-	-		-	-	-	-	-	-	3.3	-	-	-	-	-	-	-	-	-	-	5.1	-	-	-	-
bicyclogermacrene (k)	0.1	0.9	0.5	-	2.6	-	-	2.5	-	-	0.3	1	6.5	-	-	0.7	0.6	-	2	3.5	12	0.1	2.7	3	-	3.9	0.19	2.7	-	1.1	-	-	-
caryophyllene oxide (l)	4.5	1.9	-	-	5.9	-	-	2.2	-	-	-	-	-	-	6.5	24	3.8	6.6	1.2	-	-	3.7	4.2	-	-	-	0.87	-	-	4.5	-	16	2.9
epiglobulol	-	-	-	11	-	0.5	17	-	-	-	-	-	-	-	4.5	-	-	46	-	-	-	-	-	-	-	-	-	-	8.3	-	-	-	-

Source: own authors' compilation (2016).

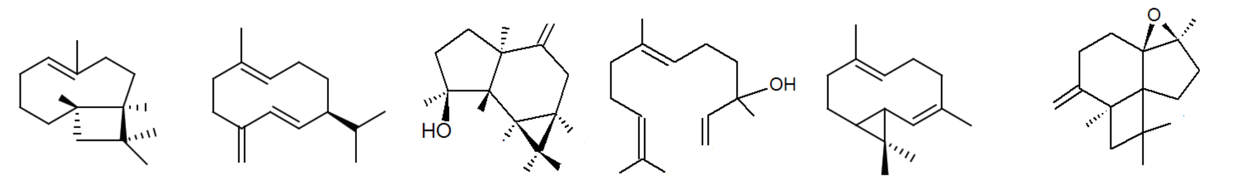
Figure 1: Major monoterpenes that were presented in essential oils of *Baccharis.*



α-pinene (a) β-pinene (b) Limonene (c) Myrcene (d) Sabinene (e) Terpinen-4-ol (f)

Source: own authors (2016).

Figure 2. Major sesquiterpenes that were found in essential oils of *Baccharis*.



β-caryophyllene (g) Germacrene-D (h) Spathulenol (i) Nerolidol (j) Bicyclogermacrene (k) Caryophyllene oxide (l)

Source: own authors (2016).

Many works have reported the occurrence of monoterpenes and sesquiterpenes compounds in the chemical composition of essential oils of *Baccharis*. According to Simões and Spitzer (2007), about 90% of the volatile oils are mainly composed by monoterpenes. However, in the reviewed studies, most species of *Baccharis* have shown sesquiterpenes as main components. Additionally, variations in their amount for each species can be widely observed.

According to Table 1, only nine samples show a predominance of monoterpenes: *B. articulata, B. cognata, B. darwinii, B. milleflora, B. oxyodonta, B. semisserrata, B. tandilensis, B. tridentata, B. uncinella*. On the other hand, two samples of *B. crispa* and *B. microcephala* have no monoterpenes in the analyzed volatile oil. Concerning the monoterpenes, special attention should be given to *B. trimera* by the presence of an unusual compound, carquejyl acetate (36%), which corresponds to the acetate of the oxygenated monoterpene carquejol (3.5%) that is observed only in this sample of *Baccharis*.

The chemical composition of these essential oils of *Baccharis* revealed a high proportion of sesquiterpenes in *B*. *articulata* from Argentina (94.0%), *B*. *crispa* collected in Paraná State, Brazil (92.7%), *B*. *crispa* collected in Argentina (92.6%) and *B*. *myriocephala* (90.2%) from Rio Grande do Sul State, Brazil. The amounts of sesquiterpenes have varied from 2.9 to 94% in the studied species.

Lago et al. (2008a) studied the chemical composition of essential oils of six *Baccharis* species collected in Campos do Jordão, Brazil. A high proportion of monoterpenes was verified in *B. schultzii* (34.93%), *B. regnelli* (35.79%) and *B. uncinella* (21.34%) while sesquiterpenes were more abundant in *B. dracunculifolia* (63.10%), *B. regnelli* (37.76%), *B. trimera* (53.52 %) and *B. microdonta* (49.91%).

It is important to highlight that the variation in the content of the essential oils have been related to the genetic pattern of the species as well as the seasonal conditions, circadian rhythms and environmental factors that influence the development of the plants. These factors are of great importance, regarding both the quantity and the quality of its constituents, since they are not constant throughout the year. Seasonal variations have influenced the content of almost every class of secondary metabolites. Essential oils can vary the concentration of certain constituents up to 80% (GOBBO-NETO; LOPES, 2007).

According to Table 1, the same species, grown and collected in different places and periods, showed considerable difference in yield and content of their chemical constituents, as observed in *B. articulata*, *B. crispa*, *B. dracunculifolia*, *B. trimera* and *B. uncinella*.

A research demonstrated the chemical composition and seasonal variation throughout one year of essential oils from leaves of *B. microdonta* and *B. elaeagnoides*. A total of 43 compounds were identified, and a predominance of oxygenated sesquiterpene derivatives was found in both species. The main components of *B. microdonta* oils were elemol (11.7-30.6%), spathulenol (4.7-9.1%), β-caryophyllene (3.7-6.2%), and germacrene-D (2.9-12.2%) (SAYURI et al., 2010). A study carried out with *B. trimera* demonstrated that a plant growing in sunny areas was able to produce at least twice the essential oil yield than a specimen growing partly in shadow (SILVA et al., 2006). A paper was performed to compare the composition and sedative properties of essential oils of *B. uncinella* obtained closer (BU-SC) and farther (BU-PR) to Laklaño Indian Reserve, Brazil. BU-SC presents a higher monoterpene/sesquiterpene ratio (0.31); α-pinene (6.42%), limonene (7.21%), caryophyllene (26.13%), spathulenol (13.39%) and caryophyllene oxide (13.26%) were identified as major components. BU-PR shows a low monoterpene/sesquitepene ratio (0.004); spathulenol (32.93%), caryophyllene oxide (27.78%), viridiflorol (5.29%) and α-cadinol (2.42%) were registered as the main compounds (FIGUEIREDO-RINHEL et al., 2013).

Budel et al. (2012) confirmed that the composition of essential oils of *B. anomala*, *B. megapotamica* and *B. ochracea* shows the remarkable tendency of *Baccharis* to biosynthesize sesquiterpenes. In addition, sesquiterpenes are usually related with a bitter taste in *Baccharis* (COBOS et al., 2001). Due to the high content of sesquiterpenes, the composition of the studied essential oils could also be used as a chemical standard to evaluate quality in bitters from these species.

The analysis of literature demonstrates a certain similarity among the volatile chemical components since 24 terpene constituents are observed with considerable frequency in 33 species of *Baccharis*. However, no chemical marker can be established to characterize *Baccharis* species. In general, sesquiterpenes are more frequent than monoterpenes in this genus. Therefore based on the results obtained in this review, there is a tendency in sesquiterpenes accumulation as main components of essential oils from *Baccharis* species.

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