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ESSENTIAL OILS OF *BACCHARIS UNCINELLA* DC.**ÓLEOS ESSENCIAIS DE *BACCHARIS UNCINELLA* DC.****Jociani Ascari¹; Domingos Sávio Nunes^{1*}; Mariza Boscacci Marques¹; Rosângela Capuano Tardivo²; Valdir Cechinel Filho³; Edesio Luiz Simionatto⁴; Alberto Wisniewski Junior⁴**

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ABSTRACT

The essential oils from the leaves of *Baccharis uncinella* collected in two distant areas of Southern Brazil were analyzed by GC-MS. The oil sample from the State of Paraná presented low monoterpene content (2.29%) and sesquiterpenes as the main components like spathulenol 17.20%, caryophyllene oxide 16.20%, caryophyllene 10.48%, α -eudesmol 7.55%, germacrene D 6.28% and α -cadinol 5.18%. The oil from the State of Santa Catarina presented a composition that is similar to published data for samples from the State of Rio Grande do Sul, showing spathulenol as the main component (15.83%) but also around 36% of monoterpenes including 12.90% α -pinene, 9.90% limonene, 5.39% γ -cadinene and 5.25% β -pinene.

Keywords: *Baccharis uncinella*. Essential oils. GC-MS.

RESUMO

Os óleos essenciais das folhas de *Baccharis uncinella* coletadas em duas áreas distantes da região sul do Brasil foram analisados por CG-EM. A amostra de óleo do estado do Paraná apresentou baixo conteúdo em monoterpenos (2,29%) e, como principais componentes sesquiterpênicos, 17,20% de espatulenol, 16,20% de cariofileno-óxido, 10,48% de cariofileno, 7,55% de α -eudesmol, 6,28% de germacreno D e 5,18% de α -cadinol. O óleo do estado de Santa Catarina apresentou uma composição similar aos dados publicados sobre amostras do estado do Rio Grande do Sul, indicando o espatulenol como principal componente (15,83%),

mas também cerca de 36% de monoterpenos, incluindo 12,90% de α -pineno, 9,90% de limoneno, 5,39% de γ -cadineno e 5,25% de β -pineno.

Palavras-chave: *Baccharis uncinella*. Óleo essencial. CG-EM.

1 Introduction

About 100 *Baccharis* species, among which at least 34 can be considered as Brazilian species, were already researched regarding their solid secondary metabolites like flavonoids, diterpenes and triterpenes (VERDI et al., 1995). The interest for the substances produced by plants of the *Baccharis* genus increased considerably in the last years, in view of the discovery of strong antioxidant compounds present in the Brazilian "green propolis", which are extracted by *Apis mellifera* bees from the sprouts of *B. dracunculifolia* (PARK et al., 2002; KUMAZAWA et al., 2003).

The essential oils of *Baccharis*, on the other hand, are also studied as possible sources of substances of industrial interest, as is the case of the oil obtained from the aerial parts of *B. dracunculifolia*, which can have a high content in (*E*)-nerolidol (CASSEL et al., 2000; FERRACINI et al., 1995; MOTL e TRKA, 1983; QUEIROGA et al., 1990). The essential oils of the aerial parts of some 38 species of this genus had their chemical compositions studied at least once a time according to current data found in the Chemical Abstracts (CAS, 2009).

Essential oils of the aerial parts of *B. uncinella* containing monoterpenes between 37% and 60% were obtained from several samples collected in the State of Rio Grande do Sul, Brazil (AGOSTINI et al., 2005; FRIZZO et al., 2001 e 2008). This plant species presents spontaneous distribution in the highlands and plateau areas of southern Brazil. Although it is not mentioned in the Brazilian traditional medicine, this plant is used in the form of a tea with alleged soothing and antihypertensive actions by the Laklaño Indians inhabiting the reservation known as Terra Indígena de Ibirama, situated in the State of Santa Catarina, Brazil (SENS, 2002). We aim to present here the results of the GC-MS analyses of essential oils obtained from leaves of *B. uncinella* collected in the State of Paraná and in the State of Santa Catarina, Brazil.

2 Material and methods

2.1 Collection of the plant materials

The leaves of *Baccharis uncinella* DC. were collected in the municipal district of Ponta Grossa, Paraná (altitude of 1,070 m, 25°07'56" South and 49°59'41" West) in November of 2005, being the voucher specimen deposited in the Herbarium of the Universidade Estadual de Ponta Grossa under the number HUPG-13105. One second collection of leaves was done at the place known as Vacas Gordas, municipal district of Urubici, Santa Catarina (altitude of 1,360 m, 28°09'44" South and 49°40'59" West) in July of 2006, registered under the number HUPG-13748.

2.2 Extraction of the essential oils

The leaves were dried in the air during 7 days at room temperature and then carefully separated from the finest branches. The essential oils were obtained by hidrodistillation in a glass apparatus for 4 hours using a 2 liters glass balloon containing 100 grams of dried and grinded leaves and 1 liter of distilled water.

2.3 GC-MS analyses of the essential oils

The oil samples were analyzed in a Varian® CP-3800 Gas Chromatograph coupled to a FID detector or to a Saturn® 2000 Mass Spectrometer using the software Saturn® GC-MS Workstation 5.51. The quantification of the components was accomplished by GC-FID. Identical analysis conditions were used, so much in the GC-MS as in GC-FID: apolar capillary column CP-Sil-8 CB Low Bleed/MS (30 m, 0.25 mm, with a film of 0.25 μ m). The temperature of the injector was 250 °C and the temperature of the oven was programmed for 60 °C in the first 3 min, going up 5 °C/min up to 220 °C and then staying in this temperature for more 15 min. The Kovàts

indices were calculated by using the data of the injection of a series of n-alkanes (C9-C26) in the same chromatographic conditions as those used for the oil samples. The components were first identified by the comparison of the obtained mass spectra with those of the equipment data bank, following the comparison of Kovats retention indices (KI) with published data (ADAMS, 1995; AGOSTINI et al., 2005; FERRACINI et al., 1995; FRIZZO et al., 2001 e 2008; PHEROBASE, 2008).

3 Results and discussion

As mentioned above, two studies were published in the last years on the composition of essential oils samples of *B. uncinella* collected in the State of Rio Grande do Sul, Brazil. The first samples collected in April produced 0.23% of an essential oil containing α -pinene 16.1%, β -pinene 15.5%, limonene 13.1% and spathulenol 9.8% as the main components (AGOSTINI et al., 2005). Two samples collected in November in the region known as Serra Gaúcha yielded around 0.2% of essential oils containing 8.1 and 12.9% of α -pinene, 10.2 and 9.8% of β -pinene, 16.8 and 14.2% of limonene and 47.7 and 23.1% of spathulenol (FRIZZO et al., 2001 e 2008). These published data could indicate that the mentioned four compounds appear in the oil of *B. uncinella* as principal components over the year, always presenting a high proportion of monoterpenes. Also a sample of *B. uncinella* collected more recently in Campos do Jordão, State of São Paulo, produced an essential oil presenting a high monoterpenes/sesquiterpenes ratio, with 13.5% of α -pinene and 6.6% of β -pinene, although no limonene could be detected in this collection (LAGO et al. 2008).

The Table 1 summarizes our results of the GC-MS analyses of the essential oils hidrodistilled from leaves of *B. uncinella* collected in the highlands of the State of Santa Catarina (SC, 0.47% yield) and in the second plateau of the State of Paraná (PR, 0.27% yield). The composition of the SC-essential oil (Table 1) shows a profile that is very similar to those observed previously for oils proceeding from collections made in the Serra Gaúcha, also when the minor components are compared and in spite of some differences mainly in the case of the spathulenol proportions, these samples keep a perceptible similarity

Table 1 - Compositions of the essential oils from leaves of *B. uncinella* collected in the Southern Brazilian States of Paraná (PR) and Santa Catarina (SC).

	PR	SC	
Components	%	%	KI*
α -thujene	-	1.43	933
α -pinene	tr	12.90	940
β -pinene	tr	5.25	982
α -terpinene	-	0.94	1019
limonene	tr	9.90	1032
γ -terpinene	-	1.03	1061
terpinolene	-	0.12	1088
linalool	0.53	-	1101
fenchol	-	0.23	1124
<i>trans</i> -pinocarveol	0.40	0.20	1146
borneol	-	0.27	1178
terpinen-4-ol	0.41	2.78	1185
<i>p</i> -cimen-8-ol	-	0.12	1192
α -terpineol	0.63	0.99	1200
mirtanal	0.22	-	1202
ciclosativene	-	0.14	1374
β -bourbonene	tr	0.11	1389
β -elemene	tr	1.64	1393
methyl eugenol	1.13	-	1401
α -gurjunene	3.43	0.20	1412
caryophyllene	10.48	0.48	1426
α -himachalene	tr	4.15	1445
α -humulene	0.40	-	1463
allo-aromadendrene	tr	0.48	1465
valencene	-	1.33	1480
germacrene D	6.28	0.32	1486
Ar-curcumene	-	0.51	1487
viridiflorene	1.35	1.20	1497
<i>trans</i> - β -guaiene	0.81	1.54	1502
cuparene	1.61	-	1510
β -curcumene	3.23	-	1515
γ -cadinene	tr	5.39	1519
δ -cadinene	tr	0.27	1524
cadina-1,4-diene	0.73	1.56	1539
α -calacorene	0.43	2.30	1548
germacrene B	-	0.85	1554
elemol	1.36	-	1555
<i>cis</i> -nerolidol	-	0.37	1564
β -calacorene	0.54	-	1570
spathulenol	17.20	15.83	1586
caryophyllene oxide	16.20	2.91	1592
viridiflorol	-	3.54	1603
γ -eudesmol	-	1.45	1633
cubenol	-	2.20	1636
α -cadinol	5.18	-	1653
α -muurolol	-	1.40	1655
α -eudesmol	7.55	1.92	1665
α -santalol	2.23	-	1679
cadalene	-	0.50	1681
aristolene	0.33	-	1749
<i>cis</i> -nuciferol	0.18	-	1765
Total (%)	82.84	88.75	

* KI data in apolar column.

in the composition (AGOSTINI et al., 2005; FRIZZO et al., 2001 e 2008).

However, the essential oil of the leaves collected in the State of Paraná (PR, in the Table 1) has only sesquiterpenes as main components, resulting in a composition that is completely different from the others: 17.20% of spathulenol, 16.20% of caryophyllene oxide, 10.48% of caryophyllene, 7.55% of α -eudesmol, 6.27% of germacrene D and 5.18% of α -cadinol. Even though the occurrence of arylprope-noid volatile derivatives in *Baccharis* species is quite rare, methyl eugenol was found in the PR-essential oil in 1.13% and solid arylprope-noids were isolated from the leaves of *B. uncinella* in another part of the present research work (ASCARI, 2007).

Recently, the essential oils of eight *Baccharis* species belonging to the section Caulopterae collected in Brazil and in Argentine (*B. articulata*, *B. crispa*, *B. microcephala*, *B. milleflora*, *B. myriocephala*, *B. stenocephala*, *B. trimera* and *B. usterii*) were analyzed to verify possible biosynthetic correlations in the volatile compositions (SIMÕES-PIRES et al., 2005). At least three of these species are popularly known as “carqueja” but in spite of the morphologic similarities, these species of the botanical section Caulopterae did not present essential oils with homogeneous profile. On the contrary, some of them showed a high differentiation degree, like *B. trimera*, the only species producing carquejyl acetate between 35% and 68% in counterbalance with ledol proportions between 5.9% and 24.2%. Although *B. trimera* and *B. crispa* are morphologically very similar, the occurrence of the carquejyl acetate was found only in the first species. In the mentioned research work (SIMÕES-PIRES et al., 2005), a lot of samples were compared but the causes of the observed variations in the composition of essential oils obtained from the same plant species, remained undetermined.

A pioneer systematic research work on the chemical composition of *Baccharis* essential oils, included seven species collected in a savannah area of the State of São Paulo, Brazil (*B. caprariaefolia*, *B. dracunculifolia*, *B. erioclada*, *B. myriocephala*, *B. platipoda*, *B. tridentata* and *B. vincaefolia*) and presented comparisons among essential oils from male and female specimens. *B. erioclada* collected in the region of Campos do Jordão showed the more remarkable differences between oils of male and female specimens: α -pinene 0.26% and 8.45%,

β -pinene 1.6% and 21.44%, limonene 2.68% and 15.16%, β -caryophyllene 10.70% and 4.21%, spathulenol 12.57% and 6.61% (FERRACINI et al., 1995). Also of great interest in the cited work is the observation in male and female *B. dracunculifolia* specimens of the daytime oil composition variations, that can therefore be assumed as another plausible cause for the differences found between oil samples compositions.

4 Conclusions

The published data discussed here suggest that the differences found in the composition of the oil distilled from leaves of *B. uncinella* collected in the State of Paraná in comparison with the one obtained from leaves collected in the State of Santa Catarina (Table 1) could be due to genetic or ecological factors. Future studies on this issue should also take in account the possible variation of the volatile composition of male and female essential oils.

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