Revista Brasileira de Ciências Farmacêuticas
Brazilian Journal of Pharmaceutical Sciences
vol. 38, n. 3, jul./set., 2002

RBCF

Essential oils from *Calyptranthes concinna, C. lucida* and *C. rubella* (Myrtaceae)

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Essential oils from Calyptranthes concinna*,* C. luci*da and* C. rubella*, collected in Southern Brazil, were analyzed by GC and GC/MS. Sixty-two compounds were identified representing about 98% of the oil contents. All samples were rich in cyclic sesquiterpenes (more than 90 %), mainly those from cadinane, bisabolane and germacrane cyclization pathway. The mainly components characterized were bicyclogermacrene (22.1% in* C. concinna*; 11.7% in* C. rubella*), cis-calamenene (10.3% in* C. concinna*), beta-caryophyllene (16.5% in* C. rubella*; 9.4% in* C. lucida*), beta-bisabolene (25.5% in* C. lucida*), spathulenol (15.4% in* C. rubella*) and caryophyllene oxide (7.6% in* C. concinna*).*

Uniterms:
- *Calyptranthes concinna*
- *Calyptranthes lucida*
- *Calyptranthes rubella*
- Myrtaceae
- Essential oil

INTRODUCTION

The american myrtaceous genus *Calyptranthes* comprises about 100 species, ranging from Mexico to Uruguay (McVaugh, 1968). Six species grow in the state of Rio Grande do Sul (Brazil; Marchiori, Sobral, 1997): *C. concinna* DC., *C. grandifolia* O.Berg, *C. lucida* Martius ex DC., *C. pileata* D.Legrand, *C. rubella* (O.Berg) D.Legrand and *C. tricona* D.Legrand.

We had previously analyzed the oil composition of fresh leaves of *C. concinna*, *C. grandifolia* (Menut *et al.*, 1997) and *C. tricona* (Menut *et al.*, 2000). The oil from *C. grandifolia* showed predominance of pinenes (55.9%) and beta-caryophyllene (10.5%). *C. concinna* oil contained a high amount of elemicine (76%). *C. tricona* was characterized by the presence of two new alpha-monomethyl chromenes derivatives, where a new biosynthetic pathway could be proposed to explain their formation in the plant.

Another Brazilian species, *C. spruceana* (Silva *et al.*, 1984), showed two chemical varieties: high contents of limonene, geranial and perillaldehyde for the variety A, and pinenes and citral to the variety B.

Herein we present the chemical composition of the fresh leaves from *Calyptranthes lucida C. rubella*. and *C. concinna.* Since *C. concinna* has previously shown a high amount of elemicine (Menut, *et al.*, 1997) which is not characteristic for this genus, such species was recollected in a different location to confirm the chemical composition of its oil. All species are trees from coastal tropical brazilian forests; *Calyptranthes concinna* grows in forests of Argentina, Paraguay, Uruguay and Brazil, where it ranges from Minas Gerais to Rio Grande do Sul; *C.lucida* is widely distributed in Brazil, ranging from the state of Pará until Rio Grande do Sul, while *C. rubella* is more geographically restricted, growing in the southern states of Santa Catarina and Rio Grande do Sul (Legrand, Klein, 1971).

MATERIAL AND METHODS

Plant material and isolation procedure

The studied species of *Calyptranthes* were collected in Rio Grande do Sul, Brazil. *C. lucid*a and *C. rubella* were collected in Dom Pedro de Alcântara, and *C. Concinna*, in São Francisco de Paula. Voucher specimens were deposited in the ICN Herbarium (UFRGS, Porto Alegre), and are as follows: *C. concinna*: Sobral *et al*. 8886; *C. lucida*: Sobral, Apel 8384a; and *C. rubella*: Sobral, Apel 8650.

The oils were obtained from fresh leaves by hydrodistillation for five hours using a Clevenger-type apparatus.

Qualitative and quantitative analysis

Quantitative and qualitative analyses of the oils were performed by capillary GC/FID and GC/MS, respectively.

Gas Chromatography: GC analysis was performed in a chromatograph (Shimadzu GC-17A) equiped with Shimadzu GC 10 software, using a fused silica capillary column (30 m x 0.25 mm x 0.25 μm, coated with DB-5). Injector and detector temperatures were set at 220 ºC and 250 ºC, respectively; the oven temperature was programmed from 60º - 300 ºC at 3 ºC/min and helium was employed as carrier gas (1 mL/min). The percentage compositions were obtained from electronic integration measurements using flame ionization detection without taking into account relative response factors.

Gas Chromatography - Mass Spectrometry: All the samples were analyzed by GC/MS in the same apparatus and chromatographic conditions as described above, using a quadrupole MS system (QP 5000) operating at 70 eV. Compound identification was based on a comparison of retention indices (determined relatively to the retention times of a series of *n*-alkanes) and mass spectra with those of authentic samples and with literature data (Jennings, Shibamoto, 1980; Henriques *et al*., 1993; Adams, 1995; Henriques *et al*., 1997).

RESULTS AND DISCUSSION

The oil contents of all species were 0.1%.

The relative amounts of each identified constituent, accounting for the range 98.2 – 99.1% of the oils contents, according to its cyclization pathway, are presented in Table I.

The analyzed samples were characterized by presence of cyclic sesquiterpene (91.6% in *C. concinna*; 98.0% in *C. lucida* and 98.2% in *C. rubella*), with predominance of hydrocarbon sesquiterpenes of the bisabolane group (25.5% of beta-bisabolene in *C.lucida*), the caryophyllane group (9.4% of beta-caryophyllene in *C.lucida* and 16.5% in *C. rubella*) and the germacrane group (22.1% of bicyclogermacrene in *C. concinna* and 11.7% in *C.rubella*). Within the oxygenated fraction, spathulenol (skeleton aromadendrane, germacrane group; 15.4 % in *C. rubella*) was the most representative.

The monoterpene fraction could not be detected in any species. Only in *C. lucida* a small fraction of acyclic sesquiterpene (10.1%) could be characterized, where the sesquiterpene (*E*)-nerolidol (8.2%) was the most abundant.

C. lucida showed predominance of products from the bisabolane (32.2%) and germacrane (28.7%) cyclization pathway, while *C. concinna* and *C. rubella* were characterized by germacrane (47.5% and 49.2 7%, respectively) and cadinane (29.9 and 20.9%, respectively) groups. The caryophyllane/humulane groups were present in important amount in all species (13.3 7% in *C. concinna*, 20.9 7% in *C. lucida* and 23.7% in *C. rubella*). The carotane group could not be detected in any sample. It is important to remark that *C. concinna* did not present elemicine as previously reported by Menut *et al.* (1997). It may be a result of the different location the samples were collected. However, to confirm the existence of two different chemotypes, further investigation should be conducted.

A scheme of the sesquiterpene pathway can be seen in Figure 1.

CONCLUSION

The analyzed species showed the predominance of cyclic sesquiterpenes, mainly those from caryophyllane, germacrane and cadinane groups. This is a common characteristic in the essential oils of *Myrciinae's* species, except in *Myrcia fallax*, characterized by presence of alpha-bisabolol (91.9%, Henriques *et al.,* 1997) which is resulting from bisabolane pathway.

TABLE I - Composition of essential oils (%) from *Calyptranthes concinna*, *C. lucida* and *C. rubella*

constituents	*C. concinna*	*C. lucida*	*C. rubella*
Monoterpene hydrocarbons	7.0	0.0	0.0
alpha-pinene	1.2		
beta-pinene	2.1		
myrcene	1.3		
limonene	1.9		
terpinolene	0.5		
Oxygenated monoterpenes	0.9	0.0	0.0
1,8-cineol	0.3		
alpha-terpineol	0.6		
Acyclic sesquiterpene	0.0	10.1	0.0
(*Z*)-alpha-bisabolene	0.9		
(*E*)-nerolidol	8.2		
(*Z*)-(*Z*)-alpha-farnesene	1.0		
Bisabolane pathway	0.0	32.2	2.4
cis-alpha-bergamotene	1.2		
beta-bisabolene	25.5	2.4	
bisabolol oxide A	3.3		
bisabolol oxide B	0.8		
beta-bisabolol	0.6		
alpha-bisabolol	0.5		
(*E*)-gamma-bisabolene	0.3		
Cadinane pathway	29.7	7.2	20.9
alpha-cubebene	0.6	0.9	
alpha-copaene	1.9	3.2	
cadina-1(6)-4-diene	0.3		
gamma-muurolene	0.7		
germacrene D	5.4	4.5	
alpha-muurolene	0.3		
gamma-cadinene	0.4	0.5	0.6
cis-calamenene	10.3		
delta-cadinene	0.5	1.0	3.4
beta-cadinene	1.1	1.7	
alpha-cadinene	0.3		
alpha-calacorene	2.6		
1-epi-cubenol	1.0	0.3	1.5
tau-cadinol	1.3	0.8	
tau-muurolol	3.0		
cubenol	0.6	2.1	
alpha-muurolol	0.6		
alpha-cadinol	2.3	4.1	

TABLE I - Composition of essential oils (%) from *Calyptranthes concinna*, *C. lucida* and *C. rubella* (continuation)

constituents	*C. concinna*	*C. lucida*	*C. rubella*
Caryophyllane pathway	12.3	12.4	19.6
isocaryophyllene	0.9	2.2	
beta-caryophyllene	3.8	9.4	16.5
gamma-himachalene	0.8		
caryophyllene oxide	7.6	3.1	
Humulane pathway	1.0	8.5	4.1
alpha-humulene	1.0	6.2	3.0
humulene oxide I	1.0		
humulene oxide II	1.3	1.1	
Germacrene pathway	47.5	28.7	49.2
beta-bourbonene	1.2	2.1	
beta-elemene	0.8	3.2	
beta-gurjunene	0.3	0.7	1.4
aromadendrene	2.5	1.6	1.0
allo-aromadendrene	1.7	2.3	0.8
beta-selinene	0.4	5.8	1.9
delta-selinene	2.9		
alpha-selinene	7.4		
bicyclogermacrene	22.1	11.7	
germacrene A	1.0		
germacrene B	0.4	0.7	
ledol	1.7		
spathulenol	5.6	0.4	15.4
globulol	6.3	3.8	3.3
epi-globulol	2.9	0.5	4.2
guaiol	0.5		
eudesmol (isomer not identified)	1.6	1.1	1.9
10-epi-gamma-eudesmol	1.0		
isospathulenol	1.3		
Hydrocarbons	0.0	0.0	2.0
n-heneicosane	2.0		
Total	98.4	99.1	98.2

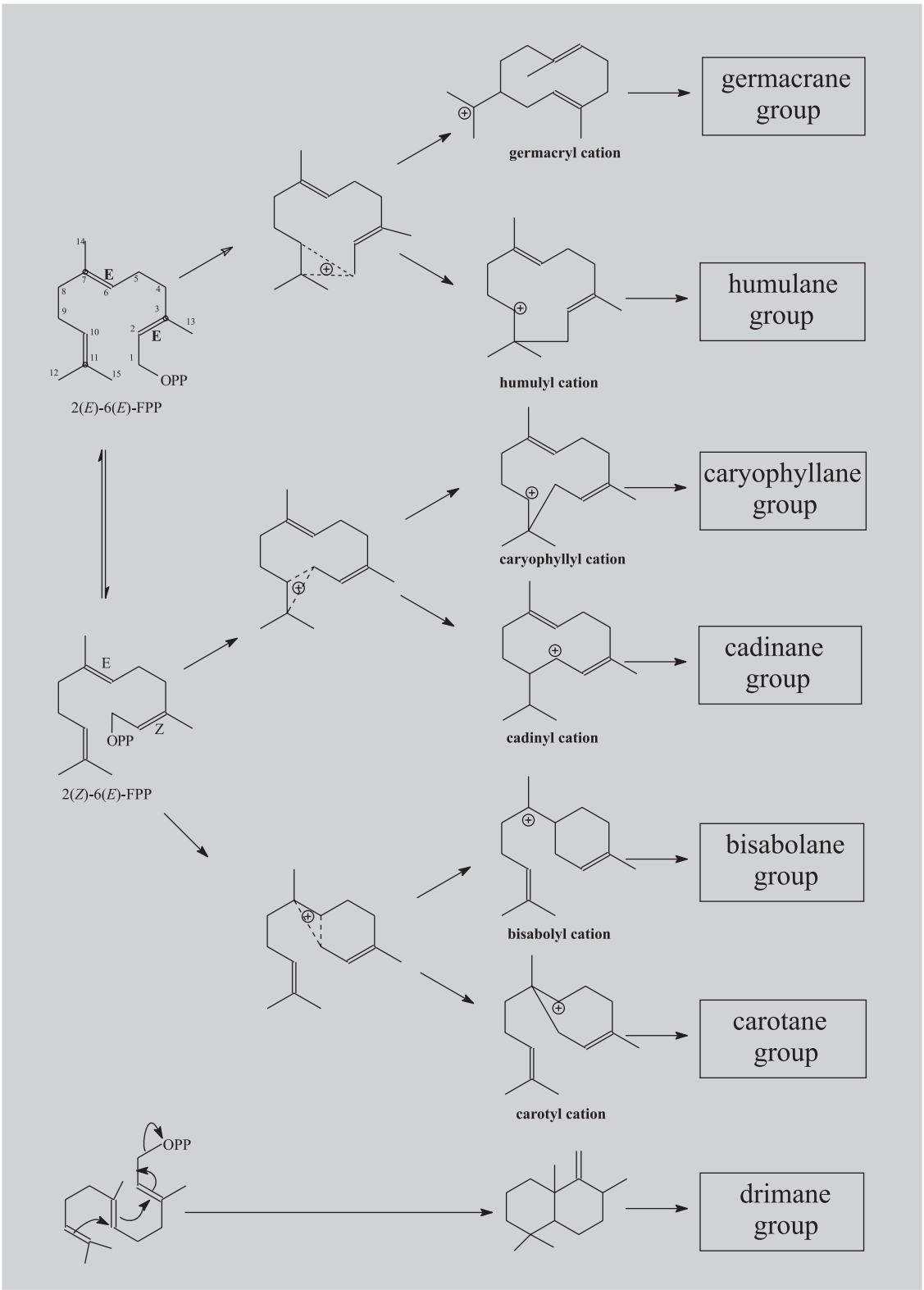

FIGURE 1 - Biosynthetic pathways for cyclic sesquiterpenes.

RESUMO

Óleos essenciais de *Calyptranthes concinna*, *C. lucida* and *C. rubella* (Myrtaceae)

Os óleos essenciais de Calyptranthes concinna, C. lucida *e* C. rubella*, coletadas no sul do Brasil, foram analisados por GC/FID e GC/MS. Sessenta e dois constituintes foram identificados representando cerca de 98% do óleo. Todas as amostras mostraram-se ricas em sesquiterpenos cíclicos (mais de 90%), principalmente aquelas da via de ciclização dos cadinanos, bisabolanos e germacranos. Os principais constituintes caracterizados foram biciclogermacreno (22,1% em* C. concinna*; 11,7% em* C. rubella*), cis-calameneno (10,3% em* C. concinna*), beta-cariofileno (16,5% em* C. rubella*; 9,4% em* C. lucida*), beta-bisaboleno (25,5% em* C. lucida*), espatulenol (15,4% em* C. rubella*) e óxido de cariofileno (7,6% em* C. concinna*).*

***UNITERMOS**:* Calyptranthes concinna. Calyptranthes lucida. Calyptranthes rubella. *Myrtaceae. Óleo essencial.*

ACKNOWLEDGEMENT

This work was supported by FAPERGS and the fellowships from CNPq.

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Recebido para publicação em 25 de julho de 2001.

O arquivo disponível sofreu correções conforme ERRATA publicada no Volume 38 Número 4 da revista.