

Seasonal variation of germacrone and atractylone in the essential oil of *Siparuna guianensis* Aublet

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RESUMO: Variação sazonal de germacrone e atractilona em óleo essencial de *Siparuna guianensis* Aublet. Relatamos recentemente os óleos essenciais de três tipos químicos amazônicos de *S. guianensis*: tipo A, rico em epi- α -bisabolol e espatulenol, tipo B rico em espatulenol e selin-11-en-4-ol, e tipo C rico em germacrone e atractilona. Neste trabalho, os óleos essenciais das folhas do tipo C foram obtidos em intervalos bimensais de Janeiro a Dezembro de 2000. Em cada coleta, o óleo foi obtido em sistema tipo Clevenger, e analisado através de CG-EM. Os maiores teores de atractilona e de germacrone foram 51,7% e 29,7%, em Março e Dezembro, respectivamente. O rendimento em óleo obtido das folhas variou de 0,9% a 1,3%.

Palavras-chave: *Siparuna guianensis*, Monimiaceae, óleos voláteis, germacrone, atractilona

ABSTRACT: In the previous study, we described the essential oil of *Siparuna guianensis* obtained from three Amazon varieties: type A, rich in epi- α -bisabolol and spathulenol, type B rich in spathulenol and selin-11-en-4-ol, and the type C rich in germacrone and atractylone. In this study, the essential oil from the leaves of the type C were obtained from January at 2 month intervals up to December 2000. At each sampling, the oil content was determined in a Clevenger-type apparatus, and examined by GC-MS. The maximum content of atractylone and germacrone were 51.7% and 29.7%, in March and January, respectively. The leaf oil yields were in the range 0.9-1.3%.

Key words: *Siparuna guianensis*, Monimiaceae, oils volatile, germacrone, atractylone

INTRODUCTION

The genus *Siparuna* (Monimiaceae) comprises ca. 150 species of shrubs and small trees of the tropical regions of Mexico, the West Indies, Central and South America. *Siparuna guianensis* Aubl. (Syn: *Citrosma campora* Tul., *C. discolor* Poepp. & Endl., *Siparuna archei* A. C. Sm., *S. arianae* Leite Pereira, *S. camporum* (Tul.) A. DC., *S. cavalcantei* Jangoux, and others), commonly known as "capitiu", "caá-pitiú", "negra-mena", "erva-santa", is most used in medicine (Berg, 1993, Branch & Silva, 1983, Milliken, 1992). The leaf, branch, and bark extracts of a specimen of *S. guianensis* were analyzed for insecticidal activity (Jacobson, 1958). The alkaloids liriodenine and cassamedine and the phytosteroids sitosterol and stigmasterol were isolated from the trunk wood of a sample of *S. guianensis* (Braz Filho *et al.*, 1976). The leaf oil of the other specimen collected at Panama was reported (Antonio *et al.*, 1984) and the major identified constituents were curzerenone and curzerenone type or products decomposing to curzerenone. The seasonal variation of the content of nerolidol in the *S. guianensis* oil were reported (Machado *et al.*, 1998) and a large seasonal variation in the nerolidol content was observed (0-

99.3%) which reached in June during flowering. The volatiles from the three chemotypes of *S. guianensis* collected at three places in the Amazon were previously reported by us (Zoghbi *et al.*, 1998). The aim of the present study was to investigate the variation of the leaf oil from *S. guianensis* during 1 year of seasonal observation.

MATERIAL AND METHOD

The samples of *S. guianensis* were collected in the campus of Museu Paraense Emílio Goeldi, Belém, state of Pará, Brasil, from the same individual shrub, approximately 3m in height. A voucher specimen (No. 150.701), has been deposited in the Herbarium of the Museu Paraense Emílio Goeldi. Samples of leaves were air-dried in a room under an air-conditioning for seven days and submitted to hydrodistillation for 3 h, using a Clevenger-type apparatus. The oil yields ranged from 0.8% to 1.3%. The total leaf oil yields were expressed as mL/100g of the dried plant material. The resulting oil was immediately used for analysis. The yield of the oil can be seen in Table 1.

The oil was analyzed by GC/MS, using a Finnigan Mat INCOS XL GC/MS instrument, with the following conditions: a WCOT DB-5MS (30 m x 0.25 mm; 0.25 mm film thickness) fused silica capillary column; temperature programmed: 60°-240°C (3°C/

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min); injector temperature: 220°C; carrier gas: He, adjusted to a linear velocity of 32 cm/sec (measured at 100°C); injection type: splitless (1 mL, of a 1:1000 hexane soln.); split flow was adjusted to give a 20:1; septum sweep was a constant 10 mL/min; EIMS: electron energy, 70 eV; ion source temperature and connection parts: 180°C. Individual components were identified by comparison of both mass spectrum and their GC retention data with those of authentic compounds previously analyzed and stored in the data system, and by comparison of mass spectra with those in the data system libraries and cited in the literature (Adams, 1995). The quantitative data were obtained by electronic integration of the TIC peak areas. The retention indices were calculated for all volatile constituents using a homologous series of *n*-alkanes. The major compounds identified in the oil are listed in Table 1.

RESULT AND DISCUSSION

The yield of essential oil were approximately

constant (0.9-1.3%) in different seasons, but the content of the components varied noticeable. The maximum value of atractylone was 51.7% in March (when the plant carried mature fruits); the minimum value was 30.5% in September. The maximum value of germacrene was 29.7% in January and the minimum value was 16.1% in November. Minimum value of germacrene B was 5.9% in March, but increased to 10.9%-12.9 in July to September. Bicyclogermacrene and germacrene D showed a similar behavior. From the results of this study it is clear that during seasonal variation the content of the components of the *S. guianensis* differed considerably, mostly due to the development of the plant (these species flowering during all the year). Seasonal variation of mono- and sesquiterpenes content were related to some species (Chalchat *et al.*, 1997; Lopes *et al.*, 1997; Machado *et al.*, 2003), but in the case of *S. guianensis* no appreciable changes in the total content of sesquiterpenoids were observed (92.5-98.9%) during the seasonal observation.

Table 1 - Mean percentage composition of the leaf oil components of *Siparuna guianensis* (January-December 2000)

	RI*	Month of sampling						
		Jan	Mar	May	July	Sept	Nov	Dec
Oil yield (%)		1.0	1.3	1.0	0.9	1.3	1.2	1.2
α -Pinene	938	0.5	0.5	0.5	1.0	0.8	0.2	0.2
β -Elemene	1390	0.6	tr	0.7	0.9	1.1	0.4	0.3
β -Caryophyllene	1418	1.2	0.4	1.0	1.6	1.7	0.5	0.6
Germacrene D	1478	8.7	8.6	14.3	11.0	12.0	13.1	13.5
Bicyclogermacrene	1492	9.6	9.8	10.5	11.1	11.4	9.2	11.7
δ -Cadinene	1522	1.1	0.7	1.1	0.8	1.2	0.7	0.8
Germacrene B	1555	8.1	5.9	8.5	10.9	12.9	9.3	12.7
Atractylone	1654	35.3	51.7	44.5	32.9	30.5	48.8	34.9
Germacrene	1690	29.7	21.8	17.6	23.8	21.7	16.1	24.2

* RI on DB5, tr = traces

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REFERENCE

ADAMS, R.P. Identification of essential oil components by gas chromatography/quadrupole mass spectroscopy. Carol Stream: Allured Publ Corp., 1995. 456p.

ANTONIO, T.M., WALLER, G.R., MUSSINAN, C.J. Composition of essential oil from the leaves of *Siparuna guianensis* (Monimiaceae). Chemistry and Industry, v.16, p.514-5, 1984.

BERG, M. E. van den. **Plantas medicinais na Amazônia:** contribuição ao seu conhecimento sistemático. Belém: Museu Paraense Emílio Goeldi, 1993. 207p.

BRANCH, L. C. SILVA, M. F. Folk medicine of alter do chão, Pará, Brasil. **Acta Amazônica**, v.13, p.737-97, 1983.

BRAZ FILHO, R., GABRIEL, S.J., GOMES, C.M.R., *et al.* Oxoaporphine Alkaloids from *Fusea longifolia* and *Siparuna guianensis*. **Phytochemistry**, v.15, p.1187-8, 1976.

- CHALCHAT, J.C., GARRY, R.P., MICHE, A. Variation of the chemical composition of essential oil of *Mentha piperita* L. during the growing time. **Journal Essential Oil Research**, v.9, p.463-5, 1997.
- JACOBSON, M. *Insecticides from Plants*. Washington: United States Department of Agriculture, 1958. 177p
- LOPES, N.P., KATO, M.J., ANDRADE, E.H. A., *et al.* Circadian and seasonal variation in the essential oil from *Virola surinamensis* leaves. **Phytochemistry**, v.46, p.689-93, 1997.
- MACHADO, S.M. F., RIBEIRO, V.A.F.A., MILITÃO, J.S., *et al.* Seasonal variation of (E)-Nerolidol in *Siparuna guianensis* Aublet and ¹³C-NMR spectral assignments of (E)- and (Z)-Nerolidol. **Journal Essential Oil Research**, v.10, p.708-10, 1998.
- MACHADO, L.B., ZOGHBI, M.G.B., ANDRADE, E.H.A. Seasonal variation in the composition of the essential oils from the leaves, thin branches and resin of *Protium spruceanum* (Benth.) Engl. **Flavour and Fragrance Journal**, v.18, p.338-41, 2003.
- MILLIKEN, W., MILLER, R.P., POLLARD, S.R., *et al.* *The ethnobotany of the Waimiri atroari Indians of Brazil*. Kew: Royal Botanic Gardens, 1992. 146p.
- ZOGHBI, M.G.B., ANDRADE, E.H.A., SANTOS, A.S., *et al.* Essential oils of *Siparuna guianensis* Aubl. **Journal of Essential Oil Research**, v.10, p.543-6, 1998.