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The first flavonoid isolated from *Bromelia laciniosa* (Bromeliaceae)

Raimundo G. de Oliveira-Júnior[1], Ana P. de Oliveira[1], Amanda L. Guimarães[1], Edigênia C. C. Araújo[1], Raimundo Braz-Filho[2], Dag O. Øvstedal[3], Torgils Fossen[4] and Jackson R. G. S. Almeida[1]*

[1]Center for Studies and Research of Medicinal Plants, Federal University of San Francisco Valley, Petrolina, Pernambuco, Brazil.
[2]Department of Chemistry of Natural Products, State University of North Fluminense, Campos dos Goytacazes, Rio de Janeiro, Brazil.
[3]Museum of Botany, University of Bergen, Bergen, Norway.
[4]Centre for Pharmacy, Department of Chemistry, University of Bergen, Bergen, Norway.

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***Bromelia laciniosa* is a native species of the Caatinga biome, popularly known as "macambira" and "macambira de porco". This paper describes the isolation and structural characterization of the first chemical constituent isolated from the leaves of *B. laciniosa*, an unprecedented flavonoid in the Bromeliaceae family. The structure was established as 5,7-dihydroxy-3,3',4'-trimethoxyflavone (quercetin 3,3',4'-trimethyl ether) on the basis of mass spectrometry and 1D and 2D nuclear magnetic resonance (NMR) experiments and further confirmed by comparison with available data in current literature.**

Key words: *Bromelia laciniosa*, Bromeliaceae, flavonoid, medicinal plants, Caatinga.

INTRODUCTION

The Bromeliaceae family has a predominantly neotropical distribution and includes about 58 genera and 3,200 species (Luther, 2010). The phytochemistry of this family is distinguished by the presence of triterpenoids and flavonoids. Other classes of compounds such as sterols, diterpenoids, cinnamic acid derivatives, substituted glycerols, lignans and nitrogen-containing compounds, among others, have also been identified in this family, although to a more limited extent. The distribution of flavonoids in leaves of species of Bromeliaceae was previously reported by Williams et al. (1978). Since the large number of species of Bromeliaceae, only few of them have been analyzed with respect to their chemical constituents so far (Manetti et al., 2009).

Several species of the genus *Bromelia* are being studied with respect to their chemical constituents and their pharmacologic activity. For example, Camacho-Hernandez et al. (2002) evaluated the antifungal activity

*Corresponding author. E-mail: jackson.guedes@univasf.edu.br. Tel/Fax: + 55 (87) 21016862.

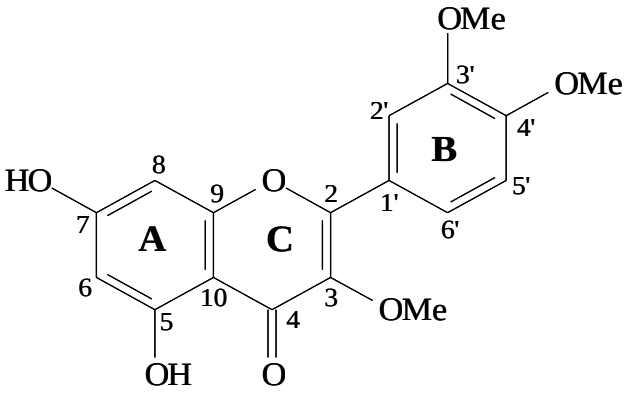

Figure 1. Chemical structure of the flavonoid quercetin 3,3',4'-trimethyl ether (1) with highlight to A, B and C rings of the generic structure of flavonoids.

of methanol extracts of pulp of *Bromelia pinguin* against various fungal strains, showing significant activity against strains of *Trichophyton* spp. and *Paecillomyces variotii*. The extracts of the leaves and branches of this species have also shown spasmodic activity, antiparasitic and cytotoxic activities (Payrol and Martinez, 2000; Raffauf et al., 1981; Geran et al., 1972). The biological potential of this species may be rationalized by the presence of diterpenes and flavonoids previously identified (Raffauf et al., 1981). Flavonoids also were identified in leaves of *Bromelia karatas* (Williams et al., 1978).

Bromelia laciniosa is a species native to the Brazilian Caatinga and is known in the Northeast region of Brazil as "macambira" and "macambira de porco". The plant is used in the alimentation of man and domestic animals, especially in times of drought (Dutra et al., 2010). From the base of the leaves is extracted a mass, wherefrom a type of bread is produced (Angelim et al., 2007). The main therapeutic indications are for treatment of child colic, diarrhea, fever, jaundice, dandruff and hepatitis (Albuquerque et al., 2007). The decoctions of the roots is also popularly used against hepatitis and intestinal disorders and as a diuretic, while the dried and powdered leaves are used in cooking as a source of proteins (Agra et al., 2007).

In the present paper, we report results of the first phytochemical study of the species *B. laciniosa* and the isolation and chemical characterization of a flavonoid described for the first time in the Bromeliaceae family.

MATERIALS AND METHODS

General experimental procedures

Mass spectra of the fraction were obtained on a gas chromatograph coupled to a mass spectrometer (QP2010 Plus, Shimadzu, Japan) with electron impact (EI) ionization, operating at an MS ionization voltage of 70 eV. The chromatograph was equipped with a fused silica capillary column FactorFour VF-5ms (30 m × 0.25 mm × 0.25 mm), and helium (He) was used as the carrier gas. The following chromatographic conditions were used: injector temperature at 250°C, detector temperature at 230°C; gas flow 1.0 ml/min; split 1/20; initial column temperature of 100°C with heating to 290°C at 3°C/min. ^{1}H and ^{13}C NMR spectra were recorded at 500.13 and 125.76 MHz for ^{1}H and ^{13}C, respectively, on a Bruker Avance DRX-500 instrument, using Methanol-D_3 (Sigma Aldrich, USA) as solvent. The residual solvent signal (^{1}H) and the solvent signal (^{13}C) were used for spectral calibration. Chemical shifts were reported in units (ppm) and coupling constants (J) in Hz. Silica gel 60 (Merck, Kiesegel 60 F_{254}) was used for analytical thin layered chromatography (TLC) and Silica gel 60 (Merck, 230 to 240 mesh) was used for column chromatography (CC). Spots on chromatograms were detected under UV light (254 and 365 nm). When necessary, vanillin sulfuric and NR + PEG reagents were used to detect the spots on the TLC plates.

Plant

The mature and healthy leaves of *B. laciniosa* Mart. ex Schult. f. (Bromeliaceae) were collected in the city of Petrolina (Coordinates 08° 59' 16.90" S and 40° 35' 20.60" W), State of Pernambuco, Brazil, in January, 2011. At the collection site, the plant was fully exposed to the sun. The samples were collected and identified by André Paviotti Fontana, a botanist from Centro de Recuperação de Áreas Degradadas da Caatinga (CRAD). A voucher specimen (6442) was deposited at the Herbário Vale do São Francisco (HVASF) of the Universidade Federal do Vale do São Francisco.

Extraction and isolation

The dried and pulverized leaves of *B. laciniosa* (879 g) were subjected to maceration with 95% EtOH for 72 h. The solution was filtered and concentrated under reduced pressure on a rotatory evaporator at 50°C, producing 39 g of crude ethanol extract (Bl-EtOH, 4.39%). For the phytochemical study, Bl-EtOH was suspended in MeOH:H_2O (3:7 v/v) and partitioned with hexane, chloroform ($CHCl_3$) and ethyl acetate (AcOEt) in increasing order of polarity to obtain the respective extracts. The chloroform fraction (Bl-$CHCl_3$) was subjected to column chromatography over silica gel eluting with hexane, $CHCl_3$, AcOEt and MeOH alone or in binary mixtures, in increasing order of polarity. In total, 113 fractions were collected (each 100 ml). The fractions were monitored by TLC and combined according to the similarity between the retention factors (R_f), resulting in different groups. The combined fractions 75 to 80 were purified by recrystallization using $CHCl_3$ to afford the flavonoid 1 (14 mg).

RESULTS AND DISCUSSION

The flavonoid 1 (Figure 1) reported in this paper was obtained as a yellow amorphous powder. The powder was dissolved in MeOH and applied to analytical TLC plate and eluted with hexane:EtOAc (70:30; v/v). Thereafter, the chromatographic plate was developed with NR + PEG reagent (NR: diphenylboric acid 2-amino-

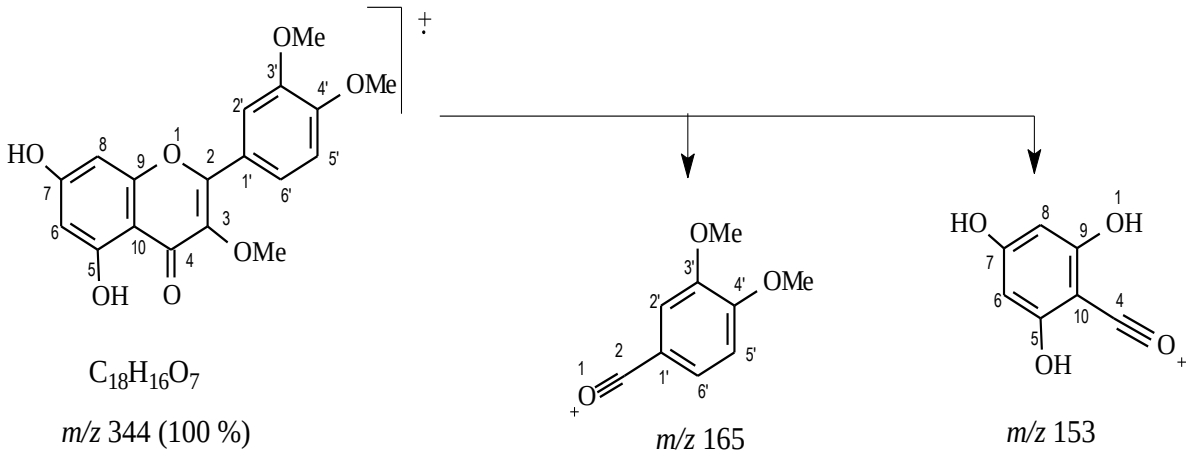

Figure 2. Main fragmentation patterns observed in the mass spectrum of 1.

ethyl ester; PEG: polyethylene glycol) and visualized at UV light at 365 nm in the dark, providing a yellow colored substance (R_f = 0.45), indicating a positive detection of a flavonoid (Wagner and Bladt, 1996).

The ^{13}C NMR spectrum of 1 (Table 1) showed eighteen signals, which were attributed to ten quaternary C (δ_C 178.8, 165.5, 162.5, 157.7, 150.3, 150.0, 147.9, 122.7, 138.5 and 106.8), five CH (δ_C 120.4, 115.3, 109.3, 91.3 and 98.0) and three CH_3 that correspond to methoxyl signals (δ_C 59.7, 55.5 and 55.6). The signals at δ_C 98.0 (C-6), 91.3 (C-8), 162.5 (C-5) and 165.5 (C-7) indicate standard oxygenation of C-5 and C-7 in the A-ring of the flavonoid (Figure 1). Furthermore, the ^1H NMR spectrum showed two signals at δ_H 6.62 (*s*, H-6) and 6.74 (*s*, H-8), confirming this data (Facundo et al., 2012).

The signals at δ_H 7.62 (*d*, J = 2.6 Hz), 6.96 (*d*, J = 8.3 Hz) and 7.56 (*dd*, J = 8.3 and 2.6 Hz) correspond to H-2', H-5' and H-6', respectively, suggesting oxygen substituents of C-3' and C-4'. This was confirmed by observation of the 3H singlets at δ_H 3.97 (3'-OMe) and 4.00 (4'-OMe). The heteronuclear multiple-bond correlation (HMBC) spectra exhibited correlations between δ_H 3.97 (3'-OMe)/δ_C 147.9 (C-3') and δ_H 4.00 (4'-OMe)/150.3 (C-4'). A correlation was also observed between signals at δ_H 3.92 (3-OMe)/δ_C 138.5 (C-3), confirming the flavone skeleton and the position of the 3-OMe substituent in the molecule. Our NMR data are relatively similar to that of closely related compounds reported in current literature (Wang et al., 1989).

The analysis of all spectral data for 1, including the 1D and 2D NMR spectra, led to the elucidation of its structure as the flavonoid 5,7-dihydroxy-3,3',4'-trimethoxyflavone. The structure was corroborated by the mass spectral data. The EIMS revealed a molecular ion at *m/z* 344, consistent with the molecular formula $C_{18}H_{16}O_7$ (11 degrees of unsaturation) compatible with a substituted flavonol skeleton. In addition, two fragment ions were observed at *m/z* 165 and *m/z* 153, suggesting the fragmentation patterns for the A-ring and the B-ring, respectively. The observed fragmentations of 1 are rationalized in Figure 2 and confirm the NMR data.

It is noteworthy that until now phytochemical studies on *B. laciniosa* have been completely absent in current literature. Furthermore, the isolation of 5,7-dihydroxy-3,3',4'-trimethoxyflavone is being reported, to the best of our knowledge, for the first time in the Bromeliaceae family. In a leaf survey of 61 species of the Bromeliaceae, an unexpectedly wide spectrum of flavonoid constituents was encountered. The family is unique amongst the monocotyledons in the frequency and variety of flavonoids with extra hydroxylation or methoxylation at the 6- or 8-position. Quercetin (5- and 7-hydroxy substituted flavone) was the most common leaf constituent and was identified as the 3-rutinoside or the 3-glucoside in some Bromeliaceae species (Williams et al., 1978). In a recent review about the secondary metabolites from Bromeliaceae family (Manetti et al., 2009), 25 flavonols were reported among 76 flavonoids identified in 83 species. Therefore, it may be considered that flavonols are widespread within the family but the occurrence of quercetin 3,3',4'-trimetyl ether was not reported.

Compound 1, quercetin 3,3',4'-trimetyl ether was originally reported as a synthesis product by Allan and Robinson (1926). Half a century later, the compound was independently isolated as a natural product from *Ericameria diffusa* (Urbatsch et al., 1976) and *Achillea santolina* L. (Khafagy et al., 1976). Since then, the compound has been reported from several plant sources including *Betula nigra* (Wollenweber, 1977), *Solanum*

Table 1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data for **1** including results obtained by heteronuclear 2D shift-correlated HMQC and HMBC spectra, in MeOD as solvent and TMS as internal reference. Chemical shifts in δ (ppm) and coupling constants (*J*, in parenthesis) in Hz.

Carbon	HMQC		HMBC	
	δ_C	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$
C				
2	150.0	-	-	H-2'; H-6'
3	138.5	-	-	MeO-3
4	178.8	-	-	-
5	162.5	-	-	-
7	165.5	-	H-6	-
9	157.7	-	-	-
10	106.8	-	-	H-6; H-8
1'	122.7	-	-	H-5'
3'	147.9	-	-	H-5'; MeO-3'
4'	150.3	-	-	MeO-4'
CH				
6	98.0	6.62 (*s*)	-	-
8	91.3	6.74 (*s*)	-	-
2'	109.3	7.62 (*d*, 2.6)	-	-
5'	115.3	6.96 (*d*, 8.3)	-	-
6'	120.4	7.56 (*dd*, 8.3 and 2.6)	-	-
MeO				
3	59.7	3.92 (*s*)	-	-
3'	55.5	3.97 (*s*)	-	-
4'	55.6	4.00 (*s*)	-	-

pubescens (Krishna et al., 1985), *Baccharis* spp. (Wollenweber et al., 1986), *Cistus* spp. (Vogt et al., 1987), *Encelia* (Proksch et al., 1988), *Artemisia monosperma* (Ismail et al., 1989), *Artemisia schimperi* (Abegaz and Herz, 1991), *Ageratina deltoidea* (Yang et al., 1991), *Sphaeranthus* spp. (Zdero et al., 1991), *Passiflora foetida* (Echeverri et al., 1991), *Artemisia roxburghiana* (Li et al., 1994), *Grindelia* spp. (Timmermann et al., 1994), *Allagopappus* spp. (Gonzalez et al., 1995), *Chrysothamnus* (Stevens et al., 1999), *Achillea santolina* (Urmanova and Komilov, 1999), *Melicope* spp. belonging to Rutaceae (Simonsen et al., 2003), wild tobacco, *Nicotiana attenuata* (Roda et al., 2003), *Ceanothus* spp. (Wollenweber et al., 2004), *Pulicaria canariensis* (Triana et al., 2005), Asteraceae spp. (Wollenweber et al., 2005), *Artemisia campestris* (Ferchichi et al., 2006), *Scyphiphora hydrophyllacea* (Dai et al., 2006), *Artemisia rupestris* (Song et al., 2006), *Conyza blinii* (Su et al., 2007), *Jasonia montana* belonging to Asteraceae (Soliman et al., 2009), *Callicarpa nudiflora* (Mei et al., 2010), *Inula japonica* (Qin et al., 2010), *Blumea balsamifera* (Chen et al., 2010), *Callicarpa longipes* (Gao et al., 2011), *Calotropis procera* (Mohamed et al., 2011), *Callicarpa kwangtungensis* (Jia et al., 2012) and *Blumea balsamifera* (Nguyen and Nguyen 2012).

In summary, in concomitance with its widespread occurrence in quite diverse plant species, quercetin 3,3',4' trimethyl ether is not a compound unique to the Bromeliaceae family. However, the compound has not previously been identified in any Bromeliaceae which may indicate a potential of compound 1 as a chemotaxonomic marker for *B. laciniosa*. Chemotaxonomic markers are sometimes used as indicators of botanical identity and their selection is crucial for the quality control of plant drugs, including authentication of genuine species (Braz et al., 2012). The identification of flavonoids in the Bromeliaceae family allows highlighting of the importance of these compounds as potential pharmacological agents and also to consider them as potential chemotaxonomic markers.

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Conflict of Interests

The author(s) have not declared any conflict of interests.

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