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Chemical constituents of *Piptadenia gonoacantha* (Mart.) J.F. Macbr (pau jacaré)

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ABSTRACT

The phytochemical investigation of *Piptadenia gonoacantha* (Mart.) J.F. Macbr. (Leguminosae-Mimosoideae), commonly known as "pau jacaré" (alligator stick), afforded sitosterol, campesterol, stigmasterol, the N-benzoyl-phenylalanine-2-benzoylamide-3-phenylpropyl ester, known as asperphenamate, sitosterol-3-O-β-D-glucopyranoside, besides three flavonoids, apigenin, 5-O-methylapigenin and 7,4′-dihydroxy-3′,5-dimethoxyflavone from its branches. From its leaves, the methyl gallate and two flavonoids, vitexin and isovitexin, were isolated. From its bark, a mixture of sitosterol, campesterol, and stigmasterol, besides a mixture of cycloartenone, cycloartan-25-en-3-one, and 24-methylene-cycloartenone, and the pure triterpenes 24-methylenecycloartanol, friedelin, lupeol and lupenone, were isolated. Their structures were established on the basis of spectral analysis, comparison with literature data and GC-MS analysis of the mixtures. The ester, flavonoids and the cycloartanes are been identified for first time in the genus *Piptadenia*.

Key words: Leguminoseae, *Piptadenia gonoacantha*, terpenoids, asperphenamate, flavonoids, "pau jacaré".

INTRODUCTION

The *Piptadenia* genus belong to Mimosoideae (Leguminosae) and have about 80 tropical species frequently occurring in South America. The *Piptadenia* species are known in Brazil as angico, and as cebil in Argentina and Paraguay. These species have been used in tannery due to the tannins, in building due to the hard and heavy wood and in the recovery of forests because they can grow in poor and degraded soil (Lorenzi 1998, Correa 1984). The scientific interest on *Piptadenia* species is motivated by their use in snuff preparation, such as *P. peregrina* that causes humans euphoria due to the indole alkaloid from its seeds (Stromberg 1954). More frequently, indole alkaloids, such as bufotenine and derivatives, have been detected by the phytochemical and pharmacological studies of *Piptadenia* to justify its popular use because of its psicotropic and alucinogenic properties (e.g. *P. colubrine* (Patcher et al. 1959), *P. falcate* (Giesbrecht 1960), *P. macrocarpa* (Legler and Tschescher 1963)). The more recent study of other parts of species of this genus did not detect alkaloids, only flavonoids such as the anadantoside (Piacente et al. 1999), cumarine, triterpene, steroids and flavonoids (Miyauchi et al. 1976) from *P. macrocarpa*. Flavonoids, chalcone, two benzoil derivatives, sitosterol, lupeol and betuline, were identified in the woods extract from *P. rigida* (M.S. Gomes, unpublished data, Nascimento et al. 2003). The *Piptadenia gonoacantha* is a tree that occurs in the South and Southeast Brazil, including Mato Grosso do Sul and the Atlantic complex. It is easily identified in the forest

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due to its salience in the bark like lamina, and owed to it the tree is named as "icarapé", "caniveteiro", "casco-de-jacaré" and mainly as "pau jacaré" (alligator stick) (Fig. 1). This is the first phytochemical study of *P. gonoacantha* in which we describe the presence of three cicloartenones, cicloartanol, three steroids, sitosterol-3-O-β-D-glycopiranoside, three pentaciclic triterpenes, methyl gallate, the ester asperphenamate, and five flavonoids, apigenin, apigenin-5-methyl ether, 7,4′-dihydroxy-3′,5-dimethoxyflavone, vitexin and isovitexin (Fig. 2).

Fig. 1 – Stalk aspect of *Piptadenia gonoacantha*, "pau-jacaré".

MATERIALS AND METHODS

General Experimental Procedure

Melting points have not been corrected. IR spectra were recorded on a Perkin-Elmer 1605 FT-IT spectrophotometer using KBr for solids and film for liquid samples (range 4000-600 cm^{-1}). ^{1}H and ^{13}C NMR spectra (including 1D and 2D specials techniques) were recorded on a Brüker AC-200 (^{1}H: 200 and ^{13}C: 50 MHz) of UFRRJ, and Brücker DRX-500 (^{1}H: 500 and ^{13}C: 125 MHz) of UFC. DMSO-d_6, CD_3OD or $CDCl_3$ with TMS as internal standard were used as solvents. Bruker Ac-200 was used in the NOEDIFF experiments. LRMS were recorded on Varian saturn 2000 instrument with ion trap at 70eV and electron ionization. The Chromatography columns were packed with silica gel (Vetec and Aldrich 0.05-0.20 mm) and Sephadex LH-20 (Sigma, USA); silica gel F254 G (Vetec) was used for preparative TLC; aluminum backed (Sorbent) silica gel plates W/UV254 were used for analytical TLC, with visualization under UV (254 and 366 nm), with $AlCl_3$-ETOH (1%), Lieberman-Burchard and/or Godin reagents, or exposure to iodine vapor.

Plant Material

The branches and leaves of *Piptadenia gonoacantha* (Mart.) J.F. Macbr (Fig. 1) were collected in UFRRJ Campus, Seropédica, Rio de Janeiro, Brazil, in 2005 by Professor Acácio Geraldo de Carvalho. A voucher specimen (RBR 6939) has been deposited at RBR Herbarium, Instituto de Biologia, UFRRJ.

Extraction and Isolation

The powdered branches (1448 g) and leaves (560 g) of *Piptadenia gonoacantha* were extracted with methanol at room temperature. The solvent was removed under vacuum to yield the residues **PGBrM** (46.4 g) and **PGLM** (19.7 g), respectively. The bark (650.0 g) was extracted with dichlorometane and methanol, and the residues **PGBaD** (5.0 g) and **PGBaM** (70 g) were obtained. The residue **PGBrM** (40.4 g) was partitioned into $CHCl_3$, ethyl acetate, and methanol:H_2O (9:1) to yield fractions **PGBrMC** (4.0 g), **PGBrMA** (4.5 g), and **PGBrMM** (24.3 g), respectively. Fraction **PGBrMC** was chromatographed on a silica gel column eluting initially with $CHCl_3$ and gradually increasing the polarity with MeOH to give 35 subfractions. The fractions **PGBrMC**-6-7, after recrystallization from MeOH, afforded a solid composed by the mixture of **4**, **5** and **6**. The subfraction **PGBrMC**-2-11 was further purified by CC eluted with $CHCl_3$ 100% to obtain **10** (31.0 mg). Subfraction **PGBrMC**-16-20 was further purified by crystallization from methanol to afford **4a** (37.2 mg). Fraction **PGBrMA** was subjected to silica gel CC eluting with $CHCl_3$:MeOH and increasing the polarity with MeOH (100%) to obtain 33 subfractions. Fractions **PGBrMA**-6-7 was purified in silica gel CC eluting with $CHCl_3$:MeOH (9:1) to afford 10 subfractions. Fraction **PGBrMA**-6-7/4 was applied to a Sephadex LH-20 gel column, eluting with $CHCl_3$:MeOH (7:3) to afford a yellow solid **11** (6.0 mg).

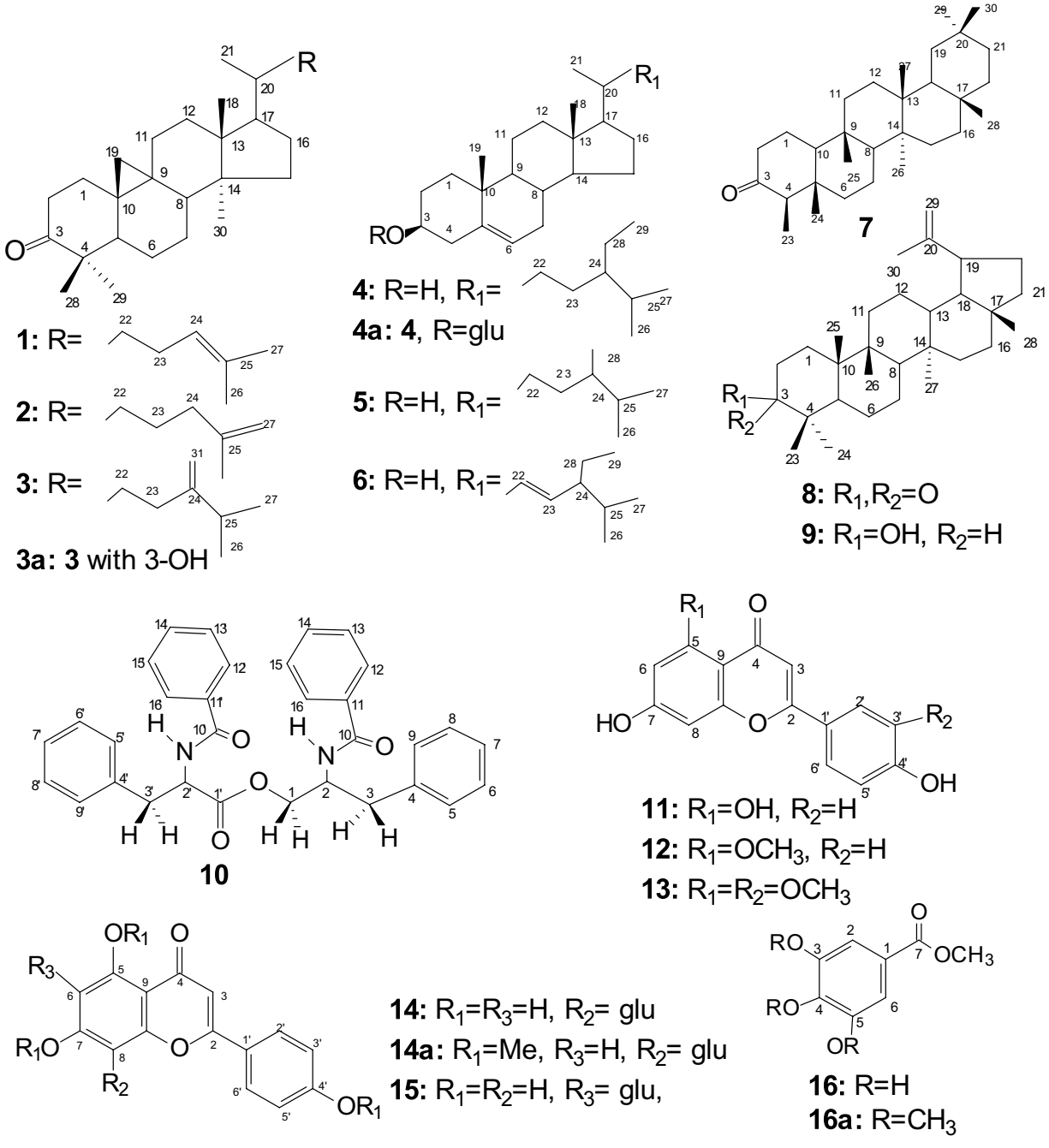

Fig. 2 – Structures of compounds isolated from *Piptadenia gonoacantha*, "pau jacaré".

Fraction **PGGMA**-12 was further purified by TLC ($CHCl_3$:AcOEt:MeOH, 7:2.5:0.5) to give **12** (5.0 mg). Fraction **PGBrMA**-21 was subjected to silica gel CC eluting with $CHCl_3$:MeOH and increasing the polarity with methanol to obtain 8 subfractions; fraction **PGBrMA**-21/6 was purified by TLC ($CHCl_3$:MeOH, 9:1) to give **13** (6.5 mg).

The residue **PGLM** (15.0 g) was extracted with $CHCl_3$ to obtain the fractions **PGLMC** (3.9 g) and **PGLMM** (10.4 g), respectively. The fraction obtained with chloroform had a mixture of hydrocarbons and steroids. The residue from the methanol fraction **PGLMM** (10.0 g) was chromatographed over silica gel, eluted with $CHCl_3$:MeOH (8:2) as eluent and increasing the polarity until MeOH 100%. Eleven fractions were collected. Fraction **PGLMM**-2 was subjected to silica gel CC eluting with $CHCl_3$:MeOH (9:1) to obtain 5 fractions, including the **PGLMM**-2/2-3 with **16** (112.0 mg). Fraction **PGLMM**-2/4 was subjected to silica gel CC eluting with $CHCl_3$:MeOH (8:2) to afford 6 fractions. Fraction **PGLMM**-2/4-4 afforded **14** (24.0 mg) and fraction **PGLMM**-2/4-5 was applied to a Sephadex LH-20 gel column eluting with $CHCl_3$:MeOH (7:3) and furnished **15** (25.0 mg).

The dichlorometane extract from the bark (**PGBaD**, 4.0 g) was fractionated on a silica gel column using hexane as the initial eluent and increasing the polarity with chloroform and methanol until methanol (100%). Sixty fractions of 25 ml were collected. The solid material obtained from the fractions 7-10 yielded **1** + **2** + **3** (54.7 mg). Fractions 11-14 yielded a solid **7** (53.4 mg). Fractions 23-25 afforded a solid **3a** (99.8 mg), and fractions 47-49 were crystallized from methanol to yield the mixture **4** + **5** + **6** (53.9 mg). The extract **PGBaM**, (70.0 g) was dissolved in methanol:water (8:2) and partitioned with dichlorometane, ethyl acetate and buthanol. The residues **PGBaMD** (2.0 g), **PGBaMA** (5.8 g), **PGBaMB** (4.9 g) and **PGBaMM** (50.3 g) were obtained from the respective solutions. **PGBaMD** (1.5 g) was fractionated on a silica gel column using chloroform as the initial eluent and increasing the polarity with methanol until methanol (100%). Thirty fractions of 25 ml were collected and analyzed by TLC plate. Fractions 15-20 (340 mg) were submitted to flash silica gel column using hexane and methanol mixture to methanol 100%. Twenty fractions of 15 ml were collected and analyzed by TLC. Fractions **PGBaMD**-15-20/3-5 yielded a solid after crystallization from methanol, which was identified as **8** (82.2 mg). Fractions **PGBaMD**-15-20/9-12 were crystallized from dimethylketone affording **9** (86.9 mg).

Tri-O-methylvitexin (5,7,4′-trimethoxy-flavone-8-C-glucopiranoside, **14a**): ^{1}H NMR (200 MHz, DMSO-d_6) δ_H: 8.09 (d, J=8.0Hz, H-2′,6′), 7.0 (d, J=8Hz, H), 6.60 (s, 2H, H-3 and H-6), 4.70 (d, J=10 Hz, H-1″), 3.92, 3.88, 3.83 (s, 3H each), 3.9-3.2 (m).

Methyl-gallate (**16**): ^{1}H NMR (200 MHz, DMSO-d_6) δ_H: 9.5 (HO), 6.96 (s, 2H), 3.72 (s, 3H); ^{13}C-NMR (50.3 MHz, DMSO-d_6): δ_C 166.7 (C-7), 145.9 (C-3,5), 138.8 (C-4), 119.7 (C-1), 108.9 (C-2,6), 51.9 (OCH_3); Methyl trimethyl-gallate: ^{1}H NMR (200 MHz, DMSO-d_6) δ_H: 7.21 (s, H-2,6), 3.82, 3.81, 3.81, 3.72 (s, OCH_3 ×4).

RESULTS AND DISCUSSION

The phytochemical investigation of the extracts from the leaves, branches and bark of *Piptadenia gonoacantha* allow the identification of four cycloartane triterpenes, cycloartenone (**1**), cycloartan-25-26-en-3-one (**2**), 24-methylene-cycloartanone (**3**) and 24-methylenecycloartanol (**3a**), three steroids, sitosterol (**4**), campesterol (**5**), and stigmasterol (**6**), a saponin, sitosterol-3-O-β-D-glucopyranoside (**4a**), three pentaciclic triterpenes, friedelin (**7**), lupenone (**8**), and lupeol (**9**), the N-benzoyl-phenylalanine-2-benzoylamide-3-phenylpropyl ester (asperphenamate, **10**), five flavonoids, apigenin (5,7,4′-trihydroxyflavone, **11**), 5-methylapigenin (**12**), 7, 4′-dihydroxy-3′, 5-dimethoxyflavone (**13**), vitexin (8-C-glucopyranosyl-5, 7, 4′-trihydroxyflavone, **14**), and isovitexin (6-C-glucopyranosyl-5,7,4′-trihydroxyflavone, **15**), and methyl gallate (**16**), Figure 2. Their structures were established on the basis of spectral analysis, comparison with literature data and GC-MS analysis of steroids and cycloartenones mixtures.

The identification of compounds **1-3**, **3a**, **4-6** and **7-9** was achieved by the analysis of IR, NMR and GC-EIMS spectra and comparison with literature data. The ^{1}H and ^{13}C NMR spectra and the use of the Olea and Roque methodology, described for the analyses of mixtures (Olea and Roque 1990), allowed the identifica-

tion of the respective series of **1-3a** (cycloartane), **4-6** (steroids) and **7-9** (pentacyclic triterpenes). Detailed analysis of ^{13}C NMR (BBD and DEPT), and comparison with literature data allowed the identification of the cycloartenones (**1-3**) and 24-methylene cycloartenol **3a** (Silva et al. 2005, Davies et al. 1992, Silveira and Pessoa 2005), friedelane (**7**), lupenes (**8, 9**) (Davies et al. 1992, Carvalho et al. 1995, Mahato and Kundu 1994) and steroids **4-6** (Dutra et al. 1992, Kojima et al. 1990, Chaurasia and Wichtl 1987). These structures were defined by the GC-MS analysis that allow the identification of three compounds in the fractions group containing the cycloartenones: cycloartenone **1** (Rt 14.29 min, $M^{+}\cdot$ 424), cycloartan-25-26-en-3-one (**2**: Rt 14.29 min, $M^{+}\cdot$424), 24-methylene-cycloartanone (**3**: Rt 15.61 min, $M^{+}\cdot$ 426); the pure compound 24-methylenecycloartanol (**3a**, Rt 16.14, $M^{+}\cdot$ 426]; the steroids in mixture: campesterol (**5**: Rt 13.20 min, $M^{+}\cdot$ 400), sitosterol (**4**: Rt 14.81, $M^{+}\cdot$ 414) and stigmasterol (**6**: Rt 16.66 min, $M^{+}\cdot$ 412). The glycoside **4a** (sitosterol-3-O-β-D-glucopyranoside) was identified mainly by ^{1}H and ^{13}C NMR (BBD and DEPT) data analysis and by comparison with literature data (Chaurasia and Wichtl 1987). The number of C, CH, CH_2 and CH_3 and comparison of the values with those from the literature (Olea and Roque 1990, Davies et al. 1992, Carvalho et al. 1995, Mahato and Kundu 1994) for **7-9** allowed to confirm the structure of the triterpenes, friedelin (**7**), lupenone (**8**) and lupeol (**9**).

The ester **10**, a solid (MP 184-186°C), was identified by IR, NMR (1D and 2D) and mass spectra analysis. The IR spectrum of **10** showed absorption bands of N-H (ν_{NH} 3310 cm^{-1}), $\nu_{C=O}$ (1750 cm^{-1}), ν_{CO} (1640 cm^{-1}), besides bands of, $\nu_{C\text{-}O}$ and bands characteristics of aromatic rings. The ^{1}H and ^{13}C NMR and 2D correlated NMR techniques, [^{1}H-^{1}H- COSY and ^{1}H-^{13}C-COSY-$^{n}J_{CH}$ (n=1, HMQC; n=2 and 3, HMBC)] were used to identify this substance and make the complete proton and carbon-13 chemical shift assignments. The analysis of ^{1}H NMR, ^{1}H-^{1}H- COSY and ^{1}H-^{13}C-COSY-$^{1}J_{CH}$ spectra allow the identification of signals of hydrogens in aromatic rings (δ_H 7.66-7.15) that were compatible with four mono substituted benzene rings, signals at δ_H 4.85-2.8 of five methylene groups and two metine [δ_H 2.85/2.93 (dd, 1H each); δ_H 3.17/3.22 (dd, 1H each), δ_H 3.96/4.47 (dd, 1H) and δ_H 4.84 (t) and 4.53 (m)] connected to carbons δ_{CH2}: 37.03, 37.20, 65.41, and with δ_{CH}: 54.50 and 50.21, respectively. Besides the signals of $^{n}J_{CH}$ detected in HMBC spectrum, the values of hydrogen and carbon-13 chemical shift of **10** were compared with those of ester described by Catalan et al. (2003), named N-benzoylphenylalanine-2-benzoylamide-3-phenylpropyl ester, isolated from *Croton hieronymi* (Catalan et al. 2003). The mass spectrum shows peaks at *m/z* (%): 355 (10), 328(50), 238 (70), 146 (100), 118 (60), 91(70) that were used to confirm the structure of **10**. This ester was isolated from *Zeyhera digitalis* (Bignoniaceae) (Faccione et al. 2004), *Piper aurantiacatum* (Piperaceae) (Banerji and Ray 1981), and *Medicargo polymorpha* (Leguminosae) (Poi and Adityachoudhury 1986). This compound has been isolated from fungus species, such as *Aspergillus flavipes* (Clark et al. 1977), *Anaphalis subumbellata* (Talapatra et al. 1983), *Penicillium* species (McCorkindale et al. 1978, Bird and Campbell 1982, Nozawa et al. 1989), and it has been named as asperphenamate.

The flavones **11-13** were identified by comparison of these ^{1}H and ^{13}C NMR data (including NOEDIFF experiments of **12** and **13**) and mass-spectra, and comparison with literature data. These compounds show positive test for flavonoids using $AlCl_3$/EtOH in TLC plate. ^{1}H NMR spectra of flavone **11** show two broad singlets at δ_H 6.44 (1H), 6.20 (1H), one singlet at δ_H 6.68 (1H), two doublets at δ_H 7.92 (J=8.0 Hz, 2H), and 6.90 (J=8.0 Hz, 2H), besides a singlet at 13.01 of quelated hidroxyl group (5-OH). These data were compared with those of 5,7,4′-trihydroxyflavone and confirmed the structure of **11** that is known as apigenin (Miyazawa and Hisama 2003). ^{1}H NMR spectrum of **12** was similar to that one of **11** only with an additional signal at δ_H 3.78 of the methoxyl group. Besides the analysis of ^{13}C NMR and ^{1}H-^{1}H-COSY data, the spectra obtained by NOEDIFF experiment show only one signal of NOE (4%) at δ_H 6.37 (H-6) by irradiation at δ_{CH3} 3.78, and NOE (14%) at δ_H 7.84 (H-2′,6′) by irradiation at δ_H 6.50 (H-3). The ^{13}C NMR data were identical to those of 5-O-methylapigenin (Wagner et al. 1976). The spectra of **13** show signal at δ_H 6.31 (brs), 6.47 (brs), 6.57 (s), 7.44 (brs, 2H) and 6.88 (d, J=8 Hz, 1H), and two singlets of OCH_3 at δ_{CH3} 3.85 and 3.75. The same NOE experiments made

with **12** were made with **13** and allow the identification of NOE at δ_H 6.31 (H-6) and 7.44 (H-2′), confirming the methoxyl group at 5 and 3′ positions. These data and analysis of ^{1}H×^{1}H-COSY, besides the LREIMS spectrum [*m/z* (%): 314 (1), 180 (100), 163 (50), 147 (10), 137 (50), 124 (20), 109(10)], allow the identification of **13** as 7,4′-dihydroxy-5,3′-dimethoxyflavone.

The ^{1}H NMR spectrum of flavonoids **14** and **15** shows signals of a flavone moiety containing four groups: three hydroxyl group and one sugar unit in both **14** and **15** as indicated by the following signals: **14**: δ_H 8.0 (d, *J*=8Hz, 2H)/6.88 (d, *J*=8Hz, 2H) (AA′BB′ system), 6.77 (H-3)/6.26(H-6), 4.68(d, *J*=10 Hz, 1H), multiplet between 3.8-3.0 and singlet at 13.2; **15** 7.90(d, *J*=8 Hz, 2H)/6.92 (d, *J*=8Hz, 2H) (AA′BB′ system), 6.75(H-3)/6.53(H-8), 4.58(d, *J*=10 Hz, 1H), multiplet between δ_H 4.5-3.0 and 13.6(s). Comparison of the ^{13}C-NMR (BBD and DEPT) data showed that all the carbon chemical shifts were similar, but small differences were δ_{CH} 93.7, δ_C 79.0, 108.5 in **15**. These data and comparison with ^{1}H and ^{13}C NMR literature data, allow the identification of **14** as vitexin (Zhou et al. 2005), and **15** as isovitexin (Pedras et al. 2003). NOEDIFF experiments confirmed these identifications. Irradiation of **14** at $\delta_{HO\text{-}5}$ (13.2) shows NOE at δ_H 6.78 (H-6), and irradiation on $\delta_{H\text{-}3}$ shows NOE at δ_H 8.0 (H-2′.6′). The same experiments were made with **15** and the obtained results were according with its identification as isovitexin. Methylation of **14** (in methanol) with diazomethane ether solution yielded **14a**, which is additional data to confirm the identification of **14**.

The IR, ^{1}H and ^{13}C NMR spectra of **16** were analyzed and compared with literature data to identify this compound as methyl gallate (Scott 1972). The tri-O-methyl derivative obtained by the treatment of **16** with diazomethane ether solution yielded **16a** (see experimental) and confirmed its identification.

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RESUMO

O estudo fitoquímico de galhos de *Piptadenia gonoacantha* (Mart.) J.F. Macbr. (Leguminosae-Mimosoideae), comumente conhecida como "pau jacaré", forneceu sitosterol, estigmasterol, o éster N-benzoilfenilalaninato de 2-N-benzoil-3-fenil-propila, conhecido como asperfenamato, 3-O-β-D-glicopiranosil-sitosterol, além de três flavonóides, apigenina (5,7,4′-triidroxiflavona), apigenina-5-O-metil éter e 7,4′-dihidroxi-3′, 5-dimetoxiflavona. Das folhas isolaram-se galato de metila e dois flavonóides, 8-C-glicopiranosil-5,7,4′-trihidroxiflavona e 6-C-glicopiranosil-5,7,4′-trihidroxiflavona, conhecidas como vitexina e isovitexina. Das cascas desta planta isolaram-se uma mistura de sitosterol, campesterol e estigmasterol; mistura de cicloartenona, cicloartan-25,26-en-3-ona e 24-metileno-cicloartanona, além dos triterpenos, 24-metilenocicloartenol, fridelina, lupeol e lupenona. As estruturas foram estabelecidas através de análise de espectros de IV, RMN ^{1}H e ^{13}C e massas, além de análise com CG-EM para identificar os componentes das misturas de cicloartanos e esteróides. O éster conhecido como asperfenamato, os flavonóides e os cicloartanos estão sendo registrados pela primeira vez em *Piptadenia*.

Palavras-chave: Leguminoseae, *Piptadenia gonoacantha*, terpenóides, asperfenamato, flavonóides, pau jacaré.

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