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A flavone dimer from *Ouratea hexasperma*

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Abstract

From the leaves of *Ouratea hexasperma*, the flavone dimer 4′,5,7-trihydroxyflavone-(6 → 8″)-4‴,5″-dihydroxy-7″-methoxyflavone was isolated in addition to methyl myoinositol. The structures were established by various analyses including 2D-NMR spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ouratea hexasperma; Ochnaceae; Flavone dimer; Methyl myoinositol; Spectral data

1. Introduction

In a previous report, we described the isolation from *Ouratea hexasperma* (Ochnaceae) (Moreira, Sobrinho, de Carvalho, & Braz-Filho, 1994) of the biisoflavonoid, hexaspermone A, from a hexane extract of roots and hexaspermones B and C and 4′,5,7-trimethoxyisoflavone from a methylene chloride extract of stem bark, together with a mixture of aliphatic esters and a mixture of aliphatic acids.

In this paper, we report the chemical investigation of the leaves of this species. The new flavone dimer 4′,5,7-trihydroxyflavone-(6 → 8″)-4‴,5″-dihydroxy-7″-methoxyflavone (**1**, 7″-*O*-methyl agathisflavone) and methyl myoinositol (**4**) were identified in the methanol extract.

The spectral data, including 2D NMR experiments ^{1}H–^{1}H-COSY and ^{13}C–^{1}H-COSY-$^{n}J_{CH}$ ($n=1$; $n=2$ and 3, COLOC) spectra were used to establish the structures and the unambiguous ^{1}H and ^{13}C-NMR assignments of **1** and its acetyl (**1a**) and methyl (**1b**) derivatives. The biflavone **1** is a monomethyl ether of agathisflavone (**2**) and an isomer of 7-*O*-methylagathisflavone (**3**) (Mashima et al., 1970; Geiger, 1994). This new biflavone **1** was a potent inhibitor of cellular growth and also of DNA and protein synthesis using Sarcoma 180-tumor cells (Grynberg et al., 1994).

2. Results and discussion

The carbohydrate methylmyoinositol (**4**) was identified by analysis of the chemical shifts of monoprotonated carbon atoms revealed in the ^{13}C NMR spectrum and comparison with values described in the literature (Breitmaier & Voelter, 1987). The ^{1}H and ^{13}C NMR spectra of **4a** (see Section 3) and comparison with an authentic sample confirmed the identity of carbohydrate **4** (Dutra, Alves, Carvalho, & Braz-Filho, 1992; Sanders & Hunter, 1993).

The molecular formula of **1** was determined as $C_{31}H_{20}O_{10}$ by analysis of its mass spectrum (m/z 552, $[M]^{\cdot +}$, 100%). Five hydroxyl groups were confirmed by formation of penta-acetyl derivative **1a**, and one methoxy group, four singlet signals corresponding to hydrogens bonded to sp^2 carbon atoms and four doublets attributed to two AA′BB′ systems in two *para*-substituted aromatic rings) were observed in the ^{1}H NMR

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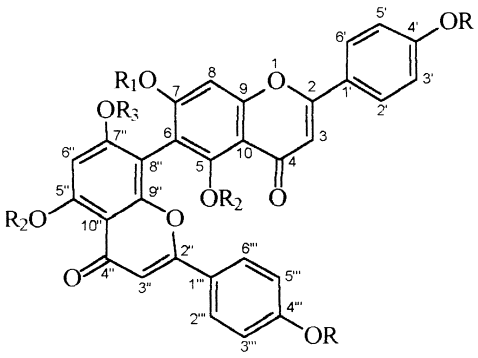
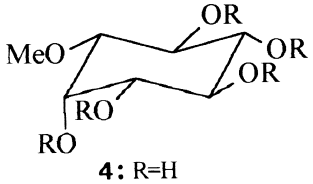


	R	R_1	R_2	R_3
1	H	H	H	Me
1a	Ac	Ac	Ac	Me
1b	Me	Me	H	Me
2	H	H	H	H
3	H	Me	H	H



4: R=H

4a: R=Ac

spectrum. The ^{13}C NMR spectrum, on the other hand, showed 27 carbon signals which are consistent with the superimposition of resonances at δ_H 129.25 (2CH-2′,6′), 129.08 (2CH-2‴,6‴) and 116.75 (2CH-3′,5′ and 2CH-3‴,5‴) correlated to four carbons involved in two AA′BB′ systems revealed by the ^1H NMR spectrum (Table 1). The IR spectrum of **1** showed absorption bands for a conjugated and H-bonded carbonyl group (ν_{max} 1654 cm^{-1}), an aromatic ring (ν_{max} 1600, 1570, 1560, 1510 cm^{-1}) and a hydroxyl group (ν_{max} 3370 and 3200 cm^{-1}).

The presence of two monosubstituted 4′,5,7-trihydroxyflavone ($C_{15}H_9O_5$) and 4′,5-dihydroxy-7-methoxyflavone ($C_{16}H_{11}O_5$) moieties in **1** was recognized by analysis of the ^1H (one- and two-dimensional ^1H–^1H-COSY) and ^{13}C (PND and DEPT) NMR spectra of **1** and **1a** (pentaacetyl derivative) in combination with the following additional data: (a) the number of bonded hydrogens for each carbon signal deduced by comparative analysis of the PND- and DEPT-^{13}C NMR spectra of **1** and its **1a** and **1b** derivatives; (b) additional data obtained from ^1H NMR (one- and two-dimensional ^1H–^1H-COSY) spectra of **1** revealing the presence of singlet signals attributed to two H-bonded hydroxyl functionalities (δ_H 13.34 (HO-5) and 13.18 (HO-5″)) and one methoxy group (δ_H 3.88),

Table 1
^1H (200 MHz) and ^{13}C (50 MHz) NMR spectral data for biflavone **1** (CD_3COCD_3) and its pentaacetyl **1a** ($CDCl_3$) and trimethyl ether **1b** ($CDCl_3$) derivatives. Chemical shifts are in δ (ppm) and coupling constants (J, in parenthesis) in Hz[a]

	1		**1a**		**1b**	
C	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
2	165.03	–	161.57	–	163.96	
4	183.54	–	176.40	–	182.85	
5	161.29	–	152.72	–	159.41	
6	104.08	–	117.38	–	105.50	
7	163.08	–	155.36	–	163.54	
9	158.18	–	157.06	–	157.78	
10	105.12	–	115.08	–	104.41	
1′	123.16	–	128.30	–	123.27	
4′	161.81	–	153.23	–	162.63	
2″	165.20	–	161.57	–	163.96	
4″	183.14	–	176.15	–	182.40	
5″	163.43	–	151.38	–	162.33	
7″	164.82	–	160.99	–	163.36	
8″	101.00	–	106.02	–	98.08	
9″	155.50	–	160.99	–	154.47	
10″	105.55	–	110.74	–	105.17	
1‴	123.16	–	128.43	–	123.57	
4‴	161.81	–	152.89	–	162.33	
AcO	–	–	169.30	–	–	
AcO	–	–	168.78	–	–	
AcO	–	–	168.70	–	–	
AcO	–	–	167.96	–	–	
AcO	–	–	167.46	–	–	
	$^{13}Cx^1H$-COSY-$^1J_{CH}$		$^{13}Cx^1H$-COSY-$^1J_{CH}$		$^{13}Cx^1H$-COSY-$^1J_{CH}$	
CH						
3	104.04	6.65 (s)	108.50	6,60 (s)	104.42	6.63 (s)
8	94.50	6.80 (s)	109.90	7.48 (s)	89.96	6.65 (s)
2′,6′	129.25	7.94(d, 6.8)	127.48	7.92 (d, 8.7)	127.98	7.86 (d, 8.4)
3′,5′	116.75	7.05 (d, 6.8)	122.27	7.27 (d, 8.7)	114.49	6.99 (d, 8.4)
3″	103.56	6.60 (s)	107.72	6.54 (s)	103.53	6.51 (s)
6″	96.03	6.54 (s)	103.87	6.72 (s)	95.47	6.48 (s)
2‴,6‴	129.08	7.62 (d, 7.1)	127.43	7.54 (d, 8.7)	127.73	7.47 (d, 8.3)
3‴,5‴	116.75	6.83 (d, 7.1)	122.09	7.06 (d, 8.7)	114.36	6.81 (d, 8.3)
CH_3						
MeO-7″	56.67	3.88 (s)	56.42	3.82 (s)	56.25	3.85 (s)
MeO-4′	–	–	–	–	55.47	3.89 (s)
MeO-7	–	–	–	–	56.16	3.83 (s)
MeO-4‴	–	–	–	–	55.38	3.79 (s)
AcO	–	–	20.98	2.46 (s)	–	–
AcO	–	–	20.98	2.34 (s)	–	–
AcO	–	–	20.88	2.24 (s)	–	–
AcO	–	–	20.69	2.13 (s)	–	–
AcO-7	–	–	20.36	1.94 (s)	–	–
HO-5	–	13.34 (s)	–	–	–	13.06 (s)
HO-5″	–	13.18 (s)	–	–	–	13.04 (s)
HO-4″	–	9.15 (br s)	–	–	–	–
HO-4‴	–	9.15 (br s)	–	–	–	–
HO-7″	–	9.10 (br s)	–	–	–	–

[a] Homonuclear 2D-^1H–^1H-COSY and heteronuclear 2D-^{13}C–^1H-COSY-$^nJ_{CH}$ ($n=1$ ($^1J_{CH}$); $n=2$ ($^2J_{CH}$) and $n=3$($^3J_{CH}$), COLOC Table 2) were also used in these assignments. Chemical shifts and coupling constants (J) of hydrogens deduced by 1D ^1H NMR spectra.

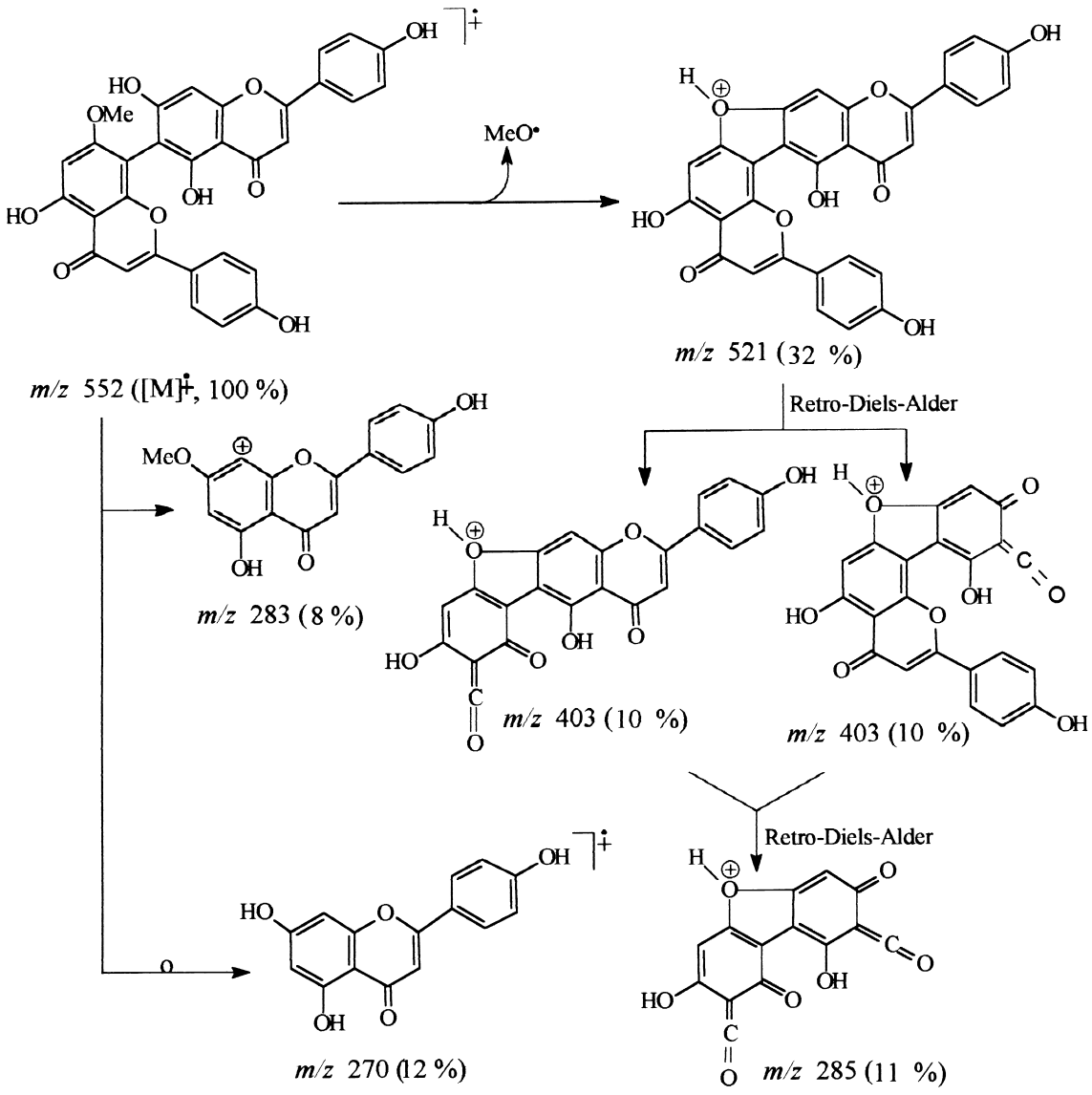
along with four isolated hydrogens attached to sp^2 carbon (δ_H 6.65 (H-3), 6.80 (H-8), 6.60 (H-3″) and 6.54 (H-6″)) and four doublet signals corresponding to eight hydrogens bonded to sp^2 carbon atoms of two AA′BB′ systems (δ_H 7.94 (d, $J=8.3$ Hz, 2H-2′, 6′), 7.05 (d, $J=8.3$ Hz, 2H-3′, 5′), 7.62 (d, $J=8.0$ Hz, 2H-2‴, 6‴), 6.83 (d, $J=8.0$ Hz, 2H-3‴, 5‴)); (c) the presence of singlet signals (δ_H 2.46, 2.34, 2.24, 2.13 and 1.94) corresponding to five acetoxy groups in the ^1H NMR spectrum of **1a** (Table 1); (d) formation of a tetramethyl ether derivative (**1b**: δ_H 3.85 (s), 3.89 (s), 3.83 (s) and 3.79 (s); δ_C 56.25 (MeO-7″), 56.16 (MeO-7), 55.47 (MeO-4′) and 55.38 (MeO-4″)) by treatment of **1** with CH_2N_2, selective methylation to obtain 5,5″-dihydroxylated derivative **1b** (δ_H 13.06 (HO-5) and 13.04 (HO-5″)); (e) connections for signals of all hydrogen and carbon atoms in the heteronuclear ^{13}C–^1H correlation via one bond ^{13}C–^1H-COSY-$^1J_{CH}$ and long-range couplings ^{13}C–^1H-COSY-$^nJ_{CH}$ ($n=2$ ($^2J_{CH}$) and 3 ($^3J_{CH}$)) spectra of **1**, **1a** and **1b** (Tables 1 and 2), along with the intensities of the signals corresponding to hydrogens 2H-2′,6′, 2H-3′,5′, 2H-2‴,6‴ and 2H-3‴,5‴ and carbons 2CH-2′,6′, 2CH-3′,5′, 2CH-2‴,6‴ and 2CH-3‴,5‴; f) the existence of major peaks (Scheme 1) at m/z 521 (32%, M-31 (MeO), $C_{31}H_{20}O_{10}$ ($[M]^{\cdot+}$)–$MeO^{\cdot}=C_{30}H_{17}O_9$), 283 (8%, $C_{16}H_{11}O_5$, corresponding to 4′,5-dihydroxy-methoxyflavone derived fragment) and 270 (12%, $C_{15}H_{10}O_5$, attributed to 4′,5,7-trihydroxyflavone derived fragment) in the EIMS of **1**, along with the molecular ion ($[M]^{\cdot+}$) at m/z 552 (100% (basic peak), $C_{31}H_{20}O_{10} \rightarrow C_{16}H_{11}O_5$ (m/z 283) + $C_{15}H_9O_5$ (m/z 270-$H^{\cdot}$)).

The connection ($6 \rightarrow 8''$) of the two flavone moieties was established by ^{13}C–^1H-COSY-$^nJ_{CH}$ [$n=2$ ($^2J_{CH}$) and 3 ($^3J_{CH}$)) spectra of **1**, **1a** and **1b**, which revealed cross-peaks showing heteronuclear long-range couplings Table 2 of C-9 (δ_C 157.06 (**1a**) and 157.78 (**1b**)) and H-8 (δ_H 7.48 (**1a**) and 6.65 (**1b**), $^2J_{CH}$) and C-6 (δ_C 104.08 (**1**) and 105.50 (**1b**)) and both HO-5 (δ_H 13.34 (**1**) and 13.06 (**1b**), $^3J_{CH}$) and H-8 (δ_H 7.48 (**1a**) and 6.65 (**1b**), $^3J_{CH}$) (Tables 1 and 2). This deduction was confirmed by additional NMR data used in the

Table 2
Heteronuclear long range coupling observed in the ^{13}C–^1H-COSY-$^nJ_{CH}$ ($n=2$ and 3) 2D NMR spectra of biflavone **1** (CD_3COCD_3) and its pentaacetyl **1a** ($CDCl_3$) and tetramethyl ether **1b** ($CDCl_3$) derivatives[a]

	1		**1a**		**1b**	
	$^{13}Cx^1H$-COSY-$^nJ_{CH}$		$^{13}Cx^1H$-COSY-$^nJ_{CH}$		$^{13}Cx^1H$-COSY-$^nJ_{CH}$	
	$^2J_{CH}$	$^3J_{CH}$	$^2J_{CH}$	$^3J_{CH}$	$^2J_{CH}$	$^3J_{CH}$
C						
2	H-3		H-3	2H-2′,6′	H-3	2H-2′,6′
4						
5	HO-5				HO-5	
6		HO-5		′H-8		HO-5, H-8
7					H-8	MeO-7
9			H-8		H-8	
10		H-6, HO-5		H-3, H-8		HO-5, H-8
1′				2H-3′,5		2H-3′,5′
4′			2H-3′,5′	2H-2′,6′		2H-2′,6′,MeO-4′
2″	H-3″		H-3″	2H-2‴,6‴	H-3″	2H-2‴,6‴
4″						
5″	H-6″,HO-5″		H-6″		HO-5″,H-6″	
7″	H-6″	MeO-7″	H-6″	MeO-7″		MeO-7″
8″		H-6″		H-6″		H-6″
9″						
10″		H-6″,HO-5″		H-3″, H-6″		HO-5″,H-6″
1‴				2H-3‴,5″		2H-3‴,5‴
4‴			2H-3″,5‴′	′2H-2″,6″		H-2‴,6‴,MeO-4‴
AcO			2.46			
AcO			2.34			
AcO			2.24			
AcO			2.13			
AcO			1.94			
CH						
6″		HO-5″				HO-5″

[a] Homonuclear 2D-^1H–^1H-COSY and ^{13}C–^1H-COSY-$^1J_{CH}$ data were also used in these assignments.



Scheme 1. Proposed mass spectral fragmentation mechanism for **1** (only shows major peaks).

location of the methoxy group at carbon atom C-7″ (vide infra).

The location of the methoxy group at carbon C-7″ and not C-7 as in 7-*O*-methylagathisflavone (**3**) (Mashima et al., 1970; Geiger, 1994), was deduced on the basis of the unambiguous assignment of the chemical shifts of the directly bound ($^1J_{CH}$) hydrogen H-6″ (δ_H 6.54 (**1**), 6.72 (**1a**) and 6.48 (**1b**)) and C-6″ (δ_C 96.03 (**1**), 103.87 (**1a**) and 95.47 (**1b**)) by cross-peaks observed in the ^{13}C–^1H-COSY-$^1J_{CH}$ spectra of **1**, **1a** and **1b** in combination with the following data obtained by ^{13}C–^1H-COSY-$^nJ_{CH}$ ($n=2$ ($^2J_{CH}$) and 3 ($^3J_{CH}$), COLOC) spectra of **1**, **1a** and **1b** Table 2: (a) spin–spin interaction of C-5″ (δ_C 163.43 (**1**), 151.38 (**1a**) and 162.33 (**1b**)) and both hydrogens H-6″ (δ_H 6.54 (**1**), 6.72 (**1a**) and 6.48 (**1b**)) and HO-5″ (δ_H 13.18 (**1**) and 13.04 (**1b**), $^2J_{CH}$); (b) coupling of carbon C-10″ (δ_C 105.55 (**1**), 110.74 (**1a**) and 105.17 (**1b**)) with the three hydrogens H-6″ (δ_H 6.54 (**1**), 6.72 (**1a**) and 6.48 (**1b**), $^3J_{CH}$), H-3″ (δ_H 6.60 (**1**), 6.54 (**1a**) and 6.51 (**1b**), $^3J_{CH}$) and HO-5″ (δ_H 13.18 (**1**) and 13.04 (**1b**), $^3J_{CH}$); (c) carbon C-7″ (δ_C 164.82 (**1**) and 160.99 (**1a**)) and both H-6″ (δ_H 6.54 (**1**) and 6.72 (**1a**), $^2J_{CH}$) and MeO-7″ (δ_H 3.88 (**1**), 3.82 (**1a**) and 3.85 (**1b**), $^3J_{CH}$) (Tables 1 and 2); (d) results obtained from NOE difference spectra of **1a** and **1b** performed with irradiations at MeO-7″ (δ_H 3.82 (**1a**) and 3.85 (**1b**)) revealing signal enhancements at δ_H 6.72 (H-6″, NOE = 10% (**1a**)) and 6.48 (H-6″, NOE = 9% (**1b**)), along with other data summarized in Table 3.

Thus, all these data were used to establish the structure of the new flavone dimer as 4′,5,7-trihydroxyflavone-(6 → 8″)-4‴,5″-dihydroxy-7″-methoxyflavone (**1**).

Table 3
$^1H\{^1H\}$-NOE difference spectral data ($CDCl_3$) for pentaacetyl **1a** and tetra-methyl ether **1b** derivatives

Compounds	Irradiated		NOE enhancement		
	^1H	δ_H	^1H	δ_H	%
1a	AcO-7	1.94	8	7.48	3
	MeO-7″	3.82	6″	6.72	10
	3″	6.54	2‴,6‴	7.54	20
1b	MeO-4‴	3.79	3‴,5‴	6.81	11
	MeO-7	3.83	8	6.65	9
	MeO-7″	3.85	6″	6.48	9
	MeO-4′	3.89	3′,5′	6.99	15

The homonuclear ^1H–^1H-COSY and heteronuclear ^{13}C–^1H-COSY-$^nJ_{CH}$ ($n=1$; $n=2$ and 3, COLOC) 2D shift-correlated and ^1H–$\{^1H\}$-NOE spectra were also used to assign the chemical shifts of all hydrogen and carbon atoms of **1**, **1a** and **1b** (Tables 1–3). These assignments were facilitated by application of the usual shift parameters (Breitmaier & Voelter, 1987; Dutra et al., 1992; Sanders & Hunter, 1993; Gunther, 1994).

The analysis of the mass spectra resulted in the proposed fragmentation for the major fragments **1** as shown in Scheme 1.

3. Experimental

M.p.'s are uncorr. NMR spectra in CD_3COCD_3 (**1**) or $CDCl_3$ (**1a** and **1b**) soln were recorded at 200 MHz for ^1H and 50.3 MHz for ^{13}C on a Bruker AC-200 spectrometer using TMS as int. standard or by reference to solvent signals $CHCl_3$ at δ_H 7.24 and $^{13}CDCl_3$ at δ_C 77.00; EIMS: direct inlet at 70 eV on a VG Auto Spec-300 spectrometer; CC: silica gel (Merck and Aldrich 0.05–0.20 mm); TLC: silica gel H or G (Merck and Aldrich) with visualization by UV (254 and 366 nm) and exposure to iodine vapour. TLC was used to analyze the frs collected from CC.

3.1. Plant material

Ouratea hexasperma (St. Hil) Bail (Ochnaceae) was collected in Amapá State, Brazil and authenticated by botanist Benedito Vitor Rabelo. A voucher specimen (No. 01519) is deposited at the Herbário Amapaense HAMAB of the Divisão de Botânica, Museu Angelo Moreira da Costa Lima (IEPA), Macapá-AP, Brazil.

3.1.1. Extraction and isolation of leave constituents

Dried and powdered leaves (1.5 kg) were successively percolated with *n*-hexane and methanol at room temp. The solvents were removed under vacuum giving residues *A* (23.4 g) and *B* (286.1 g), respectively. Residue A (23.4 g) was filtered on a $CaCO_3$ column to eliminate chlorophyll, eluted with hexane and the solvent was evaporated under vacuum giving residue *C* (6.7 g). The latter (C) was submitted to column chromatography (200 g, silica gel) eluted with *n*-hexane and *n*-hexane–$CHCl_3$ mixtures of gradually increasing polarity) and 101 frs of 100 ml each were collected. These fractions were analyzed by TLC and the compounds of interest were subsequently combined and recrystallized in methanol. Fractions 1–12 yielded a mixture of alkanes; frs 17–24 yielded a mixture of aliphatic esters and fr 37–79 produced a ppt which was washed with *n*-hexane to afford a mixture of triterpenoids (283.2 mg). Part of residue *B* (70 g) was partitioned with $CHCl_3$ to produce a $CHCl_3$-soluble portion named residue *D*. This residue (D, 28.6 g) was chromatographed on a silica gel column and eluted with $CHCl_3$ (frs 1–50, 100 ml each one) and EtOAc (frs 51 to 80, 100 ml each one); fr 53 was recrystallized from EtOAc to afford **1** (364.3 mg); frs 54–70 yielded additional quantity of **1** (466.0 mg). Frs 71–80 (120 mg) were chromatographed on silica gel (chloroform: methanol, 9:1) and 40 frs of 50 ml each one were collected; frs 3–14 (43.0 mg) were analyzed by ^1H and ^{13}C NMR spectra. Acetylation of frs 15–40 (30.0 mg) in pyridine (2 ml) and Ac_2O (2 ml) at room temperature overnight, following work-up and filtration through a silica gel column, gave pure **4a** (m.p. 218–219°C, 26.0 mg).

3.2. 4′,5,7-Trihydroxyflavone-(6→8″)-4‴,5″-dihydroxy-7″-methoxyflavone (*1*)

M.p. 227–229°C (EtOAc). $[\alpha]_D$: −2.3 (*c* 0.5, H_3CCOCH_3). UV λ_{max}^{ketone} nm (log ε): 330 (3.94), 270 (3.96), 220 (4.04), 206 (4.11). IR υ_{max} (KBr) cm^{-1}: 3370, 3200 (OH), 1654 (C=O), 1600, 1570, 1560, 1510 (aromatic rings). ^1H and ^{13}C NMR spectra: Tables 1 and 2. EIMS 70 eV: Scheme 1.

3.3. 4′,5,7-Tri-O-acetylflavone-(6→8″)-4‴,5″-di-O-acetyl-7″-methoxyflavone (*1a*)

M.p. 186–188°C (MeOH). $[\alpha]_D$: −6.2 (*c* 0.5, $CHCl_3$). UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 313 (3.28), 265 (3.26), 240 (3.17). ^1H and ^{13}C NMR spectra: Tables 1 and 2. ^1H NMR NOE difference spectra: Table 3.

3.4. 5-Hydroxy-4′,7-dimethoxyflavone-(6→8″)-5″-hydroxy-4‴,7″-dimethoxyflavone (*1b*)

M.p. 170–172°C (MeOH). $[\alpha]_D$: −1.2 (*c* 0.5, $CHCl_3$). UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 325 (4.17), 275 (14.19), 240 (3.97). ^1H and ^{13}C NMR spectra: Tables 1 and 2. ^1H NMR NOE difference spectra: Table 3.

3.5. Penta-O-acetyl-methyl myoinositol (**4a**)

M.p. 218–219°C (OEtAc). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.70(t, 2.8 Hz), 5.40, 5.30 and 5.10 (t, 10.1 Hz, 1H each one) 4.90 (dd, 10.1 and 2.8 Hz), 3.37 (dd, 10.1 and 2.8 Hz), 3.30 (s, 3H), 2.15 (s, 3H), 2.01 (s, 3H) and 1.97 (s, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C: 169.9–169.9, δ_{CH}: 77.0, 70.9, 70.7, 69.3, 69.1, 66,0 and δ_{CH_3}: 58.1, 20.7–20.3.

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