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PHYTOCHEMISTRY

Diastereomeric C-glycosyloxanthrones from picramnia antidesma

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Abstract

Nine compounds were isolated and identified from the stem of *Picramnia antidesma*. Two of the isolated compounds: mayoside and saroside, which is new, are diastereoisomeric oxanthrones. The structure of saroside has been obtained on the basis of spectroscopic evidence. The absolute configuration of this diastereoisomeric pair has been determined by CD spectra, and that of saroside was further established by X-ray crystallographic analysis.

Keywords: *Picramnia antidesma*; Simaroubaceae; Oxanthrone; Saroside

1. Introduction

Picramnia antidesma is a shrub or small tree, native to woods from middle-America, south of Mexico, Cozumel, Cuba and Jamaica, usually 6–9 meters tall. Previous phytochemical investigation of *P. antidesma* leaves has resulted in the isolation of the known anthraquinone aloe-emodin and its reduced derivative aloe-emodin anthrone, and three aloe-emodin C-glycosides named picramniosides A, B and C (Solis, Gutierrez Ravelo, Gonzalez, Gupta & Phillipson, 1995). These compounds were isolated from plant material collected in Panama, however no phytochemical data have been reported so far on the stem. In this paper, we describe the isolation and structural determination, obtained on the basis of spectroscopic evidence and confirmed by X-ray analysis, of a new oxanthrone emodin-C-glycoside, named Saroside, as well as the complete assignments of the ^{1}H and ^{13}C NMR spectra and the absolute configurations of both mayoside and saroside.

2. Results and discussion

The methanolic extract of the dried stem of *P. antidesma* was subjected to silica gel CC to yield seven known compounds, which were easily identified as chrysophanol (Danielsen, Aknes & Francis, 1992), β-sitosterol and its glucoside tetraacetyl derivative (Salama, Sanchez-Lopez, Gutierrez & Achenbach, 1987), emodin (Danielsen *et al.*, 1992; Hernández-Medel, Lopez-Marquez, Santillan & Trigos, 1996) and its glucoside (Coskum, Satake, Hori, Saiki & Tanker, 1990; Lin, Chung, Gan & Lu, 1991; Kalidhar, 1992; Kinjo, Ikeda, Watanabe & Nohara, 1994), aloe-emodin (Danielsen *et al.*, 1992), and 7-hydroxycoumarin (Duddeck and Kaiser, 1982) by comparison with authentic samples, as well as two anthraquinone emodin C-glycosides. One of the oxanthrones was identified as mayoside based on the ^{1}H and ^{13}C NMR data (Table 1 and Table 2) and by comparison with an authentic sample. This compound was reported recently from *P. hirsuta* (Hernández-Medel *et al.*, 1996). The second was named saroside (**1**) and its structure was established by X-ray analysis.

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Table 1
^{1}H NMR spectral data of mayoside and saroside (**1**) in Me_2CO-d_6.

H	Mayoside	Saroside (1)
2	6.14 *d* (2.4)	6.37 *d* (2.4)
4	6.83 *d* (2.2)	6.94 *d* (2.2)
5	7.25 *d* (1.1)	7.02 *dd* (0.5, 1.6)
7	6.74 *s*	6.49 *dd* (0.8, 1.6)
11	2.42 *s*	1.80 *s*
1′	5.82 *d* (0.9)	5.82 *d* (1.5)
2′	3.86 *s*	3.87 *m*
3′	3.86 *s*	3.92 *dd* (3.6, 8.9)
4′	3.73 *m*	3.83 *t* (8.8, 9.5)
5′	3.73 *m*	3.73 *d* (9.5)
2″,6″	7.85 *dd* (1.2, 8.3)	7.87 *dd* (1.3, 8.4)
3″,5″	7.50 *t* (7.5, 7.9)	7.54 *t* (7.3, 8.1)
4″	7.63 *tt* (1.3, 1.8, 7.3, 7.5)	7.67 *tt* (1.3, 7.3, 7.5)
OH-1	12.22 *s*	12.38 *s*
OH-8	12.18 *s*	12.06 *s*
OH-3	9.67 *br*	9.65 *br*
OH-10	6.62 *s*	*
OH-2′	4.47 *d* (2.9)	4.38 *br*
OH-3′	4.19 *d* (6.8)	*
0H-4′	5.82 *br*	*

Assignments were confirmed by COSY, HMQC and HMBC experiments. Coupling constants (*J* in Hz) in parenthesis.* Not observed.

Table 2
^{13}C NMR spectral data of mayoside and saroside (**1**) in Me_2CO-d_6.

C	Mayoside	Saroside (**1**)
1	164.23	166.13
2	101.53	103.45
3	165.12	165.31
4	105.68	108.61
5	119.39	118.41
6	150.62	148.26
7	116.93	117.71
8	161.66	162.91
9	191.06	192.89
10	75.30	76.57
1a	109.43	110.70
4a	144.53[a]	148.62[a]
5a	146.27[a]	148.83[a]
8a	113.77	114.87
11	21.45	22.00
1′	94.39	95.07
2′	69.20	70.69
3′	71.93	73.48
4′	68.73	70.18
5′	79.49	80.54
1″(C=O)	163.54	163.99
1″	129.34	*
2″,6″	129.39[b]	130.65[b]
3″,5″	128.60[b]	129.77[b]
4″	133.36	134.52

Assignments were confirmed by COSY, HMQC and HMBC experiments.[a] These assignments may be interchangeable.[b] The intensity from this signals was twice of other CH signals.* Not observed.

Compound **1** was obtained as a yellow amorphous solid, and its UV spectrum (388, 274, 258, 221, 204 nm) was characteristic of a highly conjugated system. The IR spectrum exhibited absorptions consistent with a hydroxyl (3336 cm^{-1}), carbonyl ester (1740 cm^{-1}) and chelated carbonyl group (1640 cm^{-1}). The presence of two chelated hydroxyl group was supported by the ^{1}H NMR spectrum which showed two singlets at δ 12.38 and 12.06, in addition to nine aromatic protons assignable to a benzoate group at δ 7.87, 7.67 and 7.54, and the characteristic emodin system for the protons in the 5,7 and 4,2 positions (δ 7.02, 6.49, and 6.94, 6.37, respectively). The broad signal at δ 9.65 (1H, D_2O exchangeable proton) was due to hydroxyl group in the 3 position. The presence of 24 carbons was evident from the ^{13}C NMR spectrum including two signals at δ 129.77 and 130.65 showing a double intensity characteristic of a benzene ring monosubstituted due to a benzoate group. An interesting feature of this spectrum is the presence of signals comparable to those of mayoside (Tables 1 and 2).

Correlation between protons and proton-carbon resonances was achieved by means of COSY, HMQC and HMBC connectivities (Table 3). The HMBC NMR experiment showed that the singlet at δ 5.82 corresponding to the proton on C-1′ and the doublet doublet at δ 7.87 assigned to the protons on C-2″/6″, was correlated to the carbon at δ 163.99 assigned to the carbonyl of the ester group, thus establishing the position of the benzoate at C-1′. In addition, the signal at δ 3.73 for the proton on C-5′ showed a correlation to the carbons at δ 70.18, 73.48, 76.57, 95.07, 148.62 and 148.83 (C-4′, C-3′, C-10, C-1′, C-4a or/and C-5a, respectively), corroborating the position of attachment between the aglycone and the sugar moiety.

Since the ^{1}H and ^{13}C NMR data indicated that mayoside and saroside (**1**) are two diastereoisomers and the structure of mayoside has been reported by single-crystal X-ray diffraction, saroside (**1**) was also subjected to X-ray analysis. The molecular structure of saroside (**1**) in the crystalline state is shown in the Fig. 1. The asymmetric unit of the crystal structure contains two independent molecules and acetone as solvent. The lyxose is linked to the oxanthrone system as a β-D-glycosyl residue and has a chair conformation. The A and C rings in the 1,8-dihydroxyoxanthrone system are planar within the limits of experimental accuracy. Ring B has an envelope conformation in which C-10 is raised out of the plane of the other five atoms by 0.228(4) Å and C-31 by 0.134(4) Å. The lyxose residue at C-10 is in the equatorial position and the hydroxyl group is axial. The nonplanarity of

Table 3
Spectral data for Saroside (**1**) in Me_2CO-d_6.

Position	δC	$^1H/^{13}C$ connectivity	$^1H/^{13}C$ connectivity [bond connectivities]
1	166.13		OH-1 (12.38) [2]
2	103.45	H-2 (6.37)	OH-1 (12.38) [3], H-4 (6.94) [3]
3	165.31		H-2 (6.37) [2], H-4 (6.94) [2]
4	108.61	H-4 (6.94)	H-2 (6.37) [3]
5	118.41	H-5 (7.02)	H-7 (6.49) [3], H-11 (1.80) [3]
6	148.26		H-11 (1.80) [2]
7	117.71	H-7 (2.49)	OH-8 (12.06) [3], H-5 (7.02) [3], H-11 (1.80) [3]
8	162.91		OH-8 (12.06) [2], H-7 (6.49) [2]
9	192.89		
10	76.57		H-4 (6.94) [3], H-5 (7.02) [3], H-5′ (3.73) [2]
1a	110.70		OH-1 (12.38) [3], H-2 (6.37) [3], H-4 (6.94) [3]
4a	148.62[a]		H-5′ (3.73) [3]
5a	148.83[a]		H-5′ (3.73) [3]
8a	114.87		OH-8 (12.06) [3], H-5 (7.02) [3], H-7 (6.49) [3]
11	22.00	H-11 (1.80)	H-5 (7.02) [3], H-7 (6.49) [3]
1′	95.07	H-1′ (5.82)	H-5′ (3.73) [3]
2′	70.69	H-2′ (3.87)	*
3′	73.48	H-3′ (3.92)	H-1′ (5.82) [3], H-4′ (3.83) [2], H-5′ (3.73) [3]
4′	70.18	H-4′ (3.83)	H-5′ (3.73) [2]
5′	80.54	H-5′ (3.73)	H-1′ (5.82) [3], H-4′ (3.83) [2]
1″ (C=O)	163.99		H-1′ (5.82) [3], H-2″, 6″ (7.87) [3]
1″	*		*
2″, 6″	130.65	H-2″, H-6″ (7.87)	H-2″, 6″ (7.87) [3], H-4″ (7.67) [3]
3″, 5″	129.75	H-3″, H-5″ (7.54)	H-3″, 5″ (7.54) [3]
4″	134.52	H-4″ (7.67)	H-2″, 6″ (7.87) [3]

δ-H (ppm) in parenthesis.[a] These assignments may be interchangeable.* Not observed.

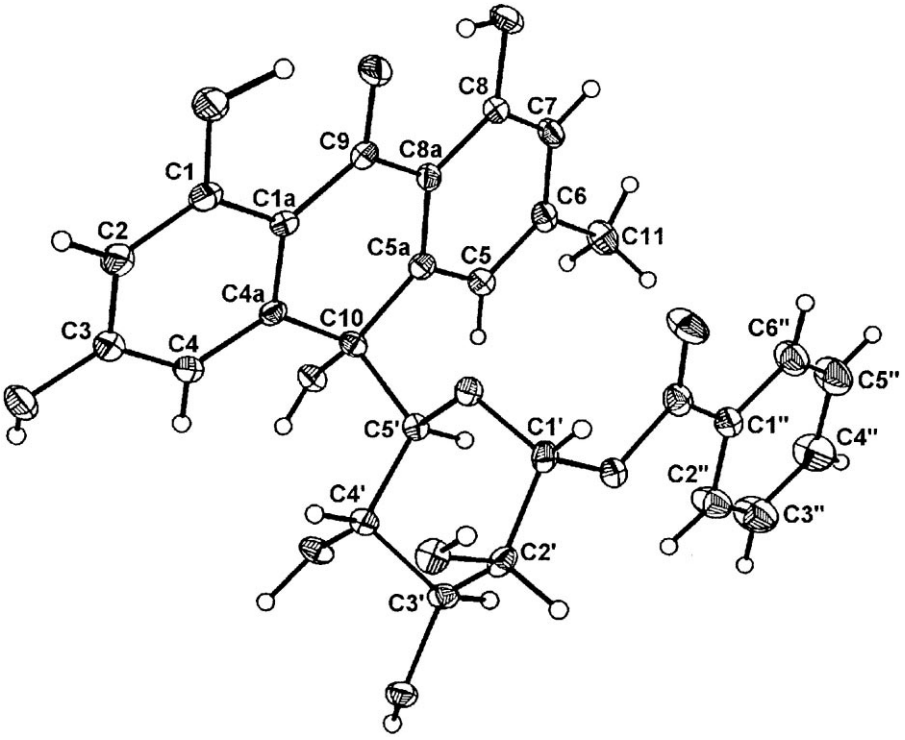

Fig. 1. Molecular structure of saroside (**1**) as determined by X-ray analysis.

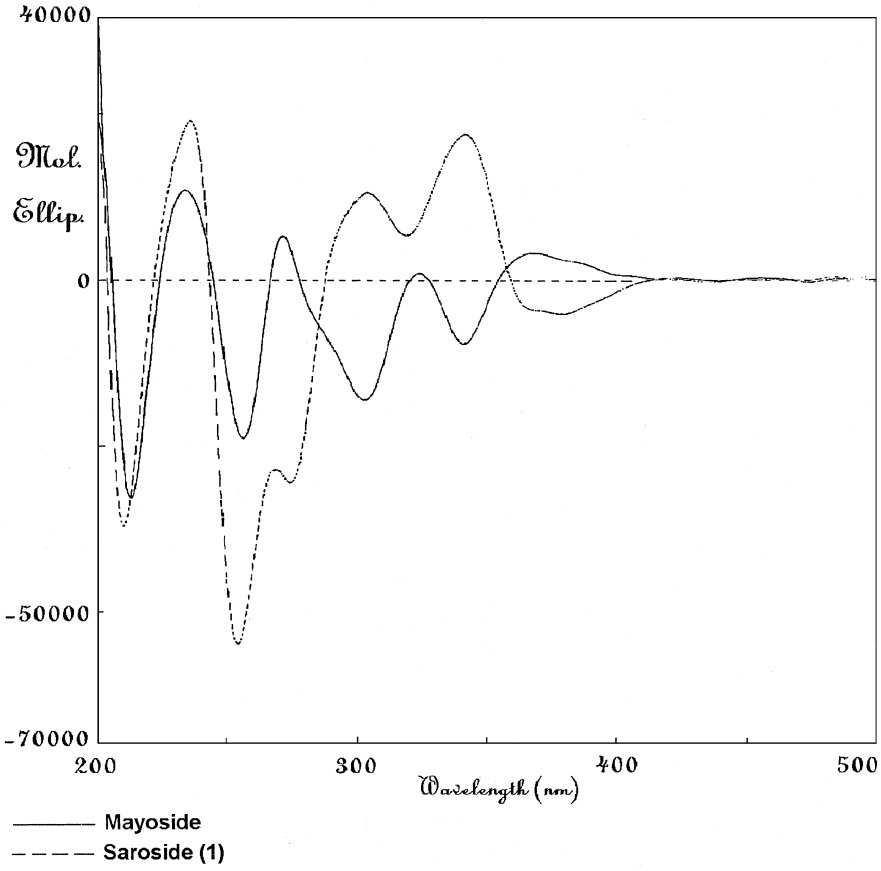

Fig. 2. CD spectra of mayoside and saroside (**1**).

ring B results in an angle of 12° between rings A and C. The torsion angles about the C-10-C-5′ bond show a staggered arrangement. The CD spectra (Fig. 2) of mayoside and saroside (**1**) show opposite Cotton effects in the ranges 270–378 nm, indicating the opposite configuration of C-10 for these oxanthrones. Thus mayoside shows a negative Cotton effect and saroside (**1**) a positive one. These results are the same as those reported for aloin A and B (Rauwald, Lohse & Bats, 1989; Manitto, Monti & Speranza, 1990), 10-hydroxyaloins A and B (Rauwald, Lohse & Bats, 1991) and cascarosides A, B, C and D (Manitto, Monti, Speranza, Mulinacci, 1993). Establishment of the configuration at C-10 for these compounds can be inferred from the NOE correlation of the anomeric proton with the H-atoms in the peri position. For compound **1**, the NOE correlation of H-5′ with H-5 and H-4′ with H-4 (Fig. 3) is indicative of the prevalent conformation both in solution and the crystalline state and therefore saroside (**1**) has the 10*S* configuration while mayoside is the 10*R* diastereoisomer.

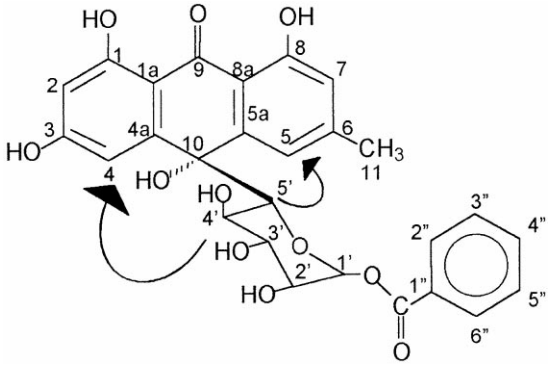

Fig. 3. NOESY correlations of saroside (**1**).

3. Experimental

3.1. General

Mp: uncorr.; TLC: Merck 60 GF_{254} of 0.2 mm thickness; CC silica gel (Merck, Kieselgel 60 particle size 0.063–0.200 mm and 0.040–0.063 mm); UV: shimadzu U-160 spectrophotometer; IR: Perkin-Elmer

16-PC-FT-IR spectrophotometer; ^{1}H and ^{13}C NMR: Jeol Eclipse + 400 in $(CD_3)_2CO$ CD: Jasco J-720 instrument.

3.2. Plant material

The stem of *P. antidesma* was collected at Yecuatla, Veracruz, México, during March 1992, and identified by C. Gutiérrez. A voucher specimen was deposited at the Herbarium of the Institute of Ecology, A.C. (XAL), Xalapa, Veracruz, México.

3.3. Isolation

The chopped stem (1.0 kg) from *P. antidesma* was soaked in MeOH at room temperature and then filtered, the MeOH extract was concentrated under vacuum and the residue (60.0 g) was submitted to CC (silica gel 60, 0.063–0.200 mm) using $CHCl_3$ and $CHCl_3$-MeOH mixtures of increasing polarities as eluent. The first fractions were further purified by CC (silica gel 60, 0.040–0.063) and crystallization which resulted in the isolation of the following compounds: chrysophanol (17 mg) (Danielsen *et al*., 1992), β-sitosterol (25 mg) (Salama *et al*., 1987), emodin (17 mg) (Danielsen *et al*., 1992; Hernández-Medel *et al*., 1996) and its glucoside (20 mg) (Coskum *et al*., 1990; Lin *et al*., 1991; Kalidhar, 1992; Kinjo *et al*., 1994), aloe-emodin (2 mg) (Danielsen *et al*., 19924), 7-hydroxycoumarin (30 mg) (Duddeck & Kaiser, 1982) β-sitosterol glucoside as its acetylated derivative (21 mg) (Salama *et al*., 1982), respectively. They were identified by comparison with authentic samples and their spectral data.

Mayoside (17 mg), yellow needles, was identified from its ^{1}H and ^{13}C NMR data (Tables 1 and 2) and comparison with an authentic sample (Hernández-Medel *et al*., 1996).

3.4. Saroside (**1**)

Yellow needles (9 mg), mp 215–218° (C_6H_6-Me_2CO). UV λ_{MAX} (MeOH)/nm: 388, 274, 258, 221, 204 nm; IR ν_{MAX} (KBr)cm^{-1}: 3336, 2930, 1740, 1640, 1618, 1266, 950, 908, 846 and 714; ^{1}H NMR and ^{13}C NMR: Tables 1 and 2.

3.5. X-ray analysis

Suitable crystals of saroside (**1**) were grown from C_6H_6-Me_2CO as light yelow prisms. Intensity data were collected at room temp on a Siemens CCD-Area-detector diffractometer using MoKα radiation ($\lambda = 0.71073$ Å) with 2θ range for data collection between 2.42–58.30°. Crystal data for **1**: $C_{27}H_{24}O_{11}$ 0.5 C_3H_6O, orthorhombic, space group $P2_12_12_1$, $a = 8.1581$ (2), $b = 19.4886$ (2), $c = 33.4698$ (5) Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 90.00°$, $V = 5321.4(2)$ Å^3, $Z = 8$. 6563 observed reflections [$F > 4\sigma(F)$]. Structure solution program was XS(SHELXTL-Ver. 5), the program used for refinement details was SHELXL (Sheldrick). The final fractional coordinates, themal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Centre.

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