Pergamon

PII: S0031-9422(96)00160-4

Phytochemistry, Vol. 43, No. 1, pp. 279–281, 1996

0031-9422/96 $15.00 + 0.00

MAYOSIDE, AN OXANTHRONE FROM *PICRAMNIA HIRSUTA*

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(*Received in revised form* 30 *January* 1996)

Key Word Index—*Picramnia hirsuta*; Simaroubaceae; oxanthrone, mayoside.

Abstract—A new oxanthrone named mayoside was isolated from the roots of *Picramnia hirsuta* and the structure established by X-ray diffraction. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Picramnia is the largest and most complex genus in the Simaroubaceae and comprises 40 species in the American tropics. *P. hirsuta* appears to be restricted to rainforests near the Isthmus of Tehuantepec, Mexico, ranging from Catemaco, Veracruz, to the Uxpanapa region of Oaxaca and Veracruz [1]. Previous investigations of the genus *Picramnia* have resulted in the isolation of several anthraquinones and triterpenoids [2–5].

RESULTS AND DISCUSSION

The extracts were subjected to repeated column chromatography on silica gel to yield compounds **1–5**. Compounds **1–4** were shown to be β-sitosterol [6], chrysophanol, emodin [7] and 7-hydroxycoumarin [8], respectively, by comparison with authentic samples and spectral data [9]. Compound **5** gave rise to a UV spectrum (218, 275, 366 and 373 nm) characteristic of a highly conjugated system, such as an anthraquinone, and the IR spectrum showed absorption bands at 3540, 3390, 1715 and 1635 cm^{-1}. The ^1H and ^{13}C NMR spectra established the presence of 24 protons and 27 carbons. The GC–mass spectrum displayed a fragmentation ion at m/z 402 $[M-122]^+$ indicating the loss of benzoic acid. The presence of an emodin system was supported by the ^1H NMR spectrum (Table 1), which showed two singlets for chelated hydroxyl groups (δ 12.17 and 12.14) and the typical AB pattern for the protons in the H-5, H-7 and H-4, H-2 positions (δ 7.20, 6.82 and 6.73, 6.09, respectively). The singlet at δ 10.44 (1H, D_2O exchangeable proton) was due to a hydroxyl group in the 3 position. There were signals for nine aromatic protons from δ 6.09–7.80 and the COSY spectrum showed three separate aromatic rings; three D_2O exchangeable protons at δ 6.14, 5.18 and 5.01 were assigned to the hydroxyl groups in the sugar moiety; and a singlet at δ 5.70 was assigned to the proton on C-1′. The two proton singlet-shaped multiplet at δ 3.70 was assigned to the protons on C-2′ and C-3′ and the two proton singlet-shaped multiplet at δ 3.54 was assigned to the protons at C-4′ and C-5′. The ^{13}C NMR assignments are presented in Table 1. The spectrum showed 25 signals, including two CH signals at δ 129.01 and δ 129.33 which showed a double intensity characteristic of a monosubstituted benzene ring. The DEPT experiment was accounted for by one methyl, 14 methine, and 12 quaternary carbons. An interesting feature of the ^{13}C NMR spectrum was the presence of one quaternary carbon resonance at δ 75.03 for C-10, indicating oxygenation at this position and hence the presence of an oxanthrone moiety. The presence of a C-glycosyde unit was confirmed by five CH signals at δ 94.52, 80.10, 71.67, 69.00 and 68.34. The full assignment of the ^{13}C NMR signals was mainly based on comparison with those of anthrones [10–11] and oxanthrones [12–13] and also on HETCOR experiments (Table 1). The above information led to the conclusion that compound **5**, named mayoside, has the structure shown in Fig. 1. The lyxose nature of the sugar moiety was established by single-crystal X-ray diffraction.

EXPERIMENTAL

General. MP: uncorr.; TLC: silica gel (Merck 60 GF_{254}; 0.2 mm thickness); CC: silica gel (Merck, Kieselgel 60 particle size 0.063–0.200 mm and 0.040–0.063 mm); ^1H and ^{13}C NMR; Varian Gemini 200

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Table 1. ^{1}H NMR and ^{13}C NMR spectral data for mayoside, **5** (DMSO-d_6, δ, ppm)

C	δ	Multiplicity* DEPT	^{1}H–^{13}C† Connectivity	Multiplicity‡ ^{1}H NMR	^{1}H–^{1}H† Connectivity
1	163.94	C			
1a	108.97	C			
2	101.63	CH	H-2 (δ 6.09)	*d* (2.0)	H-4
3	165.37	C			
4	105.94	CH	H-4 (δ 6.73)	*d* (2.0)	H-2
4a	146.17	C			
5	119.68	CH	H-5 (δ 7.20)	*s*	H-7 and H-11
5a	144.78	C			
6	150.92	C			
7	117.11	CH	H-7 (δ 6.82)	*s*	H-5 and H-11
8	161.25	C			
8a	113.54	C			
9	190.30	C			
10	75.03	C			
11	22.35	CH_3	H-11 (δ 2.40)	*s*	H-5 and H-7
1′	94.52	CH	H-1′ (δ 5.70)	*s*	H-2′
2′	69.00	CH	H-2′ (δ 3.70)	*s*	H-1′ and 2′ OH
3′	71.67	CH	H-3′ (δ 3.70)	*s*	H-4′ and 3′ OH
4′	68.34	CH	H-4′ (δ 3.54)	*s*	H-3′ and 4′ OH
5′	80.10	CH	H-5′ (δ 3.54)	*s*	H-4′
1″ (C = 0)	163.58	C			
1″	129.18	C			
2″ and 6″§	129.33	CH	H-2″/H-6″ (δ 7.80)	*d* (7.6)	H-3″/H-5″
3″ and 5″§	129.01	CH	H-3″/H-5″ (δ 7.55)	*dd* (7.6 and 7.2)	H-2″/H-6″ and H-4″
4″	133.81	CH	H-4″ (δ 7.70)	*d* (7.2)	H-3″/H-5″

*Multiplicity from DEPT ^{13}C NMR experiment.

†Assignments were confirmed by ^{1}H COSY, DEPT and HETCOR experiments.

‡Multiplicity from ^{1}H NMR experiment. Coupling constants (*J* in Hz) in parentheses.

§The intensity for this signal was twice that of the other CH signals.

instrument in $CDCl_3$ and DMSO-d_6 with TMS as int. standard.

Plant material. The root of *Picramnia hirsuta* was collected at Valle de Uxpanapa, Veracruz, México, during November 1992. A voucher specimen is deposited at the Herbarium of the Centro de Investigaciones Biológicas, Universidad Veracruzana (XALU).

Isolation. The chipped roots (1.60 kg) were soaked successively in C_6H_{14}, $CHCl_3$ and MeOH at room temp. and then filtered; the filtrates after removal of the solvents under red. pres. gave residues weighing 1.5 g, 3.2 g and 50.3 g, respectively.

The crude C_6H_{14} extract was chromatographed on silica gel. Elution with C_6H_{14}–$CHCl_3$ (4:1) yielded compound **1** (40 mg). The $CHCl_3$ extract was subjected to CC on silica gel; elution with C_6H_{14}–$CHCl_3$ (4:1) and C_6H_{14}–EtOAc (8:2, 7:3) gave compounds **2** (5 mg), **3** (7 mg) and **4** (12 mg). The crude MeOH extract (30 g) was chromatographed on silica gel, using $CHCl_3$, $CHCl_3$–MeOH (19:1, 9:1, 17:3, 4:1) as eluents to yield compounds **3** (25 mg), **4** (15 mg) and **5** (50 mg).

Compounds **1–4** were identified as sitosterol, chrysophanol, emodin and 7-hydroxycoumarin, respectively, by spectral data (^{1}H NMR and ^{13}C NMR) and direct comparison with authentic samples [7–9].

Compound **5**. Yellow needles (MeOH), mp 238–240°. UV λ_{max} (EtOH) nm: 218, 275, 366 and 373; IR (KBr) ν_{max}, (cm^{-1}): 3540 and 3390 (OH), 2940, 1715, 1635, 1610, 1250, 1155, 910, 850 and 710; GC–MS 70 eV, *m/z* (rel. int.): 524 (1) $[M]^+$, 402 (5) $[M - C_7H_6O_2]^+$ 122 (75) $C_7H_6O_2$, 77 (100) C_6H_5; ^{1}H NMR and ^{13}C NMR: Table 1.

X-ray analysis. Suitable crystals of mayoside (**5**) were grown from MeOH as prisms. Intensity data were collected at room temp. on a CAD4-Enraf-Nonius diffractometer using MoKα radiation ($\lambda = 0.71069$ Å) with the $\omega/2\theta$ data collection method in the range 2–25°. Crystal data for **5**: $C_{27}H_{24}O_{11}$, square prism, space group P1, a = 8.251 (3), b = 8.955 (3), c = 9.931 (2) Å, $\alpha = 61.83$ (2), $\beta = 70.50$ (2), $\gamma = 74.65$ (3), °, V = 604.7 (3) Å^3, Z = 1. 1768 observed reflections [$(Fo)^2 > 3\sigma(Fo)^2$], final R = 0.040, Rw = 0.039. The final fractional coordinates, thermal parameters, bond distances and angles have been deposited with the Cambridge Crystallographic Centre.

Acknowledgement—The authors thank Professor Mario Vázquez (Centro de Investigaciones Biológicas, Uni-

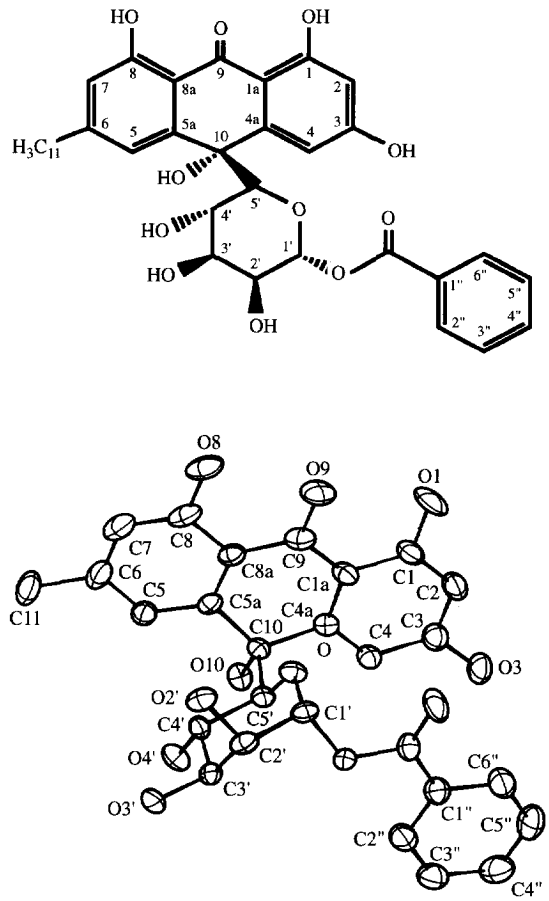

Fig. 1. Formula of mayoside (**5**), as determined by X-ray analysis.

versidad Veracruzana, México) for the identification of the plant.

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