

AN ANTHRONE FROM *PICRAMNIA ANTIDESMA*MARIA DEL R. HERNANDEZ-MEDEL,^{†*} IRMA GARCIA-SALMONES,[†] ROSA SANTILLAN[‡] and ANGEL TRIGOS[§]

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Key Word Index—*Picramnia antidesma*; Simaroubaceae; anthrone; roots; uveoside.

Abstract—A new chrysophanol anthrone C-glycoside, named uveoside and four known compounds were isolated and identified from the chloroform extract of roots from *Picramnia antidesma*. © 1998 Elsevier Science Ltd. All rights reserved

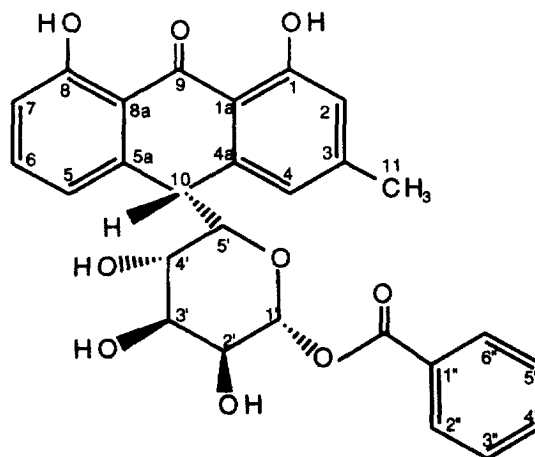
INTRODUCTION

In previous papers [1,2], we reported the isolation and characterization of two diastereoisomeric oxanthrone C-glycosides from *Picramnia* species. In this work, a new anthrone (**1**) and the known compounds, chrysophanol, β -sitosterol, emodin and 7-hydroxycoumarin were obtained from the roots of *Picramnia antidesma*. We report here on the structure elucidation of **1** a new natural product named uveoside.

RESULTS AND DISCUSSION

The chloroform extract of dried roots was subjected to repeated column chromatography on silica gel to yield four known compounds which were identified as chrysophanol [1–3], β -sitosterol [2,4], emodin [1–3] and 7-hydroxycoumarin [1,2,5] by comparison with authentic samples and spectral data. Compound **1**, had a UV spectrum (223, 268, 297 and 360 nm) characteristic of a highly conjugated system, such as an anthraquinone and the IR spectrum showed absorption bands at 3432, 1726 and 1636 cm^{-1} . The ^1H and ^{13}C NMR spectra established the presence of 24 protons and 27 carbons. The presence of an anthrone group was supported by the GC-mass spectral fragment ion at m/z 239 ($\text{C}_{15}\text{H}_{11}\text{O}_3$) [6], the ^1H NMR (δ 4.67, d, $J = 2.5$ Hz for H-10) and the ^{13}C NMR (δ 43.69 for C-10) data. The peak at m/z 122 indicating the

presence of a benzoate moiety [7]. In addition, the ^1H NMR spectrum (Table 1) shows two singlets for chelated hydroxyl protons (δ 12.08 and 11.93) assigned to OH groups on C-8 and C-1. There were signals for 10 aromatic protons at δ 6.49 to 7.86 and the COSY spectrum showed three separate aromatic rings. A doublet of doublets at 4.01 ($J = 2.5$ and 9.7 Hz) was assigned to the proton on C-5'. Three D_2O -exchangeable protons (δ 4.53, 4.23 and 4.05) were assigned to the hydroxyl groups on C-4', C-2' and C-3' in the sugar moiety; a singlet at δ 5.85 was assigned to the proton on C-1'. The two proton singlet-shaped multiplet at δ 3.88 was assigned to the protons on C-2' and C-3' and a double, double doublet at δ 3.66 ($J = 9.7, 8.6$ and

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Table 1. Spectral data for Uveoside, 1 in Me₂CO-d₆

C	δ_C (ppm)	$^1H/^13C$ connectivity (δ ppm)	$^1H/^13C$ connectivity [bond connectivities]	$^1H/^1H$ connectivity (δ ppm)	Multiplicity 1H NMR (J in Hz)
1	163.17		OH-1 (11.93) (2), H-2 (6.49) [2]		
2	116.46	H-2 (6.49)	OH-1 (11.93) (3), H-4 (6.70) [3]	H-4 (7.67), H-11 (1.88)	s
3	148.91		H-11 (1.88) [2]		
4	120.00	H-4 (6.70)	H-2 (6.49) [3]	H-2 (6.49), H-11 (1.88)	s
5	121.25	H-5 (7.20)	*	H-6 (7.54), H-7 (6.90)	d (7.3)
6	136.23	H-6 (7.54)	*	H-5 (7.20), H-7 (6.90)	m
7	116.95	H-7 (6.90)	OH-8 (12.08) [3], H-5 (7.20) [3], H-11 (1.88) [3]	H-5 (7.20), H-6 (7.54)	d (8.4)
8	163.17		OH-8 (12.08) [2]		
9	194.96		*		
10	43.69	H-10 (4.67)	*	H-5' (4.01)	d (2.5)
1a	116.05		OH-1 (11.93) [3], H-2 (6.49) [3], H-4 (6.70) [3], H-10 (4.67) [3]		
4a	142.15*		H-10 (4.67) [2]		
5a	146.75*		*		
8a	118.30		OH-8 (12.08) [3], H-5 (7.20) [3], H-7 (6.90) [3], H-10 (4.67) [3]		
11	21.64	H-11 (1.88)	H-2 (6.49) [3], H-4 (6.70) [3]	H-2 (6.49), H-4 (6.70)	s
1'	95.30	H-1' (5.85)	OH-2' (4.23) [3]	H-2'/H-3' (3.88)	s
2'	70.70	H-2' (3.88)	OH-2' (4.23) [2]	H-1' (5.85), OH-2' (4.23)	m
3'	73.56	H-3' (3.88)	H-1' (5.85) [3], OH-2' (4.23) [3]	H-4' (3.66), OH-3' (4.05)	m
4'	68.47	H-4' (3.66)	OH-4' (4.53) [2]	H-2'/H-3' (3.88), H-5' (4.01), OH-4' (4.53)	ddd (9.7, 8.6, 4.5)
5'	81.97	H-5' (4.01)	H-1' (5.85) [3], OH-4' (4.53) [3]	H-4' (3.66), H-10 (4.67)	dd (2.5, 9.7)
1'' (C = O)	164.12		H-1' (5.85) [3], H-2'', 6'' (7.85) [3]		
1''	*		*		
2'' and 6''	130.31	H-2'' and H-6'' (7.86)	H-2'', H-6'' [3], H-4'' (7.64) [3]	H-3''/H-5'' (7.54)	dd (3.1, 1.1)
3'' and 5''	129.47	H-3'' and H-5'' (7.54)	H-3'', H-5'' (7.54) [3]	H-2''/H-6'' (7.86), H-4'' (7.67)	
4''	134.21	H-4'' (7.64)	H-2'', 6'' (7.86) [3]	H-3''/H-5'' (7.54)	t (7.4)

*Not observed

4.5 Hz) was assigned to the proton on C-4'. The ^{13}C NMR assignment is presented in Table 1. This spectrum showed 27 signals, including two CH signals at δ 130.3 and 129.5 showing a double intensity characteristic of a monosubstituted benzene ring. The presence of a C-glycoside unit was confirmed by five CH signals at δ 95.3, 82.0, 73.6, 70.7 and 68.5 [1]. The full assignment of the ^{13}C NMR signals was mainly based on 1H COSY, HMQC and HMBC experiments (Table 1), as well as by analogy with the chemical shifts of anthrones [7–9]. The CD spectrum showed a negative Cotton effect at 297 nm, which agreed with that previously reported for (10*R*) aloin [8] and other anthrones [7, 9, 10]. The above information led to the conclusion that compound named uveoside has the structure 1.

Plant material

Roots of *P. antidesma* were collected at Yecuatla in Veracruz, Mexico, during March 1992. A voucher specimen is deposited at the Herbarium of the Instituto de Ecología A. C. (XAL), Xalapa, Veracruz, Mexico.

Isolation

Chipped roots (1.6 kg) were soaked repeatedly in CHCl₃ at room temperature and then filtered. The filtrate, after solvent removal under reduced pressure, gave 19 g. This CHCl₃ extract was subjected to CC on silica gel, using CHCl₃ and CHU₃–Me₂CO (9:1, 17:3, 4:1, 3:1, 7:3) as eluents to yield chrysophanol (15 mg) [1–3], β -sitosterol (20 mg) [2, 4] emodin (15 mg) [1, 2] and 7-hydroxycoumarin (10 mg) [1, 2, 5], respectively, by comparison with authentic samples and spectral data.

Compound 1, uveoside

Yellow needles (CHCl₃–Me₂CO), m.p. 228–231°C. $[\alpha/D]^{20}$ –0.20° (EtOH; *c* 0.60). UV λ_{max} (EtOH) nm: 223, 268, 297, 360 nm. IR (KBr) ν_{max} (cm^{–1}): 3432, 1726, 1636. GC-MS 70 eV, *m/z* (rel. int.): 67 (25), 69 (48), 77 (100), 81 (23), 83 (29), 97 (22), 105 (98), 122 (60), 239 (14), 240 (28), 253 (8), 265 (31), 280 (21), 446 (54), 447 (18). 1H and ^{13}C NMR in Table 1.

EXPERIMENTAL

General

TLC: silica gel (Merck 60 GF₂₅₄). CC: silica gel (Merck, Kieselgel 60 particle size 0.063–0.200 and 0.040–0.063 mm). M.p.'s uncorr. 1H and ^{13}C NMR were obtained using a Varian Gemini 200 and Jeol Eclipse + 400 instrument in CDCl₃ and Me₂CO-d₆ with TMS as an internal standard.

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