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Two anthrones and one oxanthrone from *Picramnia teapensis*

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Abstract

From the bark of *Picramnia teapensis* were isolated 7-hydroxycoumarin, emodin, the oxanthrone mayoside and three new compounds: two anthrone glycosides named picramniosides D and E and an oxanthrone glycoside named mayoside B. These new compounds were separated by recycling-HPLC and were identified on the basis of spectral data. CD was used to establish the absolute configuration of the new compounds.

Keywords: *Picramnia teapensis*; Simaroubaceae; Anthrone glycosides; Oxanthrone glycosides; Picramnosides D, E; Mayoside B

1. Introduction

Picramnia teapensis Tul. is a tree found in Central America, one of approximately 45 in the genus *Picramnia*. According to Engler, the genus *Picramnia* belongs to the Simaroubaceae, although chemotaxonomical and morphological considerations have recently led to the proposal that *Picramnia* be promoted to a new family, Picramniaceae (Fernando, & Quinn, 1995). Previous studies of the genus have led to the isolation of coumarins, anthraquinones, triterpenoids (Herz, Santhanam, & Wahlberg, 1972; Leon, & Juan, 1975; Popinigis, Moreira, Nakashima, Krambeck, & Miguel, 1980; Arana, & Julka, 1986) and, recently, anthrone and oxanthrone glycosides (Solís, Gutiérrez, González, Gupta, & Phillipson, 1995; Hernández-Medel, López-Marquez, Santillan, & Trigos, 1996). Most of these compounds have shown interesting pharmacological properties (Fairbairn, 1964; Popinigis et al., 1980; Daguilh et al., 1986; Solís et al., 1995; Yagi, Yamauchi, & Kuwano, 1997). As part of our interest in the chemistry of Simaroubaceae, we describe here our findings on *P. teapensis*.

2. Results and discussion

The ethyl acetate extract from the bark of *Picramnia teapensis* afforded 7-hydroxycoumarin (Razdan, Qadri, Harkar, & Waight, 1987), emodin (Cam, 1975) and predominantly a mixture of four emodin C-glycosides which were separated by recycling-HPLC. This mixture afforded two new anthrones named picramniosides D (**1**) and E (**2**), a new oxanthrone named mayoside B (**3**) and the oxanthrone **4**. Compound **4** gave spectral data in agreement with those published for mayoside, which has been found previously in the bark of *Picramnia hirsuta* (Hernández-Medel et al., 1996). Its structure was further substantiated by HMQC and HMBC experiments in CD_3OD (Tables 1 and 2).

Compounds **3** and **4** ($C_{26}H_{24}O_{11}$) gave similar ESI-MS and UV spectra. The ^1H NMR spectrum of **3** suggested a structure similar to **4**, showing slight differences in the aromatic pattern and chemical shifts. Notably, H-5, H-7 and H-11 were deshielded in **3**, while H-2 and H-4 were shielded Table 1. The ^{13}C NMR spectra of **3** and **4** were almost identical except for the chemical shifts of the carbons near C-10 (C-4, C-4a, C-5, C-5a, C-6 and C-11, Table 2) In view of these differences, it was concluded that **3** must be an

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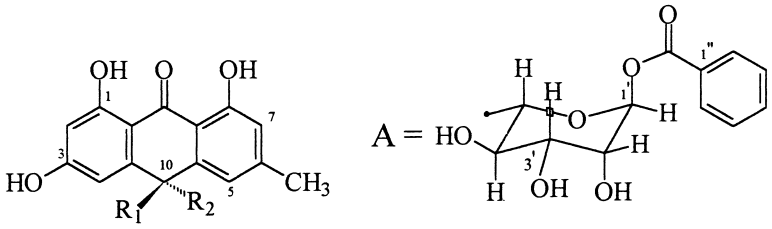

1 R_1 = A, R_2 = H
2 R_1 = H, R_2 = A
3 R_1 = A, R_2 = OH
4 R_1 = OH, R_2 = A

alternate C-10 isomeric form of **4**. The relative configuration of the sugar moiety for both compounds **3** and **4** was deduced from the chemical shift of C-1′ to C-5′ in the ^{13}C NMR, which were shown to be very closely related to those of **1** and **2**. Moreover the multiplicity and the *J* value observed for the H-1′ was very similar for all compounds suggesting the same relative configuration of the sugar moiety. Picramniosides B and C, isolated previously from *Picramnia antidesma* ssp. *fessonia* (Hernández-Medel et al., 1996), have been reported as comparable C-10 isomers.

Compounds **1** and **2** ($C_{26}H_{24}O_{12}$) showed spectral characteristics close to those of **3** and **4** and of picramniosides B and C (Solís et al., 1995). The fundamental difference between these two anthrones and the oxanthrones is at C-10. This carbon, carrying hydroxyl in **3** and **4** (δ 76.3 and 76.7, respectively), now appeared shielded (δ 44.4 for **1** and δ 43.8 for **2**, Table 2). In the HMQC spectra, C-10 signal showed correlation with the proton at δ 4.36 (d, $J = 2.1$ Hz), with a *J* value suggesting a dihedral angle with H-5′ close to 85°. In the HMBC spectra H-10 was correlated with C-4, C-5 and C-5′ (Table 3) and H-1′ and H-2″ were correlated with the carbonyl carbon of the benzoyl substituent, thus confirming the location of the sugar moiety and the exact position of the benzoate group in the glycoside. Multiplicity and *J* values clearly confirmed the xylose nature of the sugar moiety, as shown previously for the other picramniosides and mayosides.

The CD spectrum of **1** showed a positive Cotton effect at 221.8 and 359.8 nm and a negative Cotton effect at 269.0 and 300.0 nm, similar to those reported for (10*S*) picramnioside A (Solís et al., 1995). This observation allowed us to establish the absolute configuration of **1** as (10*R*) picramnioside D. Consequently, the absolute configuration of **2** is (10*S*) picramnioside E. Similar associations permitted the establishment of **3** as (10*R*) mayoside B. The absolute configuration of **4** has been previously reported as (10*S*) mayoside (Hernández-Medel et al., 1996). These results are concordant with the conformational studies of aloins

Table 1
^{1}H NMR (400 MHz) chemical shifts for compounds **1**–**4** (methanol-d_6)

H	1	2	3	4
2	6.20 d (2.1)	6.24 d (2.4)	6.15 d (2.4)	6.29 d (2.3)
4	5.94 d (2.1)	6.58 d (2.4)	6.86 d (2.4)	6.88 d (2.3)
5	6.80 br s	6.55 br s	7.26 dd (1.6, 0.6)	6.96 dd (1.5, 0.5)
7	6.57 br s	6.41 br s	6.75 dd (1.6, 0.6)	6.47 dd (1.5, 0.7)
10	4.36 d (2.1)	4.45 d (2.4)	–	–
11	2.27 s	1.79 s	2.42 t (0.6)	1.78 br s
5′	3.83 dd (9.6, 2.1)	3.89 dd (9.9, 2.4)	3.70–3.79 m	3.65 dm (8.8)
4′	3.60 t (9.6)	3.76 t (9.8)	3.80–3.92[a] m	3.81 t (8.3)
3′	3.71 dd (9.6, 3.4)	3.77–3.84 m	3.80–3.92 m	3.81–3.84 m
2′	3.76 dd (3.4, 1.5)	3.77–3.84 m	3.70–3.79[a] m	3.78 dd (3.4, 1.8)
1′	5.76 d (1.5)	5.84 d (0.8)	5.85 d (1.06)	5.80 d (1.72)
2″ and 6″	7.72 dt (8.4, 1.2)	7.82 dt (7.2, 1.4)	7.87 dt (7.4, 1.3)	7.83 dt (7.0, 1.5)
3″ and 5″	7.36 td (8.4, 1.2)	7.48 td br (7.2, 1.2)	7.50 td (7.4, 1.3)	7.50 td (7.0, 1.5)
4″	7.51 tt (8.6, 1.2)	7.63 tt (7.4, 1.2)	7.51 tt (7.4, 1.3)	7.63 tt (7.4, 1.4)
OH	12.27[b] s	12.37[b] s	12.20[b] br s	12.34[b] br s
1 and 8	12.13[b] s	12.11[b] s	12.15[b] br s	12.09[b] br s

[a] May be interchangeable.
[b] Signals observed when acetone-d_6 was used as solvent.

Table 2
^{13}C NMR (100 MHz) chemical shifts for **1**–**4** (methanol-d_6)

C	1	2	3	4
1	165.9	165.7	165.7[a]	164.8
1a	116.4	116.0	110.7	110.1
2	102.1	102.5	102.6	103.4
3	165.8	165.0	165.5[a]	166.2
4	107.9	110.1	106.5	108.4
4a	141.8	144.0	151.6	148.3
5	122.3	119.7	120.0	118.2
5a	147.3	146.0	145.6	148.1
6	149.2	147.7	147.0	148.9
7	117.3	116.4	118.0	117.8
8	165.4	162.6	163.0	162.8
8a	112.0	111.8	114.8	115.0
9	193.4	193.1	193.0	192.4
10	44.4	43.8	76.3	76.7
11	22.1	21.6	22.3	21.8
5′	82.9	82.1	80.5	80.9
4′	68.4	68.0	70.0	69.7
3′	73.6	73.7	73.0	73.7
2′	71.1	70.7	70.4	70.7
1′	96.1	95.4	95.2	95.3
1′ (C=O)	163.2	164.7	164.3	164.8
1″	130.4	130.3	130.4	130.7
2″ and 6″	130.5	130.4	130.3	130.7
3″ and 5″	129.6	129.4	129.4	129.8
4″	134.5	134.3	134.2	134.7

[a] May be interchangeable.

(Manitto, Monti, & Speranza, 1990) and cascarosides (Manitto et al., 1993).

3. Experimental

3.1. General

M.p.'s uncorr. IR (KBr, BOMEM-FT-IR); UV: (MeOH, Perkin Elmer); ^1H NMR, COSY 45 and HMQC, HMBC: 400 and ^{13}C NMR 100 MHz, containing TMS as int. standard (Bruker); EIMS (Fisons, Platform); ESI-MS (VG Platform II).

3.2. Plant material

The bark of *P. teapensis* was collected in Costa Rica, in the region of San José de la Montaña in September 1990 and a voucher (CR194274) is deposited in the herbarium of the Universidad Nacional de Costa Rica.

3.3. Isolation of constituents

Dried and powdered bark of *P. teapensis* (615 g) was macerated with EtOH 80%. The extract was filtered and concentrated under vacuum and part of this

Table 3
Selected long-range ^1H–^{13}C 2D NMR coupling data for **2**–**4**

H	C of 2	C of 3	C of 4
2	1, 1a, 4, 11	1, 1a, 4	1a, 3
4	2, 1a, 10, 11	2, 1a, 10	2, 1a, 10
5	6, 7,8a, 10	7,8a, 10, 11	7, 8a, 10, 11
7	5, 8, 8a	5, 8, 8a, 11	5, 11, 8a
10	1a, 4, 4a, 5, 5a, 8a, 5′	–	–
11	–	–	6, 5, 7
1′	2′, 3′, 5′, 1′ (C=O)	3′, 5′, 1′ (C=O)	3′, 5′, 1′ (C=O)
2″	3″, 5″, 4″, 1′ (C=O)	3″, 5″, 4″, 1′ (C=O)	3″, 5″, 4″, 1′ (C=O)

(10.3 g) was partitioned between H_2O and $CHCl_3$. The aq. layer was subsequently extracted with ethyl acetate and then with *n*-BuOH. The ethyl acetate fraction (668 mg) was submitted to vacuum chromatography over silica gel using gradient elution with CH_2Cl_2–MeOH. After reunion, 13 fractions were obtained. Fractions 2–3 afforded emodin and 7-hydroxycoumarin. Fractions 4–9 afforded different mixtures of compounds **1**–**4** (223 mg). Some of these mixtures were submitted to recycling-HPLC separation. Solutions of 15 mg ml^{-1} in MeOH were prepared and 2 ml of these solutions were chromatographed on polymeric packing (Asahipak GS-310 P, 21.5 cm ID × 50.0 cm l) using MeOH for elution (flow rate: 8 ml min^{-1}; UV detector at 254 nm). Three cycles of 60 min afforded the compounds **1**–**4**.

3.4. Picramnioside D (*1*)

White powder (4.6 mg), m.p. 198°C, decomposition. $[\alpha]_D$ (MeOH, *c* 0.0013): +5.4. UV λ_{max}^{MeOH} nm (ε): 228 (25147), 274 (7772), 364 (15074). IR (KBr) ν_{max} (cm^{-1}): 3462, 2924, 2852, 1733, 1623, 1466, 1384, 1265, 1066, 716. ^1H NMR (CD_3OD, 400 MHz): Table 1. ^{13}C NMR (CD_3OD, 100 MHz): Table 2. ESI-MS *m*/*z* (rel. int. %): 547.4 (57) $[M+K]^+$, 531.2 (100) $[M+Na]^+$, 509.1 (32) $[M+1]^+$, 467.4 (57), 387.2 (57) $[M-C_6H_5COOH]^+$, 359.3 (67). CD (MeOH, c 85.7 μM) λ nm ($\Delta\varepsilon$): 359.8 (+1.17), 269.0 (−3.17), 221.8 (+7.91).

3.5. Picramnioside E (*2*)

Yellow pale powder (44.5 mg), m.p. 205.4°C, decomposition. $[\alpha]_D$ (MeOH, *c* 0.0045): +41.7. UV λ_{max}^{MeOH} nm (ε): 226 (17319), 274 (5590), 344 (8093). IR (KBr) ν_{max} (cm^{-1}): 3440, 1712, 1632, 1610, 1483, 1028, 765, 714. ^1H NMR (CD_3OD, 400 MHz): Table 1. ^{13}C NMR (CD_3OD, 100 MHz): Table 2. ESI-MS *m*/*z* (rel. int. %): 547.2 (15) $[M+K]^+$, 528.3 (100), 467.4 (12), 387.2 (21) $[M-C_6H_5COOH]^+$, 359.3 (23).

3.6. Mayoside B (*3*)

Yellow powder, (2.4 mg), m.p. 187°C, decomposition. $[\alpha]_D$ (MeOH, *c* 0.0012): +4.2. UV λ_{max}^{MeOH} nm (ε): 224 (8729), 276 (2762), 370 (5405). IR (KBr) ν_{max} (cm^{-1}): 3444, 2920, 1724, 1625, 1610, 1483, 1266, 1033. ^1H NMR (CD_3OD, 400 MHz): Table 1. ^{13}C NMR (CD_3OD, 100 MHz): Table 2. ESI-MS *m*/*z* (rel. int. %): 563.2 (32) $[M+K]^+$, 547.2 (100) $[M+Na]^+$, 544.4 (94) $[M-3H+Na]^+$, 525.2 (30) $[M+1]^+$, 403.1 $[M-122]^+$, 359.3 (78). EIMS: 403 (0.5) $[M-C_6H_5COOH]^+$, 271 (5) [aglycone]$^+$, 123 (100) $[C_6H_5COOH]^+$, 105 (81) $[C_6H_5CO]^+$.

3.7. Mayoside (*4*)

Yellow powder (30.4 mg), m.p. 168.5°C, decomposition. $[\alpha]_D$ (MeOH, *c* 0.006): +35.2. UV λ_{max}^{MeOH} nm (ε): 226 (10066), 276 (3315), 368 (6070). IR (KBr) ν_{max} (cm^{-1}): 3434, 2923, 1734, 1619, 1482, 1266, 1163, 910, 715. ^1H NMR (CD_3OD, 400 MHz): Table 1. ^{13}C NMR (CD_3OD, 100 MHz): Table 2. ESI-MS *m*/*z* (rel. int. %): 547.2 (33) $[M+Na]^+$, 544.3 (100), 525.2 (30) $[M+1]^+$, 478.2 (10), 403.1 (25) $[M-C_6H_5COOH]^+$, 359.3 (9).

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