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PREGNANE STEROIDS FROM *TRICHILIA SCHOMBURGKII*

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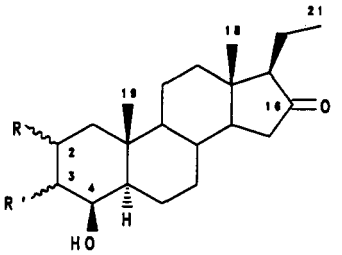
ABSTRACT.—We have reinvestigated the leaves and roots of *Trichilia schomburgkii* and, in addition to a number of known triterpenes, we have re-isolated 2β,3β,4β-trihydroxypregnan-16-one [**1**] along with the new stereoisomer 2α,3α,4β-trihydroxypregnan-16-one [**2**].

We recently reported the isolation of a number of terpenoids and a hydroxybutanolide from the leaves, stems, and roots of *Trichilia schomburgkii* DC. (Meliaceae) collected in Guyana (1). Among the terpenoids previously isolated was the novel steroid 2β,3β,4β-trihydroxypregnan-16-one [**1**] (1). We have now made a re-collection of this plant and, in addition to re-isolating **1**, a new stereoisomer 2α,3α,4β-trihydroxypregnan-16-one [**2**] was obtained. Also, from the leaves of this plant we have isolated for the first time, borjotinolone B (2), hispidol B (3–5), and cycloartane-3,24,25-triol (6).

Compound **1** was previously characterized as the monoacetate **3**, since it was more soluble in $CDCl_3$ than the free hydroxyl compound (1). We have now completed a 2D nmr study of **1** in pyridine-d_5, and the results are reported in Table 1. Confirmation for the proposed stereochemistry of ring A came from the observation of a W coupling between H-2 and H-4; this can be accounted for only on the basis of the stereochemistry shown.



1 R=β-OH, R′=β-OH
2 R=α-OH, R′=α-OH

Compound **2**, $C_{21}H_{34}O_4$, was isomeric with **1** and had ir absorptions at 3406 and 1741 cm^{-1} due to hydroxyl and a five-membered ring ketone. The ^{1}H-nmr spectrum had resonances due to one methyl triplet at δ 1.01 (J=7.5 Hz) and two methyl singlets at δ 0.56 (H_3-18) and δ 1.42 (H_3-19). Oxymethine protons had resonances at δ 4.80 (ddd, J=11.9, 4.2, 3.2 Hz), 4.62 (dd, J=3.2, 2.7 Hz), and 4.39 (dd, J=2.7, 2.5 Hz), and were assigned to H-2, H-3, and H-4 on the basis of a ^{1}H-^{1}H COSY spectrum. The protonated carbons were assigned by the use of a HETCOR experiment, while the stereochemistry followed from the coupling constants. Results are summarized in Table 1 and led to assignment of structure **2** for this new pregnane steroid. The pregnan-16-one derivatives, toosendansterols A and B, which are H-3 epimers, have previously been isolated from *Melia toosendan* (Meliaceae) (7).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—General procedures were as reported previously (1).

EXTRACTION AND ISOLATION.—Plant material identified as *T. schomburgkii* subsp. *schomburgkii* was collected at a location near the Groete Creek on the Essequibo river in March 1990. Voucher specimens are deposited in the Herbarium of the University of Guyana.

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TABLE 1. Nmr Data for Compounds **1** and **2** in Pyridine-d_5 Solution.[a]

Position	Compound			
	1		**2**	
	δ_C	δ_H	δ_C	δ_H
1	44.56	2.33, 1.22	41.82	2.11, 1.94
2	72.77	4.54(6.5, 3.5, 3.1, <1)	66.46	4.80(11.9, 4.2, 3.2)
3	72.87	3.84(3.5, 3.3)	74.94	4.62(3.2, 2.7)
4	77.20	4.18(3.3, <2.2)	77.31	4.39(2.7, 2.5)
5	50.24	1.20	44.00	1.98
6	26.58	2.13, 1.45	25.54	2.06, 1.54
7	32.76	1.59, 0.95	32.92	1.62, 0.99
8	34.11	1.51	34.08	1.48
9	56.80	0.71	56.67	0.94
10	35.71	—	37.66	—
11	20.44	1.52, 1.33	20.24	1.59, 1.31
12	38.18	1.74, 1.22	38.08	1.69, 1.17
13	42.20	—	42.14	—
14	50.56	1.30	50.53	1.27
15	38.57	2.18, 1.74	38.57	2.16, 1.71
16	218.48	—	218.56	—
17	65.15	1.63	65.12	1.61
18	13.54	0.57	13.44	0.56
19	17.47	1.60	16.05	1.42
20	18.05	1.70, 1.23	17.96	1.68, 1.22
21	13.69	1.03	13.61	1.01

[a]δ_C at 100.6 MHz and δ_H at 400 MHz.

Dried roots (5 kg) were ground and extracted with 95% EtOH, and the resulting residue, on evaporation of the solvent, was dissolved in MeOH-H_2O (9:1) and extracted with hexane. The aqueous MeOH fraction was diluted with H_2O to 40% and extracted with CH_2Cl_2, and the crude extract (51 g) was chromatographed on Si gel and eluted with $CHCl_3$ followed by $CHCl_3$-MeOH (49:1) to give **1** (38 mg) and **2** (45 mg).

The dried ground leaves (4.2 kg) were extracted with 95% EtOH and processed as above to give a crude CH_2Cl_2 extract (67 g). The extract was chromatographed on Al_2O_3 and eluted with hexane/EtOAc of increasing polarity to give niloticin (1), dihydroniloticin (1), borjotinolone B (2), piscidinol A (1), hispidol B (3–5), and cycloartane-3,24,25-triol (6). These compounds were identified by direct comparison with authentic samples or by comparison with literature data (mp, $[\alpha]_D$, ^1H and ^{13}C nmr).

COMPOUND **2**.—Mp 245–247°; $[\alpha]_D$ −95.2° (c = 0.05, MeOH); ir 3406, 1741, 1046, 1031, 1024 cm^{-1}; eims $[M]^+$ 350 (48%), 332 (17), 314 (10), 307 (22), 289 (13), 264 (100), 246 (20), 229 (40), 121 (21); exact mass 350.2460 (calcd for $C_{21}H_{34}O_4$ 350.2457); ^1H and ^{13}C nmr see Table 1.

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