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5-DEOXYSTANSIOSIDE, AN IRIDOID GLUCOSIDE FROM *TECOMA STANS**

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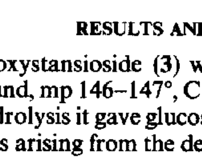
Key Word Index—*Tecoma stans*; Bignoniaceae; iridoid glucosides; plantarenaloside; stansioside; 5-deoxystansioside.

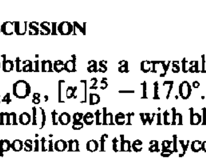
Abstract—In addition to plantarenaloside and stansioside, a new iridoid glucoside with a formyl group at C-4 has been isolated from *Tecoma stans*. The new glucoside was shown to be 5-deoxystansioside by ^{13}C NMR and ^{1}H NMR spectroscopy.

INTRODUCTION

As part of an investigation of the iridoids present in the equatorial and tropical flora, we have examined *Tecoma stans* Juss. (Bignoniaceae) because it contains many monoterpene alkaloids [1] and the biogenetic relationships between these alkaloids and the iridoids are well known [1]. In the case of *T. stans*, an unsuccessful attempt was made to demonstrate this relationship using loganin as an iridoid precursor [1]. We think that the experiment failed because an unsuitable iridoid was used. In fact, it is possible that the iridoids' precursors are plantarenaloside (1) [2], stansioside (2) [3, 4] and 5-deoxystansioside (3) [5], which we have isolated from *T. stans*, rather than loganin, which has never been detected in this plant. The structure and configuration of 5-deoxystansioside (3) was demonstrated by ^{1}H NMR and ^{13}C NMR spectroscopy.



1 R = H, R′ = Me
2 R = Me, R′ = H



3

RESULTS AND DISCUSSION

5-Deoxystansioside (3) was obtained as a crystalline compound, mp 146–147°, $C_{16}H_{24}O_8$, $[\alpha]_D^{25}$ −117.0°. On acid hydrolysis it gave glucose (1 mol) together with black products arising from the decomposition of the aglycone. Its ^{1}H NMR spectrum (Table 1 and Experimental) indicated a close structural relationship between 3 and 1 and 2. The following signals were readily assignable: a singlet (δ 9.18) due to an aldehydic proton (H-11); a doublet (1.15, $J = 6.0$ Hz) due to the protons of the C-10 methyl group; a doublet (5.54, $J = 1.5$ Hz) due to the hemiacetalic H-1; a doublet (4.88, $J = 7.5$ Hz) typical of the hemiacetalic proton of D-glucose in β-configuration; a broad singlet (δ 7.48) due to H-3. These data together with the molecular formula of 3, which differs from that of 1 and 2 ($C_{16}H_{24}O_9$) by one oxygen atom, indicated that 3 was the 5-deoxy derivative of either 1 or 2. The better correlation observed (Table 1) between the ^{1}H NMR data of 3 and 2 suggested that 3 contained a β-methyl group at C-10. In particular, the chemical shift of this methyl group together with $J_{8,10}$ was practically identical in 2 and 3. It was also significant that 2 and 3, in contrast to 1, had a measurable $J_{1,9}$. The structure and relative configuration of 3 were proved by its ^{13}C NMR spectrum (Table 2), which showed sixteen lines that were assigned using the known chemical shift rules [6, 7] and by comparison with models [8–13]. The ^{13}C NMR data were in perfect agreement with the structure proposed for 3. An important feature of the spectrum was that the chemical shift value for the C-10 methyl of 2 (δ 19.9) was the same as that shown by the C-10 methyl of 3, whereas the same carbon absorbs in 1 at δ 15.9. This proved that 2 and 3 had the same relative configuration at C-8. Assuming the usual absolute configuration at C-1, C-5 and C-9, 3 was thus shown to be the 5-deoxystansioside.

Table 1. ^{1}H NMR data of 1–3 (90 MHz, HDO as internal standard (4.70 ppm from TMS))

Assignment	1	2	3
H-1	5.93, *s*	5.77 ($J = 2.0$)	5.54 ($J = 1.5$)
H-3	7.56, *s*	7.46, *s*	7.48, *s*
Me-10	0.90 ($J = 7.0$)	1.13 ($J = 6.0$)	1.15 ($J = 6.0$)
H-11	9.23, *s*	9.18, *s*	9.18, *s*

Coupling constants in Hz.

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* Part 2 in the series "Iridoids in Equatorial and Tropical Flora". For Part 1 see refs. [3–5]. The name stanside was originally used for this compound [5].

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Table 2. ^{13}C NMR chemical shifts of **1**–**3** (20 MHz, D_2O, dioxane as internal standard (67.4 ppm from TMS))

Carbon No.	1	2	3
1	97.3	97.6	98.8
3	165.5	164.6	164.5
4	125.0	124.6	125.2
5	72.9	73.5	31.3
6	38.3	37.9	30.8
7	32.2	31.0	33.2
8	34.2	35.1	35.4
9	51.7	56.7	48.4
10	15.9	19.9	19.9
11	194.6	193.7	192.6
1′	99.4	99.7	99.7
2′	73.2	73.2	73.5
3′	76.1	76.2	76.5
4′	70.4	70.4	70.3
5′	77.2	77.2	77.2
6′	61.5	61.4	61.5

In a previous study, an iridoid, named boschnalosid, which differs from **3** only in the α-configuration of the C-10 methyl was isolated. As expected the physical data of **3** were very different from those reported for the boschnalosid [14, 15]. It is of note that plantarenaloside (**1**) has been isolated from a bignoniaceous plant, since previously it had only been isolated from the scrophulariaceous plants, *Plantago arenaria* [2] and *Leucocarpus perfoliatus* [15], under the name of yuheinosid.

EXPERIMENTAL

Column chromatography: Si gel 70–230 mesh (Merck); TLC: Si gel 60 F_{254} and cellulose pre-coated plates (Merck); PC: Schleicher & Schüll No. 2043 b Mgl paper; Spray reagents: 2N H_2SO_4, vanillin (2 g vanillin, 4 ml conc. HCl, 100 ml MeOH), resorcin (5 g resorcin, 4 ml conc. H_2SO_4, 296 ml EtOH), 2,4-DNF (0.4 g 2,4-DNF, 2 ml conc. H_2SO_4, 2 ml H_2O, 10 ml EtOH); removal of volatile materials was always performed under red. pres.

Isolation of iridoids. T. stans was collected in the summer of 1978 in Nsukka (Nigeria) when it was in flower. Voucher specimens of this plant were identified at the University of Nigeria, Nsukka and at the Istituto di Botanica dell'Universitá di Roma by Dr. Anna Francesconi. Fresh leaves (1 kg) were extracted with EtOH at room temp. for 3 days. PC in *n*-BuOH–HOAc–H_2O (63:10:27) showed two spots, R_f 0.55 (**3**) and 0.38 (**1** and **2**). The EtOH extract was concd to an aq. suspension which was treated with decolorizing charcoal (200 g). The resulting suspension was stratified on a Gooch funnel (14 cm). Monosaccharides were eluted with H_2O (6 l.); di- and oligo-saccharides with 5 % EtOH (0.5 l.), 10 % EtOH (0.5 l.) and 20 % EtOH (1 l.); **1**, **2** and small quantities of **3** with 50 % EtOH (6 l. fraction A); **3** and small quantities of **1** and **2** with 80 % EtOH (2 l. fraction B). Fraction A (4.0 g) was chromatographed on Si gel in *n*-BuOH satd with H_2O (BW) to give **3** (0.2 g) and **1** and **2** (1.7 g). Fraction B (0.56 g) on Si gel in BW gave **3** (0.4 g) and **1** and **2** (0.15 g). The fractions containing **1** and **2** were bulked and chromatographed on Si gel (6×) alternatively in BW and $CHCl_3$–MeOH (4:1). This gave 0.8 g of **1** and 50 mg of **2**. The fractions containing **3** were bulked and chromatographed on Si gel in $CHCl_3$–MeOH (9:1) to give 0.47 g of **3**. **3** was crystallized from EtOAc, mp 146–147°. $[\alpha]_D^{25}$ $-117.0°$ (MeOH; *c* 2.0). UV λ_{max}^{MeOH} nm (log ε): 249 (4.13). IR ν_{max}^{KBr} cm^{-1}: 3450, 2950, 2910, 2870, 2850, 1670, 1630, 1365, 1320, 1220, 1170, 1080, 1030, 900, 840. ^1H NMR (90 MHz, D_2O): δ 9.18 (1 H, *s*, H-11), 7.48 (1 H, *s*, H-3), 5.54 (1 H, *d*, $J_{1,9} = 1.5$ Hz, H-1), 4.88 (1 H, *d*, $J_{1',2'} = 7.5$ Hz, H-1′), 3.00 (1 H, *m*, H-5), 2.5–1.2 (6 H, C-9, C-8, C-7, C-6), 1.15 (3 H, *d*, $J_{10,8} = 6.0$ Hz, Me-10). (Found: C, 55.40; H, 7.07. $C_{16}H_{24}O_8$ requires: C, 55.80; H, 7.02 %).

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