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TWO STEROIDAL GLYCOALKALOIDS FROM *SOLANUM ARBOREUM*

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Key Word Index—*Solanum arboreum*; Solanaceae; steroidal glycoalkaloids; tomatidine glycosides.

Abstract—Two new steroidal glycoalkaloids have been found in the aerial parts of *Solanum arboreum*. Their structures have been elucidated as tomatidine 3-*O*-β-D-glucopyranoside and tomatidine 3-*O*-[*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside by a combination of 2D NMR experiments and mass spectrometry.

INTRODUCTION

In continuation of our studies on the chemistry of the *Solanum* species of Trinidad [1], we have examined the leaves and stems of *Solanum arboreum* Kunth ex Dunal, which had not been previously studied. We report herein the occurrence in the plant of two new steroidal glycoalkaloids, both of which have been characterized as their peracetates.

RESULTS AND DISCUSSION

The alkaloid fraction of the methanolic extract was chromatographed on silica gel to yield four fractions. Fractions II and IV were acetylated and subjected to repeated chromatography to afford the peracetylated derivatives **1a** and **2a**. The ^{1}H and ^{13}C NMR data for **1a** (Tables 1 and 2) indicated that it was a steroidal glycoalkaloid containing *N*-acetylated tomatidine as the aglycone [1, 2–4] and a single sugar (one anomeric proton at δ 4.59, $J = 8.3$ Hz), the ^{1}H and ^{13}C NMR shifts of which revealed that it was the tetraacetate of β-D-glucopyranose [5]. All the protons and carbons of the glucosyl moiety could be assigned using ^{1}H–^{1}H COSY and HMQC spectra. Assignment of the resonances of the acetyl groups on the glucose and those of the protons and carbons of the *N*-acetyltomatidine aglycone was achieved by a combination of ^{1}H–^{1}H COSY, HMQC and HMBC experiments [1]. The high resolution FAB mass spectrum gave a $[M + H]^+$ peak at m/z 788.4587 corresponding to $[C_{43}H_{66}NO_{12}]^+$, in agreement with the molecular formula $C_{43}H_{65}NO_{12}$,

Table 1. NMR spectral data for aglycone moieties of compounds **1a** and **2a***

	1a	
Position	δ_C	δ_H
1	36.9	0.92, 1.70
2	29.2	1.49, 1.84
3	79.7	3.54
4	34.6	1.22, 1.51
5	44.8	1.04
6	28.7	(1.27)†
7	32.3	0.87, 1.66
8	35.2	1.51
9	54.5	0.60
10	35.7	—
11	20.9	1.27, 1.48
12	39.7	1.04, 1.69
13	41.5	—
14	56.3	1.03
15	32.7	1.29, 1.98
16	78.9	4.17
17	64.7	1.62
18	16.2	0.80
19	12.3	0.79
20	38.6	3.09
21	17.8	1.19
22	101.0	—
23	28.1	1.58, 1.69
24	28.4	1.48, 1.50
25	31.7	(1.48)
26	52.1	3.30, 3.40
27	19.0	0.86
-NCOCH$_3$	170.4, 24.9	—

*NMR spectral data for **2a** are identical to those for **1a** except as described in text.

†Indicates average chemical shift for unresolved CH$_2$ groups.

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Table 2. NMR spectral data for sugar moieties of compounds **1a** and **2a**

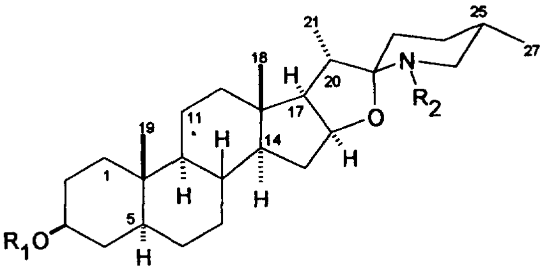
	1a		**2a**	
Position	δ_C	δ_H	δ_C	δ_H
Glc 1′	99.5	4.59	99.3	4.57
2′	71.6	4.94	71.5	4.89
3′	72.9	5.19	72.9	5.17
4′	68.6	5.07	69.1	4.91
5′	71.6	3.68	73.2	3.67
6′	62.2	4.12, 4.26	67.8	3.60 3.85
$-COCH_3$				
2′	169.3, 20.7	2.03	169.2, 20.7	2.03
3′	170.3, 20.6	2.00	170.2, 20.6	1.99
4′	169.4, 20.6	2.02	169.5, 20.7	2.02
6′	170.7, 20.8	2.07	—	—
Xyl 1″	—	—	100.6	4.47
2″	—	—	68.9	5.16
3″	—	—	70.0	5.01
4″	—	—	67.5	5.26
5″	—	—	63.0	3.60, 4.03
$-COCH_3$				
2″	—	—	169.2, 20.8	2.07
3″	—	—	170.0, 20.7	2.03
4″	—	—	170.1, 20.9	2.13

expected for peracetylated **1**. Furthermore, fragment ions in the low resolution mass spectrum at *m/z* 114 $[C_6H_{12}NO]^+$ [6], 331 $[glcAc_4]$ and 440 [*N*-acetyltomatidine − OH]$^+$ confirm the structure of **1a** as the pentaacetate of (22*S*,25*S*)-3β-{β-D-glucopyranosyloxy}-5α-spirosolane (tomatidine 3-*O*-β-D-glucopyranoside, **1**).

The FAB mass spectrum of **2a** gave ions at *m/z* 259 $[C_{11}H_{15}O_7]^+$ and 547 $[C_{23}H_{31}O_{15}]^+$, which suggested a disaccharide unit consisting of a triacetylated hexose and a triacetylated pentose. Other peaks at *m/z* 114 $[C_6H_{12}NO]^+$ [6] and 440 pointed to an N-acetylated spirosolane as the aglycone. ^{1}H and ^{13}C NMR data for **2a** (Tables 1 and 2) indicated that the aglycone was N-acetylated tomatidine [1, 2–4]. For the aglycone moiety, the ^{1}H chemical shifts were identical to those of **1a**, and the ^{13}C chemical shifts (except for C-3, δ 79.3 and C-5, δ 44.6) agreed to within 0.1 ppm. The data also indicated that the disaccharide consisted of a terminal triacetylated β-D-xylopyranose (H_1: δ 4.47, $J = 7.0$ Hz) joined 1→6 to a triacetylated β-D-glucopyranose (H_1: δ 4.57, $J = 8.0$ Hz) [4, 5]. This was corroborated by the results of the hydrolysis of **2** (see Experimental). The C-1 to C-6 coupling was confirmed by the cross-peaks observed in the HMBC spectrum between C-1 of the xylose moiety and the H-6 protons of the glucose unit. All the protons of both of the sugar units could be identified from the TOCSY spectrum [7] and then all its carbons and protons assigned with the aid of ^{1}H–^{1}H COSY and HMQC spectra. The data support the structure of **2a** as the heptaacetate of the new steroidal glycoalkaloid, (22*S*,25*S*)-3β-{*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranosyloxy}-5α-spirosolane (tomatidine 3-*O*-[*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside] (**2**). Full assignment of the ^{1}H and ^{13}C NMR spectral data for **2a** was achieved by the same combination of 2D NMR methods as used for **1a** [1].

EXPERIMENTAL

General. Mps: uncorr. TLC and prep. TLC: Silica gel 60 PF254 and 366, 0.25 and 1 mm layers, respectively. CC: Silica gel 60, 70–230 mesh. FABMS: NBA matrix, Xe atoms at 8 keV. NMR: ^{1}H, COSY, TOCSY,



1	R_1 = Glc	R_2 = H
1a	R_1 = GlcAc$_4$	R_2 = Ac
2	R_1 = Glc-^{6}-Xyl	R_2 = H
2a	R_1 = GlcAc$_3$-^{6}-XylAc$_3$	R_2 = Ac

HMCQ (optimized for $^1J_{H\text{-}C} = 140$ Hz), HMBC (optimised for $^1J_{H\text{-}C} = 8$ Hz) and NOESY at 500 MHz; ^{13}C at 100 MHz, in $CDCl_3$ with TMS as int. standard.

Plant material. Aerial parts of *S. arboreum* were collected in May 1993 at the base of the Maracas Waterfall, St. Joseph, Trinidad. Material was identified by W. Johnson of the National Herbarium of Trinidad and Tobago where a voucher specimen is deposited.

Extraction and isolation. Dried, ground aerial parts (1.3 kg) were extracted with MeOH (15 l). The crude residue of the MeOH extract was dissolved in 10% HOAc (600 ml), the soln extracted with EtOAc (3 × 200 ml) and the remaining aq. layer basified to pH 9 with aq. NH_3. The resulting ppt. was filtered and dried to yield 17.7 g of alkaloid material. This was subjected to silica gel CC ($CHCl_3$–MeOH–aq. NH_3 mixts) and sepd into 5 frs. Acetylation (Ac_2O, pyridine) of fr. II followed by CC (silica gel, hexane–CH_2Cl_2–PrOH, 50:49:1) yielded 10 mg of **1a**. Recrystallization of the solid from fr. IV (MeOH–aq. NH_3) gave needles of **2** {0.52 g, mp 260–265°, $[\alpha]_D^{23}$ −26.8° (MeOH; *c* 1.27)} which gave broad ^{1}H NMR signals (in pyridine-d_5). Acetylation of a portion of **2** (0.24 g) and purification of the product by prep. TLC (silica gel, hexane–CH_2Cl_2–PrOH, 50:47:3) yielded needles of **2a** (210 mg).

Pentaacetate of **1** (**1a**). Crystalline solid, mp 174–177°. $R_f = 0.22$ (hexane–CH_2Cl_2–PrOH, 50:47:3). $[\alpha]_D^{23}$ −13.6° ($CHCl_3$; *c* 0.44). IR ν_{max} ($CHCl_3$) cm^{-1}: 1750 (ester), 1650 (amide). LR FAB MS *m/z* (rel. int.): 788 $[M+H]^+$ (48), 440 $[M+H-glcAc_4-OH]^+$ (15), 331 $[glcAc_4]^+$ (30), 114 $[C_6H_{12}NO]^+$ (100). HR FAB MS *m/z*: 788.4587 $[M+H]^+$ ($C_{43}H_{66}NO_{12}$ requires 788.4585). ^{1}H and ^{13}C NMR: Tables 1 and 2.

Hydrolysis of **2**. A soln of **2** (0.4 g) in 10% HCl in MeOH (3.6 ml) was refluxed for 30 min. Usual workup to isolate the aglycone gave a solid (60 mg) identified as tomatidine by its mp 204–210° (lit. [4] mp 210–211°) and by comparison of its 200 MHz ^{1}H NMR spectral data with those reported [4]. TLC anal. (silica gel, EtOAc–65% *iso*PrOH, 3:7) of the residue from the aq. layer showed that it consisted of 2 sugars, whose R_f values, 0.25 and 0.32, corresponded to those of glucose and xylose, respectively.

Heptaacetate of **2** (**2a**). Needles, mp 238–240°. R_f = 0.13 (solvent as for **1a**). $[\alpha]_D^{23}$ −7.3° ($CHCl_3$; *c* 1.64). IR ν_{max} ($CHCl_3$) cm^{-1}: 1750 (ester), 1645 (amide). LR-FAB-MS *m/z* (rel. int.): 1004 $[M+H]^+$ (22), 440 $[M+H-xylAc_3-glcAc_3-OH]^+$ (13), 259 $[xylAc_3]^+$ (72), 114 $[C_6H_{12}NO]$ (100). ^{1}H and ^{13}C NMR: Tables 1 and 2.

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