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BAHAMGENIN—A STEROIDAL SAPOGENIN FROM *SOLANUM BAHAMENSE*

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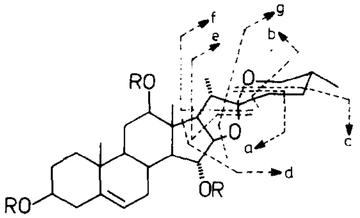
Key Word Index—*Solanum bahamense*; Solanaceae; steroidal sapogenins; spirostans; bahamgenin.

Abstract—A new spirostan sapogenin named bahamgenin has been obtained from red berries of *Solanum bahamense* and its structure elucidated by IR, NMR and mass spectral studies as (25*R*)-spirost-5-en-3*β*,12*β*,15*α*-triol.

As part of our studies on Cuban plants of medical interest as potential sources for steroidal hormone starting materials we have investigated *Solanum bahamense* L. In a previous paper we reported on the isolation of the steroidal sapogenins diosgenin, chlorogenin and isochiapagenin from red berries of this plant [1]. We now wish to report on the isolation of the new sapogenin bahamgenin (**1**) from the same source.

Acid hydrolysis of the glycosidic mixture obtained in the methanol extracts followed by Si gel chromatography yielded 0.4% of the new sapogenin, $C_{27}H_{44}O_5$ (M^+ found 446.3053; calc. 446.3032) mp 258°. Its IR spectrum showed the presence of a spirostan system [2] (968, 920, 900, 868 cm^{-1}) as well as hydroxyl groups (3450 cm^{-1}). Its EIMS fragmentation pattern was as expected [3, 4] for a spirostan sapogenin (see formulae). A peak at *m/z* 410 ($[M-2H_2O]^+$) showed the presence of at least two hydroxyl groups whilst fragments at *m/z* 374 $[\mathbf{a}]^+$ and 377 $[\mathbf{b}+H]^+$ suggested the presence of three hydroxyl groups. All these functions must be localized in the steroidal nucleus as shown by the base peak at *m/z* 139 $[\mathbf{e}]^+$. Furthermore, characteristic ions at *m/z* 168 $[\mathbf{d}]^+$ and 126 $[\mathbf{f}]^+$ indicated that one of the hydroxyl groups was located on C-15.



1 R = H
2 R = Ac

Table 1. ^{13}C NMR data of bahamgenin (**1**) and isochiapagenin (**3**) (50.33 MHz, δ-values (ppm) measured from the central solvent line ($CDCl_3$) and calculated to TMS: $\delta_{TMS} = \delta_{CDCl_3} + 77.0$ ppm)

Carbon No.	**1** ($CDCl_3$)	**3** ($CDCl_3$–CD_3OD, 1:1)	Carbon No.	**1** ($CDCl_3$)	**3** ($CDCl_3$–CD_3OD, 1:1)
1	37.2	37.2	15	78.5	31.8
2	31.6	31.6	16	89.6	80.7
3	71.2	71.6	17	58.8	61.9
4	42.2	42.1	18	11.3	10.4
5	139.9	140.8	19	19.2	19.3
6	121.7	121.3	20	41.7	42.1
7	31.2	31.4*	21	13.3	13.9
8	30.0	30.4†	22	109.4	109.5
9	49.2	49.7	23	31.2	31.3*
10	36.5	36.7	24	28.6	28.8
11	30.6	30.4†	25	30.0	30.3†
12	78.9	79.6	26	66.9	66.9
13	45.2	45.7	27	17.0	17.1
14	58.4	55.1			

*, † Values bearing the same superscript may be interchanged.

The 100 MHz ^{1}H NMR spectrum of **1** showed two singlets (3H each) at δ 0.79 and 1.04 for H_3-19 and H_3-18, angular methyl groups of a steroidal system with a Δ^5 double bond [5], two doublets (3H each, $J = 7.5$ Hz) at δ 0.75 and 0.96 corresponding to two secondary methyl groups H_3-27 (eq) and H_3-21 [6, 7], a broad signal centred at δ 3.36 (*m*, H-3α, H-12α, H_{ax}-23, H_{eq}-23), a signal at δ 4.20 (*m*, H-15β, H-16α) and a doublet at δ 5.35 for the vinylic H-6.

Acetylation of **1** with acetic anhydride–pyridine (24 hr at 20°) yielded, nearly quantitatively, the triacetate **2**.

In the 100 MHz ^{1}H NMR spectrum of **2**, one of the two protons at δ 4.20 in **1** was shifted downfield to δ 5.20 and appeared as a double doublet ($J = 11.5$ Hz, $J' = 4.2$ Hz) whereas the other remained as a double doublet at δ 4.18 ($J = 11.5$ Hz; $J' = 4.2$ Hz). These two protons belonged to the β-hydrogen at C-15 and the α-hydrogen at C-16, respectively. This was confirmed by a decoupling experiment. Furthermore, α-configuration of the hydroxyl group at C-15 was confirmed by the facts that no downfield shift for the C-18 methyl signal was observed upon acetylation of **1** [5] and that, contrary to more hindered 15β-hydroxy spirostans [8], acetylation occurred smoothly.

The ^{13}C NMR spectrum of **1** was also in agreement with a 3β,12β,15α-trihydroxylated (25*R*)-spirostan. The signal assignments were carried out via comparison (Table 1) with the corresponding data of isochiapagenin [(25*R*)-spirost-5-en-3β-12β-diol, **3**]. The assignment of the latter spectrum was done by means of the SFORD technique and comparison with the reported ^{13}C data for solanaviol [9] (rings A–D carbon atoms) and related (25*R*)- and (25*S*)-spirostans [10] (rings E and F carbon atoms).

In comparing **1** with isochiapagenin (**3**) well-known hydroxylation shifts [11] were observed (α-substituent effect for C-15; β-substituent effect for C-14 and C-16; γ-substituent effect for C-17; δ-substituent effect for C-18 methyl) which confirmed the position of the third hydroxyl group of **1** as 15α. In the course of the chromatographic isolation of bahamgenin (**1**) its 3,5-diene was obtained, probably produced as an artefact during acid hydrolysis of the glycosidic mixture. It was found to be identical in every aspect with a specimen prepared by reaction of **1** with 4 M methanolic hydrochloric acid.

EXPERIMENTAL

S. bahamense was collected in Mantanzas (Cuba) and identified by M. Sc. A. Areces. A voucher specimen is kept in the Herbarium of the National Botancial Garden of Cuba, Havana.

Isolation. Dried and powdered red berries (300 g) were extracted successively with $CHCl_3$ and MeOH in a Soxhlet. The MeOH soln was cond to dryness under red. pres. and the residue refluxed with 200 ml 2 M HCl for 3 hr, cooled and poured into an equal vol. of H_2O. The ppt was filtered off and the raw aglycone was chromatographed over Si gel. The progress of the separation was followed by TLC on Si gel ($CHCl_3$–EtOAc, 2:3). Elution with $CHCl_3$–EtOAc (1:1) gave bahamgenin (**1**). Crystals (MeOH–Me_2CO) mp 257–258°, $[\alpha]_D^{25}$ $-86.2°$ ($CHCl_3$–MeOH, 1:1; *c* 1). EIMS, 70 eV, *m/z* (rel. int.): 446 $[M]^+$ (17), 428 $[M-H_2O]^+$ (9), 410 $[M-2H_2O]^+$ (2), 395 $[M-2H_2O-Me]^+$ (31), 387 $[\mathbf{c}-H]^+$ (6), 377 $[\mathbf{b}+H]^+$, (6), 374 $[\mathbf{a}]^+$, (14), 303 (4), 168 $[\mathbf{d}]^+$ (83), 139 $[\mathbf{e}]^+$, (100), 126 $[\mathbf{f}]^+$ (91) and 115 $[\mathbf{g}+H]^+$ (56). Further spectral data are in the text.

Triacetate **2**. Needles (Me_2CO) mp 128°, $[\alpha]_D^{25}$ $-80°$ ($CHCl_3$ *c* 1.1). IR ν_{max}^{nujol} cm^{-1}: 1730 (OAc), 966, 922, 903, 868 (spirostan); EIMS (70 eV) *m/z* (rel. int.): 572 $[M]^+$ (6); ^{1}H NMR (100 MHz, TMS): δ 0.78 (*d*, $J = 7.0$ Hz, $H_{3,\,eq}$-27), 0.89 (*d*, $J = 7.0$ Hz, H_3-21), 0.92, 1.02 (*s* × 2, H_3-19, H_3-18), 2.01, 2.04, 2.06 (*s* × 3, OAc), 3.35 (*m*, H_{ax}-23, H_{eq}-23), 4.18 (*dd*, $J = 11.5$ Hz, $J' = 4.2$ Hz, H-16α), 4.57, 4.60 (m × 2, H-3α, H-12α), 5.20 (*dd*, $J = 11.5$ Hz, $J' = 4.2$ Hz, H-15β), 5.34 (*m*, H-6).

$\Delta^{3,5}$-*Diene of* **1**. This diene was obtained (0.02 %) on elution of the Si gel column with $CHCl_3$–EtOAc (4:1). Needles (Me_2CO) mp 162–164°. IR ν_{max}^{nujol} cm^{-1}: 3500 (OH), 3020, 1650 (diene), 960, 920, 900, 870 (spirostan); UV λ_{max}^{MeOH} nm (log ε): 237 (4.33). The compound was found to be identical in every aspect with a specimen prepared by refluxing **1** with 4 M HCl for 3 hr.

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