STRUCTURES OF THREE NEW STEROIDAL ALKALOID GLYCOSIDES, SOLAVERINES I, II AND III FROM *SOLANUM TOXICARIUM* AND *S. VERBASCIFOLIUM*[1)]

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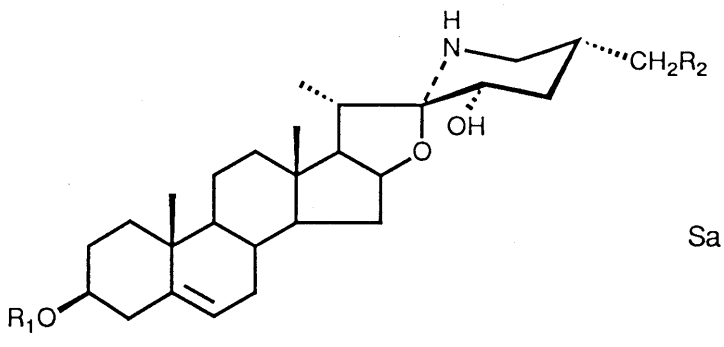
The structures of three new steroidal alkaloid glycosides named solaverines I, II and III were isolated from the aerial parts of *Solanum toxicarium* and *S. verbascifolium* and their structures, including the new sapogenols solaverols A and B, were elucidated as (22*R*,25*R*)-3β, 23α-dihydroxyspirosol-5-ene 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranoside, (22*R*,25*R*)-3β, 23α-dihydroxyspirosol-5-ene 3-*O*-α-L-rhamnopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-β-D-galactopyranoside and (22*R*,25*R*)-3β, 23α, 27-trihydroxyspirosol-5-ene 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranoside, respectively.

KEYWORDS *Solanum toxicarium; Solanum verbascifolium;* Solanaceae; steroid alkaloid; spirosolane; solaverine; solaverol

Solanum toxicarium and *S. verbascifolium* are solanaceous plants widespread in Bangladesh and are used as a plant stock for eggplant owing to their powerful propagation in Japan. Thus, research on the constituents of this plants was needed for the safe culturing of the plant stock and became a part of our systematic research on the solanaceous plants. Here we characterize the structure of three new steroidal alkaloid glycosides.

Extraction of the fresh aerial parts of *S. toxicarium* (2.2 kg) with MeOH gave a residue (61.3 g). This was partitioned between benzene and water to give an aqueous layer (44.8 g) which was subjected to MCI gel CHP 20P (water→MeOH, gradiently), silica gel ($CHCl_3$-MeOH-water=8:2:0.2→7:3:0.5) and ODS column chromatographies. These afforded two glycosides, designated solaverines I (**1**, 17.6 mg) and II (**2**, 7.1 mg). The fresh aerial parts of *S. verbascifolium* (1.5 kg) were extracted and separated in the same way, giving solaverine III (**3**, 7.6 mg) together with **1** (11.3 mg) and **2** (5.5 mg).

Solaverine I (**1**), a pale yellow powder, $[\alpha]_D$ -75.7° (pyridine), showed a positive coloration against Dragendorff reagent and a $[M-H]^-$ at *m/z* 882 in the negative FAB-MS. The ^{1}H-NMR spectrum of **1** exhibited signals due to two tertiary methyl and four secondary methyl groups at δ 0.83 (3H, d, *J*=6.2 Hz), 1.01, 1.03 (each 3H, s), 1.14 (3H, d, *J*=7.0 Hz), 1.63, 1.76 (each 3H, d, *J*=6.2 Hz) and three anomeric protons at δ 4.94 (1H, d, *J*=6.2 Hz), 5.85, 6.39 (each 1H, s), indicating that **1** is a steroid alkaloid triglycoside. Compound **1** was hydrolyzed with 1 N HCl-MeOH to yield a sapogenol named solaverol A (**4**) as a pale yellow powder, $[\alpha]_D$ -67.1° ($CHCl_3$). It showed a molecular ion at *m/z* 429, along with a characteristic fragment at *m/z* 154 $[C_9H_{16}NO]^+$ which was derived by cleavage of the



solaverol A (4) $R_1=R_2=H$
solaverol B $R_1=H$, $R_2=OH$
solaverine I (1) $R_1=Sa$, $R_2=H$
solaverine II (2) $R_1=Sb$, $R_2=H$
solaverine III (3) $R_1=Sa$, $R_2=OH$

Sa = -glc(2→4)rha, Sb = -gal(2→3)glc
rha rha

Table I. ^{13}C-NMR Chemical Data for **1**~**4**, Solasodine (**5**), Tomatidine (**6**), Solamargine (**7**) and Solasonine (**8**)

	4	**5**	**6**	**1**	**7**	**2**	**8**	**3**
C-1	37.8	37.3	37.0	37.5	37.5	37.5	37.4	37.5
2	32.6	31.5	31.5	30.1	30.1	30.1	30.1	30.1
3	71.2	71.7	71.0	77.9	78.3	77.5	78.3	77.9
4	43.4	42.3	38.2	38.9	38.8	38.8	38.8	38.9
5	141.9	140.9	44.9	140.8	140.8	140.9	140.7	140.7
6	121.0	121.3	28.6	121.8	121.7	121.7	121.6	121.8
7	32.3	32.1	32.3	32.3	32.4	32.4	32.5	32.3
8	31.6	31.5	35.0	31.4	32.4	31.9	32.5	31.5
9	50.4	50.2	54.4	50.3	50.3	50.3	50.3	50.3
10	37.0	36.7	35.5	37.1	37.1	37.2	37.1	37.1
11	21.1	20.9	21.1	21.1	21.1	21.1	21.1	21.1
12	40.4	40.0	40.2	40.3	40.1	40.4	40.1	40.4
13	41.3	40.5	40.9	41.3	40.6	41.2	40.6	41.2
14	56.7	56.6	55.8	56.6	56.7	56.6	56.7	56.6
15	32.4	32.1	32.6	32.4	31.5	32.4	31.7	32.4
16	80.1	79.0	78.5	80.1	78.7	79.4	78.7	78.6
17	62.6	62.9	62.0	62.6	63.4	62.6	63.5	62.9
18	16.7	16.4	16.9	16.6	16.5	16.7	16.5	16.6
19	19.2	19.3	12.3	19.2	19.3	19.4	19.3	19.3
20	34.7	41.3	43.0	34.7	41.6	34.6	41.5	34.6
21	15.3	15.2	15.8	15.2	15.6	15.2	15.6	15.3
22	101.1	98.4	99.3	101.1	98.2	101.1	98.2	101.6
23	68.9	34.1	26.6	68.9	34.6	69.1	34.6	69.2
24	40.4	30.3	28.6	40.3	31.0	40.6	31.1	35.4
25	31.5	31.5	31.0	31.5	31.7	31.5	31.7	40.8
26	46.7	47.7	50.2	46.7	48.0	47.0	47.9	43.2
27	19.5	19.3	19.3	19.4	19.7	19.3	19.7	65.6

	1	**7**	**2**	**8**	**3**
	glc	glc	gal	gal	glc
C-1	100.2	100.2	100.4	100.4	100.2
2	78.1	78.2	76.5	76.3	78.1
3	72.5	72.5	84.8	84.8	72.5
4	77.8	77.7	70.4	70.2	77.8
5	76.9	76.7	74.9	74.9	76.9
6	61.3	61.3	62.5	62.4	61.3
	rha	rha	glc	glc	rha
1	102.8	102.7	105.9	105.7	102.9
2	72.5	72.5	75.1	74.8	72.5
3	72.5	72.5	78.5	78.7	72.7
4	73.9	73.7	71.6	71.4	73.9
5	70.4	70.3	78.4	78.3	70.4
6	18.6	18.5	62.8	61.8	18.6
	rha	rha	rha	rha	rha
1	102.0	101.8	102.2	102.0	102.0
2	72.8	72.5	72.6	72.4	72.5
3	72.7	72.5	72.9	72.7	72.8
4	74.1	73.9	74.2	74.0	74.1
5	69.5	69.3	69.4	69.3	69.5
6	18.5	18.5	18.6	18.5	18.5

Solvents: **1**, **2**, **3**, solamargine (**7**) and solasonine (**8**) in pyridine-d_5; **4**, solasodine (**5**) and tomatidine (**6**) in $CDCl_3$.

spirosolane skeletone.[2] Its ^1H-NMR spectrum ($CDCl_3+D_2O$) revealed signals of Me-18 (3H, s, δ 0.85), Me-19 (3H, s, δ 1.03), Me-21 (3H, d, *J*=7.1 Hz, δ 0.87), Me-27 (3H, d, *J*=6.2 Hz, δ 0.93), 26-H_2 (2H, m, δ 2.63), H-3 (1H, m, δ 3.51), H-16 (1H, dd, *J*=6.2, 9.5 Hz, δ 4.36) and H-6 (1H, d, *J*=5.5 Hz, δ 5.34), in close analogy with those of solasodine (**5**). A signal at δ 3.45 (1H, d, *J*=4.8, 11.4 Hz) was ascribable to the C-23-β-proton, which is linked to the carbon bearing a hydroxyl group, when the EI-MS data of **4** were taken into account. On the basis of the chemical shifts of H-16 and H_2-26, both configurations at C-22 and C-25 were judged to be *R*.[3] The ^{13}C-NMR spectrum of **4** also provided information for the discrimination of the 22*R* (solanidine type) or 22*S* (tomatidine type). That is, whether the configuration at C-22 is *R* or *S* is decided by the chemical shift of C-26,[4]

which is not affected by the α, β and γ-effects of 23-hydroxyl group.[5] In **4**, a peak appeared at δ 46.7, which is assignable to C-26, hence the structure was cosidered to be 23α-hydroxysolasodine. The sugar moieties in the ^{13}C-NMR data of **1** were compared with those of solamargine, solasodine 3-*O*-β-chacotrioside.[6] The sugar parts of the two compounds were superimposable; thus the structure of solaverine I(**1**) was considered to be (22*R*,25*R*)-3β,23α-dihydroxyspirosol-5-ene (solaverol A) 3-*O*-α-L-rhamonopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranoside (β-chacotrioside)

Solaverine II (**2**), a pale yellow powder, $[\alpha]_D$ -74.6° (pyridine), showed a positive coloration against Dragendorff reagent and fragment peaks at *m/z* 898 $[M-H]^-$, 752 $[M-rha]^-$ and 736 $[M-rha-glc]^-$ in the negative FAB-MS. In the ^{1}H-NMR spectrum of **2**, there were signals of Me-21 (3H, d, *J*=6.2 Hz, δ 0.83), Me-27 (3H, d, *J*=7.0 Hz, δ 1.14), Me-18 and Me-19 (6H, s, δ 1.02), rha-5-Me (3H, d, *J*=6.2 Hz, δ 1.69), H-6 (1H, m, δ 5.30), and three anomeric protons (1H, d, *J*=7.7 Hz, δ 4.93; 1H, d, *J*=8.1 Hz, δ 5.20; 1H, s, δ 6.30). Acid hydrolysis of **2** provided the sapogenol which is identical with solaverol A (**4**). The signals in the ^{13}C-NMR spectrum of **2** due to the sugar part were superimposable on those of solasonine (solasodine 3-*O*-β-solatrioside).[6] So the structure of solaverine II (**2**) was determined to be solaverol A 3-*O*-α-L-rhamonopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-β-D-galactopyranoside (β-solatrioside).

Solaverine III (**3**), a pale yellow powder, $[\alpha]_D$ -66.0° (pyridine), showed a peak due to $[M-H]^-$ at *m/z* 898 in the negative FAB-MS. The ^{1}H-NMR spectrum of **3** exhibited three anomeric proton signals at δ4.93 (1H, d, *J*=6.2 Hz), and 5.87 and 6.41 (each 1H, s) together with signals due to two *tertiary* methyl groups (each 3H, s, δ 1.01 and 1.04), one *secondary* methyl group (3H, d, *J*=7.0 Hz, δ 1.15), one olefinic proton (m) and two *secondary* methyl groups of the methylpentosyl residues (each 3H, d, *J*=6.2 Hz). The ^{13}C-NMR spectrum showed signals due to one additional oxygenated carbon at δ 65.6 compared with that in **2** in the aglycone part, and signals almost identical with those of **1** in the sugar residue. The carbon at δ 65.6 was attributable to the C-27 since the ^{1}H-NMR spectrum showed no signal due to the C-25 *secondary* methyl group in **3** and the signals ascribable to C-24, C-25 and C-26 were shifted by -4.9, +9.3 and -3.5 ppm, respectively. Therefore, the structure of the solaverine III (**3**) was (22*R*,25*R*)-3β,23α,27-trihydroxyspirosol-5-ene (solaverol B) 3-*O*-β-chacotrioside. *Solanum.toxicarium* and *S.verbascifolium* included neither spirostanol or furostanol derivatives.

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