

STEROIDAL GLYCOSIDES FROM THE ROOTS OF *SOLANUM MELONGENA L.*

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Abstract: One new cholestane glycoside, six steroidal glycosides of spirostane series and one pregnane glycoside have been isolated from the roots of *Solanum melongena L.* (Solanaceae). Their structures were determined on the basis of chemical evidence and extensive spectroscopic methods including one-, two-dimensional NMR and MS analysis. In the roots of this plant the given compounds have been found out for the first time.

Keywords: steroidal glycoside, NMR analysis, *Solanum melongena L.*

Introduction

The *Solanaceae* family is a rich source of active secondary metabolites. In particular, the genus *Solanum* produces a great variety of steroidal saponins and glycoalkaloids of importance in the natural resistance of these plants against several pests [1]. Eggplant is distributed in southeast Asia, probably India and it is cultivated as a food crop in all warm areas of the world [2]. The fruit is hypotensive and helps to lower blood cholesterol levels and is suitable as part of a diet to help regulate high blood pressure [3].

The frequently observed antiviral [4], fungitoxic [5], cytostatic [6] and hypocholesterolemic [7] activities of the steroidal glycosides have aroused for years an interest of plant biochemists and physiologists. As it was reported earlier, *Solanum melongena L.* contains steroidal glycosides, so-called melongosides, which occur mainly in mature seeds [8,9]. Our interest in the chemical constituents elaborated by plants of *Solanaceae* family prompted us to take up the phytochemical investigation of the roots of *Solanum melongena L.* and report the isolation and structural elucidation of steroidal glycosides.

Results and Discussion

The water extract of roots of *Solanum melongena L.* was successively subjected to silica gel column chromatography, as well as HPLC to afford eight steroidal glycosides (**1-8**). All compounds have been isolated as amorphous powders. Their structures were determined by corresponding shifts of ¹H and ¹³C NMR spectral data.

The ¹H NMR spectrum of **1** showed signals for four steroidal methyl groups at δ 1.16 (3H, s, Me-19), 0.84 (3H, s, Me-18), 0.87 (3H, d, H-21), 0.77 (3H, d, Me-27), two methine proton signals at δ 3.62 (1H, m, H-3) and 3.94 (1H, m, H-16) indicative of secondary alcoholic functions and one double bond δ 5.41 (broad, d, 1H-6), two methylene proton signals at δ 3.43 (1H, m, H-26a) and 3.37 (1H, m, H-26b), ascribable to a primary alcoholic function, and signals for two anomeric protons at δ 4.43 (1H, d, $J = 7.5$ Hz) and 4.88 (1H, d, $J = 7.5$ Hz). The ¹³C NMR spectrum displayed four methyl groups at 12.2, 13.6, 16.7 and 16.8, two oxygenbearing methine carbon at 76.8 (C-16) and 79.8 (C-3), one carbonyl group at 218.6 (C-22), three quaternary carbons at 36.4 (C-10), 45.5 (C-13) and 140.2 (C-5), seven methine carbons at 33.8 (C-25), 36.1 (C-8), 49.9 (C-20), 54.5 (C-14), 55.6 (C-9) and 63.9 (C-17), 122.6 (C-6), and ten methylene carbons at δ 21.9, 28.3, 30.2, 31.9, 35.1, 38.2, 39.6, 41.1, 54.5 and 67.8. The HMBC disclosed the connectivities of the above functional carbons to form a cholestane skeleton. The C-25 configuration was deduced to be *R* based on the difference of chemical shifts ($\Delta_{ab} = \delta_a - \delta_b$) of the geminal protons at H₂-26 ($\Delta_{ab} = 0.06$ ppm). It has been described that Δ_{ab} is usually > 0.57 ppm in 25*S* compounds and < 0.48 in 25*R* compounds [10]. It was evident from the combination of 1D-TOCSY and DQF-COSY spectral analysis that the sugar moiety have been consisted of glucose and rhamnose. A glycosidation shift was observed for C-4_{glc} (δ 79.5). The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.43 (H-1_{glc}) and the carbon resonance at δ 79.8 (C-3 of the aglycon), the proton signal at δ 4.88 (H-1_{rha}) and the carbon resonance at δ 79.5 (C-4_{glc}). Thus, the structure of compound **1** was deduced as 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-glucopyranoside-(25*R*)-cholest-5-en, 22-one, 3 β ,16 β ,26-triol (Fig.1).

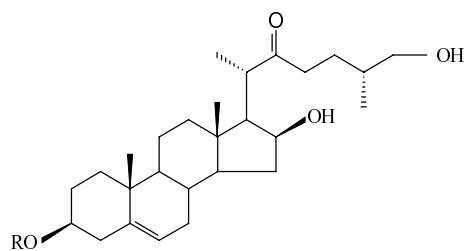


Fig. 1: R=Rha(1-4)Glc

Table. ^{13}C NMR spectral data (300 MHz, CD_3OD) of saponins (1-8)

carbon	compounds							
	1	2	3	4	5	6	7	8
1	38.2	38.2	38.0	38.2	38.0	38.3	37.9	37.9
2	30.2	32.5	30.6	32.5	30.6	32.6	30.4	30.1
3	79.8	79.7	78.3	79.7	78.3	79.4	79.0	79.1
4	35.1	39.4	34.9	39.4	34.9	40.9	34.9	39.0
5	140.2	140.4	46.2	140.4	46.2	141.8	45.8	141.3
6	122.6	122.7	32.9	122.7	32.9	122.8	32.9	121.5
7	31.9	32.6	40.8	32.6	40.8	32.6	34.6	31.8
8	36.1	31.2	36.6	31.2	36.6	31.2	36.0	30.4
9	55.6	51.4	55.6	51.4	55.6	51.6	55.2	50.8
10	36.4	37.4	36.8	37.4	36.8	37.8	36.5	37.2
11	21.9	21.6	21.6	21.6	21.6	21.4	31.0	20.9
12	41.1	40.6	40.9	40.6	40.9	40.7	40.5	35.1
13	45.5	41.2	41.2	41.2	41.2	41.4	41.8	47.2
14	54.5	57.5	57.7	57.5	57.7	57.6	57.5	57.3
15	54.5	32.2	32.4	32.2	32.4	32.5	32.3	32.9
16	76.8	82.1	82.0	82.1	82.0	82.3	82.1	147.0
17	63.9	63.7	63.7	63.7	63.7	63.4	63.7	156.0
18	13.6	16.4	16.6	16.4	16.6	16.9	16.7	15.7
19	12.2	19.4	12.8	19.4	12.8	19.5	12.5	12.3
20	49.9	42.6	43.1	42.6	43.1	42.8	42.6	199.3
21	16.8	14.5	14.3	14.5	14.3	14.4	14.2	26.8
22	218.6	109.0	110.5	109.0	110.5	110.7	110.5	
23	39.6	30.2	32.5	30.2	32.5	32.5	32.2	
24	28.3	29.5	29.5	29.5	29.5	29.7	29.1	
25	33.8	32.8	31.1	32.8	31.1	31.1	31.2	
26	76.2	67.5	67.7	67.5	67.7	67.8	67.7	
27	16.7	17.2	16.6	17.2	16.6	16.9	16.7	
1'	102.0	102.0	102.0	100.1	100.1	100.5	100.5	102.0
2'	74.9	74.9	74.9	78.9	78.9	79.5	79.5	74.9
3'	76.6	76.6	76.6	79.2	79.2	78.4	78.4	76.6
4'	79.5	80.0	80.0	71.5	71.5	80.0	80.0	79.5
5'	76.4	76.5	76.5	77.5	77.5	76.6	76.6	76.4
6'	61.7	61.5	61.5	61.8	61.8	61.8	61.8	61.7
1''	102.5	102.5	102.5	101.9	101.9	103.2	103.2	102.5
2''	72.1	72.2	72.2	71.8	71.8	72.5	72.5	72.1
3''	71.9	72.0	72.0	72.2	72.2	72.4	72.4	71.9
4''	73.5	68.9	68.9	73.5	73.5	73.8	73.8	73.5
5''	70.3	70.2	70.2	69.5	69.5	70.9	70.9	70.3
6''	17.6	17.3	17.3	17.6	17.6	15.9	15.9	17.6
1'''						102.5	102.5	
2'''						72.3	72.3	
3'''						72.5	72.5	
4'''						73.8	73.8	
5'''						69.8	69.8	
6'''						15.8	15.8	

The ^1H NMR spectrum of **2** showed signals for four steroidal methyl groups at δ 1.03 (3H, s, Me-19), 0.85 (3H, s, Me-18), 0.99 (3H, d, H-21), 0.82 (3H, d, Me-27), two methine proton signals at δ 3.62 (1H, m, H-3) and 4.44 (1H, m, H-16) indicative of secondary alcoholic functions and one double bond δ 5.42 (broad d, 1H-6), two methylene proton signals at δ 3.35 (1H, m, H-26b) and 3.47 (1H, m, H-26a), ascribable to a primary alcoholic function, and signals for two anomeric protons at δ 4.43 (1H, d, $J = 7.5$ Hz) and 4.88 (1H, d, $J = 7.5$ Hz). On the basis of the HSQC and HMBC correlations, the aglycone moiety of compound **2** was identified as (25*R*)-spirost-5-ene-3 β -ol – diosgenin. Using a combination of 1D-TOCSY and DQF-COSY spectral analysis, the sugar moiety have been identified as glucose and rhamnose. A glycosidation shift was observed for C-4_{glc} (δ 80.0). The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.43 (H-1_{glc}) and the carbon resonance at δ 79.7 (C-3 of the aglycon), the proton signal at δ 4.88 (H-1_{rha}) and the carbon resonance at δ 80.0 (C-4_{glc}). Thus, the structure of compound **2** was deduced as (25*R*)-spirost-5-ene-3 β -ol - 3 - O - α - L - rhamnopyranosyl - (1 \rightarrow 4) - β - D-glucopyranoside (Fig.2). Compound **2** has been previously reported in literature [11].

The ^1H NMR spectrum of **3** showed signals for four steroidal methyl groups at δ 0.89 (3H, s, Me-19), 0.84 (3H, s, Me-18), 1.02 (3H, d, H-21), 0.98 (3H, d, Me-27), two methine proton signals at δ 3.68 (1H, m, H-3) and 4.39 (1H, m, H-16) indicative of secondary alcoholic functions, two methylene proton signals at δ 3.29 (1H, m, H-26b) and 3.41 (1H, m, H-26a), ascribable to a primary alcoholic function, and signals for two anomeric protons at δ 4.52 (1H, d, $J = 7.5$ Hz) and 5.21 (1H, d, $J = 7.5$ Hz). On the basis of the HSQC and HMBC correlations, the aglycone moiety of compound **3** was identified as (25*R*)-5 α -spirostan-3 β -ol-tigogenin. The C-25 configuration was deduced to be *R* based on the difference of chemical shifts ($\Delta_{ab} = \delta_a - \delta_b$) of the geminal protons at H₂-26 ($\Delta_{ab} = 0.12$ ppm). 5 α configuration was deduced by HMBC correlation between the methyl signal at δ 0.89 (Me-19) and carbon resonances at δ 55.6 (C-9), 46.2 (C-5) and 38.0 (C-1). Using a combination of 1D-TOCSY and DQF-COSY spectral analysis, the sugar moiety have been identified as glucose and rhamnose. A glycosidation shift was observed for C-4_{glc} (δ 80.0). The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.43 (H-1_{glc}) and the carbon resonance at δ 78.3 (C-3 of the aglycon), the proton signal at δ 4.88 (H-1_{rha}) and the carbon resonance at δ 80.0 (C-4_{glc}). Thus, the structure of compound **3** was deduced as (25*R*) - 5 α - spirostan - 3 β -ol - 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 4) - β - D-glucopyranoside (Fig.2). Compound **3** has been previously reported in literature [12].

Compound **4**, in the positive ESIMS, showed a major ion peak at m/z 723[M + Na]⁺ and significant fragments at m/z 579 [M + Na - 146]⁺ attributable to the loss of a pentose unit. The molecular formula of **4** was unequivocally established to be C₃₉H₆₂O₁₂ by HR-MALDI-MS (m/z 725.392 [M + Na]⁺). The ^1H NMR spectrum of **4** showed signals for four steroidal methyl groups at δ 0.85 (s, 3H-18), 0.82 (d, 3H-27), 0.99 (d, 3H-21) and 1.03 (s, 3H-19), two methylene proton signals at δ 3.35 (1H, dd, H-26b) and 3.47 (1H, t, H-26a) ascribable to a primary alcoholic functions, two methine proton signals at δ 3.62 (1H, m, H-3) and 4.44 (1H, m, H-16) indicative of secondary alcoholic function and one double bond δ 5.42 (broad d, 1H-6). One primary alcoholic function at δ 67.5 (C-26), suggesting the occurrence of a glycoside spirostanol skeleton. The HMBC correlation of methyl groups clearly showed that the aglycon moiety was similar of compound **2** and was identified as (25*R*)-spirost-5-ene-3 β -ol. From 1D-TOCSY and DQF-COSY spectral analysis has been identified that the sugar moiety consists of glucose and rhamnose. The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.51 (H-1_{glc}) and the carbon resonance at δ 79.7 (C-3 of the aglycon), the proton signal at δ 5.22 (H-1_{rha}) and the carbon resonance at δ 78.9 (C-2_{glc}). The structure of compound **4** was assigned as (25*R*) - spirost - 5- ene - 3 β - ol - 3 - O - α - L - rhamnopyranosyl - (1 \rightarrow 2) - β - D- glucopyranoside (Fig.2).

The ^1H NMR spectrum of **5** showed signals for four steroidal methyl groups at δ 0.89 (3H, s, Me-19), 0.82 (3H, s, Me-18), 1.00 (3H, d, H-21), 1.12 (3H, d, Me-27). The HMBC correlation of methyl groups clearly showed that the aglycon moiety was similar of compound **2** was identified as (25*R*)- 5 α - spirostan-3 β -ol. One primary alcoholic function at δ 67.7 (C-26), suggesting the occurrence of a glycoside spirostanol skeleton. Using a combination of 1D-TOCSY and DQF-COSY spectral analysis, the sugar moiety have been determined to be identical with sugar moiety of compound **3**. The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.51 (H-1_{glc}) and the carbon resonance at δ 78.3 (C-3), the proton signal at δ 5.22 (H-1_{rha}) and the carbon resonance at δ 78.9 (C-2_{glc}). The structure of compound **5** was assigned as (25*R*) - 5 α - spirostan - 3 β -ol - 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2) - β - D-glucopyranoside (Fig.2). Compounds **4** and **5** has been previously isolated from *Hyoscyamus niger* L. [13].

The ^1H NMR spectrum of **6** showed signals for four steroidal methyl groups at δ 1.02 (3H, s, Me-19), 0.83 (3H, s, Me-18), 0.98 (3H, d, H-21), 0.83 (3H, d, Me-27). The HMBC correlation of methyl groups clearly showed that the aglycon moiety was similar of compounds **2** and **4** and was identified as diosgenin. The ^1H NMR spectrum showed signals for three anomeric protons at δ 4.53 (1H, d, $J = 7.5$ Hz), 4.87 (1H, d, $J = 7.5$ Hz), and 5.23 (1H, d, $J = 7.5$ Hz). It was evident from the ^1H and ^{13}C NMR data that the sugar chain at C-3 of **6** consisted of three sugar units. The chemical shifts of all the individual protons of the three sugar units were ascertained from a combination of 1D-TOCSY and DQF-COSY spectral analysis, and the ^{13}C chemical shifts of their relative attached carbons could be assigned unambiguously from the HSQC spectrum. These data showed the presence of one β -glucopyranosyl unit

(δ 4.53) and two α -rhamnopyranosyl unit (δ 4.87 and 5.23). A glycosidation shifts were observed for C-2_{glc} (δ 79.5) and for C-4_{glc} (δ 80.0). The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.53 (H-1_{glc}) and the carbon resonance at δ 79.4 (C-3 of the aglycon), the proton signal at δ 4.87 (H-1_{rha}) and the carbon resonance at δ 79.5 (C-2_{glc}), the proton signal at δ 5.23 (H-1_{rha}) and the carbon resonance at δ 80.0 (C-4_{glc}). Thus, the structure of compound **6** was deduced as (25*R*)-spirost-5-ene-3 β -ol-3-*O*-[[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-rhamnopyranosyl-(1 \rightarrow 4)]- β -D-glucopyranoside] (Fig.2), which has been previously isolated from *Solanum* plants [14].

The ¹H NMR spectrum of **7** showed signals for four steroidal methyl groups at δ 0.89 (3H, s, Me-19), 0.82 (3H, s, Me-18), 1.00 (3H, d, H-21), 1.12 (3H, d, Me-27). The HMBC correlation of methyl groups clearly showed that the aglycon moiety was similar of compound **3** was identified as (25*R*)-5 α -spirostan-3 β -ol. One primary alcoholic function at δ 67.7 (C-26), suggesting the occurrence of a glycoside spirostanol skeleton. The ¹H NMR spectrum showed signals for three anomeric protons at δ 4.39 (1H, d, J = 7.5 Hz), 4.56 (1H, d, J = 7.5 Hz), and 4.69 (1H, d, J = 7.5 Hz). It was evident from the ¹H and ¹³C NMR data that the sugar chain at C-3 of **7** consisted of three sugar units. The sugar chain was similar to sugar chain of compound **6**. A glycosidation shifts were observed for C-2_{glc} (δ 79.5) and for C-4_{glc} (δ 80.0). The HMBC spectrum showed key correlation peaks between the proton signal at δ 4.53 (H-1_{glc}) and the carbon resonance at δ 79.0 (C-3), the proton signal at δ 4.87 (H-1_{rha}) and the carbon resonance at δ 79.5 (C-2_{glc}), the proton signal at δ 5.23 (H-1_{rha}) and the carbon resonance at δ 80.0 (C-4_{glc}). The structure of compound **7** was assigned as (25*R*)-5 α -spirostan-3 β -ol-3-*O*-[[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-rhamnopyranosyl-(1 \rightarrow 4)]- β -D-glucopyranoside] (Fig.2), which has been previously isolated from the seeds of *Solanum melongena* L. [15].

¹H NMR spectrum of compound **8** displayed signals for three tertiary methyl groups at 0.95 (3H, s, Me-19), 1.02 (3H, s, Me-18) and 2.28 (3H, s, Me-21), one double bond δ 5.42 (broad d, 1H-6), one olefinic proton at 6.91 (1H, m, H-16) together with two anomeric protons (1H, d, 4.43; 1H, d, 4.88). On the other hand, the ¹³C NMR signals due to a total of 21 carbon signals originating from the sapogenol were composed of three methyl groups at 12.3 (C-19), 15.7 (C-18), and 26.8 (C-21), one oxygenbearing methine carbon at 79.1 (C-3), one carbonyl group at 199.3 (C-20), two quaternary carbons at 37.2 (C-10) and 47.2 (C-13), three methine carbons at 30.4 (C-8), 50.8 (C-9) and 57.3 (C-14), seven methylene carbons at δ 20.9 (C-11), 30.1 (C-2), 31.8 (C-7), 32.9 (C-15), 39.0 (C-4), 35.1 (C-12), and 37.9 (C-1), and four olefinic carbons at δ 121.5 (C-6), 141.3 (C-5), 147.0 (C-16) and 156.0 (C-17). The HMBC disclosed the connectivities of the above functional carbons to form a pregnane skeleton. The NMR data of sugar moiety was identical of compound **2**. HMBC spectrum showed key correlation picks between sugars anomeric protons and attached carbons at 4.43 (H-1_{glc}) and 79.1 (C-3 agl), 4.88 (H-1_{rha}) and 79.5 (C-4_{glc}). Thus, compound **8** was elucidated as 3-*O*- α -L-rhamnopyranosyl - (1 \rightarrow 4) - β - D - glucopyranoside - pregn - 5, 16 - dien - 20 - one, 3 β -ol (Fig.2), earlier reported in literature [16].

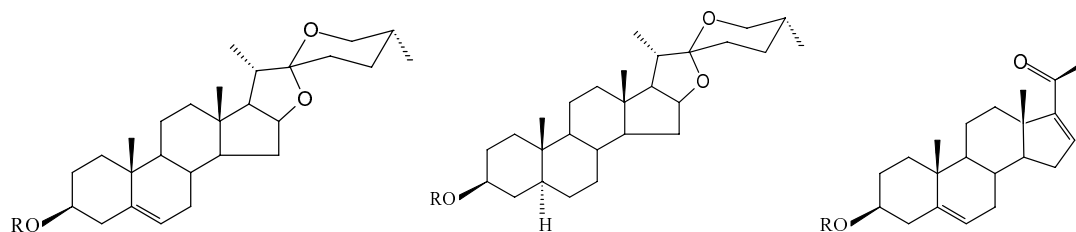


Fig. 2.

2: R=Rha(1 \rightarrow 4)Glc4: R=Rha(1 \rightarrow 2)Glc6: R=[Rha(1 \rightarrow 4)]Rha (1-2) Glc3: R=Rha(1 \rightarrow 4)Glc5: R=Rha(1 \rightarrow 2)Glc7: R=[Rha(1 \rightarrow 4)]Rha (1-2) Glc8: R=Rha(1 \rightarrow 4)Glc

Experimental

Optical rotations were measured on a Jasco DIP 1000 polarimeter. Melting points were measured on the Boetius table. Exact masses were measured by a Voyager DE mass spectrometer (Applied Biosystems, Foster City, CA). Samples were analyzed by matrix assisted laser desorption ionization (MALDI) mass spectrometry. Mass calibration was performed with the ions from ACTH (fragment 18-39) at 2465.1989 Da and Angiotensin III at 931.5154 Da as internal standards. ESI-MS analyses were performed using a ThermoFinnigan LCQ Deca XP Max ion trap mass spectrometer equipped with Xcalibur software. Samples were dissolved in MeOH (Baker) and infused in the ESI source by using a syringe pump. The capillary voltage was 43 V, the spray voltage 5 kV, and the tube lens offset 30 V. The capillary temperature was 280 $^{\circ}$ C. NMR experiments were performed at 300 K by dissolving each sample in 500 μ L of CD₃OD (Carlo Erba, 99.8 %D) (¹H, δ = 3.34 ppm; ¹³C, δ = 49.0 ppm) on a Bruker DRX-600 spectrometer equipped with a 5 mm TCI CryoProbe. All spectra were acquired in the phase sensitive mode and the TPPI method was used for quadrature detection in the ω_1 dimension. HPLC separations were carried out on a Waters 590 system equipped with a Waters R401 refractive index detector and a Rheodyne injector. TLC was performed on silica gel plates (Merck precoated silica gel 60 F₂₅₄). All solvents for chromatographic separation were of analytical

grade from Carlo Erba (Rodano, Italy). HPLC grade water (18 mΩ) was prepared using a Millipore Milli-Q purification system (Millipore Corp., Bedford, MA).

Plant Material has been collected in the scientific research field of the Institute of Genetics and Plant Physiology in October 2003 year. The voucher specimen has been deposited in the Laboratory of Genetics and Physiology of Plant Stability.

The dried and powdered roots of *Solanum melongena* L. (1000 g) were extracted three times at 100°C with water for 4 hours. Water extracts were combined and extracted with n-butanol, after that n-butanol was evaporated under reduced pressure to give a mixture of saponins (9,6 g). This mixture have been chromatographed on silica gel column (30-500 mm, 60-100μm, Merck). The column was eluted with system chloroform-methanol-water (8:2:0→20:10:1). After monitoring by TLC [Si gel plates, chloroform-methanol (85:15)] fractions showing identical characteristics were combined to give A (120 mg), B (200 mg), C (175 mg), D (230) and E (105 mg). Fractions A-E were submitted to HPLC on a Waters XTerra Prep C₁₈ column (300 x 7.8 mm i.d., the flow rate was 2 μL/min.), using a MeOH:H₂O in the ratio 85:15 for A-C, 70:30 for D and 75:35 for E (isocratic conditions). Pure **8** (6 mg, Rt = 18 min) was obtained from A, **4** (7 mg, Rt = 11 min), **5** (10 mg, Rt = 19 min) from B, **2** (9 mg, Rt = 9 min), **3** (11 mg, Rt = 17 min) from C, **6** (8 mg, Rt = 5 min), **7** (11 mg, Rt = 7 min) from D and **1** (7 mg, Rt = 15 min) from E.

1. Amorphous powder. M.p.197-198°C, [α]_D: -92.3 (c 0.3, MeOH). HRMS, *m/z* 740.653 [calculated for C₃₉H₆₄O₁₃ (M)⁺]; 594.5 [M-146]⁺; ¹H NMR (aglycon) δ 3.94 (1H, m, H-16), 3.62 (1H, m, H-3), 3.43 (1H, m, H-26a), 3.37 (1H, m, H-26b), 1.16 (3H, s, Me-19), 0.84 (3H, s, Me-18), 0.87 (3H, d, H-21), 0.77 (3H, d, Me-27). (sugars) 4.43 (d, *J*=7.5 Hz, H-1 Glc), 3.22 (dd, *J*=7.5 and 9.0 Hz, H-2 Glc), 3.49 (dd, *J*=9.0 and 9.0 Hz, H-3 Glc), 3.56 (dd, *J*=9.0 and 9.0 Hz, H-4 Glc), 3.35 (ddd, *J*=2.5, 4.5 and 9.0 Hz, H-5 Glc), 3.82 (dd, *J*=4.5 and 11.5 Hz, H-6a Glc), 3.69 (dd, *J*=2.5 and 11.5 Hz, H-6b Glc). 4.88 (d, H-1Rha), 3.87 (dd, H-2 Rha), 3.66 (dd, H-3 Rha), 3.43 (dd, H-4 Rha), 3.99 (m, H-5 Rha), 1.29 (d, H-6 Rha). For ¹³C NMR see Table.

2. Amorphous powder. M.p.230-231°C, [α]_D: -89.0 (pyridine). HRMS, *m/z* 722.345 [calculated for C₃₉H₆₂O₁₂ (M)⁺]; 576.7 [M-146]⁺; ¹H NMR (aglycon) δ 4.44 (1H, m, H-16), 3.62 (1H, m, H-3), 3.47 (1H, m, H-26a), 3.35 (1H, m, H-26b), 1.03 (3H, s, Me-19), 0.85 (3H, s, Me-18), 0.99 (3H, d, H-21), 0.82 (3H, d, Me-27). (sugars) 4.43 (d, *J*=7.5 Hz, H-1 Glc), 3.22 (dd, *J*=7.5 and 9.0 Hz, H-2 Glc), 3.49 (dd, *J*=9.0 and 9.0 Hz, H-3 Glc), 3.56 (dd, *J*=9.0 and 9.0 Hz, H-4 Glc), 3.35 (ddd, *J*=2.5, 4.5 and 9.0 Hz, H-5 Glc), 3.82 (dd, *J*=4.5 and 11.5 Hz, H-6a Glc), 3.68 (dd, *J*=2.5 and 11.5 Hz, H-6b Glc). 4.88 (d, H-1Rha), 3.87 (dd, H-2 Rha), 3.66 (dd, H-3 Rha), 3.35 (dd, H-4 Rha), 4.00 (m, H-5 Rha), 1.29 (d, H-6 Rha). For ¹³C NMR see Table.

3. Amorphous powder. M.p.233°C, [α]_D: -69.0 (MeOH). HRMS, *m/z* 725.321 [calculated for C₃₉H₆₄O₁₂ (M)⁺]; 579.7 [M-146]⁺; ¹H NMR (aglycon) δ 4.39 (1H, m, H-16), 3.68 (1H, m, H-3), 3.41 (1H, m, H-26a), 3.29 (1H, m, H-26b), 0.89 (3H, s, Me-19), 0.84 (3H, s, Me-18), 1.02 (3H, d, H-21), 0.98 (3H, d, Me-27). (sugars) 4.43 (d, *J*=7.5 Hz, H-1 Glc), 3.22 (dd, *J*=7.5 and 9.0 Hz, H-2 Glc), 3.49 (dd, *J*=9.0 and 9.0 Hz, H-3 Glc), 3.56 (dd, *J*=9.0 and 9.0 Hz, H-4 Glc), 3.35 (ddd, *J*=2.5, 4.5 and 9.0 Hz, H-5 Glc), 3.82 (dd, *J*=4.5 and 11.5 Hz, H-6a Glc), 3.68 (dd, *J*=2.5 and 11.5 Hz, H-6b Glc). 4.88 (d, H-1Rha), 3.87 (dd, H-2 Rha), 3.66 (dd, H-3 Rha), 3.35 (dd, H-4 Rha), 4.00 (m, H-5 Rha), 1.29 (d, H-6 Rha). For ¹³C NMR see Table.

4. Amorphous powder. M.p.238-240°C, [α]_D: -99.0 (pyridine). HRMS, *m/z* 722.533 [calculated for C₃₉H₆₂O₁₂ (M)⁺]; 576.5 [M-146]⁺; ¹H NMR (aglycon) δ 4.44 (1H, m, H-16), 3.62 (1H, m, H-3), 3.47 (1H, m, H-26a), 3.35 (1H, m, H-26b), 1.03 (3H, s, Me-19), 0.85 (3H, s, Me-18), 0.99 (3H, d, H-21), 0.82 (3H, d, Me-27). (sugars) 4.51 (d, *J*=7.5 Hz, H-1 Glc), 3.38 (dd, *J*=7.5 and 9.0 Hz, H-2 Glc), 3.49 (dd, *J*=9.0 and 9.0 Hz, H-3 Glc), 3.28 (dd, *J*=9.0 and 9.0 Hz, H-4 Glc), 3.26 (ddd, *J*=2.5, 4.5 and 9.0 Hz, H-5 Glc), 3.89 (dd, *J*=4.5 and 11.5 Hz, H-6a Glc), 3.68 (dd, *J*=2.5 and 11.5 Hz, H-6b Glc). 5.22 (d, H-1 Rha), 3.94 (dd, H-2 Rha), 3.69 (dd, H-3 Rha), 3.42 (dd, H-4 Rha), 4.16 (m, H-5 Rha), 1.27 (d, H-6 Rha). For ¹³C NMR see Table.

5. Amorphous powder. M.p.241-242°C, [α]_D: -56.0 (MeOH). HRMS, *m/z* 725.451 [calculated for C₃₉H₆₄O₁₂ (M)⁺]; 579.7 [M-146]⁺; ¹H NMR (aglycon) δ 4.41 (1H, m, H-16), 3.77 (1H, m, H-3), 3.47 (1H, m, H-26a), 3.34 (1H, m, H-26b), 0.89 (3H, s, Me-19), 0.82 (3H, s, Me-18), 1.00 (3H, d, H-21), 1.12 (3H, d, Me-27). (sugars) 4.51 (d, *J*=7.5 Hz, H-1 Glc), 3.38 (dd, *J*=7.5 and 9.0 Hz, H-2 Glc), 3.49 (dd, *J*=9.0 and 9.0 Hz, H-3 Glc), 3.28 (dd, *J*=9.0 and 9.0 Hz, H-4 Glc), 3.26 (ddd, *J*=2.5, 4.5 and 9.0 Hz, H-5 Glc), 3.89 (dd, *J*=4.5 and 11.5 Hz, H-6a Glc), 3.68 (dd, *J*=2.5 and 11.5 Hz, H-6b Glc). 5.22 (d, H-1 Rha), 3.94 (dd, H-2 Rha), 3.69 (dd, H-3 Rha), 3.42 (dd, H-4 Rha), 4.16 (m, H-5 Rha), 1.27 (d, H-6 Rha). For ¹³C NMR see Table.

6. Amorphous powder. M.p.275-277°C, [α]_D: -115.0 (EtOH). HRMS, *m/z* 868.343 [calculated for C₄₅H₇₄O₁₆ (M)⁺]; 722.4 [M-146]⁺; 576 [M-2x146]⁺; ¹H NMR (aglycon) δ 4.43 (1H, m, H-16), 3.62 (1H, m, H-3), 3.45 (1H, m, H-26a), 3.34 (1H, m, H-26b), 1.02 (3H, s, Me-19), 0.83 (3H, s, Me-18), 0.98 (3H, d, H-21), 0.83(3H, d, Me-27). (sugars) δ4.53 (d, *J*=7.4 Hz, H-1 Glc), 3.42 (dd, *J*=7.4 and 9.0 Hz, H-2 Glc), 3.61 (dd, *J*=4.0 and 9.0 Hz, H-3 Glc), 3.55 (dd, *J*=2.5 and 4.0 Hz, H-4 Glc), 3.35 (ddd, *J*=2.5, 2.5 and 4.5 Hz, H-5 Glc), 3.82 (dd, *J*=4.5 and 12.0 Hz, H-6a Glc), 3.67 (dd, *J*=2.5 and 12.0 Hz, H-6b Glc); 4.87 (d, H-1Rha), 3.86 (dd, H-2 Rha), 3.65 (dd, H-3 Rha), 3.43 (dd, H-4 Rha), 3.95 (m, H-5 Rha), 1.29 (d, H-6Rha); 5.23 (d, H-1 RhaI), 3.95 (dd, H-2 RhaI), 3.68 (dd, H-3 RhaI), 3.43 (dd, H-4 RhaI), 4.95 (m, H-5 RhaI), 1.28 (d, H-6 RhaI). For ¹³C NMR see Table.

7. Amorphous powder. M.p.268-269°C, [α]_D: -73.0 (MeOH). HRMS, *m/z* 870.576 [calculated for C₄₅H₇₆O₁₆ (M)⁺]; 724.3 [M-146]⁺; 578.2 [M-2x146]⁺; ¹H NMR (aglycon) δ 4.43 (1H, m, H-16), 3.62 (1H, m, H-3), 3.45 (1H, m, H-26a), 3.34 (1H, m, H-26b), 0.89 (3H, s, Me-19), 0.82 (3H, s, Me-18), 1.00 (3H, d, H-21), 1.12 (3H, d, Me-27). (sugars) δ4.53 (d, *J*=7.4 Hz, H-1 Glc), 3.42 (dd, *J*=7.4 and 9.0 Hz, H-2 Glc), 3.61 (dd, *J*=4.0 and 9.0 Hz, H-3 Glc),

3.55 (dd, $J=2.5$ and 4.0 Hz, H-4 Glc), 3.35 (ddd, $J=2.5$, 2.5 and 4.5 Hz, H-5 Glc), 3.82 (dd, $J=4.5$ and 12.0 Hz, H-6a Glc), 3.67 (dd, $J=2.5$ and 12.0 Hz, H-6b Glc); 4.87 (d, H-1Rha), 3.86 (dd, H-2 Rha), 3.65 (dd, H-3 Rha), 3.43 (dd, H-4 Rha), 3.95 (m, H-5 Rha), 1.29 (d, H-6Rha); 5.23 (d, H-1 RhaI), 3.95 (dd, H-2 RhaI), 3.68 (dd, H-3 RhaI), 3.43 (dd, H-4 RhaI), 4.95 (m, H-5 RhaI), 1.28 (d, H-6 RhaI). For ^{13}C NMR see Table.

8. Amorphous powder. M.p.233-237 $^{\circ}\text{C}$, $[\alpha]_{\text{D}}$: -69.0 (c 0.7, MeOH) HRMS, m/z 618.623 [calculated for $\text{C}_{33}\text{H}_{50}\text{O}_{11}$ (M) $^{+}$]; 472.241[M-146] $^{+}$; ^1H NMR (aglycon) 6.91 (1H, m, H-16), 3.69 (1H, m, H-3), 0.95 (3H, s, Me-19), 1.02 (3H, s, Me-18), 2.28 (3H, d, H-21). (sugars) 4.43 (d, $J=7.5$ Hz, H-1 Glc), 3.22 (dd, $J=7.5$ and 9.0 Hz, H-2 Glc), 3.49 (dd, $J=9.0$ and 9.0 Hz, H-3 Glc), 3.56 (dd, $J=9.0$ and 9.0 Hz, H-4 Glc), 3.35 (ddd, $J=2.5$, 4.5 and 9.0 Hz, H-5 Glc), 3.82 (dd, $J=4.5$ and 11.5 Hz, H-6a Glc), 3.69 (dd, $J=2.5$ and 11.5 Hz, H-6b Glc). 4.88 (d, H-1Rha), 3.87 (dd, H-2 Rha), 3.66 (dd, H-3 Rha), 3.43 (dd, H-4 Rha), 3.99 (m, H-5 Rha), 1.29 (d, H-6 Rha). For ^{13}C NMR see Table.

Conclusion

One new cholestane glycoside, six steroidal glycosides of spirostane series and one pregnane glycoside have been isolated for the first time from the roots of *Solanum melongena* L. During the investigation their structures have been determined as 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D- glucopyranoside-(25R)-cholest-5-en, 22-one, 3 β ,16 β ,26-triol for compound 1, (25R)-spirost-5-ene-3 β -ol - 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 4) - β - D-glucopyranoside for compound 2, (25R) - 5 α - spirostan - 3 β -ol - 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 4) - β - D-glucopyranoside for compound 3, (25R)-spirost- 5-ene-3 β -ol-3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-glucopyranoside for compound 4, (25R) - 5 α - spirostan - 3 β -ol - 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2) - β - D-glucopyranoside for compound 5, (25R)-spirost-5-ene-3 β -ol-3-O-[[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-glucopyranoside] for compound 6, (25R) - 5 α - spirostan - 3 β -ol -3-O-[[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-rhamnopyranosyl-(1 \rightarrow 4)- β -D-glucopyranoside] for compound 7 and 3-O- α -L-rhamnopyranosyl - (1 \rightarrow 4) - β - D - glucopyranoside - pregn - 5, 16 - dien - 20 - one, 3 β -ol for compound 8. Compounds 2-8 are known steroidal glycosides and their physico-chemical data coincide with literature ones.

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