STRUCTURES OF TWO NEW STEROIDAL GLYCOSIDES, SOLADULCOSIDES A AND B FROM *SOLANUM DULCAMARA*¹⁾

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The structures of two new steroidal glycosides named soladulcosides A and B, isolated from the aerial parts of *Solanum dulcamara* including new sapogenols, were elucidated as (22*R*,25*R*)-3 β ,15 α ,23 α -trihydroxy-5 α -spirostan-26-one 3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranoside and (22*R*,25*R*)-3 β ,23 α -dihydroxy-5 α -spirostan-26-one 3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]- β -D-glucopyranoside, respectively.

KEYWORDS *Solanum dulcamara*; Solanaceae; steroidal glycoside; soladulcoside

A European crude drug, *Solanum dulcamara* L. has been used to treat cancers, tumors, and warts since the old time of Galen.²⁾ The constituents steroidal alkaloid glycosides²⁾ and steroidal glycosides³⁾ have been known. Now we have obtained two novel spirostanol steroidal glycosides, named soladulcosides A and B, which have a lactone ring in the sapogenol moiety, from the aerial parts of the above plant.

Soladulcoside A (**1**), a white powder, $[\alpha]_D -73.8^\circ$, showed a peak due to $[M+Na]^+$ at m/z 793 ($C_{39}H_{62}O_{15}Na$) in the positive FAB-MS and the IR spectrum showed an absorption band at 1764 cm^{-1} suggesting the presence of a carbonyl group. Acid hydrolysis of **1** provided glucose and rhamnose as sugar components. The $^1\text{H-NMR}$ spectrum displayed signals due to two tertiary methyl [δ 0.91(3H, s) and 0.99 (3H, s)] and three secondary methyl[1.16(3H, d, $J=6.2\text{ Hz}$), 1.29(3H, d, $J=6.6\text{ Hz}$) and 1.77(3H, d, $J=5.7\text{ Hz}$)] groups and two anomeric protons [δ 5.07(1H, d, $J=7.3\text{ Hz}$) and 6.37(1H, s)], indicating that **1** was a steroid diglycoside. Moreover, the $^{13}\text{C-NMR}$ spectrum showed an α -rhamnopyranosyl-(1 $\rightarrow$ 2)- β -glucopyranosyl moiety (Table I), an ester carbonyl signal at δ 180.6, four oxygenated methine signals at δ 76.8, 77.7, 79.0 and 92.0, and a spiroketal carbon signal at δ 109.9, which was closely analogous to tigogenin glycoside.⁴⁾ In the $^1\text{H-}^1\text{H}$ COSY spectrum, there were correlations in a sequence of H_3 -21 [δ 1.29], H-20 [δ 2.78(dq, $J=6.6, 6.6\text{ Hz}$)], H-17 [δ 2.15(dd, $J=6.6, 8.4\text{ Hz}$)], H-16 [δ 4.99(1H, dd, $J=3.9, 8.4\text{ Hz}$)] and H-15 [δ 4.38(dd, $J=3.9, 10.0\text{ Hz}$)] and in a sequence of H_3 -27 [δ 1.16], H-25 [δ 2.99(m)], H_2 -24 [δ 1.94(m) and 2.98(m)] and H-23 [δ 4.69(br d, $J=8.8\text{ Hz}$)]. The evidence indicated two hydroxyl groups attached to C-15 and C-23 on tigogenin. All carbon signals in **1** could be assigned as listed in Table I by the $^{13}\text{C-NMR}$ and $^1\text{H-}^{13}\text{C}$ COSY, and signals at C-1~13 showed chemical shifts similar to those of tigogenin 3-*O*-glycoside.⁴⁾ The location of the lactone ring was determined in the $^1\text{H-}^{13}\text{C}$ long-range COSY spectrum. Cross peaks were observed between H_3 -27 and C-26 (δ 180.6), and H-25 and C-26, indicating that the lactone ring was in F-ring. NOE's in **1** were observed between H_3 -18 (δ 0.99) and H-15; H-23 and H-25, and between H_3 -27 and H_2 -24, showing that the configurations of the two hydroxyl groups at C-15 and C-23 and methyl group at C-25 were α . Moreover, the CD spectrum ($[\Theta]_{222} -6.63 \times 10^2$) revealed that

the C-22 configuration was R .⁵⁾ So the structure of soladulcoside A (1) was (22*R*,25*R*)-3 β ,15 α ,23 α -trihydroxy-5 α -spirostan-26-one 3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranoside.

Soladulcoside B (2), a white powder, $[\alpha]_D -79.2^\circ$, showed a peak due to $[M+Na]^+$ at m/z 923 ($C_{45}H_{72}O_{18}Na$) in the positive FAB-MS. The IR spectrum showed an absorption band at 1762 cm^{-1} . Acid hydrolysis of 2 yielded rhamnose and glucose. The $^1\text{H-NMR}$ spectrum exhibited three anomeric proton signals at δ 4.93(1H, d, $J=6.2\text{ Hz}$), 5.85(1H, s) and 6.37(1H, s) together with signals due to two tertiary methyl groups (each 3H, s, δ 0.86 and 0.92), four secondary methyl group [each 3H, d, δ 1.20($J=7.3\text{ Hz}$), 1.29($J=7.0\text{ Hz}$), 1.62($J=5.9\text{ Hz}$) and 1.75($J=5.9\text{ Hz}$)]. In the $^{13}\text{C-NMR}$ spectrum, signals due to the C-1~13 and C-19~27 showed chemical shifts similar to those of 1, but signals due to C-14, C-15, C-16 and C-17 were similar to the chemical shifts of tigogenin, suggesting that the aglycone in 2 should be a 15-dehydroxy derivative of 1. Signals due to the sugar part in the $^{13}\text{C-NMR}$ spectrum of 2 were superimposable on those of solamargine (solasodine 3-*O*- β -chacotrioside).⁶⁾ Consequently, the structure of soladulcoside B (2) was determined to be (22*R*,25*R*)-3 β ,23 α -dihydroxy-5 α -spirostan-26-one 3-*O*- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 4)]- β -D-glucopyranoside.⁷⁾

TABLE I. ^{13}C -NMR Data for **1**, **2** and Tigogenin (in pyridine d_5)

	1	2	Tigogenin		1	2
C-1	37.4	37.2	37.5	Glc 1'	99.8	99.8
2	30.0	29.9	32.5	2'	79.6	78.7
3	76.8	76.9	70.6	3'	78.1	77.9
4	34.4	34.4	39.3	4'	71.9	78.0
5	44.6	44.6	45.2	5'	78.3	77.9
6	29.2	28.9	29.1	6'	62.8	61.4
7	32.8	32.4	32.5	Rha 1"	102.2	102.1
8	35.9	35.0	35.4	2"	72.5	72.4 ^a
9	54.6	54.3	54.5	3"	72.8	72.6 ^b
10	36.1	35.8	35.8	4"	74.1	73.8 ^c
11	21.3	21.2	21.1	5"	69.5	69.4 ^d
12	40.9	40.1	40.3	6"	18.7	18.4 ^e
13	41.4	41.4	40.8	Rha 1' "		102.9
14	60.7	56.3	57.6	2' "		72.5 ^a
15	79.0	32.4	32.1	3' "		72.7 ^b
16	92.0	82.1	81.1	4' "		74.0 ^c
17	60.3	62.9	63.1	5' "		70.4 ^d
18	18.1	16.7	16.7	6' "		18.6 ^e
19	12.5	12.5	12.5			
20	37.3	37.2	42.0			
21	15.6	15.6	15.0			
22	109.9	110.0	109.2			
23	77.7	77.2	31.9			
24	31.1	31.1	29.3			
25	34.1	34.1	30.6			
26	180.6	180.7	66.9			
27	16.3	16.3	17.3			

Assignments a-e may be interchangeable.

REFERENCES AND NOTES

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