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STEROID ALKALOID GLYCOSIDES FROM *SOLANUM COCCINEUM**

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Key Word Index—*Solanum coccineum*; Solanaceae; aerial parts; steroid alkaloid glycosides; xylosylsolamargine; xylosyl-β-solamarine.

Abstract—In addition to solamargine, isoanguivine and solasonine, two new steroid alkaloid glycosides, xylosylsolamargine and xylosyl-β-solamarine, have been isolated from the aerial parts of *Solanum coccineum*, the structures of which have been elucidated as (25*R*)-3β-{*O*-β-D-xylopyranosyl-(1 → 2)-*O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranosyloxy}-22α*N*-spirosol-5-ene and (25*S*)-3β-{*O*-β-D-xylopyranosyl-(1 → 2)-*O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranosyloxy}-22β*N*-spirosol-5-ene.

INTRODUCTION

From the aerial parts of *Solanum coccineum* Jacq., solamargine (yield 0.042%), isoanguivine (yield 0.028%), solasonine (yield 0.016%) and two new steroid alkaloid glycosides, xylosylsolamargine (yield 0.005%) and xylosyl-β-solamarine (yield 0.005%), have been isolated, for which the structures **1**, (25*R*)-3β-{*O*-β-D-xylopyranosyl-(1 → 2)-*O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranosyloxy}-22α*N*-spirosol-5-ene, and **2**, (25*S*)-3β-{*O*-β-D-xylopyranosyl-(1 → 2)-*O*-α-L-rhamnopyranosyl-(1 → 4)-*O*-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranosyloxy}-22β*N*-spirosol-5-ene, have been established.

RESULTS AND DISCUSSION

The electrospray ionization mass spectra (ESI-MS, positive ions) of the two alkaloids suggested glycoside structures. Peaks at *m/z* 414, $[C_{27}H_{43}NO_2 + H]^+$, were in agreement with the assumption of spirosolenols as aglycones. Intense $[MH]^+$ peaks (*m/z* 1000) were observed. The ^{13}C NMR spectrum of **1** indicated that the aglycone was solasodine (Experimental, cf. ref. [2]), and that of **2** corresponded to tomatidenol (Experimental, cf. ref. [3]; for consideration of the 5-double bond see refs [4, 5]). The assignments of the signals were supported by APT measurements. The ^{13}C signals of the oligosaccharide portions of **1** and **2** had the same values, indicating identical structures. Therefore, only the carbohydrate structure of **1** was studied (Table 1). The ^1H signals of the oligosaccharide portion (Table 1) were assigned by ^1H–^1H 2D DQF COSY NMR spectra, and the sugars were recognized. The D-configurations were assumed for xylopyranose and glucopyranose, while for the rhamnopyranose moieties L-configurations were expected. The coupling constants $J_{1,2}$ of xylose and glucose corresponded to β-configurations. Cross peaks in the ROESY spectrum of **1** (in pyridine-d_5) relating H-1 and the axial H-5 of xylose as well as of glucose agreed with this conclusion, while the absence of such cross peaks for the rhamnose moieties indicated α-configurations. The ^{13}C signals of the sugar components were assigned by HMQC measurements (in pyridine-d_5).

Finally, the connections of the sugar components had to be determined. This was in part carried out by analysing long-range heteronuclear coupling recognized in the HMBC spectrum (in pyridine-d_5). Correlations were found between H-1 of xylose and C-2 of 4-*O*-rhamnose, H-2 of 4-*O*-rhamnose and C-1 of xylose, H-1 of 4-*O*-rhamnose and C-4 of glucose, H-1 of 2-*O*-rhamnose and C-2 or C-3 of glucose (nearly equal chemical shifts and no unequivocal assignments, cf. Table 1) as well as H-3 of solasodine and C-1 of glucose. Thus, the sequence was established with the exception of one rhamnose, which could be connected to the 2- or 3-position of glucose. The study of NOEs using ROESY measurements gave the same results. H-1 of xylose showed a strong effect to H-2 of 4-*O*-rhamnose, H-1 of 4-*O*-rhamnose to H-3, H-4 and H-5 of glucose (indicating a 1 → 4 bond), H-1 of 2-*O*-rhamnose to H-2 or/and H-3 of glucose (equal chemical shifts, cf. Table 1) and H-1 of glucose to H-3 of solasodine. All ^{13}C signals and the signals of H-1–H-4 of glucose had the same chemical shifts as the corresponding atoms of the 2,4-branched glucose in solamargine (measured in pyridine-d_5 [1]). In comparison with a

*Part 135 in the series '*Solanum* Alkaloids'. For part 134 see ref. [1].

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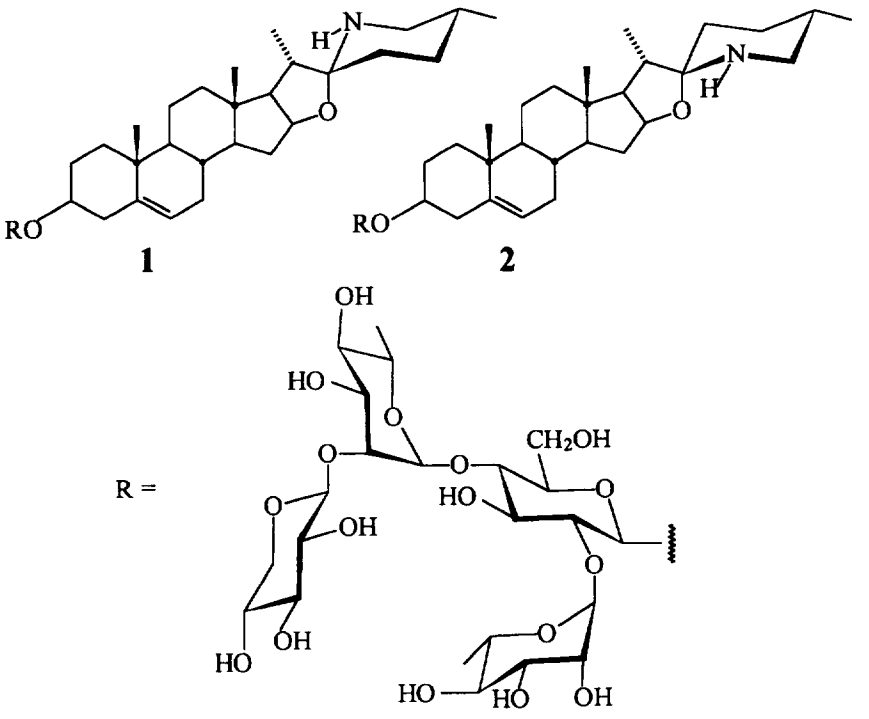

terminal glycopyranose moiety (e.g. in tomatine [3]) the signals of C-2 and C-4 were shifted downfield, whereas C-3 displayed a signal at nearly the same position. Therefore, it was concluded that the second rhamnose had a 2-position. Compounds **1** and **2** are the first *Solanum* steroid alkaloids containing an inner rhamnose moiety.

EXPERIMENTAL

Seeds of *S. coccineum* were obtained from the Botanical Garden of St Gallen. Plants were grown in a field in Halle (Saale) and harvested in September 1992. Identification of the species was confirmed by Dr U. Braun, herbarium, curator, Institute of Geobotany, University of Halle. A voucher specimen is retained in the Institute of Plant Biochemistry, Halle.

Isolation of alkaloids. Aerial parts were dried at 60°, ground and extracted with 95% MeOH at room temp. This soln was extracted with petrol, the MeOH evapd and the aq. soln extracted with EtOAc, followed by *n*-BuOH. Evapn of *n*-BuOH *in vacuo* gave a residue which was partitioned between aq. $KHCO_3$ and $CHCl_3$–EtOH (2:1). Evapn of the organic solvents *in vacuo* gave a mixt. of alkaloids. This was chromatographed over Merck silica gel with $CHCl_3$–MeOH–conc. NH_3 (12:5:4, 30:11:10 or 300:103:100, lower phase) and over Merck LiChroprep RP-8 with MeOH–0.4% HOAc (1:1). The alkaloids were purified by HPLC, performed on a Eurosil Bioselect 100-10 C8 column, 250 × 32 mm, 7.6 MPa, 20 ml min^{-1} detection at 200 nm, elution with MeOH-buffer soln [1:1, buffer soln: 0.1 M $(NH_4)H_2PO_4$, H_3PO_4 added to pH 3.0] or MeCN-buffer soln (1:3). Frs containing alkaloids were basified with conc. NH_3, MeOH or MeCN evapd *in vacuo*, the aq. soln extracted with $CHCl_3$–EtOH (2:1) and the solvents evapd *in vacuo*. Prep. TLC [Merck PLC plates, Silica gel 60 $F_{254}S$ with concentrating zone precoated for prep. layer chromatography, $CHCl_3$–MeOH–conc. NH_3 (3:3:1 or 12:5:4)] was also used. TLC: Merck TLC aluminium sheets, Silica gel 60 $WF_{254}S$, $CHCl_3$–MeOH–conc. NH_3 (3:3:1), detection by Dragendorff's reagent [R_f(1), solamargine: 0.54, isoanguivine: 0.40, solasonine: 0.29] or Merck TLC plates RP-8 $F_{254}S$, MeOH–buffer soln (2:1, buffer soln: 50 g NH_4OAc dissolved in 50 ml H_2O, 560 ml 1 M HCl and 720 ml H_2O added, detection by I_2 vapour [R_f(2), solamargine: 0.45, isoanguivine: 0.47, solasonine: 0.45]. Analyt. HPLC: Eurosil Bioselect 100–10 C8, 250 × 4 mm, 10 MPa, 1 ml min^{-1}, detection at 200 nm, MeOH–buffer soln [1:1, buffer soln: 0.1 M $(NH_4)H_2PO_4$, H_3PO_4 added to pH 3.0] [RR_t related to solanine, solamargine: 1.75, isoanguivine: 1.56, solasonine: 1.48].

Xylosylsolamargine, (25R)-3β-{O-β-D-*xylopyranosyl*-(1 → 2)-O-α-L-*rhamnopyranosyl*-(1 → 4)-O-[α-L-*rhamnopyranosyl*-(1 → 2)]-β-D-*glucopyranosyloxy*}-22αN-*spirosol*-5-*ene*, **1**. Yield 0.005%, amorphous. $[\alpha]_D^{22}$ −57.5° (pyridine; *c* 0.43). R_f(1) 0.41, R_f(2) 0.45, RR_t 1.35. ^{1}H NMR (500 MHz, pyridine-d_5, TMS): δ0.83 (*d*, *J* = 5.2 Hz, H_3-27), 0.88 (*s*, H_3-18), 1.06 (*s*, H_3-19), 1.09 (*d*, *J* = 7.0 Hz, H_3-21), 3.92 (*m*, H-3), 4.44 (*m*, H-16), 5.31 (*d*, *J* = 4.9 Hz, H-6), oligosaccharide signals: *cf* Table 1. ^{13}C NMR (126 MHz, pyridine-d_5, TMS): δ15.7 (C-21), 16.5 (C-18),, 19.4 (C-19), 19.8 (C-27), 21.1 (C-11), 30.1 (C-2), 31.1 (C-24), 31.6 (C-25), 31.7 (C-8), 32.3 (C-15), 32.6 (C-7), 34.7 (C-23), 37.1 (C-10), 37.5 (C-1), 38.9 (C-4), 40.1 (C-12), 40.6 (C-13), 41.6 (C-20), 48.0 (C-26), 50.3 (C-9), 56.7 (C-14), 63.5 (C-17), 78.0 (C-3), 78.8 (C-16), 98.4 (C-22), 121.8 (C-6), 140.8 (C-5), oligosaccharide signals: cf. Table 1.

Table 1. NMR spectral data (δ values, J Hz) for compounds **1** and **2** (oligosaccharide portions, 500 MHz for ^{1}H, 126 MHz for ^{13}C)

		1				2	
Sugar	Position	δ_H*	J(H, H)*	δ_H†	J(H, H)†	δ_C†	δ_C†
Xylose	1	4.49	7.9 (1, 2)	5.25	7.3 (1, 2)	107.5	107.6
	2	3.38	9.1 (2, 3)	4.10	—	75.6	75.6
	3	3.56	9.1 (3, 4)	4.16	—	78.5	78.5
	4	3.48	10.1 (4, 5a)	4.16	10.4 (4, 5a)	71.0	71.0
	5	3.20 (axial)	5.3 (4, 5e)	3.70 (axial)	4.1 (4, 5e)	67.4	67.4
		3.87 (equatorial)	11.2 (5a, 5e)	4.32 (equatorial)	10.7 (5a, 5e)		
2-*O*-Rhamnose	1	5.19‡	1.5 (1, 2)	6.43	0.0 (1, 2)	102.0	102.0
	2	3.92§	3.3 (2, 3)	4.86	3.8 (2, 3)	72.6	72.6
	3	3.66	9.4 (3, 4)	4.65	9.4 (3, 4)	72.8	72.8
	4	3.39	9.5 (4, 5)	4.39	—	74.1	74.1
	5	4.12	6.2 (5, 6)	4.98	6.1 (5, 6)	69.5	69.5
	6	1.24		1.80‖		18.6	18.6
4-*O*-Rhamnose	1	5.07‡	0.0 (1, 2)	6.01	0.0 (1, 2)	101.4	101.4
	2	3.84§	3.4 (2, 3)	4.69	3.5 (2, 3)	81.8	81.8
	3	3.66	9.2 (3, 4)	4.56	10.0 (3, 4)	72.8	72.8
	4	3.38	9.2 (4, 5)	4.25	—	74.3	74.4
	5	3.94	6.2 (5, 6)	4.98	6.1 (5, 6)	69.9	69.9
	6	1.24		1.59‖		18.3	18.3
Glucose	1	4.37	7.3 (1, 2)	5.00	—	100.2	100.2
	2	3.25	8.8 (2, 3)	4.25	—	77.9¶	77.9**
	3	3.30	9.2 (3, 4)	4.25	8.2 (3, 4)	77.8¶	77.8**
	4	3.48	9.2 (4, 5)	4.45	8.2 (4, 5)	78.8	78.6
	5	3.30	4.6 (5, 6)	3.75	2.0 (5, 6)	77.2	77.2
	6	3.64	1.8 (5, 6')	4.26	2.0 (5, 6')	61.3	61.3
		3.80	12.0 (6.6')	4.38	—		

*In CD_3OD.
†In pyridine-d_5.
‡‖¶**May be exchanged.
§Has to be exchanged if the signal for H-1 is reversed.

Xylosyl-β-*solamarine*, (25*S*)-3-β-{O-β-D-*xylopyranosyl*-(1 → 2)-O-α-L-*rhamnopyranosyl*-(1 → 4)-O-[α-L-*rhamnopyranosyl*-(1 → 2)]-β-D-*glucopyranosyloxy*}-22βN-*spirosol*-5-*ene*, **2**. Yield 0.005%, amorphous. $[\alpha]_D^{22}$ −54.8° (pyridine; *c* 0.74) R_f(1) 0.41, R_f(2) 0.56, RR_t 1.29. ^{13}C NMR (126 MHz, pyridine-d_5, TMS): δ16.2 (C-21), 16.8 (C-18); 19.4 (C-19), 19.8 (C-27), 21.1 (C-11), 27.0 (C-23), 29.3 (C-24), 30.0 (C-2), 31.4 (C-25), 31.6 (C-8), 33.1 (C-15), 32.4 (C-7), 37.1 (C-10), 37.4 (C-1), 38.9 (C-4), 40.1 (C-12), 40.7 (C-13), 43.0 (C-20), 50.3 (C-9), 50.6 (C-26), 56.0 (C-14), 62.2 (C-17), 78.0 (C-3), 78.6 (C-16), 99.4 (C-22), 121.8 (C-6), 140.8 (C-5), oligosaccharide signals: cf. Table 1.

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