Pergamon

PII: S0031-9422(96)00575-4

Phytochemistry, Vol. 44, No. 4, pp. 731–734, 1997

0031-9422/97 $17.00+0.00

STEROIDAL ALKALOID GLYCOSIDES FROM *SOLANUM UPORO**†

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(*Received in revised form* 8 *July* 1996)

Key Word Index—*Solanum uporo*; Solanaceae; roots; steroidal alkaloid glycosides; (23*S*)-23-hydroxyanguivine; (23*S*)-23-hydroxyisoanguivine.

Abstract—In addition to solamargine, anguivine and isoanguivine, two new steroidal alkaloid glycosides, (23*S*)-23-hydroxyanguivine and (23*S*)-23-hydroxyisoanguivine, have been isolated from roots of *Solanum uporo*, the structures of which have been assigned by comparison with literature data as (23*S*,25*R*)-3β-{*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-β-D-glucopyranosyloxy}-22α*N*-spirosol-5-en-23-ol and (23*S*,25*R*)-3β-{*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-β-D-galactopyranosyloxy}-22α*N*-spirosol-5-en-23-ol.

INTRODUCTION

From the roots of *Solanum uporo* the solasodine glycosides solamargine [2] (yield 0.007%), anguivine (**3**) [3] (yield 0.027%), isoanguivine (**5**) [3] (yield 0.051%) and two new (23*S*)-23-hydroxysolasodine glycosides, (23*S*)-23-hydroxyanguivine (yield 0.021%) and (23*S*)-23-hydroxyisoanguivine (yield 0.007%), have been isolated, for which the structures (23*S*,25*R*)-3β-{*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-β-D-glucopyranosyloxy}-22α*N*-spirosol-5-en-23-ol (**4**) and (23*S*,25*R*)-3β-{*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-β-D-galactopyranosyloxy}-22α*N*-spirosol-5-en-23-ol (**6**) have been assigned by comparison with literature data. Two further (23*S*)-23-hydroxysolasodine (solaverol A) glycosides, solaverine I and II, have previously been isolated from *S. toxicarium* and *S. verbascifolium* [4].

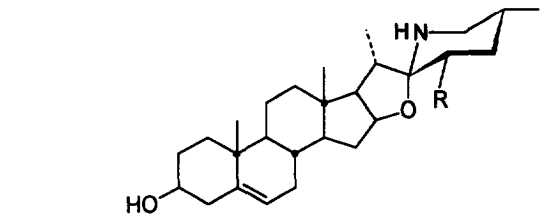
RESULTS AND DISCUSSION

(23*S*)-23-Hydroxysolasodine glycosides were easily separated from solasodine alkaloids by reverse-phase chromatography, because the 23-hydroxyl group increased their mobility to a large extent (R_f (2) 0.55–0.59, RR_t 0.51–0.55, see Experimental) in comparison with spirosolane glycosides unsubstituted in ring F (R_f(2) 0.29–0.36, RR_t 1.46–1.82 [5] under identical conditions).

The structures of compounds **4** and **6** were recognized by comparison of their ^{13}C NMR spectra (Table 1) with those of (23*S*)-23-hydroxysolasodine (**2**) [6], anguivine (**3**) [3] and isoanguivine (**5**) [3]. The signals of alkaloid **2** in pyridine-d_5 were assigned by comparison with the spectra of solasodine (**1**) (C-1–C-19 [7]) and solaverine I (C-20–C-27 [4]) in pyridine-d_5, and also with the spectrum of compound **2** in $CDCl_3$ [6]. The signal of C-20 showed a remarkable upfield shift of 7.1 ppm compared with the corresponding signal of solasodine (δ 41.6 [7]), whereas the signal of C-25 was only shifted by −0.5 ppm (δ 31.6 for solasodine [7]). This could be explained by a γ-gauche interaction between C-20 and the 23-hydroxyl group on one hand and the γ-anti arrangement between C-25 and the 23-hydroxyl group on the other. The structures of glycosides **3** and **5** have previously been elucidated by liquid secondary ion mass spectra and by NMR measurements (APT, ^{1}H–^{1}H two-dimensional COSY, ROESY, HMBC) [3]. The aglycone signals of (23*S*)-23-hydroxyanguivine (**4**) and (23*S*)-23-hydroxyisoanguivine (**6**) corresponded with those of compound **2** (Table 1), when the shifts expected by glycosylation were considered. The agreement of the sugar signals of compounds **4** and **6** with the analogous signals of anguivine (**3**) and isoanguivine (**5**) (Table 1), respectively, indicated identical sugar moieties. All ^{13}C signal assignments were supported by APT measurements. In the electrospray ionization mass spectra (ESI-MS), compounds **4** and **6** gave rise to intense $[M+H]^+$ peaks.

* Part 138 in the series '*Solanum* Alkaloids'. For part 137 see ref. [1].

† Dedicated to Professor K. Schreiber with best wishes on the occasion of his 70th birthday.



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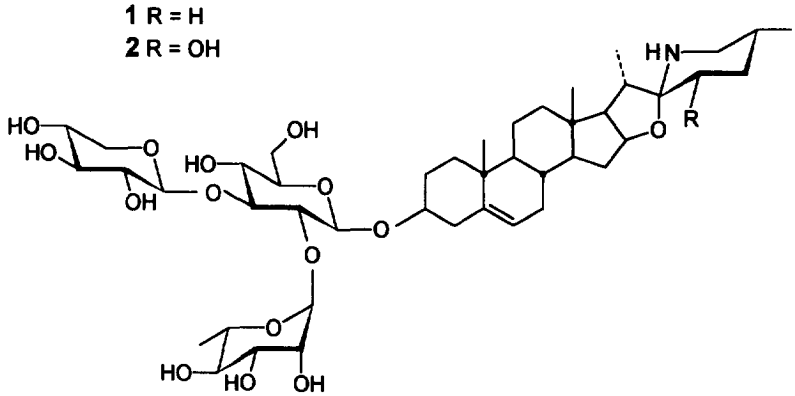

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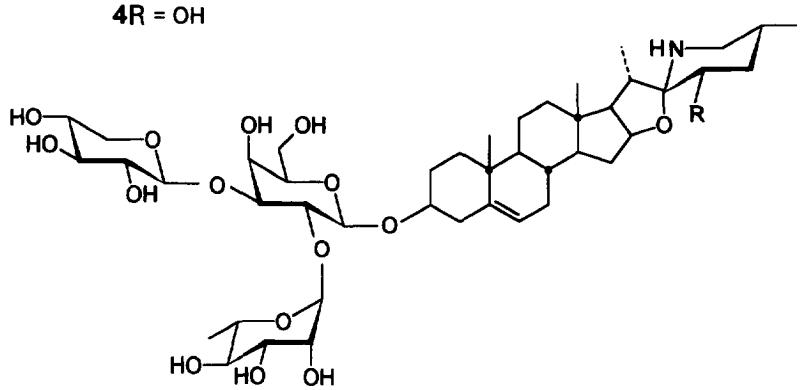
4R = OH



5R = H
6R = OH

EXPERIMENTAL

Seeds of *S. uporo* Dun. were obtained from the Botanical Garden of Besançon. Plants were grown in a field in Halle (Saale) and harvested in September 1992. A voucher specimen is retained in the Institute of Plant Biochemistry, Halle.

Isolation of alkaloids. Roots were dried at 60°, ground and extracted with MeOH at room temp. Evapn of MeOH *in vacuo* gave a residue which was partitioned between H_2O and benzene–Et_2O (1:1). After addition of $KHCO_3$ to the aq. layer, the latter was extracted with $CHCl_3$–EtOH (2:1). Evapn of 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, lower phase) and over Merck LiChroprep RP-8 with 1% HOAc–MeOH (3:2). Frs containing alkaloids were made alkaline with conc. NH_3, the MeOH evapd *in vacuo*, the aq. soln extracted with $CHCl_3$–EtOH (2:1) and the solvents evapd again *in vacuo*. TLC: Merck TLC aluminium sheets silica gel 60 WF_{254S}, $CHCl_3$–MeOH–conc. NH_3 (3:3:1), detection by Dragendorff's reagent [R_f(1): solamargine 0.42; anguivine 0.34; isoanguivine 0.26] or Merck TLC plates RP-8 F_{254S}, MeOH–buffer soln (3:2; buffer soln: 50 g of NH_4OAc dissolved in 50 ml of H_2O, 560 ml of 1 M HCl and 720 ml of H_2O added, detection by I_2 vapour) [R_f(2): solamargine 0.36; anguivine 0.33; isoanguivine 0.36]. Analytical HPLC: Eurosil Bioselect 100-10 C8, 250 × 4 mm, 8.2 MPa, 1 ml min^{-1}, detection at 210 nm, MeOH–buffer soln [1:1, buffer soln: 0.1 M $(NH_4)H_2PO_4$, H_3PO_4 added to pH 3], RR_t related to solanine (RR_t: solamargine 1.71; anguivine 1.82; isoanguivine 1.58).

Table 1. ^{13}C NMR of alkaloids **2–6** (pyridine-d_5, TMS, 76 MHz)

	C	2	3*	4	5*	6
Aglycone	1	37.8	37.5	37.4	37.5	37.5
	2	32.40[a]	30.1	30.0	30.2	30.1
	3	71.3	77.7	77.7	77.5	77.5
	4	43.5	38.7	38.6	38.8	38.8
	5	141.9	140.7	140.7	140.8	140.9
	6	121.0	121.9	121.8	121.7	121.7
	7	32.6	32.6	32.3	32.6	32.4
	8	31.6	31.7	31.5	31.7	31.5
	9	50.4	50.3	50.3	50.3	50.3
	10	37.0	37.2	37.1	37.2	37.1
	11	21.2	21.2	21.1	21.1	21.1
	12	40.5	40.1	40.4	40.1	40.4
	13	40.8	40.6	40.7	40.6	40.8
	14	56.7	56.7	56.6	56.6	56.6
	15	32.36[a]	32.4	32.3	32.4	32.4
	16	79.2	78.9	79.2	78.8	79.2
	17	62.9	63.5	62.9	63.5	62.9
	18	16.7	16.5	16.6	16.5	16.6
	19	19.5	19.4	19.3	19.4	19.32[a]
	20	34.5	41.6	34.5	41.6	34.5
	21	15.3	15.7	15.2	15.7	15.2
	22	101.0	98.3	101.0	98.3	101.0
	23	69.2	34.6	69.1	34.6	69.1
	24	41.2	31.0	41.1	31.0	41.2
	25	32.1	31.6	32.0	31.6	32.1
	26	47.1	48.0	47.0	48.0	47.0
	27	19.4	19.8	19.3	19.8	19.29[a]
Rhamnose	1		102.4	102.3	102.2	102.2
	2		72.4	72.4	72.5	72.5
	3		72.8	72.8	72.8	72.9
	4		74.1	74.0	74.1	74.2
	5		69.4	69.4	69.4	69.4
	6		18.7	18.6	18.6	18.6
Xylose	1		105.4	105.4	106.8	106.8
	2		74.6	74.6	75.0	75.0
	3		78.4	78.3	78.3	78.3
	4		70.7	70.6	70.3	70.3
	5		67.2	67.2	67.0	67.1
Glucose	1		99.9	99.9		
	2		77.9	77.8		
	3		88.2	88.1		
	4		69.6	69.6		
	5		77.3	77.3		
	6		62.3	62.3		
Galactose	1				100.4	100.5
	2				76.4	76.4
	3				85.0	85.0
	4				71.0	71.0
	5				74.7	74.7
	6				62.2	62.2

[a] May be exchanged.
* From ref. [3].

(23S)-23-*Hydroxyanguivine*, (23S,25R)-3β-{O-α-L-*rhamnopyranosyl*-(1 → 2)-O-[β-D-*xylopyranosyl*-(1 → 3)]-β-D-*glucopyranosyloxy*}-22αN-*spirosol*-5-*en*-23-ol (**4**). From MeOH–H_2O; yield 0.021%. Mp 215–222° (dec.). $[\alpha]_D^{22}$ −94.0° (pyridine, *c* 0.71). R_f (1) 0.34, R_f (2) 0.55, RR_f 0.55. ^1H NMR (300 MHz, pyridine-d_5, TMS): δ 0.81 (*d*, J = 6.0 Hz, H_3-27), 1.00 (*s*, H_3-18, H_3-19), 1.10 (*d*, J = 7.2 Hz, H_3-21), 1.74 (*d*, J = 6.0 Hz, H_3-6 of rhamnose), 3.67 (*dd*, J = 10.7 and 10.7 Hz, H-5a of xylose), 3.84 (*m*, H-5 of glucose), 3.96 (*dd*, J = 8.8 and 8.8 Hz, H-2 of xylose), 4.87 (*m*, H-2 of rhamnose), 4.97 (*d*, J = 6.9 Hz, H-1 of glucose and

xylose), 5.29 (*d*, $J = 5.2$ Hz, H-6), 6.32 (*s*, H-1 of rhamnose). ^{13}C NMR: Table 1. ESI-MS (positive ion): 870 $[M+H]^+$.

(23S)-23-*Hydroxyisoanguivine*, (23S,25R)-3β-{O-α-L-*rhamnopyranosyl*-(1 → 2)-O-[β-D-*xylopyranosyl*-(1 → 3)]-β-D-*galactopyranosyloxy*}-22αN-*spirosol*-5-*en*-23-ol (**6**). From MeOH–H_2O needles; yield 0.007%. Mp 225–230° (dec.). $[\alpha]_D^{26}$ −90.1° (pyridine, *c* 0.56). $R_f(1)$ 0.26, $R_f(2)$ 0.59, RR_t 0.51. ^{1}H NMR (300 MHz, pyridine-d_5, TMS): δ 0.81 (*d*, $J = 6.0$ Hz, H_3-27), 1.00 (*s*, H_3-18, H_3-19), 1.10 (*d*, $J = 7.1$ Hz, H_3-21), 1.67 (*d*, $J = 6.0$ Hz, H_3-6 of rhamnose), 3.62 (*dd*, $J = 11.0$ and 9.8 Hz, H-5a of xylose), 3.90 (*dd*, $J = 8.0$ and 8.0 Hz, H-2 of xylose), 3.97 (*m*, H-3), 4.51 (*m*, H-16), 4.59 (*dd*, $J = 9.2$ and 3.4 Hz, H-3 of rhamnose), 4.72 (*dd*, $J = 9.5$ and 7.9 Hz, H-2 of galactose), 4.78 (*d*, $J = 3.0$ Hz, H-4 of galactose), 4.90 (*m*, H-2 of rhamnose), 5.28 (*d*, $J = 5.2$ Hz, H-6), 6.29 (*s*, H-1 of rhamnose). ^{13}C NMR: Table 1. ESI-MS (positive ion): 870 $[M+H]^+$.

Acknowledgements—This work was supported by the Ministerium für Bildung, Wissenschaft, Forschung und Technologie, Bonn. We are grateful to Mrs I. Knolle for technical assistance and Dr A. Porzel for NMR and Mrs I. Horn for mass spectrometry measurements. We thank the Botanical Garden of Besançon for the supply of seeds.

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