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3-DESAMINO-3β-HYDROXYSOLANOCAPSINE—A STEROIDAL ALKALOID FROM *SOLANUM ACULEATUM**

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Key Word Index—*Solanum aculeatum*; Solanaceae; steroidal alkaloids; 3-desamino-3β-hydroxysolanocapsine.

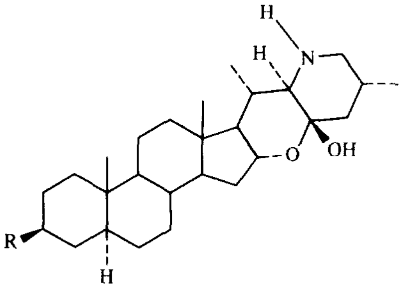
Abstract—A new steroidal alkaloid has been obtained from roots of *Solanum aculeatum* and its structure elucidated by IR, NMR and mass spectral studies as 3-desamino-3β-hydroxysolanocapsine.

Steroidal alkaloids of the solanocapsine type are very seldom found in the plant kingdom. Up to now, solanocapsine (**1**) has been isolated from *Solanum pseudocapsicum*, *S. capsicastrum*, *S. hendersonii* [1] and *S. tucumanense* [2], solacasine from *S. pseudocapsicum* [3] and solanoforthine from *S. seaforthianum* [3]. We now report the isolation and structure elucidation of the new alkaloid 3-desamino-3β-hydroxysolanocapsine (**2**) from *Solanum aculeatum* Jacq., an endemic species from Cuba.

Acid hydrolysis of the glycosidic mixture obtained in the methanol extracts of dried roots followed by Si gel chromatography yielded 0.01 % of the new alkaloid, $C_{27}H_{45}NO_3$ (M^+ found 431.3370; calc. 431.3399) mp 204°. Its IR spectrum showed the presence of hydroxyl groups (3400–3550 cm^{-1}). The high resoluted EIMS exhibited the same fragmentation pattern as solanocapsine [4] for the D–F rings with ions at *m/z* 179, 168, 157, 142, 139, 130, 112, 84 (bp) and 70. However, the ions at *m/z* 431, 413 and 398 appear one unit higher. These data, together with the lack of the fragment at *m/z* 56 characteristic of 3β-aminosteroids [4, 5], suggested a substitution of the 3β-amino group of solanocapsine by a hydroxyl group for the new alkaloid.

Also, the 200 MHz ^1H NMR spectrum of **2** was very similar to that reported for solanocapsine [2] but showed a well-defined seven-line signal at δ 3.54 typical for the axial H-3α of a 3β-hydroxy-5α-steroid [6].

In the ^{13}C NMR spectrum of **2** signal assignments were carried out by means of the SFORD spectrum and by comparison (Table 1) with the published data of tomatidine and solanocapsine (cf. refs. [3, 7, 8]). The chemical shift values of the ring A and B carbon atoms were in good agreement with the corresponding data for tomatidine. The remaining signals in the spectrum of **2** correspond to those of ring C–F carbon atoms of solanocapsine and were assigned in the same way with the exception of C-15 and C-25, the assignments of which were reversed due to the multiplicities of the SFORD spectrum.



1 R = NH_2
2 R = OH

All these data suggest the alkaloid to be 3-desamino-3β-hydroxysolanocapsine (22,26-epimino-16α,23-epoxy-5α, 22α*H*,25β*H*-cholestan-3β,23β-diol, **2**). This was finally confirmed by direct comparison with a synthetic sample obtained earlier from solanocapsine [3]. In addition to **2**, the known alkaloid 25-isosolafloridine [3] was isolated in 0.15 % yield.

EXPERIMENTAL

S. aculeatum Jacq. was collected in Guantanamo (Cuba) and identified by M. Sc. A. Areces. A voucher specimen is kept in the Herbarium of the National Botanical Garden of Cuba, Havana.

Isolation. Dried and powdered roots (1.2 kg) were extracted successively with $CHCl_3$ and with MeOH in a Soxhlet. The MeOH soln was concd to dryness under red. pres. and the residue was dissolved in 20 % HOAc and extracted × 3 with C_6H_6–Et_2O to remove pigments. The aq. layer was basified with NH_3, the glycosidic mixture extracted with EtOH and the obtained soln concd to dryness under red. pres. The residue was refluxed with 1 N HCl for 2.5 hr and poured into water. The aglycones were

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*Part 111 in the series "Solanum Alkaloids". For Part 110 see ref. [2].

Table 1. ^{13}C NMR chemical shifts of 3-desamino-3β-hydroxysolanocapsine (**2**), [50.33 MHz, δ-values (ppm) measured from the central line ($CDCl_3$) and calculated relative to TMS: $\delta_{TMS} = \delta_{CDCl_3} + 77.0$ ppm].

Carbon No.		Carbon No.		Carbon No.	
1	36.8 (*t*)	10	35.6 (*s*)	19	12.3 (*q*)
2	31.5* (*t*)	11	20.5 (*t*)	20	33.0 (*d*)
3	71.3 (*d*)	12	39.2 (*t*)	21	15.1 (*q*)
4	38.2 (*t*)	13	41.8 (*s*)	22	68.8 (*d*)
5	45.0 (*d*)	14	54.8 (*d*)	23	96.0 (*s*)
6	28.6† (*t*)	15	28.4† (*t*)	24	46.2 (*t*)
7	31.8* (*t*)	16	74.5 (*d*)	25	30.0 (*d*)
8	34.9 (*d*)	17	60.4 (*d*)	26	55.0 (*t*)
9	54.8 (*d*)	18	13.6 (*q*)	27	18.7 (*q*)

*, †Values bearing the same sign may be interchanged.

extracted with $CHCl_3$–EtOH (19:1). Evaporation of the organic phase gave a residue which was chromatographed over Si gel (Merck). The progress of the separation was followed by TLC on Si gel (Merck) ($CHCl_3$–MeOH, 9:1). Elution with $CHCl_3$–MeOH (17:3) gave 3-desamino-3β-hydroxysolanocapsine (**2**). Needles (MeOH–H_2O) mp 204°, $[\alpha]_D^{25} + 20.1°$ ($CHCl_3$; *c* 1). EIMS 70 eV *m/z* (rel. int.): 431 $[M]^+$ (6), 413 $[M - H_2O]^+$ (22), 398 $[M - Me]^+$ (12), 179 (5), 168 (7), 157 (50), 142 (25), 139 (20), 130 (58), 112 (24), 84 (100) and 70 (52); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ0.72 (*s*, H_3-18), 0.79 (*s*, H_3-19), 0.85, 0.92 (*d* × 2, each $J = 6.5$ Hz, H_3-27 and H_3-21), 3.54 (*septet*, H-3α), 4.45 (*m*, H-16β). Further spectral data in the test.

25-*Isosolafloridine.* This alkaloid was obtained (0.15%) on elution of the Si gel column with $CHCl_3$–MeOH (9:1). Needles (Me_2CO) mp 165°. IR ν_{max}^{nujol} cm^{-1}: 3500 (OH), 1650 ($>C{=}N$). The compound was found to be identical in every aspect with a synthetic [3] specimen.

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