Phytochemistry, Vol. 27, No. 9, pp. 3031–3032, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00

SOLANUDINE, A STEROIDAL ALKALOID FROM *SOLANUM NUDUM*

A. USUBILLAGA

Instituto de Investigación, Facultad de Farmacia, Universidad de Los Andes, Mérida, Venezuela

(*Received* 2 *December* 1987)

Key Word Index—*Solanum nudum*; solanaceae; steroidal alkaloid; solanudine.

Abstract—The structure of solanudine, a new steroidal alkaloid isolated from green berries of *Solanum nudum*, was determined on the basis of spectral data to be (22*R*, 23*S*, 25*R*)22,26-epimino-4,23-dihydroxycholest-4-en-3-one.

The title plant is a small tree native to the Venezuelan Andes. Solanudine (**1a**), presented IR absorption for hydroxyl (3580, 3430 cm^{-1}) and α,β-unsaturated ketone groups (1650 cm^{-1}). No molecular ion peak was observed in its mass spectrum but the parent peak at *m/z* 114 was indicative of a hydroxy-methyl-piperidine side chain [1]. An explanation for the unusually low frequency of the carbonyl band was found in the UV spectrum which showed strong absorption at 278 nm (log ε 4.3); this absorption agrees with the calculated maximum (279 nm) for an enone with an exocyclic double bond and an hydroxyl substituent at the α-carbon [2]. The ^1H NMR spectrum did not show any olefinic protons but the ^{13}C NMR spectrum showed two sp^2 carbons at δ 140.9 and 141.4 which were assigned to C-4 and C-5. The other ^{13}C NMR values agreed quite well with those found for deacetoxysolaphyllidine (A. Usubillaga, unpublished results).

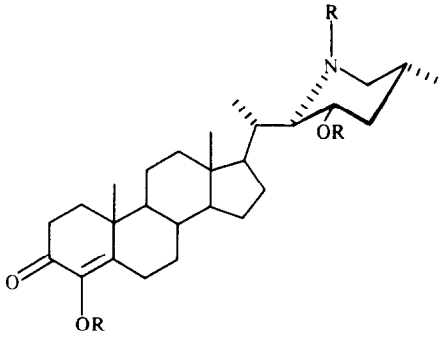
A mild acetylation of **1a** yielded the *O*,*N*-triacetyl derivative (**1b**). The ^1H NMR spectrum of **1b** showed two *O*-acetyl and one *N*-acetyl group. The mass spectrum showed the molecular ion at *m/z* 555 ($C_{33}H_{45}NO_5$), the most aaundant fragments at *m/z* 198 (71%) and 156 (100%) indicated the conversion of the side chain to an *O*,*N*-diacetyl derivative.

Based on these evidences a 22,26-epimino-4,23-dihydroxycholest-4-en-3-one structure is proposed for this alkaloid. Considering that compound **1a** is a probable biological precursor of solaphyllidine and related alkaloids [3, 4], the configurations of the side chain chiral centres should be 22*R*, 23*S* and 25*R*. A comparison of the ^{13}C NMR spectra of **1a** and **1b** with those of some 4-keto steroidal alkaloids and their acetylated derivatives supports this proposition. Several biologically active compounds which possess a similar enone moiety have been reported, like cucurbitacine E [5], α- and β-pipitzol [6], and taxodione [7].

EXPERIMENTAL

Mps: uncorr. The ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ soln with TMS as int. standard.

Isolation of solanudine (**1a**). Green berries of *S. nudum* (2 kg fr. wt) were collected at La Soledad (Merida, Venezuela) in April 1986. A voucher specimen is kept at the MERF Herbarium. The juice was shaken with $CHCl_3$. The $CHCl_3$ extract was conc under vacuum and the residue was dissolved in MeOH. Compound **1a** crystallized as needles mp 225°, $[\alpha]_D^{23}$ 352° (*c* 1.02, dioxane). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH) and 1650 (CO). MS: $[M]^+$ not visible, *m/z* 114 (base peak, $C_6H_{12}NO$). UV λ_{max}^{EtOH}: 278 nm (4.3). ^1H NMR: δ 0.75 (3H, *s*, H_3-18), 0.86 (3H, *d*, $J = 7$ Hz, H_3-27), 0.91 (3H, *d*, $J = 7$ Hz, H_3-21), 1.17 (3H, *s*, H_3-19), 2.95 (1H, *d*, $J = 10$ Hz, H-22). ^{13}C NMR: see Table 1.



1a R = H
1b R = Ac

Table 1. ^{13}C NMR chemical shifts of solanudine (**1a**) and its *O*, *N*-triacetate (**1b**)

C	1a	1b
1	34.4	34.7
2	31.8	33.3
3	193.2	190.4
4	141.1	155.8
5	140.5	139.1
6	22.9	24.1*
7	30.9	30.8
8	33.2	35.1
9	54.3	53.7
10	37.3	39.0
11	20.9	21.0
12	39.4	39.4
13	42.1	42.8
14	53.9	53.7
15	24.0	24.3*
16	27.3	28.4
17	55.6	55.5
18	11.5	12.2
19	17.0	17.6
20	35.1	35.1
21	12.1	14.5
22	63.3	60.7
23	66.9	71.0
24	42.8	37.8
25	31.1	30.1
26	52.9	54.3
27	18.5	19.7
4 (O–Ac)	—	171.5
	—	20.1
23(O–Ac)	—	168.5
	—	20.6
N–Ac	—	170.2
	—	21.0

* Could be exchanged.

Solanudine acetate (**1b**). Mild acetylation of **1a** yielded **1b**, mp 162–165°. UV λ_{max}^{EtOH}: 244 nm (3.99). MS: *m/z* 555 (M^+, $C_{33}H_{49}NO_6$, 0.1%), 198(71), 156(100). ^1H NMR: δ 0.70 (3H, *s*, H_3-18), 0.82 (3H, *d*, $J = 7$ Hz, H_3-27), 1.03 (3H, *d*, $J = 7$ Hz, H_3-21), 1.20 (3H, *s*, H_3-19), 2.00 (3H, *s*, C-23 O-Ac), 2.09 (3H, *s*, N-Ac), 2.20 (3H, *s*, C-4 O-Ac), 3.25 (1H, *m*, H-22), 5.05 (1H, *m*, H-23). ^{13}C NMR: see Table 1.

Acknowledgements—The author is indebted to Consejo de Desarrollo Científico, Humanístico y Tecnológico of the University of Los Andes, for financial support, and to Mr Jaime Bautista for his kind help in the collection of the plant. I would also like to thank Mrs C. E. Benitez (UCV-Maracay) for the botanical identification and Dr T. Nakano of IVIC (Caracas) for optical rotation measurements.

REFERENCES

1. Budzikiewicz, H. (1964) *Tetrahedron*, **20**, 2267.
2. Fieser, L. F. and Stevenson, R. (1954) *J. Am. Chem. Soc.* **76**, 1728.
3. Usubillaga, A., Seelkopf, C., Karle, J., Dale, J. and Witkop, B. (1973) *J. Am. Chem. Soc.* **92**, 700.
4. Usubillaga, A. (1984) *J. Nat. Prod.* **47**, 52.
5. Kupchan, S. M., Gray, A. H. and Grove, M. D. (1967) *J. Med. Chem.* **10**, 337.
6. Walls, F., Padilla, J., Joseph-Nathan, P., Giral, F., Escobar, M. and Romo, J. (1966) *Tetrahedron* **22**, 2387.
7. Kupchan, S. M., Karim, A. and Marcks, C. (1969) *J. Org. Chem.* **34**, 3912.