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SOLADUNALINIDINE, A NEW STEROIDAL ALKALOID FROM *SOLANUM DUNALIANUM*

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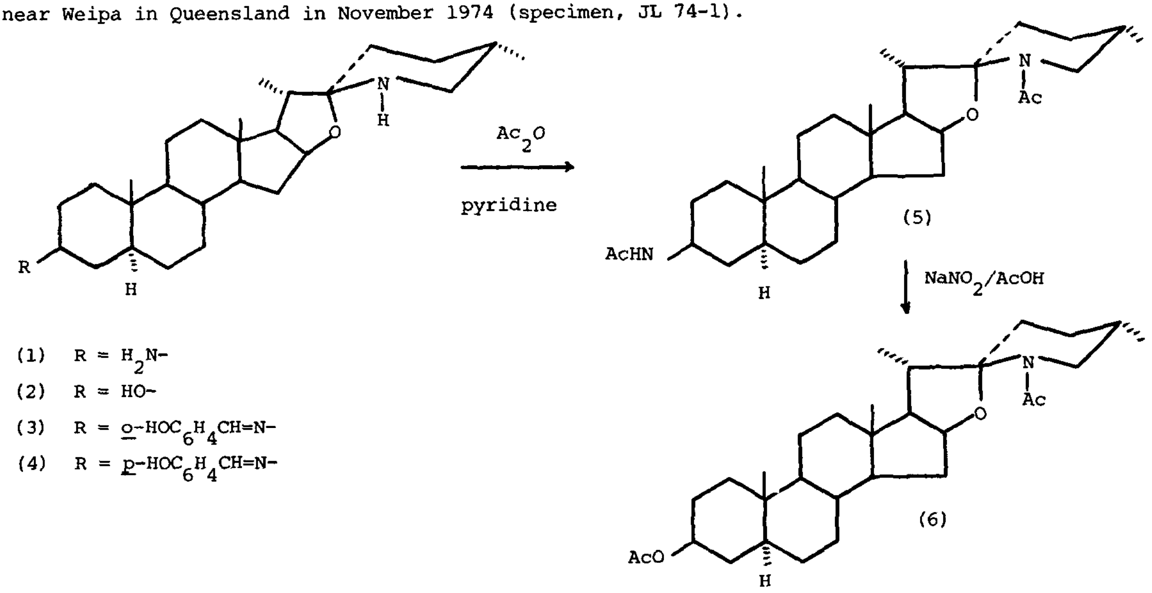
A new steroidal alkaloid, soladunalinidine (1) has been obtained by counter-current distribution of the crude aglycone extract from *Solanum dunalianum* Gaud., which was collected near Weipa in Queensland in November 1974 (specimen, JL 74-1).



(5)

(6)

(1) R = H_2N-
(2) R = HO-
(3) R = o-HOC_6H_4CH=N-
(4) R = p-HOC_6H_4CH=N-

Soladunalinidine (1) $C_{27}H_{46}N_2O$, was obtained as a colourless non-crystalline solid, m.p. 145-153°, $[\alpha]_D^{35}$ + 1.30° (c, 0.46 in $CHCl_3$). The infrared spectrum showed strong absorption at 3420 cm^{-1} (NH), and the 90 MHz p.m.r. spectrum showed a singlet at δ 0.82 (18-Me, 19-Me); doublets at 0.85 (27-Me) and 0.96 (21-Me); an apparent doublet at 2.73 for the protons at C-26 and multiplets at 3.01 (H3α) and 4.14 (H16α), the spectrum being similar to that of tomatidine (2). The mass spectrum showed a molecular ion m/e 414 and fragmentation peaks at m/e 138 and 114, consistent with a spirosolane structure.[1] It formed a picrate, m.p. 235-255° d., and the formation of a salicylidene derivative (3), m.p. 227-229°, $[\alpha]_D^{35}$ + 18.1° (c, 0.96 in $CHCl_3$); λ_{max} (EtOH) 224 (ϵ 15900), 255 (ϵ 12860), 316 (ϵ 4100), 400 nm (ϵ 1070); ν_{max} (Nujol) 1620, 1600, 1570, 1490, 750 cm^{-1}, and a p-hydroxybenzylidene derivative (4), m.p. 238-240°, $[\alpha]_D^{35}$ + 12.2° (c, 1.10 in $CHCl_3$); λ_{max} (EtOH) 220 (ϵ 11620), 271 (ϵ 18660), 384 nm (ϵ 4190); ν_{max} (Nujol) 3100, 1610, 1580, 1490, 810 cm^{-1}, confirmed the presence of a primary amino group. Acetylation of soladunalinidine gave the diacetyl derivative (5), m.p. 286-288°, $[\alpha]_D^{35}$ + 4.6° (c, 0.66 in $CHCl_3$); ν_{max} (Nujol) 3280 (NH), 1660 (NAc), and 1620 and 1540 cm^{-1} (NHAc). The tentative assignment of the 22.62 MHz ^{13}C m.r. spectrum of soladunalinidine* is as follows, with carbon atom number followed by chemical shift (p.p.m. with respect to $SiMe_4$): 1, 38.0;

2, 32.5; 3, 51.5; 4, 39.4; 5, 45.7; 6, 29.1; 7, 32.5; 8, 35.3; 9, 54.6; 10, 35.8; 11, 21.3; 12, 40.5; 13, 41.1; 14, 56.0; 15, 32.9; 16, 78.8; 17, 62.4; 18, 17.1; 19, 12.5; 20, 43.0; 21, 16.1; 22, 99.4; 23, 27.0; 24, 29.0; 25, 31.4; 26, 50.5; 27, 19.7. The chemical shifts for all carbon atoms correspond to those of tomatidine (2)[2,3] except those in ring A. This indicated that soladunalinidine (1) has the same structure as tomatidine (2) except that a 3-amino group is substituted for the 3-hydroxyl group. This was confirmed by a comparison of the chemical shift values for the carbon atoms of ring A with those for 3β-amino-5α-cholestane. The C.D. of the salicylidene derivative (3), measured in dioxan showed positive Cotton effects at 253 nm (Δε + 1.3) and at 316 nm (Δε + 0.8), consistent with published data for derivatives of 3β-amino-steroids.[4]

Verification of the structure was achieved by a chemical correlation between soladunalinidine (1) and tomatidine (2). Diacetylsoladunalinidine (5) was nitrosated with sodium nitrite in acetic acid and the product underwent a rearrangement to eliminate N_2, giving a mixture of alkenes and O-acetates. O,N-Diacetyltomatidine (6) was isolated from the mixture and its identity confirmed by comparison with an authentic sample.

Soladunalinidine is the first naturally occurring 3-aminospirosolane isolated from a *Solanum* species. The other known dibasic *Solanum* alkaloids are solanocapsine,[5] solacasine,[6] solacallinidine,[7] and solanogantine.[8]

Acknowledgments

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References

* The solvent used was d^5-pyridine.

1. H. Budzikiewicz, Tetrahedron, 20, 2267 (1964).
2. R. J. Weston, Hugo E. Gottlieb, E. W. Hagaman, and E. Wenkert, Aust. J. Chem., 30, 917 (1977)
3. R. Radeglia, G. Adam, and H. Ripperger, Tetrahedron Lett. (No. 11), 903 (1977).
4. H. E. Smith, E. P. Burrows and Fu-Ming Chen, J. Org. Chem., 41, 704 (1976).
5. K. Schreiber, and H. Ripperger, Tetrahedron Lett. (No. 27), 9 (1960).
6. L. A. Mitscher, J. V. Juvarkar, and J. L. Beal, Experientia, 32, 415 (1976).
7. G. J. Bird, D. J. Collins, F. W. Eastwood, B.M.K.C. Gatehouse, A. J. Jozsa and J. M. Swan, Tetrahedron Lett. (No. 40), 3653 (1976).
8. S. C. Pakrashi, A. K. Chakravarty and E. Ali, Tetrahedron Lett. (No. 7), 645 (1977).