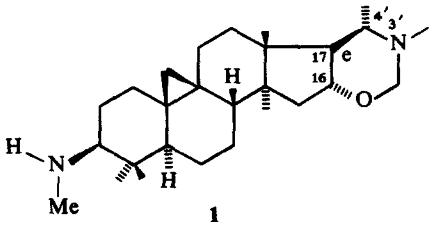
suggesting some modification of the α-amino-C_{17}-side chain of the pregnane backbone. The arguments presented, biogenetic considerations and the requirement for 6 loci of unsaturation would allow postulation of the structural formula of the base under investigation as being **1**.

To verify this suggestion the **1** was hydrogenized to afford cyclovirobuxine-C [8] (**2**) identical in all respects with the authentic specimen. This experiment produced evidence not only the correctness of the proposed structure, but also proof of the stereochemical arrangement of the alkaloid designated buxozine-C. The semisystematic name of this alkaloid of a new type is (4′S)-3′,4,4,4′,14α-pentamethyl-3β-methylamino-9,19-cyclo-5α-androstano-[16β,17α-e] tetrahydro-13-oxazine.



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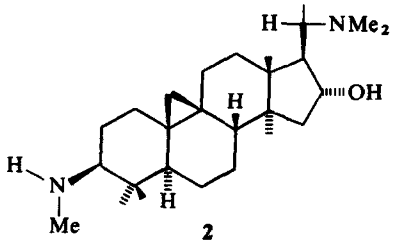

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SOLAQUIDINE, A NEW STEROIDAL ALKALOID FROM *SOLANUM PSEUDOQUINA*

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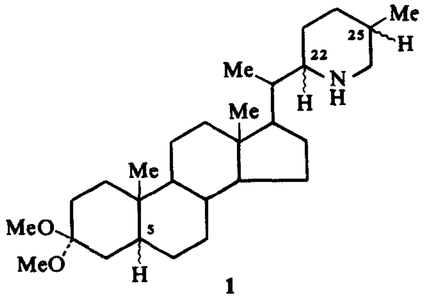
Key Word Index—*Solanum pseudoquina*; Solanaceae; fruits; *3,3-dimethoxy-22,26-epiminocholestane*; stereoidal alkaloids.

Solanum pseudoquina St. Hil was identified by Alfredo Paredes, and a voucher kept at Escuela Politécnica, Quito; trivial name, pululo. This was obtained from the Ecuadorian Andes, on the outskirts of Quito. In previous work, tests have been made for steroidal alkaloids [1]. In the present work green berries of this plant were crushed and extracted with MeOH. Chromatography of the alkaline $CHCl_3$ extract yielded solaquidine (**1**) as colourless needles, mp 278–281°. The PMR spectrum showed the presence of two OMe groups, (δ 3.10 and 3.15), a most unusual feature in steroidal *Solanum* alkaloids. The MS showed a parent peak at *m/e* 444. Since an elementary analysis indicated the presence of only one N the true MW was established as 445 ($C_{29}H_{51}NO_2$). The base peak at *m/e* 98 showed the presence of a Me piperidine side chain [2], and the two very abundant fragments at *m/e* 101 (60%) and *m/e* 127 (32%) indicated that both OMe groups were located at C-3. It has been demonstrated that an ethylene ketal function at C-3 produces mainly fragments at *m/e* 99 and 125, if rings A and B of a steroid are not substituted [3]. Since solaquidine has two OMe groups at C-3 instead of an ethylene ketal, the fragmentation proceeds in a similar manner, but it produces fragments two a.m.u. greater, *m/e* 101 instead of 99, and *m/e* 127 in place of 125. The fact that both OMe groups are attached to the same carbon produces some shielding and explains why these protons appear at higher field than normally expected. The IR of the acetate (**2**) showed a strong *N*-



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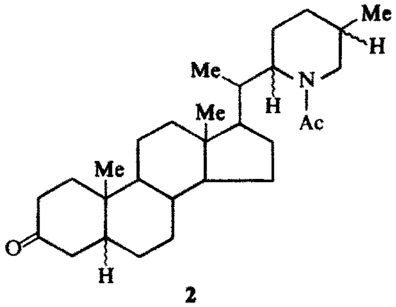
acetyl band at 1630 cm^{-1} and a ketone band at 1710 cm^{-1}. The PMR spectrum of **2** showed no OMe bands and only one *N*-acetyl group at 2.09. The shift of the angular C-19 Me resonance from δ 0.78 to 0.99 agreed with the presence of a ketone at C-3 [4]. The MS of **2** confirmed the absence of the two OMe groups since it showed an M$^+$ at *m/e* 441 ($C_{29}H_{47}NO_2$) and no fragments at either *m/e* 101 or 127. Based on these data a 3,3-dimethoxy-22β,25ξ-22,26-epimino-5ξ-cholestane structure (**1**) was assigned to solaquidine. The small amount of material isolated did not permit the determination of the absolute configuration at C-5, C-22, and C-25.



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EXPERIMENTAL

Mps are not corrected. IR spectra were recorded as KBr pellets, PMR (60 MHz) spectra were determined in $CDCl_3$ with TMS as internal standard. MS were recorded by Mrs. M. Hazos at I.V.I.C. (Caracas) and the elementary analysis were performed by A. Bernhard, Analytical Laboratories.

Isolation. Green berries (4 kg) were crushed and extracted several times with cold MeOH, the extract was concd under vacuum and the last traces of MeOH eliminated by steam distillation. Dil. HCl was added and the solid residue removed by centrifugation. The supernatant was made alkaline with NH_3 and the precipitated alkaloids redissolved in MeOH–H_2O. Extraction with $CHCl_3$ and subsequent evaporation yielded 3.1 g of crude alkaloids which were chromatographed on Si gel (150 g). The column was eluted with $CHCl_3$–EtOH–NH_4OH (2.2 1), 100 ml fractions were taken. Fractions 6 and 7 contained solaquidine (**1**) 27 mg, mp 278–281° (from MeOH); ν_{max} 1050 and 1100 cm^{-1}; PMR δ 0.69 (3H, *s*, C-18), 0.78 (3H, *s*, C-19), 0.92 (3H, *d*, $J = 7$ Hz, C-21), 1.1 (3H, *d*, $J = 7$ Hz, C-27) found. C, 77.56; H, 11.25; N, 2.97%; $C_{29}H_{51}NO_2$ requires: C, 78.20; H, 11.46; N, 3.15%. Electron impact (70 eV) MS, M$^+$ *m/e* 444, base peak *m/e* 98, fragments *m/e* 430, 414, 398, 316, 127 (32%) and 101 (60%). Field desorption MS shows a M$^+$ +1 peak at *m/e* 446. The acetate (**2**) was prepared (15 mg) with Ac_2O–C_5H_5N and purified on a small Al_2O_3 column. It crystallized from Me_2CO–C_6H_{14}, mp 129–134°, ν_{max} 1630 and 1710 cm^{-1}; PMR δ 0.7 (3H, *s*, C-18), 0.99 (3H, *s*, C-19), 0.86 (3H, *d*, $J = 7$ Hz, C-21), 0.92 (3H, *d*, $H = 7$ Hz, C-27), 2.09 (3H, *s*, N-COMe), 3.4 (2H, *m*); found: C, 77.95; H, 11.04; N, 3.05%; calculated for $C_{29}H_{47}NO_2$. C, 78.91; H, 10.66; N, 3.17%; M$^+$ *m/e* 441, fragments *m/e* 427, 398, 300, 140 (97%), and 98 (100%).

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