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SOLANOGANTINE, A NOVEL 3-AMINO-22βH-SOLANIDANE FROM SOLANUM GIGANTEUM

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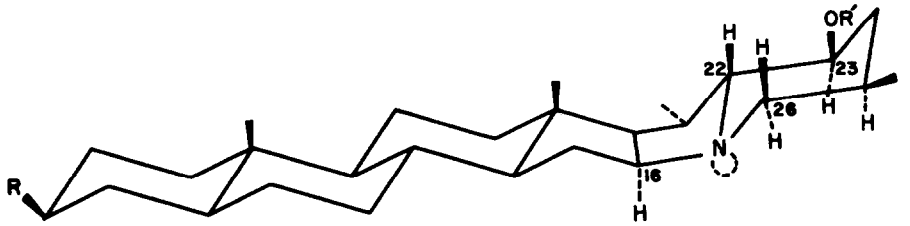
All the naturally occurring solanidanes so far isolated possess the same 16αH, 22αH stereochemistry with trans E/F ring fusion[1]. Herein we report the isolation of a new base, solanogantine, from the leaves of S.giganteum Jacq.[2], with the unusual 22βH configuration. Incidentally, this is also the first 3-amino solanidane encountered in nature.

Solanogantine (I), $C_{27}H_{46}N_2O$ (M^+, m/e 414), obtained as a glass, is best characterised as its N,N-dimethyl derivative (II), m.p. 111-112°, $[\alpha]_D$ +41.3° ($CHCl_3$), ν_{max}(nujol) 3300, 3120(OH) cm^{-1}, or the N,O-diacetyl derivative (III), m.p. 219-221°d, $[\alpha]_D$ +27.2° ($CHCl_3$), ν_{max}(nujol) 3200, 1640, 1550(NHAc), 1725, 1255 (OAc) cm^{-1}. The mass spectra of compounds I and II showed fragments[3] for 3-amino-5,6-dihydro steroids (m/e 56, 82 from I and m/e 84, 110 from II) and for solanidane skeleton with an OH group at ring E or F (m/e 166, 204). The NMR spectra (Fig.1) of compounds II and III showed that (a) the OH group is secondary, equatorial and located at C-23 and (b) one of the bridgehead protons (16-H or 22-H) is cis to the lone pair of electrons on nitrogen. It thus became apparent that the stereochemistry of solanogantine at the D/E/F ring junctions must be different from that of solanidane.

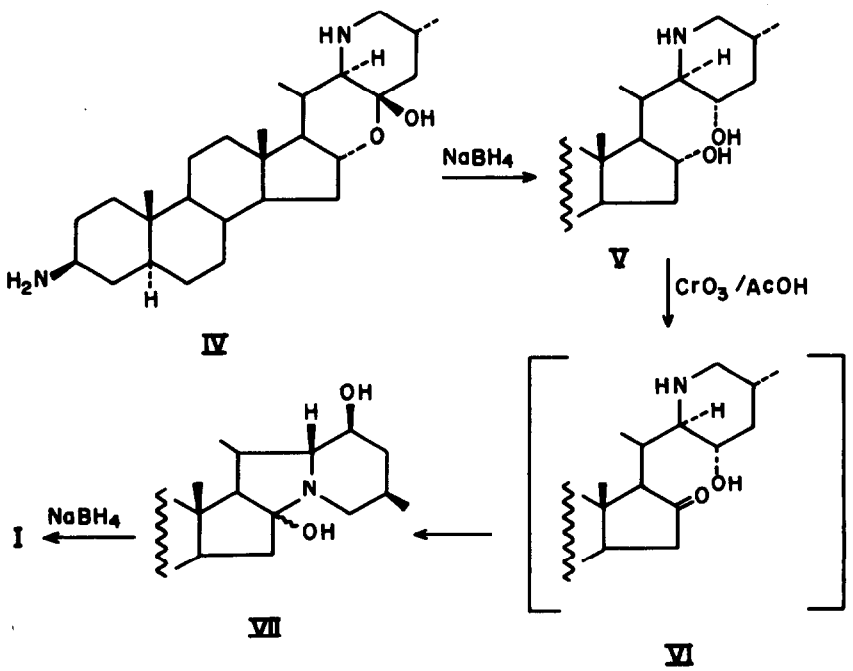
The structure I for solanogantine was then proved by its partial synthesis as follows from solanocapsine (IV), the structure and stereochemistry of which are well established[4]. Sodium borohydride reduction (EtOH, r.t.) of solanocapsine afforded the diol V, m.p. 287-289°d (N,N',O,O'-tetraacetate: etherate, m.p. 151-153°), the 23-OH group of which was assigned the equatorial orientation from mechanistic considerations. Oxidation of V with CrO_3/AcOH (r.t.) led to the hydroxy-ketone VI which was not fully characterised but from

its IR (no carbonyl absorption) and mass spectrum (no fragments arising by cleavage of C_{20}-C_{22}) could be concluded to exist in the carbinolamine from VII. Sodium borohydride reduction or catalytic hydrogenation of VII yielded solamogantine (I), the identity of which was established through the diacetate III. Since reduction of VII is expected to occur from the less hindered α side, this synthesis established the stereochemistry of I in all centres except that of N_b.

Since solamogantine (I) and the diacetate (III), unlike 22-isosolanidanes (22β<u>H</u> with <u>cis</u> E/F ring junction)[5], underwent facile mercuric acetate oxidation



I R = NH_2, R' = H II R = NMe_2, R' = H III R = NHAc, R' = Ac



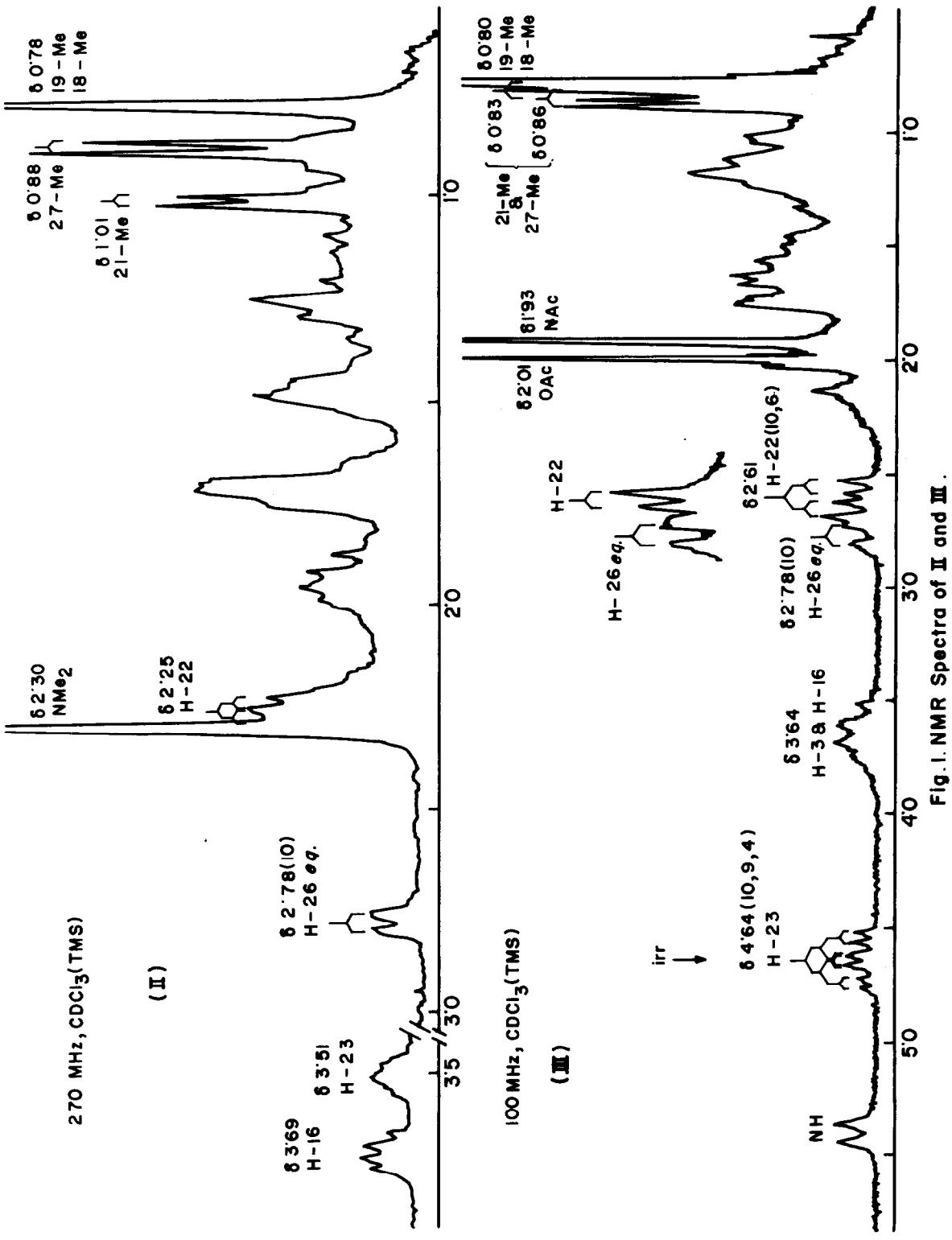


Fig. 1. NMR Spectra of II and III.

(50% AcOH, steam-bath temp.), the B/F ring junction must be trans. Such a stereochemistry is also compatible with the NMR spectra of II and III. Of the four -N-CH- protons on C-16, C-22 and C-26, the signals for two protons in case of II and for three protons in case of III are in the accessible regions of the spectra. A broad doublet (J_{gem} = 10 Hz) at δ 2.78 in both the spectra could be assigned to the equatorial proton at C-26. The signal for 22-H is masked by the N-Me signal in the spectrum of II but is obtained as a clear double doublet ($J_{22,23}$ = 10 Hz, $J_{20,22}$ = 6 Hz) at δ 2.61 in the spectrum of III. This assignment was confirmed by spin decoupling of 23-H. The chemical shift of this proton indicates that it could not be cis to the nitrogen lone pair. The third signal at δ 3.64 in III (δ 3.69 in II) must then be assigned to 16-H which from its abnormally down field chemical shift must be cis to the nitrogen lone pair[6].

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