STRUCTURE OF SOLAPARNAINE, A NEW SPIROSOLANE ALKALOID FROM THE GREEN BERRIES OF SOLANUM ASPERUM VAHL

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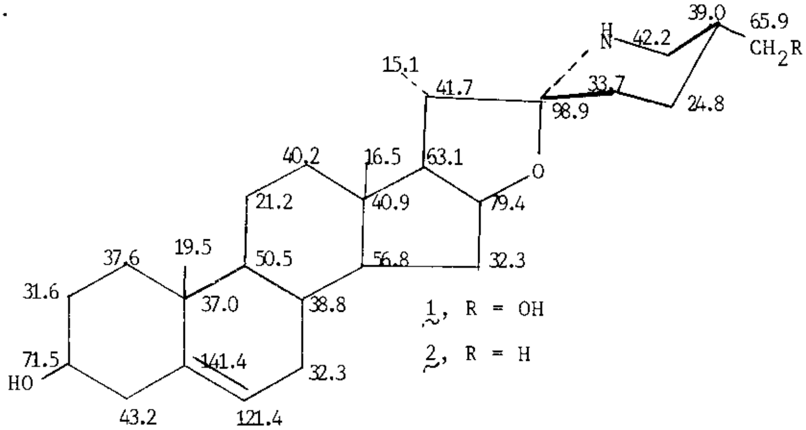
Abstract - The structure of a new spirosolane alkaloid, solaparnaine, isolated from the green berries of Solanum asperum Vahl as an aglycone has been determined mainly with the aid of ^{13}C NMR spectroscopy and MS.

During the search for a rich source of solasodine from the local species of Solanum, we isolated solaparnaine, $C_{27}H_{43}NO_3$, (M^+ 429), mp 228-230°C, $[\alpha]_D^{23}$ -77.8° (MeOH), along with spirosola-3,5-diene and the target compound from the green berries of Solanum asperum Vahl[1]. In this communication, we wish to report the structure of solaparnaine as 1 mainly with the aid of ^{13}C NMR spectroscopy and MS. Solaparnaine represents the first spirosolane alkaloid with oxygenation in the piperidine ring at C-27.



The IR spectrum of solaparnaine in KBr shows a broad absorption band at 3400 cm^{-1} for the OH along with characteristic bands at 975, 965, 910 and 884 cm^{-1} for a spiroaminoketal system[2].

The MS of solaparnaine shows, in addition to the molecular ion at 429, two abundant fragments at m/z 154 and 130 (100%). The molecular formula of solaparnaine shows the presence of an O-atom more than that of solasodine (2) which is corroborated by the appearance of the M^+ in the former at 429; 16 mass units higher than that of solasodine (M^+ 413). The presence of the fragments at m/z 154 and 130, both of which having 16 mass units higher than the typical fragments at m/z 138 and 114 (100%) for the spirosolane alkaloids such as solasodine (2)[2] indicates that the O-atom must be located at the piperidine ring (ring F) of solaparnaine.

The ^{13}C NMR spectrum of solaparnaine (20 MHz; $CDCl_3$/TMS) showed 26 signals for 27 carbons in the molecule; the signal at 32.3 ppm represents two carbons. The assignments of the chemical shifts (ppm) which are shown on structure 1 were made with the aid of complete and partially decoupled (SFORD) spectra, direct analysis of the non-protonated centers[3] and the attached proton test (ATP)[4]. The spectrum of solaparnaine shows the presence of three CH_3 groups instead of four, as are common in all the spirosolane alkaloids. The appearance of a triplet at 65.9 ppm for a primary carbinol carbon and the absence of one CH_3 group in the region of 19.0 ppm, characteristic of the C-27-CH_3 of the spirosolane alkaloids is obviously owing to the presence of a CH_2OH group at that position. This assignment is supported by the fact that the doublet for C-25 in solaparnaine is shifted downfield to 39.0 ppm instead of the usual chemical shift of 31.5 ppm in solasodine (2)[5] due to the β-effect of the C-27-OH group. Also, the triplets for C-24 and C-26 in solaparnaine are shifted upfield to 24.8 and 42.2 ppm respectively, from their usual positions at 30,4 and 47.7 ppm respectively, in solasodine[5] owing to the γ-effect of the C-27-OH group. Comparison of the rest of the chemical shifts of the carbons of solaparnaine with those of solasodine supports the (25R)-22αN-spirosola-5-en-3β,27-diol structure 1 for the former.

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