

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

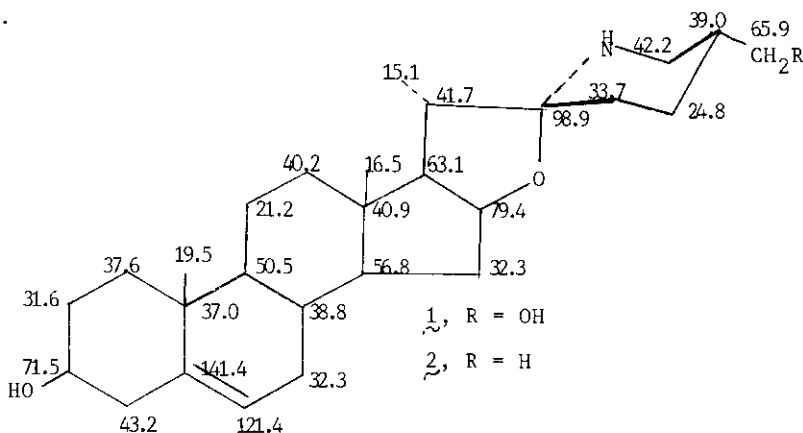
Jnanabrata Bhattacharyya

Laboratorio de Tecnologia Farmaceutica, Universidade Federal da Paraiba, 58.000

Joao pessoa, Paraiba, Brazil

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, $\text{C}_{27}\text{H}_{43}\text{NO}_3$, (M^+ 429), mp 228-230°C, $[\alpha]_D^{23} -77.8^\circ$ (MeOH), along with spirosola-3,5-diene and the target compound from the green berries of Solanum asperum Vahl¹. 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 system².

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 centers³ 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 solasodine⁵ 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)-22 α N-spirosola-5-en-3 β ,27-diol structure 1 for the former.

ACKNOWLEDGMENTS

The financial support of CNPq and FINEP is gratefully acknowledged. Thanks are due to Ms. Lucia d'Avila Freire de Carvalho and Maria de Fatima Agra for the identification of the plant material. We also thank Dulce Goncalves de Oliveira for technical assistance and Prof. Delby Fernandes de Medeiros, Director of the Laboratory for his encouragement.

REFERENCES

1. J. Bhattacharyya, J. Natl. Prod., 1984, 47, 1059.
2. H. Ripperger and K. Schreiber, 'The Alkaloids' ed. by R. G. A. Rodrigo, Academic Press, New York, 1981, vol. 19, p. 81.
3. E. Wenkert, A. O. Clouse, D. W. Cochran and D. Doddrell, J. Amer. Chem. Soc., 1969, 91, 6879.
4. S. L. Platt and J. N. Shoolery, J. Mag. Res., 1982, 46, 535.
5. G. J. Bird, D. J. Collins, F. W. Eastwood and R. H. Exner, Austr. J. Chem., 1979, 32, 783.

Received, 23rd August, 1985