STRUCTURE AND CONFIGURATION OF STENANZINE

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From the total alkaloids isolated by chloroform extraction of the epigeal part of Rhinopetalum stenantherum a new base has been isolated - stenanzine - with mp 203-205°C, [α]D --44 °C, C27H43NO3. On the basis of a study of the IR, NMR, and mass spectra of stenanzine and its conversion products the configuration and structure of 3β,23α-dihydroxy-5α-veratr-12-enin-6-one have been established for this alkaloid.

From the combined alkaloids obtained by the chloroform extraction of the epigeal part of Rhinopetalum stenantherum by chromatography on a column of alumina, a new alkaloid stenanzine with mp 203-205°C [α]D --44 °C, C27H43NO3, (I), has been isolated.

The IR spectrum of (I) shows absorption bands at (cm⁻¹) 3425-3125 (--OH, NH--), 2930-2830, 1475, 1455, 1420 (--CH3; --CH2--); 1713 (C=O). The mass-spectrometric fragmentation of stenanzine took place similarly to that of veratrmine: peaks were observed with m/z 96, 114 (100%), 115, 141, 256, 315, (M-1)+, 429 M+ [3-5].

The acetylation of stenanzine with acetic anhydride in pyridine yielded 0,0',N-triacetylstenanazine (II), the IR spectrum of which had absorption bands at (cm⁻¹) 1740, 1245 (C=O, ester); 1717 (C=O), and 1648 (N--COCH3) and no absorption bands of hydroxy groups. When 0,0',N-triacetylstenanazine was saponified in a methanolic solution of caustic soda, N-acetylstenanazine (III) was obtained with M+ 471. Its IR spectrum contained absorption bands at (cm⁻¹) 3450 (OH); 2970-2860, 1455, 1430 (--CH3; --CH2--); 1717 (C=O); and 1595 (N--COCH3), and the absorption bands of the ester carbonyl group had disappeared.

The reduction of stenanzine with sodium tetrahydroborate led to a dihydro derivative C27H43NO3 (IV), M+ 431. Details of the NMR spectra of (I) and (II) are given in Table 1.

A comparison of the NMR and mass spectra of stenanzine and of peimisine (V) (see Table) [3] shows that stenanzine belongs to the C-nor,D-homosteroid alkaloids of the jervine group [3-5]. The NMR spectrum of (I) shows the signals from two protons geminal to hydroxy groups at 3.76 ppm (br.s, W1/2 = 6 Hz) and 3.65 ppm (W1/2 = 22 Hz). Consequently, both hydroxy groups have a secondary nature, as was confirmed by the production of 0,0',N-triacetylstenanazine. In the mass spectrum of (I), together with the peak of the molecular ion with m/z 429, the peak of an ion with m/z 114 (100%) is also observed, which shows the position of one of the hydroxy groups in ring F [4, 5]. The hydroxy group may occupy one of the two possible positions at C23 and C24. Of these, from biogenetic considerations, the position at C23 is most suitable.

The position of the other secondary hydroxy group and of the carbonyl group was determined by comparing the chemical shifts of the 19-CH3 group of stenanzine (I) and its acetate with those of the 19-CH3 groups in the spectra of peimisine (V) and its acetyl derivative.
From the value of its chemical shift and the half-width of the C₃-H signal, the hydroxy group at C₃ is present in the equatorial orientation (C₃-H is α-axial). This is confirmed by the existence of a multiplet at 4.61 ppm from C-3aH in the NMR spectrum of 0,0',N-triacetylstenanzine [6, 7].

The signal of a second proton geminal to an acetoxy group at 5.04 ppm in the NMR spectrum of 0,0',N-triacetylstenanzine shows the axial orientation of the C₃₂-H group and the equatorial orientation of C₂₃-H [4, 8, 9]. The orientations of the methyl groups at C₂₀ and C₂₅ were determined on the basis of the following facts. The chemical shifts of the 21-CH₃ and 27-CH₃ groups of stenanzine and of peimisine are almost identical (see Table 1), which shows the identical orientations of these methyl groups [3, 9].

On the basis of the facts given, for stenanzine we propose as the most probable structure and configuration that of 3β,23α-dihydroxy-5α-veratr-12-enin-6-one [10].

The mass spectra of stenanzine and its derivatives confirmed the correctness of the proposed structure and permitted the structural features of similar compounds to be studied.

The fragmentation of stenanzine under electron impact forms the ions given in the following scheme: