DEOXYDELCORINE – A NEW ALKALOID FROM Delphinium corumbosum

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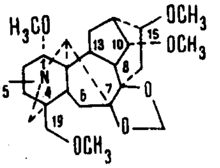
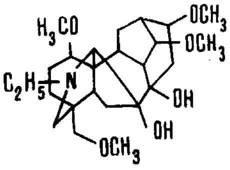
We have previously reported the isolation from Delphinium corumbosum of a base $C_{26}H_{41}NO_6$ with mp 93-95°C [1]. The alkaloid contains a N-ethyl group (3 H, triplet at 1.01 ppm), four methoxy groups (3 H, singlets at 3.22, 3.25, 3.30, and 3.36 ppm), and a methylenedioxy group (1 H, singlets at 4.86 and 4.96 ppm). The closeness of the NMR and mass spectra of this base and delcorine, the absence in the IR spectra of the former of the absorption band of hydroxy groups, and also the difference in their molecular weights by 16 amu permitted the assumption that the base is deoxydelcorine, i.e., it differs from delcorine by the absence of the hydroxy group. The mass spectrum of deoxydelcorine (I) is characteristic for alkaloids with the lycoctonine skeleton and the maximum peak is that of an M−31 ion, which shows the presence of a methoxy group at C_1 [2].

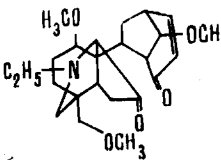
The presence in the NMR spectrum of the alkaloid of a one-proton triplet at 3.6 ppm with a coupling constant of ~5 Hz enables the second methoxy group to be placed at C_{10} and, at the same time, excludes the location of any substituents at C_9 and C_{11} [3, 4]. Heating (I) with 10% sulfuric acid gave demethylenedeoxydelcorine (II) $C_{25}H_{41}NO_6$, in the NMR spectrum of which there are no signals of the protons of a methylenedioxy group. When demethylenedeoxydelcorine was oxidized with one mole of periodic acid, compound (III), $C_{24}H_{35}NO_6$, was obtained with an IR spectrum showing the absorption bands of carbonyl groups in a five-membered ring (1730 cm^{-1}) and in a six-membered ring (1680 cm^{-1}). Analysis of the mass spectrum (M 417) and of the NMR spectrum (3 H, singlet at 3.13 ppm, and 6 H, singlet at 3.21 ppm; 3 OCH_3) shows that as a result of the reaction, in addition to the cleavage of the diol system, the elimination of a molecule of methanol takes place. Features of the UV spectrum ($\lambda_{max}^{C_2H_5OH}$ 228 nm; log ε 3.8) and the IR spectrum 1680 cm^{-1}) show that the double bond formed is conjugated with the carbonyl group in the six-membered ring. In the NMR spectra of (III) and of demethylenesecodemethanoldelcorine there are the signals of two olefinic protons in the form of a one-proton doublet at 5.98 ppm (J = 9 Hz) with additional splitting of ~1.5 Hz and a one-proton quadruplet at 6.81 ppm with $J_{AX} = 9$ Hz, $J_{BX} = 7$ Hz. It follows from the facts given that the α-diol system in (II) and the methylenedioxy group in (I) are located at C_7 and C_8, and the ready elimination of a molecule of methanol shows the location of the third methoxy group at C_{15} [5]. If the lycoctonine skeleton of deoxydelcorine and its empirical and expanded formulas are taken into account, the remaining methoxy group must be located at C_{19} [1].



I



II



III

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