THE STRUCTURE OF EXCELSINE

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UDC 547.944/945

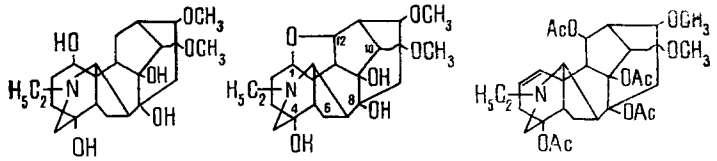
From the roots of Aconitum excelsum (Leucostomum) we have isolated a new base which we have called excelsine, $C_{22}H_{33}NO_6$ (I), mp 103-105°C (ether–methanol, mol. wt. 407.2317). The NMR spectrum of the alkaloid contains the signals of a N-ethyl group (three-proton triplet at 1.01 ppm) and of two methoxy groups (three-proton singlets at 3.13 and 3.18 ppm; figures given in the δ scale).

The acetylation of the base with acetic anhydride in the presence of p-toluenesulfonic acid gave a triacetate (mol. wt. 533), in the NMR spectrum of which there was the signal of three acetyl groups (nine-proton singlet at 1.99 ppm), and acetylation with acetyl chloride gave a chloro tetraacetate with mp 216-218°C, mol. wt. 611 (12-proton signal at 1.92, 1.94, 1.96 ppm).

The reduction of (I) with Raney alloy in an aqueous methanolic solution of caustic soda at the boiling point for 20 h led to the formation of a product with mp 206-207°C identified by its IR and mass spectra, and also by means of a mixed melting point, as lappaconidine (II) [1]. Excelsine was not hydrogenated by Adams' method, nor with sodium tetrahydroborate and lithium tetrahydroaluminate.

From what has been said above, we may conclude that the alkaloid contains the lycoctonine skeleton with two methoxy and three hydroxy groups and a N-ethyl group and that it also has an oxygen bridge.

In an aqueous solution of hydrochloric acid at the boil, excelsine adds HCl with the formation of two epimers, $C_{22}H_{34}NO_6Cl$ – one amorphous and one crystalline with mp 117-119°C – and in sulfuric acid is obtained a crystalline product $C_{22}H_{33}NO_6$ with mp 180-182°C, forming on acetylation a tetraacetate (III). The NMR spectrum of (III) has the signals of four acetyl groups (3 H at 1.92 ppm, 6 H at 2.02 ppm, and 3 H at 2.05 ppm), two olefinic protons (1 H, doublet at 6.06 ppm, J 9 Hz, and 1 H, quadruplet at 5.57 ppm, J_1 9 Hz, J_2 4 Hz, with additional splitting having $J_3 \approx 1.5$ Hz), and also of a proton geminal to a methoxyl at C-10 in the form of a doublet at 4.82 ppm, J 5 Hz (analogous to the signal observed in lappaconine triacetate), and a one-proton signal in the form of a doublet at 5.11 ppm (J 4 Hz). Such a nature of the splitting of the olefinic protons can be explained (under the conditions of the retention of the lycoctonine skeleton) only if the double bond is located at C-1 and C-2 or at C-2 and C-3 of ring A.



The absence from the mass spectrum of (I) of the peak M−17 [2], and also a study of the product (III) shows that C-1 is one of the ends of the oxygen bridge in excelsine. We came to the same conclusion in a study of the products of the Kiliani oxidation of (I), one of which is a substance $C_{22}H_{31}NO_6$, mp 207-209°C (decomp.) containing a carbonyl in a five-membered ring, ν_{max} 1740 cm^{-1}. In view of the production of lappaconidine on the hydrogenation of excelsine, we consider that in (I) there is no free hydroxy group at C-1, and on oxidation the diol system at C-8 and C-9 undergoes cleavage [3].

Institute of the Chemistry Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 129-130, January-February, 1973. Original article submitted June 13, 1972.

When (I) was treated with periodic acid at room temperature for 48 h, a crystalline derivative deposited: $C_{22}H_{33}NO_6$, mp 223-224°C (decomp.), molecular weight equal to that of the initial base, IR spectrum containing the absorption band of a carbonyl group at 1754 cm^{-1} (cyclopentanone). Consequently, the product was formed as the result of a rearrangement in which the oxygen of the bridges takes part and the carbonyl group in the five-membered ring is the second end of the bridge. In this case, two positions remain for it: C-12 and C-6. The latter must be excluded, since a consideration of a model shows that the formation of a bridge between C-1 and C-6 is impossible. On the basis of what has been said, structure (I) is proposed for excelsine.

LITERATURE CITED

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