STRUCTURE AND ABSOLUTE CONFIGURATION OF (+)-EXCELSINE

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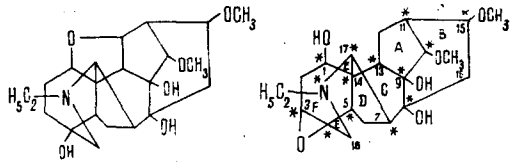
The alkaloid excelsine has been isolated previously from Aconitum excelsum (Leucostomum) [1]. In order to achieve an objective determination of its structural formula and to establish the absolute configuration of this alkaloid we have performed an x-ray structural study of the hydrate of the hydriodide of (+)-excelsine $C_{22}H_{33}NO_6 \cdot HI \cdot H_2O$ (the presence of the water was shown in the course of the present investigations). Crystalsrhombic, space group $P2_12_12_1$, $a = 10{,}970$ (7), $b = 20$, 194 (9), $c = 10{,}747$ (7) Å, $V = 2381$ Å^3, mol. wt. = 535.5, $d_{meas} = 1.56$ g/cm^3, $d_{calc} = 1.55$ g/cm^3 for $z = 4$. The results of the experiments (2900 independent reflections) were obtained on a Hilger–Watts automatic diffractometer (λCuK_α, graphite monochromate, ω-scanning, ordinate analysis, absorption factor not taken into account). The coordinates of the iodine atom were determined in a three-dimensional Patterson synthesis and the positions of the other nonhydrogen atoms were found by the successive approximations of electron-density series. The structure of the alkaloid was refined by the method of least squares in the isotropic approximation, R = 0.125.



I II

The results obtained show that excelsine has structure (II), differing somewhat from the structure (I) proposed previously [1]. The structure of excelsine is remarkable for a three-membered epoxy ring. The absolute configuration of (II) was determined with respect to 20 Friedel pairs by a published method [2]. According to the Cahn–Ingold–Prelog nomenclature [3], the 15 asymmetric centers of the molecule (including the tetrahedral N nitrogen atom) possess the following configurations: 1 (S), 3 (S), 4 (R), 5 (S), 7 (S), 8 (S), 9 (S), 10 (S), 11 (R), 13 (S), 14 (R), 15 (S), 17 (R), N (S).

The conformation of the rings is [4] as follows: five-membered ring A – envelope ^{10}E; six-membered ring B – boat $^{10,16}B$; six-membered ring C (atoms 7, 8, 9, 13, 14, and 17) – chair $^9C_{17}$; five-membered ring D (atoms 5, 6, 7, 17, and 14) – envelope ^{17}E; six-membered piperidine ring E (atoms 4, 5, 14, 17, N, and 18) – chair $^4C_{17}$; six-membered ring F – boat $^{2,5}B$. The lengths of the bonds and the valence angles are as usual.

LITERATURE CITED

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