STRUCTURE AND ABSOLUTE CONFIGURATION OF (−)-PSEUDOCOPSININE

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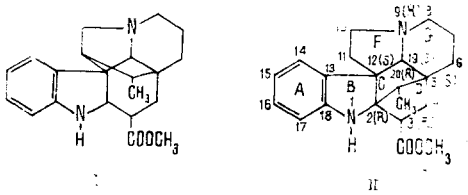
The alkaloid (−)-pseudocopsinine was first isolated from the epigeal part of Vinca erecta Rgl. et Schmalh. [1]. To achieve an objective and independent determination of the structure of this alkaloid, and also to establish its absolute configuration, we have made an x-ray structural study of the hydrate of the hydrobromide of (−)-pseudocopsinine $C_{21}H_{26}N_2O_2 \cdot HBr \cdot H_2O$ (the presence of one molecule of water was shown in the performance of the present investigation).

Crystals rhombic, $a = 9{,}777$ (6), $b = 16{,}056$ (8), $c = 12{,}714$ (6) Å, $V = 1996$ Å^3, $M = 437.4$, $d_{meas} = 1.46$ g/cm^3, $d_{calc} = 1.46$ g/cm^3 for $z = 4$, space group $P2_12_12_1$. The intensities of 3160 independent reflections with $c|F|^2 \geq 3\sigma(|F|^2)$ were measured on a Hilger–Watts automatic diffractometer (λCuK_α, graphite monochromator, ω-scanning, ordinate analysis, absorption not taken into account).



II

The structure of the alkaloid was interpreted by the heavy-atom method and refined by the method of least squares in the isotropic approximation to $R = 0.102$. The absolute configuration was determined with respect to 24 Friedel pairs by a published method [2].

The results obtained permitted the objective establishment of the fact that (−)-pseudocopsinine has formula (II), which differs somewhat from formula (I) proposed previously [1].* The absolute configuration of this alkaloid with seven asymmetric centers [including the N_9 nitrogen atom] is denoted by 2 (R), 3 (R), 5 (S), N (9) (R), 12 (S), 19 (S), 20 (R).

The benzene ring A is planar, the conformation of the pyrrolidine ring B is envelope ^2E, that of the five-membered ring C half-chair $^{20}T_5$, that of the five-membered ring D envelope ^{20}E, that of the cyclohexane ring E (atoms 2, 3, 4, 5, 19, and 12) boat $^{2,5}B$, that of the pyrrolidine ring F envelope ^{10}E, and that of the piperidine ring G twisted boat $^5S_7$. The linkage of rings B/C is trans, C/F cis, C/G trans, and F/G cis. The lengths of the bonds and the angles are the usual ones.

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*Structure (II) is also confirmed by recent NMR-spectroscopic investigations of [^{13}C]dihydrovindolinine [3], which is a complete analog of pseudocopsinine.

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