X-RAY STRUCTURAL INVESTIGATION OF ALKALOIDS
VI. CRYSTAL STRUCTURE OF THE ALKALOID PARFUMINE

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A complete x-ray structural investigation of the alkaloid parfumine has been performed. The lengths of the bonds and the valence angles have the usual values. Benzene rings A and D are planar, B a distorted half-chair C$_6$H$_5$N, and rings C and E are flattened envelopes, E$_{C(14)}$ and C$_{C(18)}$E, respectively.

We have previously determined the crystal structure of the alkaloid sibiricine, which crystallizes in a centrosymmetrical space group [1]. In the present paper we consider the determination of the crystal structure of the related alkaloid parfumine, isolated from Fumaria parviflora in order to confirm the structure proposed previously [2] and to determine the configuration of the spiro center. Parfumine differs from sibiricine by the absence of a hydroxy group in the five-membered ring, and also by the presence of hydroxy and methoxy groups in place of the methylenedioxy group at C(2) and C(3).

The structure of the parfumine molecule is shown in Fig. 1, which also shows the solvate ethanol molecule. The form of the thermal ellipsoids of the carbon atoms of ethanol clearly shows the unorderedness of the ethyl group of this molecule in the crystal. The lengths of the bonds and the valence angles are given in Table 1.

Figure 2 gives a sketch of the parfumine molecule with the torsion angles in the ring. The benzene ring A is somewhat deformed. Thus, the deviations of the atoms of the ring from its mean plane amount to 0.03 Å, and the departure from this plane of the closest atoms of the substituents is $-0.07$ Å (for C(5), see Table 2, which gives the characteristics of the planes of the fragments of the molecule). The other benzene ring, D, is planar to within 0.01 Å, including the closest atoms of the substituents. The dihedral angle between the planes of benzene rings A and D is 99.6°, i.e., somewhat greater than in the molecules of sibiricine (89.9°) and of other related alkaloids - ochrobirine [3] and ochotensine [4] (about 90°). The six-membered pyridine ring B has a distorted half-chair conformation C$_6$H$_5$N in Schwarz's symbols [5], but the nature of the distortion differs from that found in the sibiricine molecule. The five-membered ring C has a flattened envelope conformation E$_{C(14)}$ (the C(14) atom departs from the plane of the C(6) C(17) C(18) C(13) atoms by $-0.093$ Å), while in the sibiricine molecule this ring has a half-chair conformation.

The difference in the conformations of rings B and C in the parfumine and sibiricine molecules indicates a conformational flexibility of these rings, leading to the realization of different methods of reducing strain in these polycyclic condensed systems.

The other five-membered (dioxolane) ring E also has a flattened envelope conformation C$_{C(18)}$E as in sibiricine: the C(19) atom departs from the plane of the other atoms of the ring by 0.125 Å.

The nitrogen atom has a pyramidal conformation (sum of the valence angles 334°; the departure of N from the C(6) C(14) C(21) plane amounts to $-0.441$ Å). All the C−N bond lengths [from 1.45(1) to 1.47(1) Å] are the same and coincide with the standard value for an ordinary C−N bond of 1.472 Å [6]. The C−C interatomic distances in aromatic rings A and D have a scatter of 1.33(1) to 1.44(1) Å, which exceeds 3σ and is apparently the consequence of the general strain of the skeleton of the molecule or, rather, of the failure to take libration errors into account. All the interatomic distances coincide, within the limits of accuracy, with those found for the sibiricine molecule and are the usual ones for the corresponding types of bonds.

The parfumine and ethanol molecules each have one "active" hydrogen atom which, in the crystal, participates in the form of hydrogen bonds. The hydroxy group of parfumine plays the role of donor in a O(1)-H...O(4) hydrogen bond with the hydroxy group of ethanol, the O(1)...O(4) distance being 2.65(1) Å, the O(1)-H(01) distance 1.06 Å, and the H(01)...O(4) distance 1.62 Å, and the angle at the H(01) hydrogen atom is 164°, i.e., this bond of medium strength is close to linear. The hydrogen atom of the hydroxy group of ethanol participates in a H bond with the nitrogen atom of the parfumine molecule obtained from a basis translation a. The O(4)...N distance is 2.84(1) Å, this hydrogen bond also, apparently, being close to linear (the hydrogen atom at O(4) could not be objectively localized), since the angles between the O(4)...N vector and the nitrogen-atom bonds N-C(14), N-C(6), and N-C(21) are 123.7(5), 102.9(5), and 94.5(5)°, respectively, i.e., they do not greatly differ from one another and from the tetrahedral angle. Thus, the hydrogen bonds with the participation of the ethanol molecule join the parfumine (IV) molecules into endless chains along the a axis: ...O(A)--H...N(11) O(1)--H...