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X-RAY CRYSTAL STRUCTURE OF DELNUDINE, A NOVEL ALKALOID.

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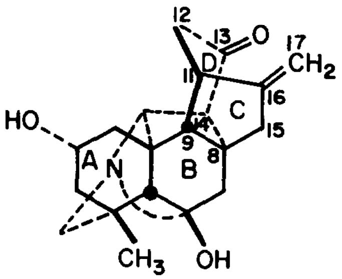
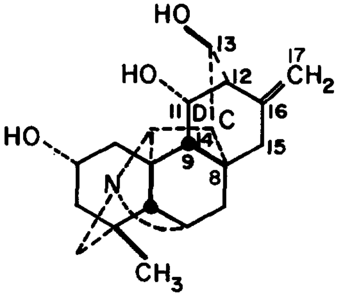
Delnudine, $C_{20}H_{25}NO_3$, was isolated from the seeds of *Delphinium denudatum* by Götz and Wiesner(1). Since its structure was not fully known it was decided to carry out this X-ray analysis.

The free base crystallized by slow evaporation from an acetone:ethyl acetate solution in the orthorhombic space group $P2_12_12_1$. However, these crystals were not suitable for data collection and therefore delnudine hydrochloride, $C_{20}H_{25}NO_3 \cdot HCl$, was prepared. The hydrochloride yielded well developed, long, prismatic crystals from an ethanol:water:pentane mixture. The crystals are monoclinic, space group $P2_1$ with 2 molecules in the unit cell and the cell dimensions are: $a = 9.528$, $b = 10.332$, $c = 9.505$Å, and $\beta = 108.50°$. The data were collected on a Picker automatic diffractometer with MoKα radiation and 1835 reflections were observed out of the 2151 reflections with $2\theta \leq 55°$.

The structure was determined to be I by a combination of the heavy-atom method and tangent refinement(2). The positional and thermal parameters of the non-hydrogen atoms have been refined by the least-squares method and the reliability factor, R, is now 8%. The refinement is being continued.



I



II

The stereochemistry and the conformation of delnudine can be seen from formula I and the Figure. It is a novel type of skeleton, but it is related to that of hetisine (II)(3). The conformation of ring A is the only one which is not governed by fusion with other rings and the ring adopts the chair form with

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the hydroxyl group in the axial position. The latter is stabilized by a hydrogen bond to the chloride ion. The ring systems of delnudine and hetisine differ in the C and D rings since in the former C(16) is joined to C(11) while in the latter it is joined to C(12). Ring C in I is five-membered and envelope-shaped, while the corresponding ring in II (C(8), C(9), C(11), C(12), C(16), C(15)) is a six-membered boat. The six-membered ring D (C(8), C(9), C(11), C(12), C(13), C(14)) adopts the chair conformation in delnudine while in hetisine it occurs in the boat form.

As mentioned by Götz and Wiesner(1), the U.V. spectrum of delnudine shows a somewhat higher intensity at 300 mμ than would be normal for a saturated ketone. It may, therefore, be of interest to indicate the distances between, and the relative orientation of, the carbonyl and the exocyclic methylene groups: C(13)···C(16) 2.90, C(17)···O 4.42Å, tilt of the C=O bond with respect to the C=C bond is 34°.

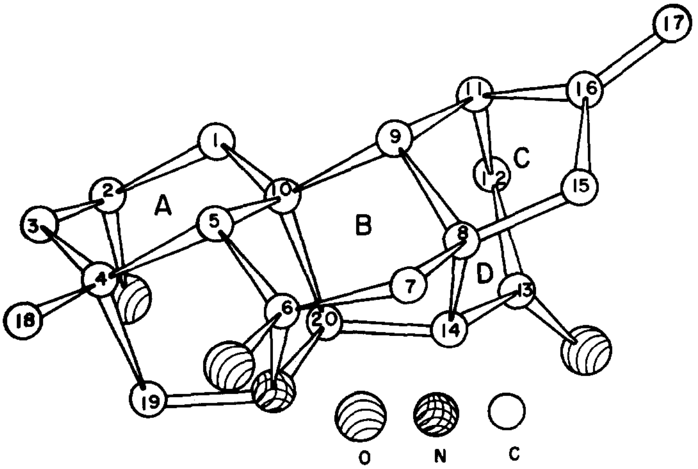

Figure. View of the molecule along the b-axis.

Complete results of this analysis will be published elsewhere.

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