Tetrahedron Letters No.50, pp. 4373–4375, 1969. Pergamon Press. Printed in Great Britain.

THE CRYSTAL STRUCTURE OF DENUDATINE

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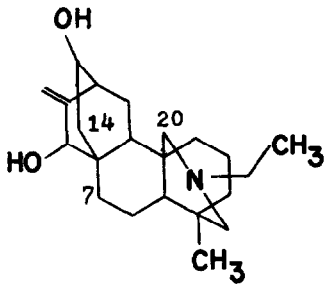
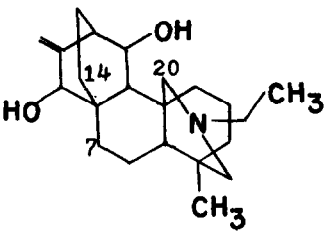
(Received in USA 22 September 1969; received in UK for publication 25 September 1969

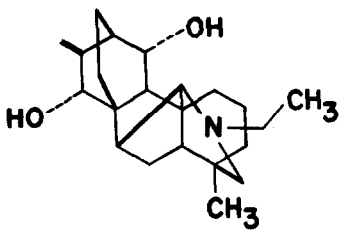
After Singh, Singh and Malik (1), Götz and Wiesner (2) recently investigated the alkaloid denudatine isolated from Delphinium denudatum. The latter group of workers established its molecular formula to be $C_{22}H_{33}NO_2$ and concluded that the structure could be either (I) or (II), where C(20) could be connected to C(14) or to C(7).



(I)



(II)



(III)

To clear up this uncertainty Dr. Wiesner of the University of New Brunswick sent us some crystals of denudatine for an X-ray structure determination.

Suitable crystals were obtained by slow evaporation from an ethanol solution. Precession photographs showed the crystals to be monoclinic with cell dimensions: a = 14.229, b = 7.296, c = 9.552 Å and β = 107.64°. The space group is $P2_1$ and

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there are two molecules per unit cell.

Three dimensional intensity data were collected with an automatic Picker diffractometer and a General Electric XRD_5 manual diffractometer. Of the 2247 possible independent reflections, 2084 were observed. The phases of 245 reflections, with normalized structure factors E greater than 1.50, were determined by the symbolic addition procedure for non centrosymmetric crystals (3). An E-map computed at this stage yielded a partial structure containing 11 atoms. The phases calculated from the 11 atom portion were refined by the use of the tangent formula (4). A final E-map gave all the 25 non hydrogen atoms. The atomic parameters were refined by the least-squares procedure using the programs written for the IBM/360 system by Dr. F.R. Ahmed of this laboratory. After 5 cycles of isotropic temperature factors refinement followed by 4 cycles of anisotropic refinement the agreement index decreased to 8.6%. Although the refinement is still in progress there is no doubt that the structure was correctly established and this was done without any chemical assumptions.

The molecular structure of denudatine viewed along the b-axis is shown in Figure 1, and corresponds to (III). Denudatine is thus a diterpene alkaloid with a new type of skeleton which was postulated by Wiesner and Valenta (5) as a possible intermediate in the biogenetic transformation of the atisine steleton into the skeleton of the aconitine type of alkaloids.

The bond distances for denudatine compare well with the generally accepted values for the different bond types except for the distance C(7)-C(20) which is 1.578±0.008 Å. Although the average angle for 5-membered rings is 100° and 109° for 6-membered rings, the individual angles between bonds of tetrahedrally coordinated C atoms vary widely between 94° and 125°.

The complete results of the X-ray analysis will be published elsewhere.

Acknowledgements. I wish to thank Dr. M. Przybylska for suggesting this problem to me and Dr. K. Wiesner for supplying the crystals of denudatine. I am also grateful to Dr. C.P. Huber for her assistance with the computations.

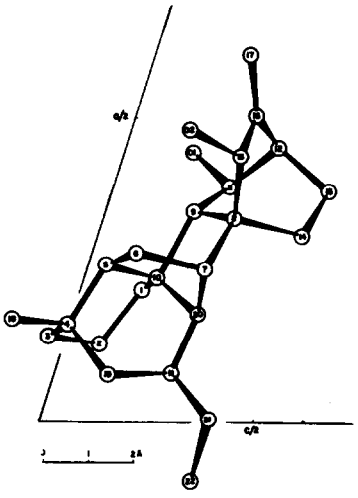

Fig. 1 View of the molecule along the b-axis.

REFERENCES

1. N. Singh, A. Singh and M.S. Malik, Chemistry and Industry, 1909 (1961).
2. M. Götz and K. Wiesner, Tetrahedron Letters, this issue.
3. H. Hauptman and J. Karle, Acta Crystallographica, 9, 45 (1956).
4. J. Karle, Acta Crystallographica, B24, 182 (1968).
5. K. Wiesner and Z. Valenta, Progress in the Chemistry of Natural Products XVI (1958), Wien, Springer-Verlag.