

CRYSTAL STRUCTURE OF CORYNOLINE P-BROMOENZOATE

By T. Kametani, T. Honda, M. Ihara, H. Shimanouchi, and Y. Sasada

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai, Japan and Laboratory of Chemistry of Natural Products, Tokyo Institute of Technology, Ookayama, Meguroku, Tokyo, Japan

(Received in Japan 12 July 1972; received in UK for publication 25 July 1972)

Corynoline, one of the benzo[c]phenanthridine alkaloids isolated from C. incisa Pers.¹⁻⁴ has been assigned a structure (1) by Takao⁵ on the basis of the chemical evidences. It was deduced from infrared absorption bands at 3100 - 3250 cm⁻¹ that an intramolecular hydrogen bond between the hydroxyl group at C-12 and the nitrogen atom is formed and therefore the B/C ring junction should be cis-fused. The nmr studies⁴ suggested that the cis B/C ring takes half chair - half chair conformation for this alkaloid and half chair - twist half boat conformation for its acetate (2). Comparison of the nmr spectra of 1, 2, and 3, it is also suggested that the B and C ring in the benzoate take the same conformation as 2.

To establish the three-dimensional molecular structure of the alkaloid, we have undertaken the X-ray analysis of p-bromobenzoate.

Crystal data: C₂₈H₁₈BrNO₆, m.p. 179 - 180°, M = 546.37, monoclinic, a = 12.598, b = 14.868, c = 13.592 Å, β = 115.30°, U = 2362.65 Å³, D_m = 1.53, D_c = 1.54 g/cm³, Z = 4, space group P2₁/c.

Intensity data were collected on a four-circle diffractometer using CuKα radiation, and the intensities of 1161 reflexions were larger than 3σ where σ is the standard deviation from counting statistics. The structure was solved by the heavy atom method. The positional and thermal parameters of the atoms were refined by the least-squares method. The final R factor was 0.165 for the observed reflexions. The perspective drawing of the molecule is shown in Figure 1. The B/C ring junction is unambiguously cis-fused, and the dihedral angle between the A and D rings is 73.2°. The B and C rings take a half chair and a twist half boat conformations, respectively.

On the basis of the present X-ray work and the spectral properties above mentioned, it may be concluded that a conformational change occurs by breaking its intramolecular hydrogen bond and corynoline itself takes the cis B/C half chair - half chair conformation as shown in Figure 2. This hydrogen bond plays an important role in stabilizing the conformation possessing the cis B/C

ring junction. The present result may provide a clue to estimate the effect of intramolecular hydrogen bond on the ring conformation of the related compounds.

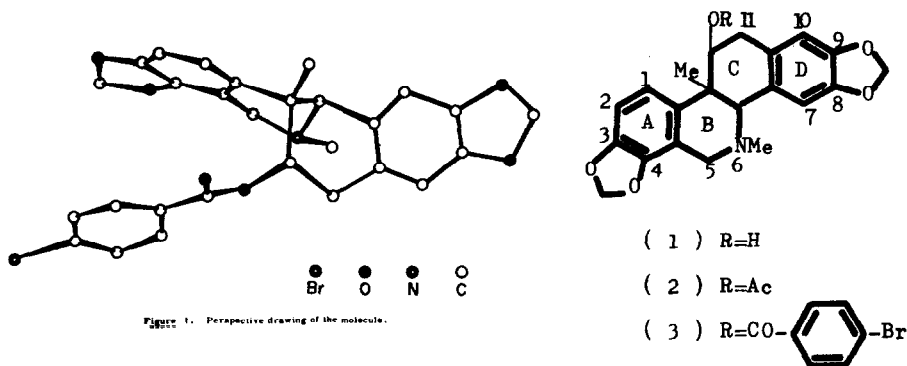


Figure 1. Perspective drawing of the molecule.

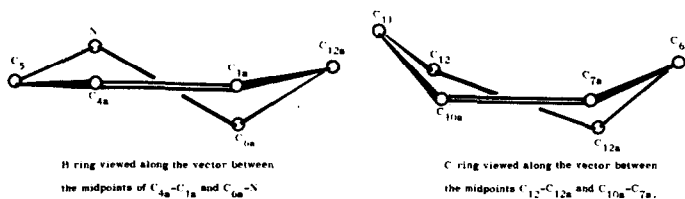


Figure 2

References

- 1 T. Kametani, M. Ihara, and T. Honda, *Phytochemistry*, 1971, 10, 1881.
- 2 R. H. F. Manske, *J. Amer. Chem. Soc.*, 1950, 72, 3207.
- 3 C. Tani and N. Takao, *J. Pharm. Soc. Japan*, 1962, 82, 594.
- 4 S. Naruto, S. Arakawa, and H. Kaneko, *Tetrahedron Letters*, 1968, 1705.
- 5 N. Takao, *Chem. and Pharm. Bull. (Japan)*, 1963, 11, 1306.