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AN X-RAY DETERMINATION OF THE STRUCTURE OF MIYACONITINE HYDROBROMIDE DIHYDRATE

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As mentioned in the accompanying report (1), the structure of miyaconitine, one of the Aconitum alkaloid, has not been established by means of the chemical and spectral methods. Therefore, an X-ray analysis was undertaken in order to reveal the structure. A heavy atom derivative, miyaconitine hydrobromide dihydrate (I), was kindly supplied by Professor Ichinohe.

Crystals of I were grown from methanol solution as colourless scale-like plates. Crystallographic and physical data are: $C_{23}H_{29}O_6N \cdot HBr \cdot 2H_2O$, M. W. = 532.4, monoclinic, a = 10.41, b = 13.85, c = 9.63 Å, β = 113.8°, space group $P2_1$, D(obs.) = 1.399, D(calc.) = 1.391 $g \cdot cm^{-3}$, Z = 2.

The intensity data were collected from equi-inclination Weissenberg photographs and measured visually. Owing to the relatively large temperature factors the number of reflexions with measurable intensity was about 1100. Accuracies of intensity data were rather low, because only very thin crystals were available. Using the phases of the bromine atom, the Fourier synthesis was carried out, but the interpretation of the resulting map was not easy, partly because of the poor intensity data, and partly because of a pseudo-mirror plane. Twenty-three light atoms were first assigned by using the criterion of the tetrahedral arrangement of peaks with suitable distances. After the refinement of the structure it was found that nine of them were incorrect. Successive Fourier syntheses revealed the molecular skeleton step by step, but some of the substituent atoms did not appear on the electron-density maps in these stages. Calculations of difference syntheses gave finally all the non-hydrogen atoms. Although it was difficult to distinguish the atomic species, it finally became possible by considering the shifts of the temperature factors of atoms in several least-squares refinements and the hydrogen-bonding system in the crystal structure. The final R factor is 0.151. The absolute

configuration was also determined using anomalous dispersion effect of the bromine atom. The structure thus determined is illustrated in the Figure. Accordingly, the structure of miyaconitine hydrobromide dihydrate can be indicated as II. Chemical aspects of the structure are given in the accompanying paper (1). Full account of the structure determination will be presented in the near future.

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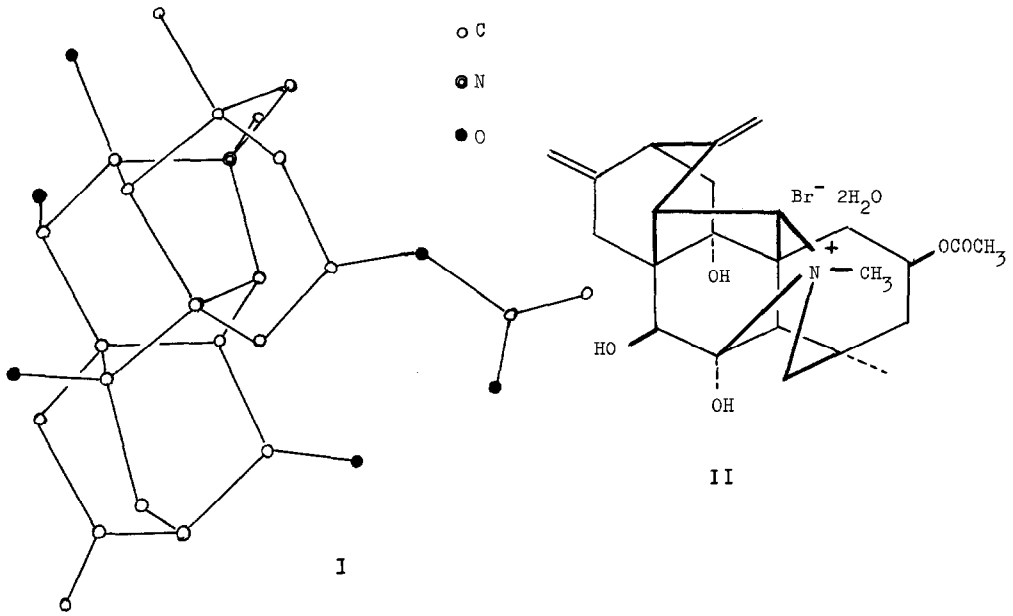

I II

Figure

Reference

1) Y. Ichinohe, M. Yamaguchi, N. Katsui and S. Kakimoto, the preceding paper.