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A NOVEL TYPE OF FRAMEWORK FOUND IN AN ALKALOID FROM DAPHNIPHYLLUM MACROPODUM

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Three kinds of crystalline salts of alkaloids were obtained by two of the present authors (T. N. & Y. T.) from the bark of Daphniphyllum macropodum Miq. in the form of iodo-methylates, of which the melting points and approximate formulae from chemical analysis are given in Table 1.

TABLE 1

	melting point	approximate formula
I	286° - 287°C	$C_{31}H_{50}O_5NI$
II	306° - 307°C	$C_{29}H_{48}O_3NI$
III	264° - 265°C	

The present communication contains one of the remarkable results obtained from the x-ray analysis of II.

II crystallizes in the monoclinic space group $P2_1$ with the lattice constants $a = 15.17$, $b = 12.01$, $c = 8.23\text{Å}$, $\beta = 97.5°$. The observed density 1.37 ± 2 g/cm^3 suggests that the unit cell contains two formula units of II. Three-dimensional intensity data were obtained visually from equi-inclination Weissenberg photographs about the b- and c-axes, taken at room temperature using Cu Kα radiations. The number of independent reflections actually observed were about 1900.

The positional parameters of the iodine ions were derived from a three-dimensional Patterson distribution as $x = 0.1583$, $y = 0$ (arbitrarily chosen), $z = 0.095$. A minimum function based on the iodine-iodine vector indicated about **forty** sets of light atom positions accompanied by the corresponding spurious peaks, the latter having been introduced by the false symmetry plane at $y = 0$. These light atom positions agreed very well with the first three-dimensional Fourier map phased on the heavy atom only. The next problem of selecting the true peaks by rejecting the false ones was not straightforward since only little was known at that time about the molecular structure of this alkaloid. The method adopted was essentially that of trial and error, assuming reasonable values for interatomic distances and angles, and was helped by sets of ordinary and difference Fourier syntheses, the latter having been used as error syntheses. The agreement between calculated and observed F-values was improved gradually until R = 0.145 for about 600 reflections within the range ($\sin\theta/\lambda)^2 \leq 0.13$. From this point the refinement was continued on an IBM 7090 computer using the diagonal least-squares program ERBR1. After several cycles the R factor for 1500 reflections dropped to 0.195. All the computations except those on the IBM 7090 were performed on an OKITAC 5090 using the programs written by one of the authors (N. K.).

Fig. 1 shows the electron density near the atomic centers shown projected along the c-axis, from which it is concluded that a novel type of framework sketched in Fig. 2 or its optical antipode is contained in the alkaloid II. It consists of two cage structures, linked by a flexible C-C chain. The larger one contains two chair-shape and one boat-shape six-membered rings fused together with two five-membered rings, while the smaller one consists of one chair-shape six-membered ring and one five-membered ring. Bond distances and bond angles are reasonable considering the complicated framework structure and the present stage of refinement.

The nitrogen and oxygen atoms shown in Fig. 2 were suggested partly by the approximate chemical formula and partly from structural considerations including bond distances and the values of electron density at the atomic centers. The chemical formula corresponding to this assignment is $C_{31}H_{49}O_3NCH_3^+ I^-$.

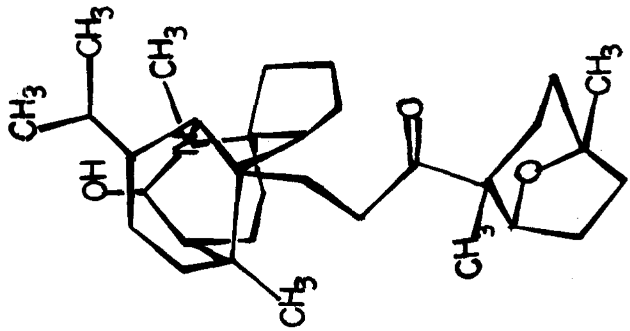

FIG. 2

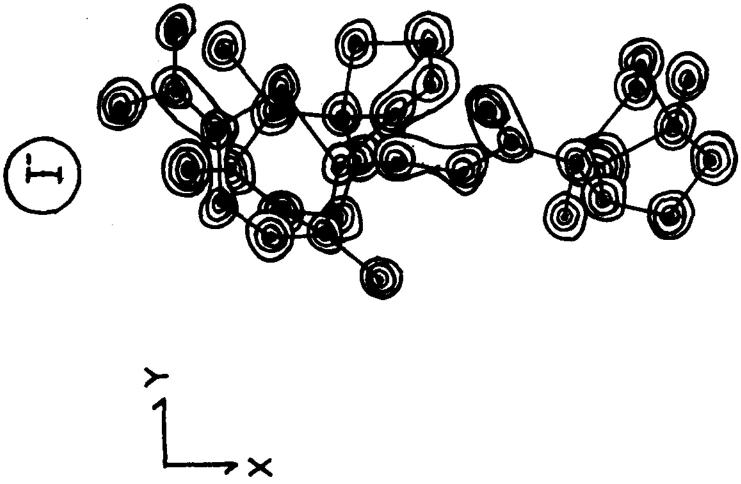

FIG. 1