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X-Ray Analysis of an Unusual Amino Acid Isolated from the Hydrolysate of a New Antibiotic, Enduracidin

Enduracidin is a new antibiotic peptide¹⁻³⁾ produced by a strain of *Streptomyces fungicidicus*, No. B-5477. It contains non-ionic chlorine atoms in an unusual amino acid component, which was obtained on hydrolysis of the antibiotic with 6N hydrochloric acid and successive chromatographic fractionation of the hydrolysate.

For the elucidation of the structure of this unusual amino acid (tentatively named K2), X-ray analysis was undertaken in parallel with chemical synthetic study.⁴⁾ Compound K2 ($C_8H_7NO_4 \cdot Cl_2$) exists in two crystalline modifications in compliance with different stage of crystallization. Needles, mp 208–210° (decomp.), obtained from an aqueous methanolic solution at an early stage of crystallization are trigonal, whereas prisms or pillars, mp 211–212° (decomp.), grown slowly from the mother liquor, are monoclinic. A preliminary study indicated that the latter, which contains one molecule of water of crystallization in the asymmetric unit, is more suitable for X-ray analysis than the former.

The unit cell of the latter with cell dimensions, $a=11.93$, $b=10.08$, $c=8.76\text{Å}$ and $\beta=95^\circ 30'$, contains four molecules of K2, the space group being $P2_1/a$ (C^5_{2h}). The crystals are, therefore, of the racemic K2. Some degree of racemization had occurred during the acid hydrolysis.

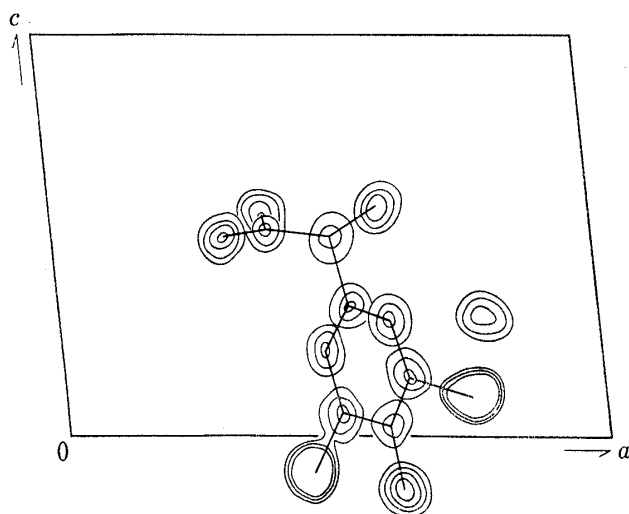


Fig. 1. The Third Three-dimensional Electron Density Distribution Projected on (010)

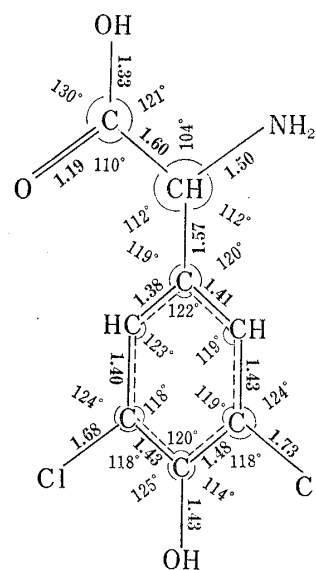
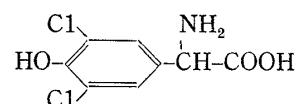


Fig. 2. Interatomic Distances and Angles

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Intensities of 1225 reflections were measured with MoK α radiation on Hilger & Watts' linear diffractometer. Coordinates of the two chlorine atoms were derived from careful analysis of the three dimensional Patterson function. A three dimensional minimum function method and a heavy-atom method were carried out for the elucidation of the positions of light atoms. The structure thus obtained was refined by three dimensional Fourier syntheses and the least squares method. The *R* factor is 17.5% at the present stage.

In Fig. 1 is given the third three dimensional electron density distribution shown by means of superimposed contour sections projected on (010). The bond lengths and angles (Fig. 2) together with intermolecular contact are reasonable considering the present stage of refinement. The structural formula corresponding to Fig. 1 is thus, or α -amino-3,5-dichloro-4-hydroxyphenylacetic acid. The existence of this new amino acid in enduracidin would be one of the proofs that the antibiotic has a unique structure.



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Partial Synthesis of Priverogenin B from Camelliagenin A

Recently, in the study of genuine sapogenins of the root of *Bupleurum falcatum* L., Kubota and Hinoh described¹⁾ the synthesis of saikogenin E^{1,2)} (IIIa) from longispinogenin (Ia) via 11-hydroxy-longispinogenin (IIa). In the present communication, we wish to forward our observations of similar line which lead the partial synthesis of priverogenin B^{3,4)} (IVa) from camelliagenin A^{4,5)} (Ib) (=dihydropriverogenin A^{3,6,7)}, the former being one of the genuine sapogenins of *Primula veris* L. root, while the latter has been known as one of the common sapogenins of some *Theaceous*^{4,5,8,9)} and *Primulaceous* plants.^{3,6)}

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