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Crystallographic data of three modifications of carbobenzoxy-* glycyl-L-prolyl-L-leucyl-glycyl-L-proline.

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Recently carbobenzoxy-glycyl-L-prolyl-L-leucyl-glycyl-L-proline has been synthesized, which is the simplest crystalline substrate for collagenase (Nagai & Noda, 1959; Nagai, Sakakibara, Noda & Akabori, 1960; Sakakibara & Nagai, 1960). Present account deals with the diffraction measurements of this crystalline compound. It is hoped that such structural studies will throw light on the structure of crystalline part of collagen because of their similar behavior towards the action of collagenase.

It was found that this substance shows at least three modifications. The crystal data of each modification were obtained from oscillation and Weissenberg photographs about the principal axes. Accurate measurement by counting procedure was made using single crystal orienter of G.E. XRD-6. Densities were obtained by flotation method. The results are listed in Table 1.

(1) α-Modification; very unstable platelet crystal obtained from water saturated ethyl acetate solution, easily turning opaque on exposure to the air. Photographs were taken with crystal sealed in glass capillary.

(2) β-Modification; stable platelet crystal, obtained from ethyl acetate solution containing water less than 1%.

(3) γ-Modification; very unstable cube-like crystal, obtained from ethyl acetate solution freed from water. Although photographs were also taken with crystal sealed in glass capillary, diffraction spots were accompanied by some streaks.

It may be added that no crystalline reflexion was observed when the solvent is completely taken off from the crystal in high vacuum.

From the cell dimensions and densities, apparent formula weights were calculated as shown in Table 1. These values obtained indicate that there must exist one molecule of ethyl acetate and three or four molecules of water per peptide as crystallization solvent, at least, in the α- and β-modifications. It was confirmed by Sakakibara & Nagai (1960) that ethyl acetate was actually present in these crystals.

Table 1. *Crystallographic data of carbobenzoxy-glycyl-L-prolyl-L-leucyl-glycyl-L-proline* ($C_{28}H_{39}O_8N_5$, $M = 573$)

	α-Modification	β-Modification	γ-Modification
a	13·54 ± 0·07 Å	26·28 ± 0·04 Å	26·33
b	14·73 ± 0·05 Å	14·63 ± 0·02 Å	14·43
c	10·28 ± 0·03 Å	10·30 ± 0·02 Å	10·33
β	105·6 ± 0·1°	—	—
Space group	$P2_1$	$P2_12_12$	$P2_122$
Density	$1{\cdot}22_3$	$1{\cdot}21_7$	—
Z	2	4	4
Apparent formula weight	727	726	—

* Carbobenzoxy = benzyloxycarbonyl.

Previously we have reported that the stepwise removal of the amino acid residues from this compound gave rise to regular decrease of axial length properly chosen (Sasada, Tanaka, Ogawa & Kakudo, 1961). From this it was considered to suggest that their molecules show some extended form in the crystals. If the pentapeptide molecule should assume also the extended form in the crystal, the length of an axis would have been expected to be about 32 Å. As the longest axis actually found is, however, 26 Å in the case of pentapeptide, we have to assume that the molecule is not fully extended, but that it somewhat curls up as a whole in the crystal. The density of this crystal is somewhat smaller than those of the lower peptides, and this may also have something to do with the above mentioned view.

It is observed that there are certain rational relations among the corresponding cell lengths of these three modifications. This suggests that in these three modifications the molecule has essentially the same shape. The occurrence of such polymorphism may be due to some complicated interaction between the peptide molecules and to that between the molecules and the solvent molecule of crystallization.

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On the symmetry and structure of the two modifications of anhydrous $CoSO_4$.

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In a recent paper by Pistorius (1961) are given the lattice constants and the space groups of the two polymorphic modifications of anhydrous $CoSO_4$, but a certain doubt is expressed in the choice of the most probable space