Acta Cryst. (1954). 7, 518

The unit-cell dimensions and the space group of L-glutaminyl-L-asparagine.*

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(*Received* 11 *March* 1954)

The dipeptide L-glutaminyl-L-asparagine is a component of the naturally occurring octapeptide oxytocin (du Vigneaud, Ressler, Swan, Roberts, Katsoyannis & Gordon, 1953). A sample of this dipeptide was kindly provided by Prof. du Vigneaud; it had been crystallized from water–ethanol solutions (du Vigneaud, private communication), and contained small orthorhombic needles. They were used for a preliminary X-ray survey, the result of which is presented in this communication.

Rotation photographs and zero-layer Weissenberg and precession photographs were taken for two crystal specimens; the density of the material was measured by the flotation method. The space group, determined by the observed systematic absences—($h00$), ($0k0$), ($00l$) absent for odd values of h, k, or l, respectively—is $P2_12_12_1$, and the unit cell dimensions are

$$a = 4\cdot88,\ b = 14\cdot12,\ c = 16\cdot27\ \text{Å} \pm 0\cdot5\%\,.$$

The density calculated for 4 molecules in the unit cell is 1·54 g.cm.$^{-3}$ and the measured density 1·52(5) g.cm.$^{-3}$.

These data are rather similar to those of glycyl-L-asparagine (Pasternak, Katz & Corey, 1954): space group $P2_12_12_1$, $a = 4\cdot81$, $b = 12\cdot85$, $c = 13\cdot52$ Å, density 1·51 g.cm.$^{-3}$, and it seems likely that the crystal structures of the two peptides are closely related.

A determination of the structure of glutaminyl-asparagine is not contemplated at present.

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* Contribution No. 1887 from the Gates and Crellin Laboratories. This investigation was supported by a research grant, RG-1987, from the National Institutes of Health, Public Health Service.

Acta Cryst. (1954). 7, 518

The unit-cell dimensions and space groups of some simple peptides.

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(*Received* 15 *April* 1954)

A number of simple crystalline peptides have been studied by X-ray methods during the last few years. The completed structures so far published have all been those of peptides having at least one residue of glycine. The packing arrangements of the larger side chains have so far been largely undetermined.

The results reported here are of preliminary observations on three glutamyl dipeptides, and on two crystalline forms of a tripeptide, the amino acids of which form a part of the gramicidin *S* sequence (Work & Harris, 1948). The dipeptides were synthesized and kindly provided by Drs Le Quesne & Young (1950*a*, *b*), and the tripeptide by Dr Work. Of these, α-L-glutamyl-L-valine was considered to be the most suitable for X-ray analysis, and this is now in progress (jointly with Dr I. G. Edmunds, Manchester College of Technology). No further work on any of the other peptides is at present contemplated.

Unit-cell dimensions were measured from rotation photographs about the main crystallographic axes, or from zero-layer Weissenberg photographs. The accuracy of these figures is estimated to be better than ±0·5% for the dipeptides, while for the two forms of the tripeptide it is considerably worse than this, owing to the very poor quality of the crystals. The density, where measured, was of about the same accuracy, flotation methods being employed.

α-L-Glutamyl aspartic acid monohydrate, α-L-glutamyl-L-valine, α-L-glutamyl-L-leucine

Crystals of these three dipeptides were grown from aqueous ethanolic solutions. Unit-cell dimensions, space groups and other data are shown in Table 1. An accurately measured density was obtained only for the second dipeptide and this is the figure given. Calculated densities are shown for the other two, and these values have been checked roughly by observing the behaviour of crystals in drops of liquid of known density.

The structural arrangements of the last two peptides appear to be closely related but with the magnitudes of a and b reversed and c somewhat longer in the larger peptide. Both crystals are positively birefringent with γ at some rather small angle to c. The refractive indices α and β are reversed, β being parallel to b in α-L-glutamyl-L-valine and α parallel to the screw axis in α-L-glutamyl-L-leucine. These observations suggest that in both crystals the molecule is elongated roughly in the c direction and that the non-polar side chain lies approximately along the length of the molecule.

α-L-Glutamyl-L-aspartic acid is hydrated and the higher density indicates a more compact structure,

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Table 1. *Cell dimensions*

Peptide	Habit	Symmetry	a (Å)	b (Å)	c (Å)	β (°)	Space group	Density (g.cm.$^{-3}$)	$n_{\text{calc.}}$	Symmetry number
A	Prisms {110}, {100}	Orthorhombic	7·92	20·56	7·56	—	$P2_12_12_1$	1·510	—	4·00
B	Needles or plates on {001}	Monoclinic	6·57	5·49	16·94	98	$P2_1$	1·350	2·00	2·00
C	Plates on {001}	Monoclinic	5·44	6·48	20·36	91·5	$P2_1$	1·203	—	2·00
D	(1) Needles or plates on {010}	Orthorhombic	22·37	23·34	11·34	—	$A2_122$	1·28	7·98	8·00
	(2) Needles	Orthorhombic	18·26	28·04	11·42	—	$P22_12$	1·29	7·97	4·00

A α-L-Glutamyl aspartic acid monohydrate.
B α-L-Glutamyl-L-valine.
C α-L-Glutamyl-L-leucine.
D *p*-Brombenzoyl-L-leucyl-D-phenylalanyl-L-proline methyl ester.

presumably owing to the increased possibilities of hydrogen bonding.

p-Brombenzoyl-L-leucyl-D-phenylalanyl-L-proline methyl ester

The original sample consisted of very small orthorhombic needles and plates on (010), *c* the needle axis. The space group was found to be $A2_122$. The density of the crystals obtained experimentally and unit-cell dimensions are shown in Table 1. The calculated number of molecules in the unit cell is 7·98, that required by symmetry being 8·00.

Attempts were made to grow larger crystals from ethyl acetate/petrol ether mixture and from a number of other organic solvents. A second crystalline form was always obtained, consisting of rosettes of long, thin, fibrous needles. The symmetry of this form is also orthorhombic, but the space group is now $P22_12$.

The measured density is 1·29 g.cm.$^{-3}$ and the number of molecules in the unit cell computed from the figures in the table is 7·97. This is twice that required by the crystal symmetry and hence there must be two independent molecules in the asymmetric unit.

When it was first examined it was hoped that the tripeptide unit might show some form of intramolecular hydrogen bonding and thus might suggest a configuration for folded polypeptide chains. Infra-red studies, however, have shown the molecule to have an extended configuration, at least in the first crystalline form (Abbott & Ambrose, 1953).

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Acta Cryst. (1954). **7**, 519

The accuracy of electron-density maps in X-ray analysis: correction.

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(*Received* 19 *May* 1954)

Incorrect formulae for the standard deviations of the x and z atomic coordinates in a monoclinic cell have been given by Cruickshank (1949), equation (11·14). These lead to the unlikely result that errors are larger in monoclinic than in orthorhombic cells. On assuming statistical spherical symmetry of the $|F(hkl)|$ errors in reciprocal space ($\sigma(A_h) = \sigma(A_k) = \sigma(A_l)$), and spherical symmetry of the atomic peak ($A_{hh} = A_{kk} = A_{ll}$), a revised analysis allowing for the correlation of A_h and A_l (covariance $(A_h, A_l) = \cos\beta\sigma^2(A_k)$) shows that

$$\sigma(x) = \sigma(y) = \sigma(z) = \sigma(A_k)/A_{kk}\,.$$

Reference

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