Conformation of the "V" Amylose Helix

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Summary *X*-Ray analysis demonstrates that the "V" amylose helix is left-handed, that oxygen(6) is in a *gauche–trans* conformation in "V" amylose dehydrate, and that the helix undergoes a net 30° rotation upon hydration.

SINCE the original description of amylose in its "V" form as a compact helix with six glucose residues per turn,[1] various structural features have been advanced from studies with models[2] and from potential-energy calculations.[3] A structure analysis based on comparisons of observed versus calculated *X*-ray diffraction intensities is now reported.

Oriented filaments of "V" amylose dehydrate were prepared by the method of Zobel, French, and Hinkle,[4] and yielded the orthorhombic lattice constants, $a = 12{\cdot}9$, $b = 22{\cdot}4$, and c (fibre axis) $= 7{\cdot}95$ Å. Although the cell dimensions are pseudo-hexagonal, systematic absences imply that the space-group is $P2_12_12_1$ in the dehydrate and in other amylose species.[4] Intensity square-roots from the observed diffraction maxima of the zero and first levels are given in Table 1; these data were separately processed by means of the error function, $E = \Sigma \mid I_{calc}^{\frac{1}{2}} - I_{obs}^{\frac{1}{2}} \mid / \Sigma I_{obs}^{\frac{1}{2}}$, which is similar to a reliability index.

Intensity calculations were made by assigning a six-fold screw symmetry to the "V" helix and a temperature factor of 4·0 to all atoms in the unit cell. In constructing a mathematical model of helix, the geometry of the α-D-glucose residue was taken from single-crystal studies.[2,5] The other variables in the structure analysis are the angle of rotation of the glucose residue about the O(1)–O(4) line, the location of O(6), helix chirality, and the rotational and translational position of the helix within the unit cell.

Numerical values of the error function were computed for six helix models at increments of the helix rotation angle and the angle of rotation of the glucose residue about the O(1)–O(4) line using *hk*0 data, in order to test chirality of the helix and the alignment of the C(6)–O(6) bond vector with respect to the C(5)–C(4) and C(5)–O(5) bond vectors. The minimum values of E for left-handed helices having O(6) aligned *gauche–trans*, *trans–gauche*, and *gauche–gauche* were 0·14, 0·20, and 0·21, respectively; the lowest numerical values of E found for right-handed helices with O(6) in these same alignments were 0·24, 0·45, and 0·23, respectively. When the non-systematically-absent maxima were treated independently from the observed zero-level reflections, the left-handed helix with O(6) in the *gauche–trans* conformation

TABLE 1

Observed and calculated intensity square-roots

hkl	$I_{obs}^{\frac{1}{2}}$	$I_{calc}^{\frac{1}{2}}$
110,020	14	16
120	0	0
130,200	24	21
210	0	0
220,040	14	18
140	0	0
230	0	1
150,240,310	43	44
320	0	2
330,060	4	1
011	0	0
101	0	2
111,021	25	34
121	4	6
031	0	4
201,131	20	16
211	0	2
221,041	19	19
141	0	4
231	0	4
051	0	2
301	0	5
151,241,311	6	12
321	0	6
331,061	14	2
251	0	2
161	0	5
341	0	5
261,401	0	7
071	0	4
411	0	3
171,351,421	12	10

yielded better agreement than the other models with respect to the positional results obtained from the two data groups. Calculations made with *hkl* data located the translational position of the helix; and, moreover, the conclusion based on zero-level intensity comparisons, that the helix is left-handed and O(6) is aligned *gauche–trans* in "V" amylose dehydrate, was confirmed.

TABLE 2

Fractional atomic co-ordinates of the reference residue in "V" amylose dehydrate

Atom	*x*	*y*	*z*
C(1)	0·624	0·919	0·096
C(2)	0·590	0·869	−0·023
C(3)	0·481	0·852	0·017
C(4)	0·468	0·836	0·203
C(5)	0·511	0·886	0·314
C(6)	0·520	0·863	0·496
O(1)	0·556	0·968	0·067
O(2)	0·602	0·889	−0·194
O(3)	0·450	0·800	−0·078
O(5)	0·617	0·898	0·264
O(6)	0·561	0·907	0·601

Table 2 lists atomic parameters for a reference glucose residue of a left-handed helix within the orthorhombic unit-cell of "V" amylose dehydrate; the calculated intensity square-roots given in Table 1 were obtained using the parameters of Table 2. Oxygen(6) is in a *gauche–trans* conformation and the rotational position of the glucose residue about the O(1)–O(4) line, or tilt angle, is such that C(6) is closer to the helix axis than O(3). Placement of the residue was determined from plots of error functions against the positional variables, and space-filling models substantiated the helix location. The residue listed has a geometry found in the cyclohexa-amylose molecule,[2] and the helix has a glycosidic linkage angle of 116°. The helix location and the tilt angle were not significantly altered when the residue geometry from the α-D-glucose molecule[5] was used in calculating intensities. A very detailed specification of structure is not warranted because of the broadness of the minima encountered in the error function treatment. Tolerances for the positional variables obtained by examining the plots of error functions are ±4° for helix rotation, ±0·05 *c* for helix translation, and ±7° for tilt angle. It is estimated that the O(6) position might vary by ±20° of rotation about the C(5)–C(6) line.

Diffraction data from oriented filaments of "V" amylose hydrate, where $a = 13{\cdot}6$, $b = 23{\cdot}6$, and $c = 8{\cdot}01$ Å were also analysed. Although there is a net 30° rotation in the helix position, the dehydrate to hydrate transition brings about only small differences in the fibre-axis spacing and tilt angle. The enlargement in the *a* and *b* lattice constants upon hydration is due to an increase in packing diameter, while the helix conformation is essentially unchanged.

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