Studies on the Helical Structure of β-D-1,3 Xylan

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Structure of β-D-1,3 Xylan

The structure of β-D-1,3 xylan has been studied in detail. Atomic coordinates in the unit cell are determined. A method for calculating structure factors for the triple helical structure of β-D-1,3 xylan which is suitable for computer and which avoids Bessel function is described. The structure is further refined by least square method. The R-value and Φ-value are minimized at 0.41 and 4.417.

Introduction

The structure of β-D-1,3 xylan was studied by various workers [1–5]. Frei *et al.* [1] proposed unit cell dimensions in the dry state ($a = c = 13.7$ Å, $\beta = 60°$, $b = 5.85$ Å) and ($a = c = 15.4$ Å, $\beta = 60°$, $b = 6.12$ Å) in the wet state (lattice). A new helical structure has been proposed by Atkins *et al.* [8] in the light of helical diffraction theory and some new x-ray diffraction data together with IR absorption results. The structure proposed by Frei *et al.* [1] was rejected by these workers. They also rejected a four strand model of β-D-1,3 xylan. From infra-red and model building Atkins *et al.* [6] proposed a novel system of H-bonding in this material. Sathyanarayana *et al.* [7] studied the non bonded interaction energy for a pair of D-xylose residue joined through a β-1,3 linkage, the two strand model of Frei *et al.* [1] and the triple helix of Atkins *et al.* [8]. The energy was computed for all four helices (two strand right-handed helix, two strand left handed-helix, three strand right-handed helix, three strand left-handed helix) by considering the interaction of all the neighbouring residues in all of the strands of a particular helical conformation. The results indicated that the triple strand molecules had the minimum energy.

The present work describes:

i) A method for calculating structure factors for the triple helical structure of β-D-1,3 xylan which is suitable for computer, and which avoids Bessel function.

ii) Determination of coordinates representing the standard configuration of glucopyranose ring in the unit cell.

iii) Refinement by least square method.

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Several programs were written in Algol 60 code and KDF9 computer was used throughout this work.

A Computer Method for the Calculation of Structure Factors for the Triple Helix of Xylan

The structure factor can be given by

$$F_{hkl} = f_{IT} \exp 2\pi i\,(x X + y Y + z Z) \qquad (1)$$

where $x\,y\,z$ are the dimensioned coordinates and $X\,Y\,Z$ are the coordinates in reciprocal space.

f_{IT} = Atomic scattering factor (corrected for temperature).

The x, y, z and X, Y, Z can be related to cylindrical coordinates in dimensional and reciprocal space as follows:

$$x = r_I \cos \Theta_I, \quad y = r_I \sin \Theta_I, \quad z = z_I \qquad (2)$$

$$X = R' \cos \psi, \quad Y = R' \sin \psi, \quad Z = Z \qquad (3)$$

where ψ, R' are angular and radial coordinates of a lattice in reciprocal space, r_I, Θ_I, z_I are the real space cylindrical coordinates of Ith atom in the repeating unit.

Put (2) and (3) in (1), ther expresion (1) becomes:

$$F_{(R\,\psi\,Z)} = \Sigma f_{IT} \exp i\pi 2 R' r_I \cdot (\cos \Theta_I \cos \psi + \sin \Theta_I \sin \psi + z_I Z). \qquad (4)$$

The xylan polymer chains are interwined with line symmetry sr, (s – is a screw displacement, that is a translation parallel to the helix together with a rotation of $2\pi/M$ radians about helix axis, where M is a rotational number. r is a rotation of $2\pi/N$ radians about the helix axis, where N is any positive number greater than one), each individual helix having six xylose residues per turn in a pitch of 18.36 Å. The axial rise per residue is 3.06 Å. The

unit cell is hexagonal with space group $P6_3$ and dimensions $a = b = 15.4$ Å, $c = 6.12$ Å (fibre axis), $\beta = 120°$. There is one such triple helix per unit cell. The odd order 001 reflections will be absent. Hence the expression for structure factors can be given by

$$F_{(R'\psi Z)} = f_{IT} \exp 2\pi i z_I Z \left(\exp(i a \cos\mu) + \exp\left(i a \cos(\mu + 2\pi/3)\right) + \exp\left(i a \cos(\mu + 4\pi/3)\right) + (-1)^l \cdot \exp\left(-i a \cos(\mu + 4\pi/3)\right) + \exp\left(-i a \cos(\mu)\right) + \exp\left(-i a \cos(\mu + 2\pi/3)\right)\right) \quad (5)$$

where $a = 2\pi r_I R'$, $\mu = \Theta - \Psi$.

The expression (5) can further be simplified for A and B parts for l = even and l = odd for the calculations of structure factors.

Advantages of the Method

The Bessel function method involves an infinite series of term. Economic but accurate termination of the series present some difficulties. The present method gives expressions which are finite and exact. The coordinates of Atkins *et al.* [8] ($A-P$ system) were used to calculate structure factors for right handed triple strand. A temperature factor of 0.03 Å ($B/4 = 0.5922$) was applied [15]. The speed of execution is about 15 times faster than the same calculations which involve the use of Bessel function. A comparison is given in Table I.

Measurement of intensities

Atkins *et al.* [8] measured the intensities by taking the peak heights of the observed peaks. Therefore intensities were remeasured by the x-ray diffraction photograph [1, 8]. The area of individual reflections were taken by tracing the reflection using Joyce Loebl microdensitometer. The usual correction factors were applied to the area under the curve [14]. The observed values of the composite reflections were divided according to the calculated values [14].

Determination of coordinates of the glucopyranose ring

The detailed mathematical procedures are given elsewhere [9]. Starting from the atomic coordinates in the reference frame of Ramachandran *et al.* [16] (O-XYZ-system I [10]), the coordinates are obtained in second reference frame with O_3 as origin O′, O_3O_1 lying along $O'Y'$ axis and C_5 in the plane of $X'O'Y'$ (system II – Fig. 1). Turning to Atkins *et al.* system [8] we define a coordinate frame III in the identical manner to that used for system II. The Ramachandran *et al.* [16] coordinates in system II for the atoms of glucopyranose residue when transferred to system III define our $A-P-R$ hybrid structure. Finally we use the inverse transformation to change the coordinates from system III back to those basic system defined by the hexagonal unit cell (Fig. 2).

Table I. Calculated structure factors from two different sources (Bessel function and this work).

Reflection	Structure factors ** (Bessel function)	Structure factors (this work)
100	81.6	81.3
110	41.5	43.5
200	39.1	39.1
300	9.2	9.6
400	11.0	10.3
301	35.8	35.3
401	24.5	25.0
102	10.4	9.6
112	37.7	37.7
202	54.1	53.8
302	24.8	24.7

** Data kindly provided by E. D. T. Atkins.

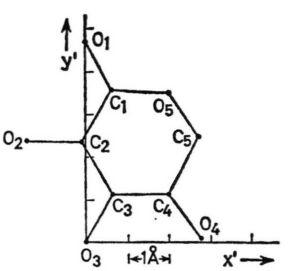

Fig. 1. 001 projection of β-D-1,3 xylan unit in system II, O_3 as origin, O_3-O_1 lying allong O′Y′ and C_5 in the plane X′O′Y′.

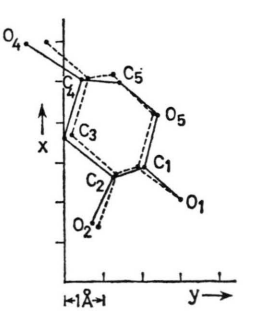

Fig. 2. Projections of β-D-1,3 xylan unit as determined by Atkins *et al.* [8] (shown as continuous lines) and as obtained in A–P–R system (shown as dotted lines).

Refinement by least square method [11]

The detailed mathematical procedure are given elsewhere [9]. The following parameters are used: i) $P1 = \Theta$ (radians) $P2$ = temperature factor, $P3$ = scaling factor. Φ [13], and R [12] values were computed after each cycle of refinement [14].

Results

The $A-P-R$ coordinates were used to calculate the structure factors. It was found by trial that the best values for the parameters Θ, and R' are -0.02 radians and -8%. The R-value was found to be 0.41. $A-P$ coordinates [8] gave an R-value of 0.45. The three parameters $P1$, $P2$ and $P3$ were used to refine the structure starting from $A-P-R$ system. The Φ was minimized at 4.417 from 4.785. The results are given in Table II.

Table II. Refinement by least square method.

	$P1$	$P2$	$P3$	R	Φ
Initial values	−0.02	0.5922	0.01955	0.41	4.785
Final values (13th cycle)	−0.051	0.6429	0.01573	0.41	4.417

Discussion

In this work a start has been made to refine the structure of β-D-1,3 xylan. Atkins *et al.* [8] gave an R-value of 0.29 for their structure. The calculated values from two different sources (Bessel function and this work) do not agree with the reported calculated values [8]. The sources of inaccuracies in their paper appears to arise out of the graphical method which they used to obtain structure factors at specific points from the continuous transforms. The remeasured values in the present work agree reasonably well with those of Atkins *et al.* [8]. It seems clear that both observed and calculated structure factors the values presented here are much more reliable. The R was calculated using the remeasured values (observed and calculated) and found to be 0.45. The parameters $P1$, $P2$ were varied by trial and R-value was reduced to 0.4. For best results a radial contraction of the transform was found with no change in Θ. This result can be compared with the statement of Atkins *et al.* [8] that their best fit when a radial expansion of 10% was allowed. In other words Atkins *et al.* [8] thought of a molecule which was some 10% larger in radial coordinates (r) than

hkl	|KFc| (K=scaling factor)	|Fo|
110	0.666	0.364
200	0.756	0.644
300	0.292	0.0
220	0.543	0.424
400	0.193	0.0
500	0.175	0.0
330	0.236	0.843
600	0.383	0.0
101	0.593	0.605
301	0.612	0.678
221	0.988	0.523
401	0.404	1.347
102	0.271	0.0
112	0.526	1.183
202	0.742	0.652
302	0.645	0.665
210	0.443	0.358
120	0.003	0.003
310	0.534	0.621
130	0.598	0.696
320	0.122	0.152
230	0.363	0.454
410	0.119	0.897
140	0.117	0.886
420	0.397	0.692
240	0.359	0.625
510	0.768	1.011
150	0.58	0.764
430	0.134	0.0
340	0.355	0.0
520	0.107	0.086
250	1.0	0.8
610	0.538	0.601
160	0.526	0.588
211	0.945	1.214
121	0.839	1.077
311	0.609	0.589
131	1.413	1.367
321	0.465	0.45
231	0.336	0.326
411	0.169	0.156
141	0.658	0.607
212	0.258	0.148
122	1.016	0.581

Table III.
A comparison of observed structures (Fo) and calculated structure factors (Fc) as obtained in the present work.

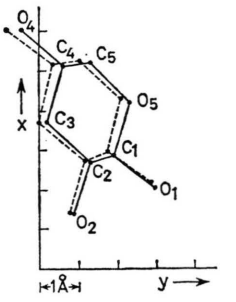

Fig. 3. Projections of β-D-1,3 cylan unit as determined in A−P−R system (shown as continuous lines) and as obtained in the present work by least square method (shown as dotted lines).

the figure quoted in their table. The present results seem to suggest that the molecule should be 8% smaller in radius. The $A-P-R$ coordinates gave an R-value of 0.41 and $\Phi = 4.785$ for $\Delta R'/R' = -8\%$ and $d\Theta = -0.02$ radians. Three parameters $P1$, $P2$, $P3$ were used to refine the structure. R remained the same, but Φ was minimized at 4.417. The results are given in Table III.

A comparison of the structure is also given in Fig. 3.

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