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

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β-D-1,3 Xylan

The triple helical structure of β-D-1,3 xylan is described. The ∅-value is reduced to 3.447 from 4.417 by number of small modifications to the structure including variations in the position of water molecule. The R-value after the refinement is found to be 0.37. The present calculations indicate that water is certainly involved with the structure possibly in a more complicated way as proposed by earlier workers. The present work supports the previous finding of Haleem and Parker that the molecule should be 8% smaller in radius.

Introduction

The little informations which are now available on the naturally occurring polysaccharide indicate that it is right handed triple helical structure of β-D-1,3 xylan [1–3]. Atkin *et al.* proposed a novel system of H-bonding in this material [4]. Haleem and Parker [5] used a new method for calculating the structure factors for the triple helical structure which is suitable for computers and which avoids the bessel function. These workers redetermined the coordinates which represented the standard configuration of glucopyranose ring in the unit cell. The structure was refined by least square method. The R-value [6] and ∅-value [8] were found to be 0.41 and 4.417 respectively. The present work describes:

1. Calculations of structure factors of the triple helical structure [5] and variants namely (a) Real space cylindrical coordinates (O) (b) R′-radial coordinates of the lattice in reciprocal space (c) Rotation of molecular chain along O_1-O_3 axis (d) Redetermination of temperature factor.
2. Determination of the position of water molecule in the helix
3. Calculations of R [6] and ∅-value [8] after parameter variation
4. Calculations of bond length and angles of the xylan unit.

Several programs [7] were written in *basic* language and Sord computer was used throughout this work.

Method of calculations

The xylan polymer chains are interwined with line symmetry sr [5], each individual helix having six residues per turn in a pitch of 18.36 A°. The unit cell is hexagonal with space group $P6_3$ with dimensions $a = b = 15.4$ A° and $c = 6.12$ A° (fibre axis), $\beta = 120°$. The axial rise per residue is 3.06 [2] A°.

The computer method [5] was used to calculate structure factors. The advantages of the method are given elsewhere [5].

The following parameters were used:

1. P1 = Change in the real space cylindrical coordinates (O) [5].
2. P2 = Change in the radial coordinates (R′) in reciprocal space [5].
3. P3 = Rotation of molecular chain along O_1-O_3 axis.
4. P4 = Temperature factor.
5. P5 = Change in the position of water molecule.

The intensities for composite reflections were divided in proportion according to the calculated values [9]. The xylan residue was rotated along O_1-O_3 (O_3 as origin) at different intervals. The general relationship for the rotation is given elsewhere [10]. Cartesian atomic coordinates were computed at each interval. The coordinates were then related to cylindrical coordinates in dimensional and reciprocal space [5].

Results

The projections of β-D-1,3 xylan unit as determined by Haleem and Parker [5] and as obtained in the present work are given in Fig. 1 and Fig. 2. The distances between C5, O5 atoms of the xylan residue and the water molecule are also given in Fig. 1. A

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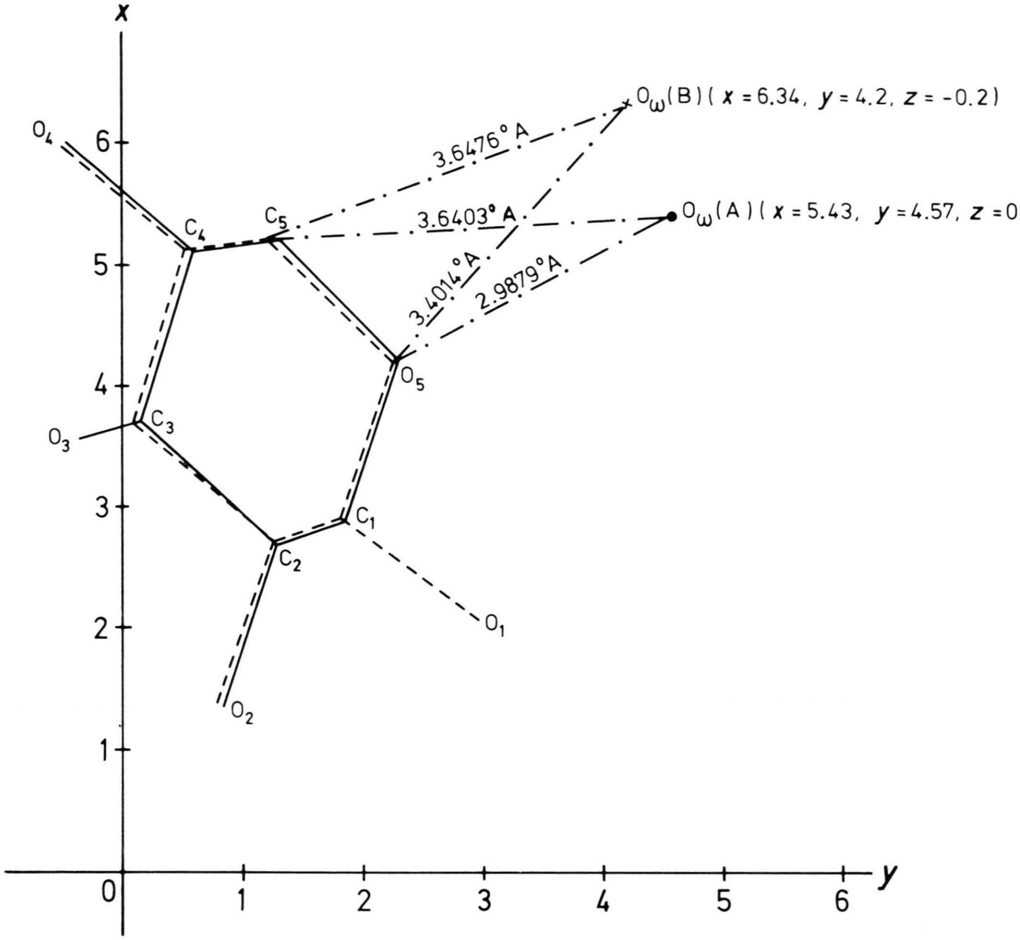

Fig. 1. 001 projections of β-D-1,3 xylan unit as determined by Haleem and Parker [5] (shown as continuous lines) and as obtained in the present work (shown as dotted lines). A and B represent the position of water molecule as determined by Haleem and Parker [5] and as obtained in the present work. The figure also shows distance between C5(– – –) and Ow(A), C5(– – –) and Ow(B), O5(– – –) and Ow(A), O5(– – –) and Ow(B).

comparison of observed and calculated structure factors is given in Table I. The bond lengths and angles are also given in Table II.

Discussion

The parameters P1, P2, P3 and P4 were adjusted by trial in order to reduce discrepancies between observed and calculated structure factors. The values obtained are as follows: P4 = 1.8, P3 = 0, P1 = −0.015 and P2 = −0.08 (−8%). R [6] and ∅ [8] values were found to be 0.41 and 5.004 respectively. The values are close to the values determined by Haleem and Parker [5]. The position of water molecule (P5) was then adjusted in order to reduce the discrepancies. The new position of water is found to be $r = 7.6$, $\theta = 0.585$ and $z = -0.2$, r, θ, z are the real space cylindrical coordinate of the water. At this stage R [6] and ∅ [8] values were minimized at 0.37 and 3.447 respectively. The parameters P1-P4 do not produce any significant change in the R [6] and ∅ [8] values. However, when the position of the water molecule was varied the R [6] and ∅ [8] values were changed significantly. It appears that water is certainly involved with structure, possibly in a more complicated way by Atkin *et al.* proposed [1]. The

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

h	k	l	|K Fc|	|Fo|	|△ F|=‖Fo|−K|Fc‖
1	1	0	0.6210	0.3640	0.2570
2	0	0	1.1164	0.6440	0.4724
3	0	0	0.4718	0.0000	0.4718
2	2	0	0.4516	0.4240	0.0276
4	0	0	0.4147	0.0000	0.4147
5	0	0	0.0472	0.0000	0.0472
3	3	0	0.1127	0.8430	0.7303
6	0	0	0.1052	0.0000	0.1052
1	0	1	0.7408	0.6050	0.1358
3	0	1	0.7893	0.6780	0.1113
2	2	1	0.9419	0.5230	0.4189
4	0	1	0.5298	1.3470	0.8172
1	0	2	0.1385	0.0000	0.1385
1	1	2	0.7304	1.1830	0.4526
2	0	2	0.7708	0.6520	0.1188
3	0	2	0.8483	0.6650	0.1833
2	1	0	0.3795	0.2228	0.1567
1	2	0	0.4776	0.2803	0.1973
3	1	0	0.5184	0.5290	0.0106
1	3	0	0.7531	0.7685	0.0155
3	2	0	0.2807	0.2065	0.0742
2	3	0	0.5874	0.4322	0.1553
4	1	0	0.6265	1.1335	0.5070
1	4	0	0.3042	0.5503	0.2461
4	2	0	0.3431	0.9144	0.5713
2	4	0	0.0677	0.1803	0.1127
5	1	0	0.2419	0.3143	0.0724
1	5	0	0.9454	1.2284	0.2830
4	3	0	0.3618	0.0000	0.3618
3	4	0	0.1109	0.0000	0.1109
5	2	0	0.0819	0.0816	0.0003
2	5	0	0.8036	0.8008	0.0028
6	1	0	0.4465	0.4357	0.0108
1	6	0	0.7384	0.7206	0.0179
2	1	1	1.1950	1.2194	0.0244
1	2	1	1.0496	1.0711	0.0214
3	1	1	0.6918	0.6102	0.0816
1	3	1	1.5399	1.3582	0.1816
3	2	1	0.3374	0.4213	0.0839
2	3	1	0.2906	0.3628	0.0722
4	1	1	0.2235	0.3226	0.0991
1	4	1	0.3725	0.5376	0.1651
2	1	2	0.1281	0.1226	0.0054
1	2	2	0.6122	0.5863	0.0259

distance between Ow (A) -- 05 (B), Ow(A) -- C5(B), Ow(B) -- 05(B), Ow(B) -- C5(B) is 2.988 A°, 3.64 A°, 3.401 A° and 3.648 A° respectively (A refers to the position of the atoms determined by Haleem and Parker [5] and B refers to the position of the atoms obtained in the present work, Ow repres-

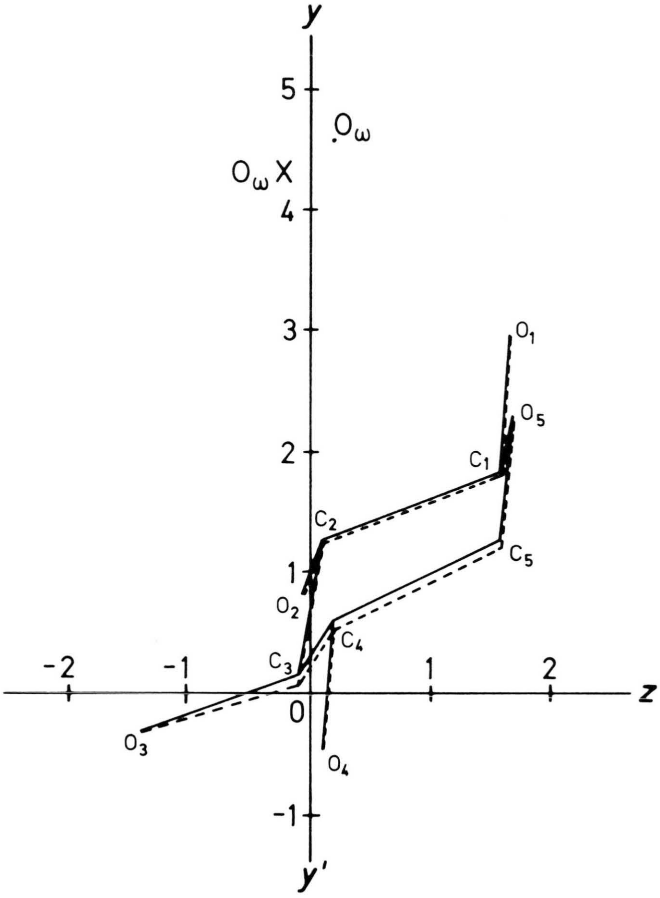

Fig. 2. 100 projections of β-D-1,3 xylan unit as determined by Haleem and Parker [5] (shown as continuous lines) and as obtained in the present work (shown as dotted lines). Dot (.) and cross (×) represent the position of water molecule as determined by Haleem and Parker [5] and as obtained in the present work respectively.

Table II. Bond lengths and bond angles of β-D-1,3 xylan unit.

Interatomic distances [A°]		Bond angles [°]	
C1−C2	1.52	C1−C2−C3	109.5
C2−C3	1.52	C2−C3−C4	111.4
C3−C4	1.51	C3−C4−C5	110.4
C4−C5	1.53	C5−O5−C1	114.3
C5−O5	1.41	O1−C1−C2	108.9
C1−O5	1.42	C1−C2−O2	110.4
C1−O1	1.38	O2−C2−C3	111.3
C2−O2	1.41	C2−C3−O3	109.8
C3−O3	1.40	O3−C3−C4	110.6
C4−O4	1.41	C3−C4−O4	111.1
C5−O5	1.41	O4−C4−C5	110.2
		O1−C1−O5	107.8
		C4−C5−O5	110.2
		O5−C1−C2	109.6

Table III. Interatomic distances.

Interatomic distances A°	
C5(A)−−Ow(A)	3.57
C5(A)−−Ow(B)	3.59
C5(B)−−Ow(A)	3.64
C5(B)−−Ow(B)	3.65
O5(A)−−Ow(A)	2.95
O5(A)−−Ow(B)	3.39
O5(B)−−Ow(A)	2.99
O5(B)−−Ow(B)	3.40

Ow = water molecule; A = position of the atom as obtained by Haleem and Parker [5]; B = position of the atom as obtained in the present work.

ents position of the water molecule). The results are summarized in Table III for the atoms A and B. The calculated value for the shift of Ow(A) is 1.1 A°. It is felt that water will certainly play a role in determining the chirality of the triple helical structure of β-D-1,3 xylan. Further work on the inter molecular bonding arrangement will be required.

The $O2^{I} -- O2^{II}$ distance in the structure is 2.8 A°, I and II denote the individual helical chains in the structure. (O2 radial coordinate obtained in the present work is 1.63). Atkin and Parker [2] suggested an O2 radial coordinate of 1.65 A° for the separation of 2.9 A°.

A comparison of observed and calculated structure factors indicate that the overall fit is better as compared to earlier model [5] (Table I). However the comparison indicates large discrepancies for the following planes 300, 400, 500, 330, 401, 102, 420, 240, 430, 340. The results obtained in the present work confirms the previous findings [5] that the molecule should be 8% smaller in radius. Furthermore the relationships [5] for calculating structure factors are suitable for mini computers.

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