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Preliminary communication

X-Ray diffraction data for (1→3)-α-D-glucan

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(1→3)-α-D-Glucan, previously mentioned in connection with dental caries[1], is one of the eight homopolymers of D-glucopyranose. The chain conformation of three of these polysaccharides, *i.e.* cellulose[2–4], amylose[2–4], and (1→3)-β-D-glucan[5,6], has been established by X-ray analysis. From conformational calculations, the chain conformation of (1→3)-α-D-glucan was predicted to be an extended, ribbon-like[7,8], single helix[8], double, or triple helix[9]. We report the unit-cell parameters of 1 (1→3)-α-D-glucan based on X-ray diffraction data.

The sample of (1→3)-α-D-glucan used in this study was prepared by mild periodate degradation of a water-insoluble α-D-glucan produced by *Streptococcus salivarius* TTL-LP1 incubated in a 5% sucrose medium[10]. The backbone of the purified D-glucan ($[\alpha]_D$ +225° in M NaOH) was found to consist exclusively of (1→3)-α-linked D-glucose residues with short chains of (1→6)-α- and (1→4)-α-linked D-glucose residues[11,12]. After oxidation with 0.05M sodium periodate for 14 days at 5°, reduction with sodium borohydride at room temperature, and hydrolysis with 50mM sulfuric acid for 20 h at 25°, the degraded D-glucan was still water-insoluble. In ultracentrifugal analysis, a 0.5% solution of the D-glucan in M sodium hydroxide showed a single and symmetrical peak ($S_{20,\,NaOH}$ 2.472 s), indicating that the D-glucan was homogeneous. Methylation analysis showed a linear molecule consisting solely of (1→3)-α-D-glucosidic linkages. The D-glucan was hardly soluble in dimethyl sulfoxide, even at a high temperature (80°), but gave clear solutions in aqueous alkali, hydrazine hydrate, and *N*-methylmorpholine *N*-oxide–dimethyl sulfoxide, respectively. Attempts to prepare a continuous film or a well-oriented fiber from these solutions were not successful. Therefore, a sample of the D-glucan was acetylated four successive times[13]. A 5% solution in chloroform of the part of the D-glucan acetate having a degree of substitution of 2.9 (n.m.r.) was deposited onto a polyethylene terephthalate film and left to evaporate. The D-glucan acetate film thus prepared could easily be peeled off from the base film. A well-oriented film was obtained by stretching a strip of the acetylated D-glucan

6.5 times at ~150° in glycerin. The stretched film was immersed into 2M sodium methoxide–methyl alcohol for 17 h at room temperature, the length of the film being kept constant. The film was subsequently washed with methyl alcohol and water; the *O*-deacetylation was complete (i.r.), and a well-oriented X-ray fiber-pattern was observed. The crystallinity of the film was remarkably improved by annealation in water at 140°, in a sealed bomb, as for (1→3)-β-D-glucan[6]. The density was measured for a solution of carbon tetrachloride–*m*-xylene by a flotation method, and the X-ray patterns were recorded in a flat-film camera with a Shimadzu GX-3B X-ray diffractometer using Ni-filtered CuKα radiation generated at 40 kV and 15 mA.

Fig. 1 shows the X-ray diffraction pattern of the annealed D-glucan film when the sample was irradiated *in vacuo*, and the X-ray data are given in Table I. All the 28 reflections on the 0, 1st, 2nd, 3rd, and 4th layer lines could be indexed in terms of axial lengths and the angle of a monoclinic (pseudo-orthorhombic) system: $a = 8.23 \pm 0.04$; $b = 9.55 \pm 0.06$; c (fiber axis) = 8.44±0.02 Å; and $\gamma = 90°$*. The volume of this cell (0.663 nm^3) and the density (1.544 g/cm^3) observed for an annealed D-glucan film that had been kept *in vacuo* overnight are in good agreement with the values calculated for four D-glucose residues per

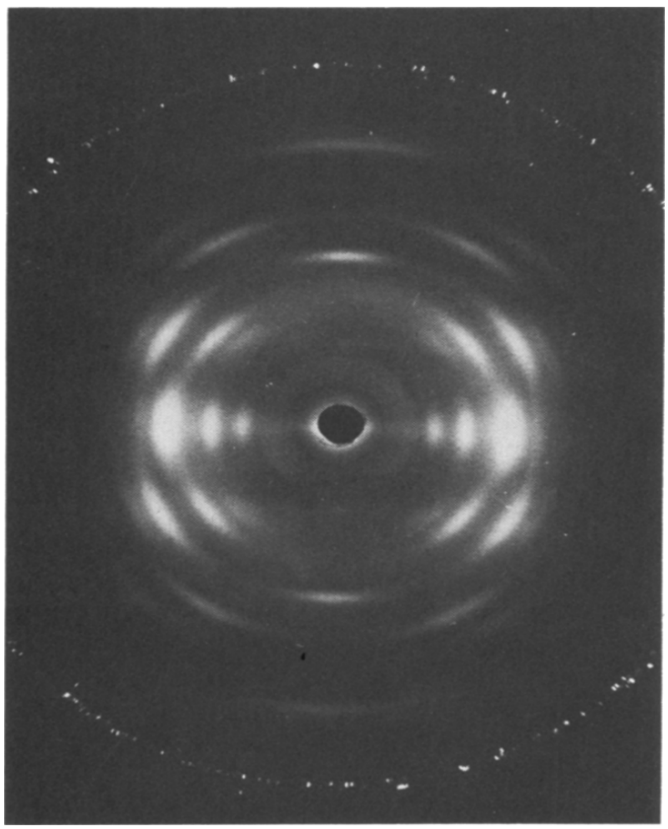

Fig. 1. The X-ray diffraction pattern of the annealed D-glucan film after sample irradiation *in vacuo*.

*Lattice parameters were obtained by a least-squares refinement program.

TABLE 1

OBSERVED SPACINGS AND INTENSITIES FOR THE ANNEALED (1→3)-α-D-GLUCAN *in vacuo*

h	*k*	*l*	*Spacing (Å)*		*Intensity*[a]	*h*	*k*	*l*	*Spacing (Å)*		*Intensity*[a]
			Calc.	*Obs.*	*(Obs.)*				*Calc.*	*Obs.*	*(Obs.)*
0	1	0	9.55			0	0	2	4.22	4.22	s
1	0	0	8.23	8.21	s	0	1	2	3.86		
1	1	0	6.24	6.28	s	1	0	2	3.76	3.77	vw
0	2	0	4.77	4.76	vs	1	1	2	3.49	3.48	s
1	2	0	4.13	4.10	m	0	2	2	3.16	3.14	m
2	0	0	4.12			1	2	2	2.95	2.95	vw
2	1	0	3.78	3.73	w	2	0	2	2.95		
0	3	0	3.18			2	1	2	2.82	2.75	w
2	2	0	3.12	3.11	w	0	3	2	2.54	2.54	w
1	3	0	2.97			0	0	3	2.81		
3	0	0	2.75	2.75	vw	0	1	3	2.70	2.76	s
0	0	1	8.44	8.44	vw	1	0	3	2.66	2.65	w
0	1	1	6.32			1	1	3	2.56	2.55	vw
1	0	1	5.89	5.87	w	0	2	3	2.42	2.42	w
1	1	1	5.01	5.03	s	0	0	4	2.11	2.10	vw
0	2	1	4.15	4.14	vs	0	1	4	2.06		
1	2	1	3.71	3.71	m	1	0	4	2.04		
2	0	1	3.70			1	1	4	2.00	2.00	w
2	1	1	3.45	3.38	w						
0	3	1	2.98	2.99	w						
2	2	1	2.93								
1	3	1	2.80								
3	0	1	2.61								
3	1	1	2.52	2.53	w						

[a]Abbreviations: vs, very strong; s, strong; m, medium; w, weak; and vw, very weak.

unit cell. Examination of the meridional reflections revealed the presence of a very weak (001), a strong (002), and a very weak (004) reflection, the (003) reflection being absent. Despite the lack of precision of these meridional reflections, a two-fold screw axis along the *c*-axis has been incorporated into the (1→3)-α-D-glucan backbone conformation. A space group $P2_1$ is suggested as, by tilting the D-glucan film, the (002) and (004) reflections became strong, but the (001) did not. The presence of the very weak (001) reflection is likely due to a slight disorder of OH-6 along the D-glucan chain as for [14] D-mannan I. Comparison of the values of the helical parameters, $n=2$ and $h=4.22$ Å, with the data of Rees and Scott[7], and of Sathyaranayana and Rao[8], suggests that the (1→3)-α-D-glucan molecule is extended along the fiber axis.

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