

Note to the Editor

Structural polymorphism of (1→4)-β-D-Xylan

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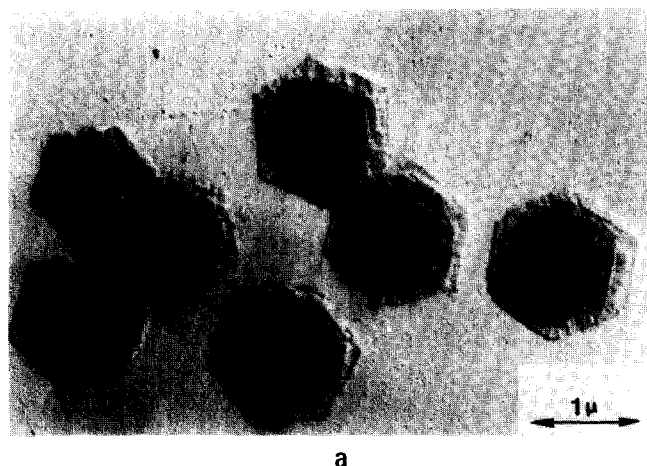
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A number of X-ray examinations on (1→4)-β-D-xylan-type materials have been reported over the years¹⁻⁷. Although the source of xylan varies, all crystallographic data are in good agreement with the structure proposed by Nieduszynski and Marchessault¹ for the xylan hydrate. The structure was a hexagonal unit-cell with the chains in a three-fold helical conformation stabilized by water molecules. It was noticed that cell parameters were sensitive to hydration conditions⁶, but in the hydrated state, where best crystalli-

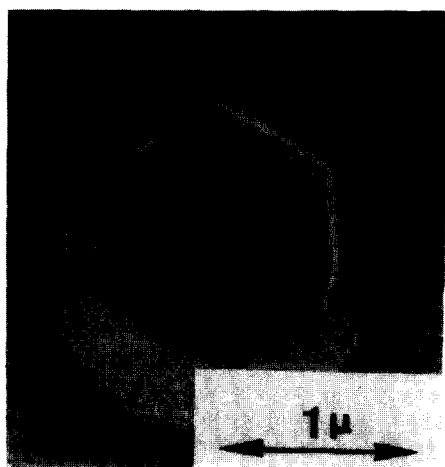
nity is achieved, all (1→4)-β-D-xylans crystallize in the hexagonal unit-cell structure. Except for the hydrate and dry forms, no other polymorphs are known for (1→4)-β-D-xylan.

The authors have obtained single crystals of a new polymorph of (1→4)-β-D-xylan and are reporting, herein, crystallographic data obtained from electron and X-ray diffraction. Xylan was extracted from esparto grass according to the method described by Chanda *et al.*. Procedures described by Marchessault *et al.*⁹ to obtain hexagonal xylan single crystals were used. A 0.05% (w/w) aqueous suspension of linear, acid-free xylan was autoclaved at 120°C for 4 h and cooled to room temperature. The clear solution then crystallized after 6 to 48 h. After centrifugation and washing with water, observation of the sediment by electron microscopy revealed hexagonal single crystals of the type shown in *Figure 1a*. The crystals are similar to those obtained by Marchessault *et al.*⁹ and the electron diffraction pattern (*Figure 1c*) corresponds to that of Atkins *et al.*¹². It can be indexed on a trigonal array and corresponds to a real lattice spacing of $a = b = 9.2 \text{ \AA}$. This value is in good

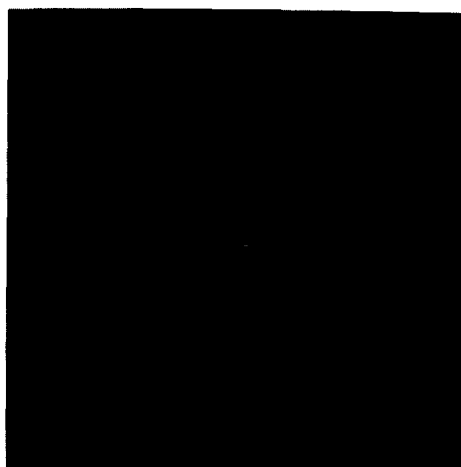


a

Figure 1 (a) Electron micrograph of (1→4)-β-D-xylan - form I; single crystals. (b) Enlarged single crystal of (1→4)-β-D-Xylan - form I and (c) an electron diffraction pattern of an hydrated specimen appropriately oriented with respect to the crystal



b



c

Table 1 X-ray and electron diffraction *d* spacings (Å) for (1 → 4)-β-D-Xylan - form II

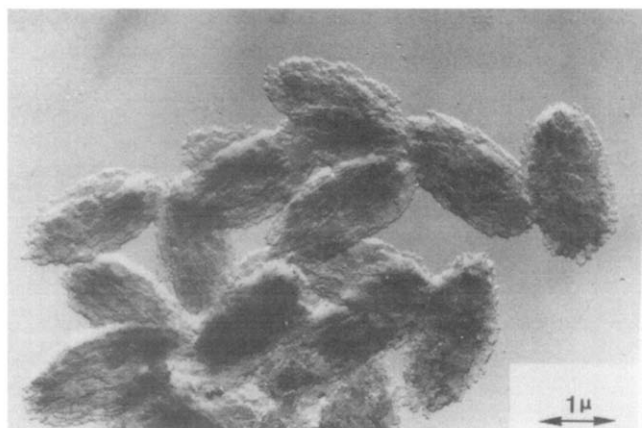
X-ray diffraction	Electron diffraction (Miller Index)
8.02	
7.00	
6.12	6.10 (120)
5.77 S	5.75 (200) S
5.36	5.32 (210)
4.48 VS	4.49 (220), 4.47 (130) VS
4.08	
3.69	3.67 (230), 3.60 (040)
3.43	3.43 (140)
3.26	
3.06	(240)
2.89	(400)
2.70	(420)
	2.41 (060)
	2.23 (260)

agreement with the 9.16 Å reported by Marchessault and Nieduszynski¹ for (1 → 4)-β-D-xylan hydrate using X-ray fibre diffraction.

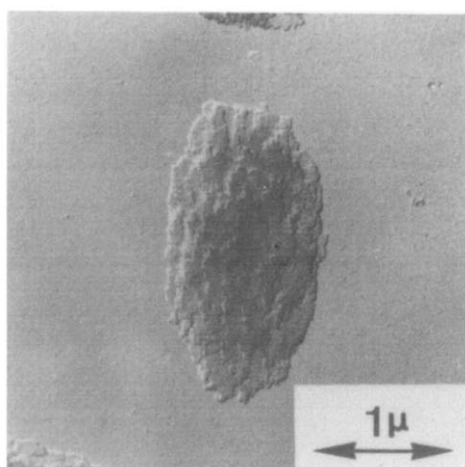
A 0.05% (w/w) aqueous suspension of hexagonal xylan single crystals obtained as above, was autoclaved at 140°C for 4 h. After cooling to room temperature, the solution became turbid readily and was immediately centrifuged and washed with water. The sediment was shadowed and ob-

served in a Philips-300 transmission electron microscope. Typical single crystals observed are shown in Figure 2a. The crystals consist of lamellar stacks (each lamellae about 100 Å in thickness) and the overall shape is clearly oval. Figures 2b and 2c show, respectively, an enlarged single crystal of (1 → 4)-β-D-xylan and the electron diffraction pattern appropriately oriented with respect to the crystal. The diffraction spots can be indexed on an orthogonal array and correspond to real lattice spacings of *a* = 11.5 Å and *b* = 14.4 Å. The strongest spot was indexed as the (130) reflexion.

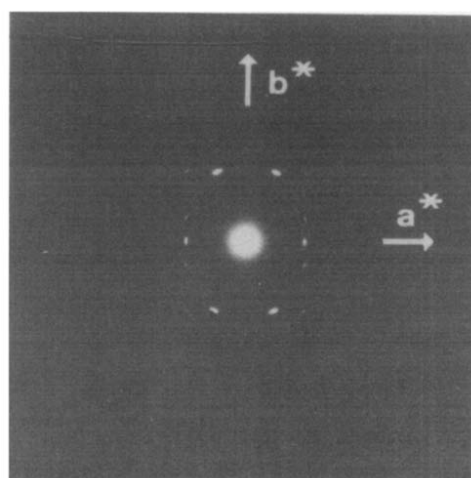
The initial hexagonal shape of the crystal prior to the second autoclave treatment has completely vanished and the electron diffraction pattern is considerably modified. It is now an orthogonal array compared to the initial trigonal array. The real lattice spacings changed from *a* = *b* = 9.2 Å to *a* = 11.5 Å and *b* = 14.4 Å. Furthermore, the new crystalline form shows no susceptibility to hydration. In the case of hexagonal xylan single crystals, maintenance of the sample in a hydrated state is conducive to high crystallinity as revealed by electron diffraction (Figure 1c). This electron diffraction pattern was obtained using the method of the frozen hydrate described by Taylor *et al.*³ If the water of crystallization is removed from the crystal, one obtains a rather poor diffraction pattern but the trigonal array is still recognizable. In the case of the oval-shaped xylan crystals, no noticeable changes in crystallinity and cell parameters were observed with hydration. The hexagonal and oval-shaped xylan crystals are named respectively (1 → 4)-β-xylan - form I and form II. Sugar analysis on the oval-type single crystals gave 100% molar composition of xylan sugar residue, thus proving the new crystalline form is due to xylan. The degree of polymerization (\overline{DP}_n) is less than 18 since \overline{DP}_n measurements on the hexagonal single crystals, prior to the second autoclave treatment, gave a value of 18. However, we do believe that we are not dealing with xylan oligomers (up to xylohexaose). Comparisons of the crystallographic data of this new xylan crystalline form with those of crystalline xylose oligosaccharides¹⁰



a



b



c

Figure 2 (a) Electron micrograph of (1 → 4)-β-D-xylan - form II single crystals. (b) Enlarged single crystal of (1 → 4)-β-D-xylan - form II and (c) an electron diffraction pattern approximately oriented with respect to the crystal

show no agreement. Furthermore, xylose oligosaccharides are known to be water soluble¹¹. No dissolution occurs with the (1 → 4)-β-D-xylan – form II, even when the suspension is heated to 100°C for several hours. Further treatments with the autoclave at 140°C cause no modifications to the crystals. They seem unlikely to redissolve even at this high temperature.

Crystallographic data for (1 → 4)-β-D-xylan – form II are tabulated in *Table I*. Calculations of *d* spacings from X-ray and electron diffraction are in good agreement. From the X-ray powder diagram, four reflexions could not be indexed as *hk0* reflexions and they correspond to *d* spacings: 8.02, 7.00, 4.08 and 3.26.

This is not the first time that a different crystalline form than the hexagonal crystal structure for (1 → 4)-β-D-xylan is reported.

Roelofsen², in an attempt to obtain more information on β(1 → 4) xylan crystals described by Yundt⁵ observed a different crystalline morphology. His X-ray data compare favourably with those we are reporting in this paper.

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