Note

On the hydration of β-D-(1→4)-xylan

F. A. BETTELHEIM
Chemistry Department, Adelphi University, Garden City, N. Y. 11530 (U. S. A.)

(Received August 19th, 1971; accepted October 12th, 1971)

In a recent article Nieduszynski and Marchessault[1] proposed that the hexagonal unit cell of β-D-(1→4)-xylan isolated from white birch provides a columnar lattice site along the fiber axis which can accommodate occasional side chains of 4-*O*-methyl-D-glucuronic acid and a column of water molecules. It is a peculiar aspect of this empty columnar lattice site that it can laterally expand and, thereby, accommodate different numbers of water molecules at different degrees of hydration. The accommodation apparently occurs without change in unit-cell symmetry, although the presence of the water molecule will give stability to the unit cell. This was deduced from the increasing degree of crystallinity obtained with increasing water content[2,3].

It is interesting that β-D-(1→4)-xylan isolated from oat hulls[3] contains twice as many side chains as that from white birch, although it has essentially the same unit cell. (The side chains of oat-hull xylan are composed of L-arabinose and D-galactose residues beside the preponderant 4-*O*-methyl-D-glucuronic acid residue). In Table I the spacings of two xylan hydrates are compared. The birchwood xylan hydrate showed 14 reflections[4] when a good fiber was prepared, although in previous preparations[2] only seven reflections could be observed. Here are reproduced only those reflections which are equivalent to the reflections of the oat-hull xylan. Thus, it is

TABLE I

OBSERVED SPACINGS OF XYLAN HYDRATES

Spacing (Å)		*Indices*[a]
Oat-hull xylan	*White-birch xylan*[a]	
8.21	7.85	110
7.02	7.02	111
5.41	5.43	112
4.70	4.64	200
3.89	3.91	202
3.55	3.53	222
2.84	2.79	115

[a] Ref. 4.

probable that unit-cell symmetry depends only on the xylan backbone, since the empty columnar space can accommodate other and more numerous side chains.

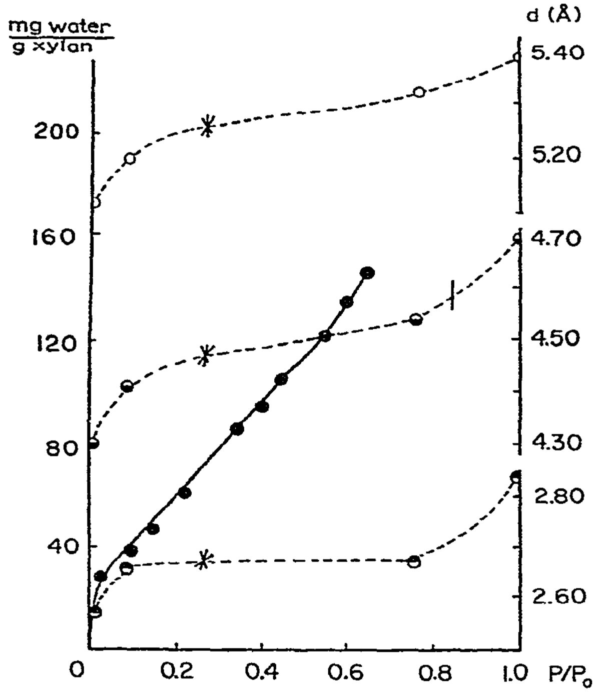

Fig. 1. Water-vapor sorption isotherm ●——● of oat-hull xylan at 29°. Change in the spacings originating from the planes ◒– – –◒ (200) ○– – –○ (112), and ⊖– – –⊖ (025) of the xylan unit-cell as a function of relative vapor pressure (P/P_0).

On the other hand, hydration studies indicate that, at least in the oat-hull[1] xylan, the water density may vary along the columnar sites. In Fig. 1, the water-vapor sorption isotherm of oat-hull xylan at 29° is presented. At the same time, the change in the X-ray reflection spacings as a function of relative vapor pressure (hence, water content) is also given for three different reflections. The change in the spacings indicates that most of the structural changes in the unit cell occur at the beginning and at the end (saturation) of the water-vapor sorption process. Analysis of the isotherm in terms of the BET[5] or Hailwood and Horrobin[6] model gave a "monolayer" uptake of 0.5 mole of water per monomer or 3 moles of water per unit cell assuming that all the xylan is crystalline. However, as is the case for most polymers, xylan is only semicrystalline and, since the amorphous part usually sorbs water with greater ease, these hydration figures can be taken as an upper limit. "Monolayer" here means the amount of water sorbed on the energetically favorable hydrophilic surface of the polymer[7]. It is obvious that the change in unit-cell parameters due to swelling is not as great after "monolayer" coverage as it was during the establishment of the "monolayer" (point marked by asterisks in Fig. 1.). Furthermore, isosteric heats of sorption rapidly decrease beyond the "monolayer" uptake[3], which indicates multilayer formation. Thus, not all water molecules in the unit cell are hydrogen bonded to the polar groups of xylan.

One may argue that the more numerous side chains in oat-hull xylan would be the primary binding sites of water. This is contradicted by the fact that water has a similar crystal-organizing effect in both birch-wood and oat-hull xylans, which indicates an interaction with the polymer backbone.

It seems that the "empty" lattice sites can accommodate water molecules hydrogen-bonded to the polymer ("monolayer") as well as water molecules hydrogen-bonded to other water molecules only. The xylan hydrate for which Marchessault and Settineri[4] have established the unit cell dimension as $a = b = 9.16$ Å; $c = 14.84$ Å; $\gamma = 120°$ (see vertical line mark on Fig. 1) would have 7 molecules of water in the unit cell as an upper limit. However, due to the amorphous content of the polymer, it is probably closer to 6 molecules of water per unit cell, in agreement with the values quoted for birch-wood xylan[2].

REFERENCES

1 I. Nieduszynski and R. H. Marchessault, *Nature*, 232 (1971) 46.
2 R. H. Marchessault and T. E. Timell, *J. Phys. Chem.*, 64 (1960) 704.
3 F. A. Bettelheim, Ph. D. Dissertation, University of California, Davis, 1956.
4 R. H. Marchessault and W. J. Settineri, *J. Polymer Sci., Part B*, 2 (1964) 1047.
5 S. Brunauer, P. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, 60 (1938) 309.
6 A. J. Hailwood and S. Horrobin, *Trans. Faraday Soc.*, 42 D. Suppl. (1946) 84 and 94.
7 F. A. Bettelheim, A. Block, and L. J. Kaufman, *Biopolymers*, 9 (1970) 1531.