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Communications to the Editor

Crystal Structure of Native Cellulose

The first X-ray diffraction pattern of native cellulose was taken by Nishikawa and Ono in 1913.[1] Thereafter, many works have been done for the structural study of native cellulose. In 1931, Meyer and Misch proposed the antiparallel structure model containing two chains with the opposite directions in a unit cell.[2] The antiparallel structure had been accepted until, in 1972, Gardner and Blackwell[3] and Sarko and Muggli[4] proposed simultaneously the parallel structure, in which two chains in a unit cell assume the same direction. Recently, many problems are pointed out for the parallel structure from the viewpoints of solid-state high-resolution NMR studies.[5,6] In the present study, the crystal structure of the native cellulose was reexamined by using the ramie cellulose. The crystal region of native cellulose is composed of a rather random stacking of up and down sheets, which are formed by hydrogen bonding the up and the down molecules, respectively. The order and disorder on the stacking of two kinds of sheets, up and down, may bring about the crystal structure difference among the species, for example, ramie, valonia, cotton, and woods.

A fiber specimen was prepared by bundling the ramie fibers. X-ray measurements were carried out by using Cu Kα radiation monochromatized by a pyrolyzed graphite. The fiber diagrams were taken in vacuo by cylindrical cameras with 5 and 10 cm radii. The Weissenberg photographs were also taken according to Norman's method.[7] The integrated intensities were mainly estimated by a drum scanner (Optronics). Intensities of some very weak reflections were visually estimated, and strong reflections were measured by a PSPC (position-sensitive proportional counter). Some of the overlapped reflections were resolved into individual reflections by using the curve resolution procedure assuming the Gauss-Cauchy function.[8] Thus, 50 independent reflection intensities were measured. The number of data is about twice as many as 24 data for ramie cellulose reported by Mann et al.[9] and is more than 39 data for valonia cellulose measured by Gardner and Blackwell.[3]

The observed reflections could be indexed by a monoclinic unit cell with parameters a = 8.34 Å, b = 7.71 Å, c (fiber period) = 10.37 Å, γ = 97.6°, and the space group $P2_1 - C_2^2$, which is essentially the same as those reported by Meyer and Misch. Two molecules contained in the unit cell locate at the center and corner and are symmetrically independent although the molecule possesses a 2-fold screw axis. Through the present study, the refinements were made by the constrained least-squares method[10-12] by using the accepted bond lengths and bond angles[13] under the assumption that two molecules at the center and the corner assume the same conformation but with different heights and different azimuthal angles. The models p1, p2, a1, and a2 reported by Gardner and Blackwell were reexamined, but the R-factor did not improve to the value less than 21% for each model. Therefore, the statistical models (sw1, sw2, sw3, sw4) are built up, in which up- and down-pointing molecules coexist at a crystal site with different probabilities. This type of statistical structure is found in the case of poly(vinylidene fluoride)[14] and silk.[15] The models sw1, sw2, sw3, and sw4 are different from each other with respect to the relative heights of up and down molecules statistically coexisting at a crystal site. In model sw2, the pyranose rings of the up and down molecules almost coincide with each other, and the down-molecule shifts up by $-c/4$ in the model sw1, by $c/4$ in sw3, and by $c/2$ in sw4. Therefore, the pyranose rings in the sw1 and sw3 models are staggered with respect to the heights, while, in the sw2 and sw3 models, the rings have almost the same height. The center chain shifts up by $c/4$ with respect to the corner chain in the same direction. The refinements started from every 60° of χ values, the internal rotation angle of the hydroxymethyl group, in order to determine which of the six possible conformations is the case. The existence probabilities of the up and down molecules at the center site were refined independent of those at the corner. Among these models, sw1 gives the lowest R-value 16.9% (sw2, 19.1%; sw3, 19.4%; sw4, 19.3%). The crystal structure (model sw1) is shown in Figure 1. The up and down molecules statistically coexist at both the corner and center sites with almost the same probability. From the calculation of the interatomic distances, the hydrogen bonds were concluded to be formed only between the molecules having the same direction in the ac plane. The hydrogen-bonding networks are shown in Figure 2. It should be noted that the intramolecular hydrogen bond is formed only between O(3) and O(5) atoms, and the hydroxymethyl group is associated only with the intermolecular hydrogen bonds.

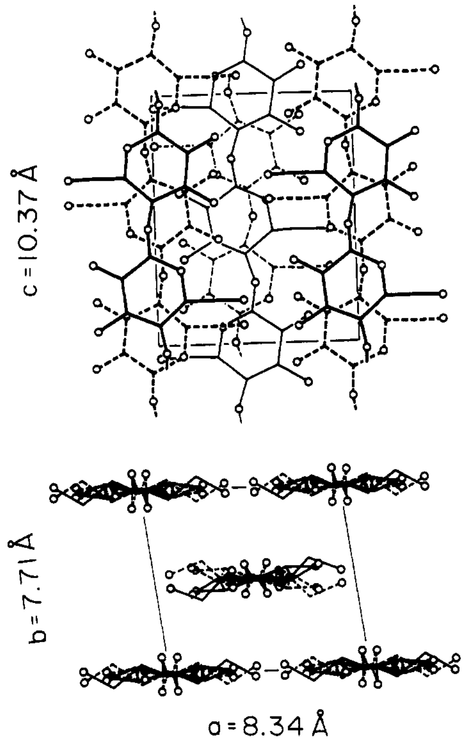

Figure 1. Crystal structure of native cellulose.

On the basis of the above-mentioned structure (sw1 model), the refinement was made for the valonia cellulose

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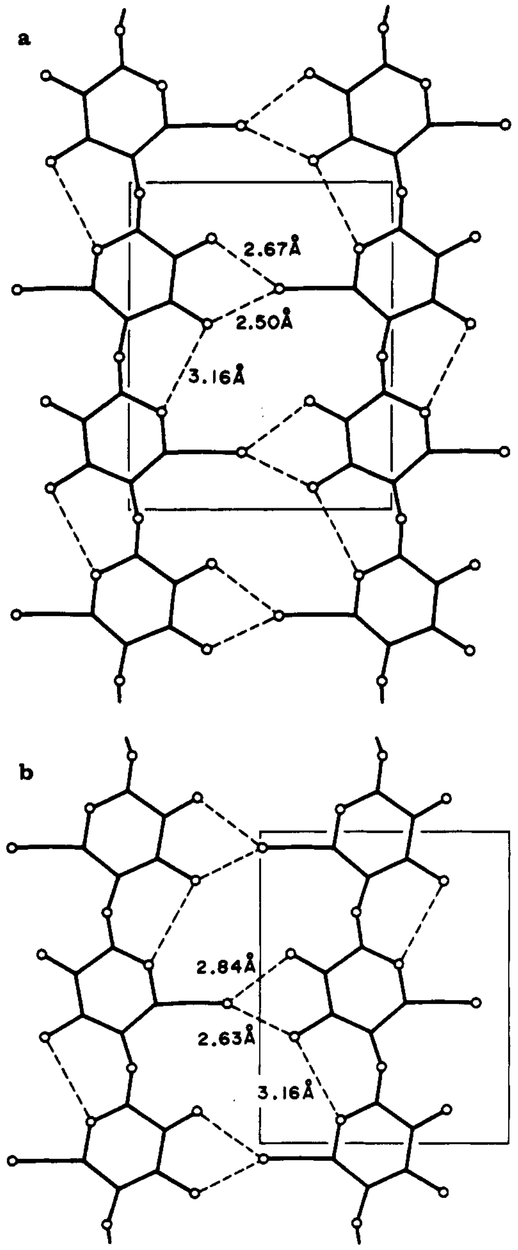

Figure 2. Hydrogen-bonding networks formed (a) by the corner chains and (b) by the center chains.

by using 36 observed reflections reported by Gardner and Blackwell. The R-factor improved to 11.7%, which is far better than 17.9% obtained for the parallel chain model by Gardner and Blackwell in spite of the same data. The ratios of the up to down molecules are 0.7 to 0.3 at the corner and 0.5 to 0.5 at the center of the unit cell. The difference in the probability should be attributed to a short-range order in stacking of the up and down sheets. In fact, on the X-ray diffraction pattern of valonia cellulose, the weak superlattice spots, which cannot be indexed by the two-chain unit cell but can be indexed by the eight-chain unit cell,[16] were found. These spots show the existence of the order having the period longer than a two-chain unit. The crystal structure difference among the other celluloses of different origins may also be attributed to the different existence probabilities, i.e., different orders in stacking of the up and down sheets. A schematic representation of the stacking of the sheet structure in the crystalline region is shown in Figure 3.

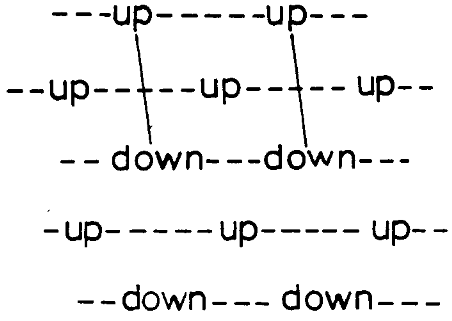

Figure 3. Schematic representation for stacking of the up- and down-sheet structures.

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