Comments on the Proposed Helical Structure of Cellulose I

The bases on which Viswanathan and Shenouda[1] propose that native cellulose has a helical conformation would seem to be in error, leaving such a structure without apparent foundation.

Their reported value of 10.3912 Å for the $O(1')-O(4)$ distance in cellobiose is obtained if, during the conversion from crystallographic to ångström coordinates, the β angle of 90.83° is not considered. When one calculates the interoxygen distance using the β angle and the other data given by Chu and Jeffrey,[2] a value of 10.35 Å results. This distance is not significantly different from the 10.34 ± 0.02 Å fiber repeat spacing reported by Wellard[3] for all cellulose polymorphs. It follows that it is not necessary for the cellobiose molecule to tilt in order to meet the fiber repeat spacing.

Equatorial intensity calculations presented by the authors as evidence for a helical structure were based on an incorrect formula which does not account for destructive interference from a more or less centered cell. The expression for the structure factor (not the intensity) should have been

$$F_{h0l} = \sum_{j=1}^{168} f_c e^{2\pi i (hx_j + lz_j)} + \sum_{m=1}^{140} f_o e^{2\pi i (hx_m + lz_m)}.$$

This formula correctly accounts for the presence of two chains of seven cellobiose residues in a new cellulose unit cell. F_{h0l} would then be expected to vary widely, depending upon the exact relationship of the two chains.

If the cellulose molecule were arranged as they propose, the true fiber repeat distance would be 72 Å, and six additional layer lines would then be theoretically possible between each of the observed layer lines. While it is possible that these additional layer lines might have generally lower intensity, no evidence of any extra layer lines in cellulose examined by x-ray or electron diffraction has been reported.

Finally, the "angle of helix" is not directly indicated on fiber diagrams of helical molecules by the arcing of the diffraction maxima. Arcing is due to statistical ordering of crystalline regions, not helical ordering of subunits within a unit cell. To verify this point, one need only examine the diagrams of a well-established helical structure. V Amylose structures[4,5] for example, have a very large helix angle but the arc length is comparable to that of ramie diagrams.

References

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ALFRED D. FRENCH*

Southern Regional Research Laboratory
Southern Marketing and Nutrition Research Division
Agricultural Research Service
U.S. Department of Agriculture
New Orleans, Louisiana 70179

* National Research Council Post-Doctoral Research Associate.