

Some Explanatory Remarks on the Helical Structure of Cellulose I

Our paper on the helical structure of cellulose I published earlier in this journal¹ has aroused some scientific curiosity as well as criticism. In the light of these, some further elucidation of the proposed structure was felt necessary. Hence this note.

Norman² has estimated the distance between the terminal oxygen atoms of a cellobiose molecule to be 10.4 Å. He also pointed out the need for fitting this value into the widely accepted repeat period of 10.3 Å for the cellulose chain. The proposed helical structure is a distinct possibility answering Norman's suggestion while no claim is made in our work to have established the same unequivocally. Now that a helical structure has, however, been postulated with a repeat distance of seven times the apparent unit cell, it is possible to refine the proposed structure through a rigorous calculation of intensities more appropriate to helical structures than the one based on the first principles. It may then become easier also to explain the system of hydrogen bonds noticed for the helical structure.³

In the derivation of the helical structure itself, coordinate geometry has been extensively employed, especially transformation of axes: first from the orthogonal coordinates (X, Y, Z) in the cellobiose structure to polar coordinates (r, θ, ϕ) so as to facilitate the determination of coordinates (X', Y', Z') after rotation of the cellobiose molecule about the helical axis and tilting the cellobiose molecule in the YZ plane; then a transfer of the origin from the terminal atom O_1 of a cellobiose residue to the center of the circle which forms the basal plane for the helical structure; and finally a transformation of the coordinates (X'', Y'', Z'') thus obtained into system of cylindrical coordinates (R, Ψ, Y), which is most convenient for computing the positions of identical atoms in a full turn of the helix and consequently the x-ray intensities as well as hydrogen bonds. It has not been possible, for obvious reasons, to elaborate all these steps in the published work.^{1,3}

Given that the cellulose molecule is not a straight or even a regular zigzag chain in the same way as many proteins are, it is none too easy to define the helical angle precisely in terms of the glucose rings. When the helical structure was first proposed, however, for cellulose I, the temptation to associate the value of the orientation angle of 8° for the IDEALLY (or nearly so) oriented ramie fibre with the helical angle of the cellulose molecule was too great to resist. The experimental observation might still be interpreted in this manner, if it is assumed that *all* the molecular chains in ramie were held parallel and consequently there was no dispersion of the long axis of the crystallites about the fiber axis. But it seems to be extremely difficult, if not impossible, to separate the only experimentally observed composite line profile into its three constituents, viz., (i) the angle of helix of an individual cellulose molecule; (ii) the angle (varying in different layers?) at which the agglomerate molecules, i.e., fibrils or crystallites, spiral around the fiber axis with frequent reversals; and (iii) angle of dispersion of the crystallites about the mean inclination to the fiber axis.

It has nevertheless been possible to schematically represent the influence of the crystallite dispersion angle α and the spiral angle ϕ as defined by DeLuca and Orr⁴ on the composite x-ray diffraction profile. Figure 1 is reproduced here from the work of Shenouda.⁵ The first row represents the ideal cases of no dispersion of crystallites with the spiral angle increasing, say, from 0° to 20°. The first diagram of the middle row is similar to that obtained from ramie for which the spiral angle is nearly zero and the angle of crystallite dispersion is perhaps 5°–10°. (Hermans' orientation angle is a measure quite different from the spiral angle defined by DeLuca and Orr.) Most cottons, native or mercerized, with a spiral angle ranging from 10° to 20° and crystallite dispersion from 15° to 20°, give x-ray diagrams similar to the second one of the bottom row. In a few cases where the spiral angle is relatively larger compared to that of crystallite dispersion, an azimuthal splitting is observed, which arises from the well-oriented

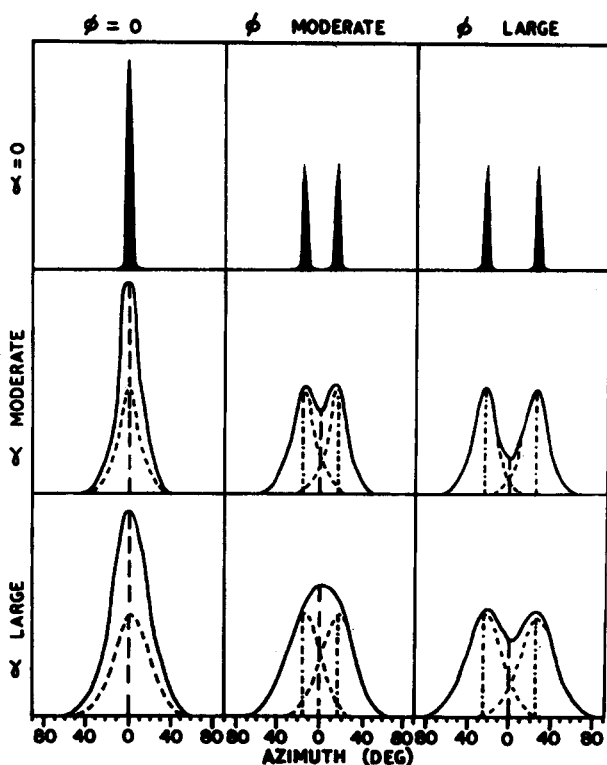


Fig. 1. Schematic diagram representing the influence of spiral angle ϕ and crystallite dispersion angle α on the composite x-ray line profile.

crystallites at the front and rear surfaces of the fibers exposed to x-rays. Then the diagram would correspond to the last one in the bottom row.

The results of an investigation on orientation—both Hermans' x-ray orientation factor and DeLuca's spiral angle—in cottons have been reported elsewhere.⁶ Scanning electron microscopy might possibly yield valuable information on the aspects discussed here.

References

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