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The Helical Structure of Cellulose I

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Synopsis

The unit cell dimension along the crystallographic *b*-axis of cellulose is widely accepted to be 10.3 Å, as against the distance of 10.3912 Å between the terminal oxygen atoms of a cellobiose molecule, estimated from the now well-established crystal structure of cellobiose. Since cellulose is only a polymer of the cellobiose residue, it has been possible to derive the crystal structure of cellulose I from that of cellobiose. The strict application of stereochemical principles to the successive residues in the cellulose chain and a consideration of the formal geometric characteristics of a helix suggest a helical form to the cellulose molecule, with seven cellobiose residues per turn, radius $r = 1.5830$ Å, and angle of helix 7°51′ which is close to the x-ray orientation angle of 8°21′ observed in ramie, the best-oriented native cellulose. An analysis of intensity data both for the equatorial and for the meridional reflections leads to a unit cell with central reversed and corner chains and a relative shift between them of one fourth of the repeat length along the *b*-axis.

INTRODUCTION

Cellulose I is the principal constituent of many naturally occurring fibrous substances. Of these, cotton has been widely studied through x-ray diffraction, but it is not, however, the ideally suited fiber for a verification of any theoretical model proposed for the crystalline structure of cellulose I. The structure of cotton is extremely complicated by the deposition of cellulose in spirals and the frequent reversals in the direction of such deposition occurring at irregular intervals. Even as early as 1922, this spiral structure was believed to exist in every growth ring.[1] Among the unsolved problems concerning the structure of cellulose, three may be mentioned here: (a) the exact nature of the spiralling cellulose chain, (b) alternating directions of the adjacent molecules, and (c) the possibility of chain folding. In this paper, an attempt is made to define a helical path for the cellulose molecule and to compare the computed intensities with the observed ones for the prominent equatorial and meridional reflections from ramie, which is acknowledged to be the best oriented naturally occurring cellulosic fiber and where there is no spiral growth or convolution. Chain folding will not be discussed in this paper, although reversal of direction in the adjacent helical molecules is considered for the purpose of intensity calculation.

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LITERATURE BACKGROUND

Meyer and Misch[2] were the first to describe the unit cell dimensions for cellulose and assign the following values: $a = 8.35$ Å, $b = 10.30$ Å (fiber axis), $c = 7.90$ Å, $\beta = 84°$. The two cellulose chains passing through the unit cell were also stated by these authors to be antiparallel, the relative shift between the two systems of cellulose chains being 2.9 Å. Several modifications have since then been suggested in order to bring about a better agreement between theory and experiment. From the recent literature, a few of the structures proposed may be cited. Ellis and Warwicker[3,4] described a larger unit cell in 1958, with $a = 16.78$ Å, $b = 10.30$ Å, $c = 15.88$ Å, $\beta = 82°$, but proposed another in 1962 with $a = 10.85$ Å, $b = 10.30$ Å, $c = 12.08$ Å, and $\beta = 93°14'$. Warwicker and co-workers[5,6] in their recent researches seem, however, to have come back to the conventional Meyer-Misch model. Munekata and Sobue[7] reported success in obtaining single crystals of cellulose which on examination by electron diffraction revealed hexagonal or nearly orthorhombic structure with $a = c = 10.4$ Å, $b = 10.3$ Å, $\beta = 60°$. Jones,[8] for cellulose in ramie has used $a = 8.17$ Å, $b = 10.34$ Å, $c = 7.85$ Å, and $\beta = 83°36'$, which do not differ considerably from the values given by Meyer and Misch.[2] Thus, there still seem to be some doubts about the unit cell dimensions because of the difficulties in resolving satisfactorily the several overlapping reflections.[9] In the circumstances, therefore, it seems reasonable to assume as a starting point for the purposes of the present study the crystallographic dimensions of $a = 8.20$ Å, $b = 10.30$ Å, $c = 7.90$ Å, and $\beta = 83°18'$, assigned recently by Ellefsen.[10]

It may be noted from the foregoing that the repeat length along the fiber (*b*-axis) has been widely accepted to be 10.30 Å. Another equally accepted fact is that a cellulose molecular chain is constituted by repetition of the monomer —$C_6H_{10}O_5$— or of a glucose residue. As has been indicated by one of us elsewhere,[11] while chemically the glucose residue constitutes the repeat unit, a pair of such residues, or simply a cellobiose residue, would form a repeat pattern in the structural configuration of cellulose. Therefore, although the crystal structure of β-D-glucose has been worked out by Ferrier,[12] the crystal structure of cellobiose first described by Jacobson and co-workers[13] and Brown[14] assumes a greater importance for the present study. Chu Shirley and co-workers[15] recently have further refined the structure of cellobiose and found the unit cell dimensions to be $a = 10.972$ Å, $b = 13.048$ Å, $c = 5.091$ Å, and $\beta = 90°50'$. They have given the coordinates for all the atoms (including hydrogen) in the cellobiose molecule. These are utilized in the present work for deriving a cellulose chain. Before proceeding to derive this, it seems worthwhile to mention that a two-fold screw axis is frequently referred to in the literature, both in relation to the two glucose residues in the same molecular chain of cellulose and also in relation to the arrangement of the individual chains with reference to each other. Ellis and Warwicker[4] have, however,

shown that it is not necessary to stipulate the twofold screw axis (in the chain) assumed in the Meyer-Misch model. This approach shall be retained in the present study.

WHY A HELICAL STRUCTURE?

The approach to the structure of crystalline cellulose I is based on the following facts:

The repeat unit along the fiber axis in cellulose is widely accepted to be 10.30 Å. The distance between the terminal oxygen atoms of a cellobiose molecule works out to be 10.3912 Å from the data of Chu Shirley and co-workers.[15] Jacobson and his associates[13] noted this to be 10.27 Å, which from their own data should read 10.40 Å, as pointed out by Norman.[16] If a cellulose molecule should be merely an extended chain of cellobiose residues, as is well known, the question now arises: Is it possible to envisage a structure in which *every* cellobiose residue in the molecular cellulose chain is inclined at an angle β to the fiber axis or the crystallographic b-axis given by $\cos \beta = 10.30/10.3912$? The answer to this question is in the affirmative if, instead of a linear shape, the cellulose molecule itself is assumed to have a helical form. Then a screw axis becomes inevitable for locating the successive glucose residues along the same chain. Should this screw axis be twofold or different? As indicated by Ellis and Warwicker[3] the removal of a twofold screw axis would itself enable the postulation of other possible structures. It is interesting to remark here that al-

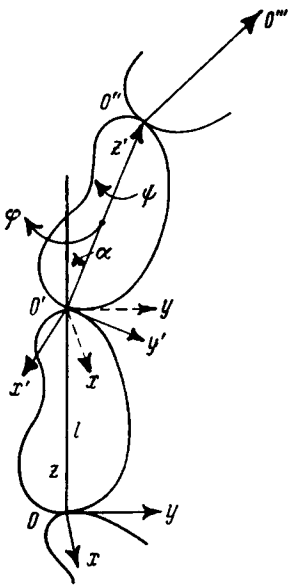

Fig. 1. Geometric characteristics of a most general type of helical structure, after Vainshtein.[18] See text for explanation of symbols.

though Mann and Marrinan[17] envisaged a helical molecule with two glucose residues per unit turn, they excluded this possibility on an analysis of the infrared spectra.

A second portent toward a helical structure comes from considerations of the most general type of this structure. Vainshtein[18] discusses some formal geometric characteristics of a helical chain molecule. According to him, the requirements are three angles: χ, the angle turned by the second residue along the chain about its own axis with reference to the first residue; α, the inclination of the axes of the two adjacent residues; and ϕ, the angle formed by turning the axis of the second residue about that of the first. The most general type of a helical structure occurs when $\chi \neq 0$, $\alpha \neq 0$, $\phi \neq 0$. Figure 1 gives the schema of such a helical construction. Ramachandran and co-workers[19] have also found that a helical symmetry will result if the angle of rotation is the same for every point of linkage along the chain. Now in the structure of cellobiose, it was shown by Jacobson and co-workers[13] that the nearly planar glucopyranose rings are twisted to each other at an angle of about 26°, and the bond angle between the two basic units is 117.5°. In the notation of Vainshtein, these two angles correspond to $\chi = 180° + 26° = 206°$ (and not 26° since the carbon atom C-6 projects in alternate directions from the successive glucose residues) and $\alpha = 117.5°$.

Taking the two observations made above, viz., constant inclination β of the axis of the cellobiose residue to the fiber axis and the constancy of the angles χ and α, a helical path for the bridge oxygen atom for the entire length of the molecule can be considered likely. The helical parameters for such a path are derived in the next section.

Parameters for the Helical Structure

In a helical structure, all monomers should have identical stereochemistry[20]: what applies to the first two glucose residues in a cellulose chain must be strictly valid also for any two adjacent glucose residues. The pitch of this helix will be determined by the distance (measured parallel to the helical axis) between any two consecutive, identically oriented glucose residues. Since $\chi = 206°$, it can be easily seen that 14 glucose residues (or seven cellobiose residues) are required to make one full turn about the helical axis. Accordingly, the helical pitch for the cellulose molecule will be $7 \times 10.3 = 72.1$ Å, and the number of cellobiose residues per helical turn is seven.

The radius of the helix can be determined by a transformation of the coordinate axes employed for the cellobiose structure. The origin is now fixed at O_1', one of the two terminal oxygens of the cellobiose molecule, and the y-axis is taken at an inclination of $\beta = 7°36'$ (given by $\cos \beta = 10.30/10.3912$) to the line $O_1'O_4$ joining the terminal bridge oxygen atoms corresponding to the cellobiose molecule. The projection of the line $O_1'O_4$ on the basal plane (a plane perpendicular to the y-axis) has a length equal to $10.3912 \sin 7°36' = 1.3737$ Å, as shown in Figure 2. If the molecule

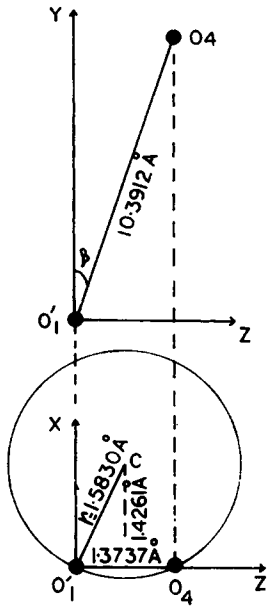

Fig. 2. Projection of the cellobiose molecular length on the yz and xz planes.

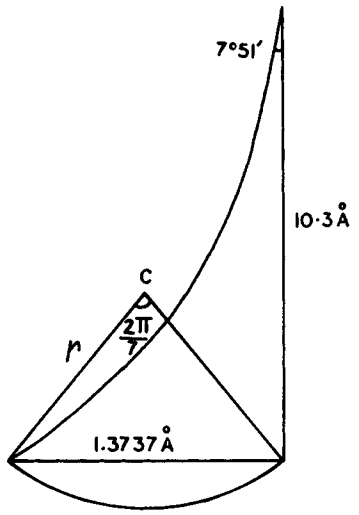

Fig. 3. Relation of the helical angle to the helical radius and the *b*-axis repeat length.

is helical, the projections of all successive terminal bridge oxygen atoms of cellobiose residues shall also lie on the same circle whose radius is readily seen to be $r = 1.5830$ Å from Figures 2 and 3. The helical angle β_0 can be derived as shown in Figure 3 and is found to be 7°51′.

Thus, the parameters of the helical structure are determined to be: helical radius, 1.5830 Å; helical angle, $\beta_0 = 7°51'$; helical pitch, 72.1 Å;

and number of cellobiose residues per turn, seven. The validity of the helical structure proposed can be examined by comparing the theoretical and the experimental intensities. For this purpose, the coordinates of all the atoms in the seven cellobiose residues must first be determined.

Coordinates of the Atoms in the Cellobiose Residue in the Helical Configuration

Table I gives the coordinates (expressed in Ångström units) of the 12 carbon and 11 oxygen atoms of a cellobiose molecule calculated from the data given by Chu Shirley and co-workers[15] taking the origin at O_1', the y-axis coinciding with $O_1'O_4$, and the z-axis lying in the plane passing through the bridge oxygens O_1', O, and O_4. Figure 4 gives the projections of a cellobiose molecule in xy, yz planes. The coordinates of the 23 atoms with reference to the helical axis passing through C (Fig. 2) can only be arrived at in two stages: (1) Rotate the plane $O_1'OO_4$ (which initially is the same as the yz plane) about the line $O_1'O_4$, through an angle ϕ such that the bridge oxygen O of the cellobiose residue also falls on the surface of the helical cylinder. (2) Transfer the origin from O_1' to C, making the y-axis coincide with the helical axis. The determination of the angle ϕ presented the most difficult of all problems encountered in the derivation

TABLE I
Coordinates, in Ångström Units, of the Carbon and Oxygen Atoms in a Cellobiose Molecule

Atom	x, Å	y, Å	z, Å
C_1	−0.2804	6.4504	1.1787
C_2	−0.3194	7.4621	2.3188
C_3	−0.6295	8.8366	1.7294
C_4	0.4155	9.1992	0.6614
C_5	0.5628	8.0716	−0.3648
C_6	1.7730	8.2964	−1.2536
C_1'	0.2163	1.2131	0.6222
C_2'	0.9945	2.1462	−0.2942
C_3'	1.1257	3.5199	0.3461
C_4'	−0.2182	4.0587	0.8220
C_5'	−1.0051	3.0160	1.6294
C_6'	−2.4165	3.4194	1.8996
O	0.0000	5.1792	1.7074
O_2	−1.2346	7.0377	3.3197
O_3	−0.7186	9.8435	2.7361
O_4	0.0000	10.3912	0.0000
O_5	0.7813	6.8075	0.2976
O_6	2.0894	7.1525	−2.0235
O_1'	0.0000	0.0000	0.0000
O_2'	2.3099	1.6607	−0.4853
O_3'	1.7547	4.3278	−0.6521
O_5'	−1.0654	1.7864	0.8883
O_6'	−3.0557	2.5647	2.8346

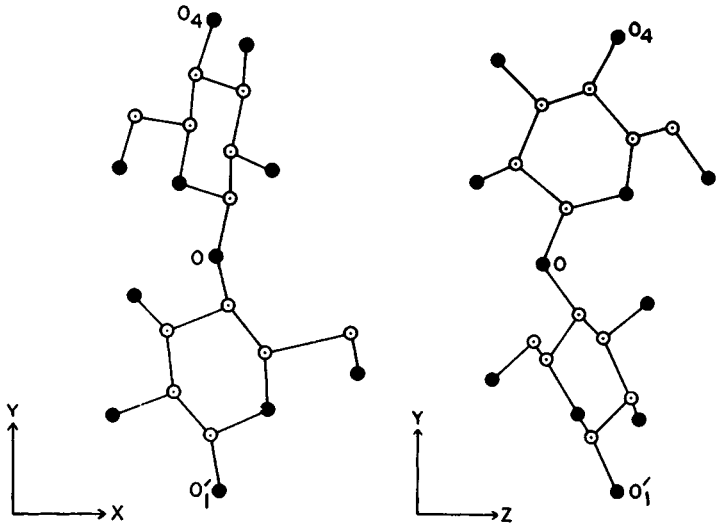

Fig. 4. Projections of cellobiose molecule on (a) the xy plane and (b) the yz plane.

of the helical structure, and this was finally solved satisfactorily with the help of an IBM 1620 computer using the following three basic equations:

$$(x\text{-}1.4261)^2 + (z\text{-}0.6869)^2 = r^2 = (1.5830)^2 \quad (1)$$

$$x^2 + (y\text{-}5.1336)^2 + (z\text{-}0.6852)^2 = s^2 = (1.7074)^2 \quad (2)$$

$$x^2 + y^2 + z^2 = d^2 = (5.4535)^2 \quad (3)$$

where x, y, and z are the coordinates of the bridge oxygen O with reference to the origin at O_1' which, on satisfying all the above three equations, will lie on the surface of the same cylinder as O_1' and O_4. As already seen, r is the radius of the helix, s is the perpendicular distance of O from the y-axis and therefore the radius of the circle described by O rotating about $O_1'O_4$, and d is the distance between O_1' and O which remains unaltered. The coordinates of C and the projection of O upon $O_1'O_4$ are involved respectively in the first and the second equations. The basic assumption made here is that the shape of the cellobiose molecule remains intact in the cellulose I structure as well. The values for x, y, and z satisfying all the three equations are 0.8413 Å, 4.9372 Å, and 2.1579 Å, respectively. From these coordinates and those of O before rotation, the angle ϕ between the two planes yz and $O_1'OO_4$ is seen to be given by $\cos \phi = \pm 0.8703$, corresponding to four values for angle of rotation $\pm\phi$, $\pi \pm \phi$, where ϕ is equal to 29°31′.

Now the transfer of the origin from O_1' to C is relatively simple. The coordinates, expressed as fractions of the cellulose unit cell dimensions, for the atoms in the first residue of cellobiose, are given in Table II. The coordinates for the atoms in the succeeding residues can be fixed up by a

TABLE II
Coordinates of the Carbon and the Oxygen Atoms, Expressed as Fractions of the Cellulose Unit Cell Dimensions in the Helical Configuration ($-\phi$ Rotation)

Atom	x	y	z
C_1	−0.2894	0.6094	0.1332
C_2	−0.3779	0.6946	0.2733
C_3	−0.3685	0.8350	0.2124
C_4	−0.1882	0.8753	0.1660
C_5	−0.0972	0.7773	0.0434
C_6	0.0868	0.8012	0.0248
C_1'	−0.1900	0.1084	0.0148
C_2'	−0.0482	0.2035	0.0218
C_3'	−0.0842	0.3277	0.0799
C_4'	−0.2529	0.3828	0.0576
C_5'	−0.3875	0.2784	0.0799
C_6'	−0.5477	0.3231	0.0285
O	−0.2976	0.4793	0.1875
O_2	−0.5403	0.6479	0.3192
O_3	−0.4522	0.9213	0.3344
O_4	−0.1838	1.0000	0.0876
O_5	−0.1211	0.6469	0.1085
O_6	0.1762	0.6977	0.0594
O_1'	−0.1641	0.0000	0.0875
O_2'	0.0969	0.1506	0.0309
O_3'	−0.0489	0.4127	0.0229
O_5'	−0.3374	0.1687	0.0261
O_6'	−0.6771	0.2345	0.0771

combination of rotation through $2\pi/7$ about the y-axis and translation of 10.3 Å (repeat length of cellulose b-axis). The figures given in Table II correspond to a rotation of $-\phi$. Similar data were also obtained for rotations of $+\phi$, $\pi - \phi$, and $\pi + \phi$. The reason for the choice of $-\phi$ as

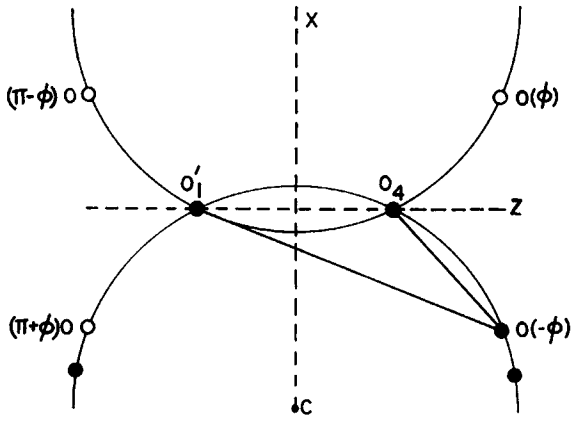

Fig. 5. Projections of bridge oxygen O for the four possible helical configurations corresponding to ϕ, $\pi - \phi$, $\pi + \phi$, and $-\phi$ rotations.

representative of the transformations will be clear in the next section while discussing the intensities to be expected from the four configurations envisaged. Figure 5 represents the projections on the basal plane of the possible helical configurations.

INTENSITY CALCULATIONS

The helical structure is bound to affect the intensities of the various reflections, since the positions of the atoms in the succeeding cellobiose residues are not identical, as has been tacitly assumed so far by other workers. Fortunately, Wilson[21] has discussed similar phenomena: (a) crystalline lattices with one of the lattice parameters varying sinusoidally while the unit cell contents remain the same; (b) crystalline lattices where, instead of the lattice parameter, the structure amplitude varies sinusoidally. In the present instance, intensities have to be worked out on the basis of a change in the coordinates of the oxygen bridge at the center of cellobiose residues, and the structure therefore falls into the second category mentioned above: identical unit cell dimensions and contents, but due to the varying atomic positions inside the unit cell, structure amplitude changing from one cell to the other, except for those which are separated by seven units in between. The intensities have been computed both for some equatorial and meridional reflections. It is worth mentioning here that in view of the facts that two cellulose chains are passing through the unit cell—one at the corner and a second at the center—and that there could be a relative shift between the two, somewhat different procedures are necessary to calculate the intensities for the equatorial and the meridional reflections.

Equatorial Reflections (*hOl*)

Since these planes are all parallel to the crystallographic *b*-axis, but the *x*- and *z*-coordinates are different (for one and the same atom) from one residue to the next, the *x*- and *z*-coordinates for all the seven residues are needed in the calculation of the intensity F according to the formula

$$F_{(hOl)} = 2\left[\sum_{j=1}^{j=12} f_c \, e^{-2\pi i(hx_c{}^j + lz_c{}^j)} + \sum_{m=1}^{m=10} f_o e^{-2\pi i(hx_o{}^m + lz_o{}^m)}\right] \qquad (4)$$

where $x_C{}^j$ and $z_C{}^j$ are the coordinates of the jth carbon atom, $x_O{}^m$ and $z_O{}^m$ are the coordinates of the mth oxygen atom, f_C and f_O are the atomic scattering factors of the carbon and oxygen atoms, respectively, corresponding to the Bragg angle for the (*hOl*) reflection. In the above expression, the two cellulose chains passing through the unit cell have been taken into account. It may also be noted that whereas there are 11 oxygen atoms in a cellobiose molecule, there are only ten oxygen atoms in the cellobiose residue, and the coordinates of the 11th oxygen (terminal) atom were verified to be the same as those of the first oxygen atom in the second residue.

Table III gives the calculated intensities for the seven residues individually, for a few equatorial reflections, for the $-\phi$ rotation only by way of illustration, and Table IV gives the mean values of intensities computed for the seven residues for all the four possible helical structures. In view of the poor resolution of adjacent peaks, following Mann and co-workers,[22] reflections other than the most frequently quoted ones are also included in Tables III and IV, and it is seen that they could be as intense as the (002) reflections. However, their intensities are grouped together for ease of

TABLE III
Computed Intensities for Seven Consecutive Units Cells for $-\phi$ Rotation

	Intensity I							
(h0l)	1st	2nd	3rd	4th	5th	6th	7th	Mean
(101)	15176	34322	234	1625	44141	2886	58	14063
(10$\bar{1}$)	418	90	21649	11642	681	3137	40882	11214
(200)	39	7581	12589	462	1258	22041	1530	6500
(002)	17005	597	811	18263	1447	3	4776	6129
(201)	1696	18542	1493	147	8435	8159	118	5513
(102)	16017	1530	41	3497	15731	348	816	5554
($\bar{2}$01)	121	1399	13915	1102	249	6337	9730	4693
($\bar{1}$02)	1368	258	4257	13169	108	933	13547	4806

TABLE IV
Mean Value of Intensities from the Seven Residues for Equatorial Reflections

(h0l)	ϕ	$-\phi$	$\pi + \phi$	$\pi - \phi$
(101)	20477	14063	10074	17860
(10$\bar{1}$)	14026	11214	11715	14520
(200)	4043	6500	14838	8335
(002)	3243	6129	14049	7757
(201)	2717	5513	13311	6942
(102)	2340	5554	12443	6890
($\bar{2}$01)	1572	4693	9636	5489
($\bar{1}$02)	1400	4806	8646	6515

TABLE V
Comparison of Computed and Observed Intensities of Equatorial Reflections

Configuration	$I_{(101)+(10\bar{1})}$	$I_{(002)}$[a]	Ratio
ϕ	34500	15320	0.44
$-\phi$	25280	33200	1.31
$\pi + \phi$	21790	72920	3.35
$\pi - \phi$	32380	41930	1.29
Our data	28000	37000	1.3
Mann and Marrinan[17]	7000	25000	3.6

[a] Includes also intensities of other reflections: (200), (201), (102), ($\bar{2}$01), and ($\bar{1}$02).

comparison with data available in the literature on the unresolved (101) + (10$\bar{1}$) and (002) reflections and are presented in Table V.

In order to determine which of the four possible helical configurations is the correct one that corresponds to the observed intensities, the equatorial reflections were recorded by an x-ray diffractometer using an unoriented ramie sample, in powder form compressed into a cake. A pulse height discriminator and proportional counter were employed to get the optimum conditions of monochromatizaton of the x-rays and resolution of the adjacent peaks. After applying all the necessary corrections, namely, air scattering, specimen absorption, polarization, and incoherent scattering, the intensities were normalized and replotted in electron units, as described elsewhere.[23] The observed integrated intensities of the unresolved reflections (101) + (10$\bar{1}$) and (002) are also included in Table V.

From column 4 of Table V, it is seen that $-\phi$ rotation gives the best agreement with experiment, the $\pi - \phi$ rotation giving a value only slightly lower for the ratio $I_{(002)}:I_{(101)+(10\bar{1})}$. The other two possibilities seem to be totally ruled out. But the data of Mann and co-workers[22] seem to conform best to the rotation $\pi + \phi$. The possibility of a further choice can be decided after an analysis of the meridional reflections. The ratio of the peak values alone observed in the present study compares favorably with that reported by Mann and co-workers. However, since the crystalline reflections in the Fourier space are not point-like in the case of polymers, a comparison of the integrated intensities is to be preferred, and then the same order of intensities (in absolute electron units) is obtained both by experiment and by computation, as is evident from Table V.

Meridional Reflections (O*k*O)

As the intensity for the meridional reflections would be dependent only on the y-coordinates, it is sufficient to take note of the atomic positions for a single residue. But, on the other hand, since there might be a reversal in direction ($\bar{Y}$) and shift (S) parallel to the b-axis in adjacent chains passing through the same unit cell, both $\bar{Y}$ and S must be taken into account. For this purpose, the expression $I = A^2 + B^2$ was used, where

$$A = \sum_{j=1}^{j=12} f_C \left[\cos 2\pi k y_j + \cos 2\pi k \, (S \pm y_j) \right] + \sum_{m=1}^{m=10} f_O \left[\cos 2\pi k y_m + \cos 2\pi k (S \pm y_m) \right] \quad (5)$$

and B is a similar function for the sine values. The positive sign inside the brackets applies to the case of parallel chains and the negative sign to antiparallel chains. The intensities were computed for the reflections corresponding to $k = 1, 2, 3, 4, 6, 8$, and 9 using axial shifts of 0.00 to 0.50 with and without a reversal. Table VI gives the intensities for the $-\phi$ rotation for a few selected values of the shift.

TABLE VI
Intensities of Meridional Reflections for the $-\phi$ Configuration for Selected Values of Relative Shift (S) With Reversal ($\bar{Y}$) and Without Reversal (Y)

	Intensity I						
S	(010)	(020)	(030)	(040)	(060)	(080)	(090)
$\bar{Y}$							
0.00	50	3448	115	862	876	5	25
0.15	19	694	7	1050	1059	89	66
0.20	10	73	56	4	242	137	0
0.25	4	102	115	862	203	5	67
0.35	0	1821	99	2557	564	34	55
0.50	18	3448	19	862	876	6	43
Y							
0.00	68	3550	135	2765	1079	174	68
0.15	54	1226	3	264	976	114	14
0.20	44	338	13	1810	706	17	45
0.25	34	0	67	2765	0	174	34
0.35	14	1226	131	264	976	114	54
0.50	0	3549	0	2765	1079	174	0

In order to obtain experimentally the meridional reflections for comparing the intensities, it has been necessary to use the oriented ramie fiber bundle. Even so, only three orders of reflections, namely, (020), (030), and (040) could be obtained with sufficient intensities using a texture goniometer.[24] The ratio of these intensities is found to be 1:0.9:9 and can be compared with the theoretical ones. Figure 6 is an adoption from the work of Kast[25] giving the relative intensities of (020), (030), and (040) reflections computed in the present work (for $-\phi$ rotation) as a function of the shift (S), only for the case of antiparallel chains. Table VII gives

TABLE VII
Comparison of Computed and Observed Intensities of Meridonal Reflections

Configuration	Relative position	$I_{(020)}$	$I_{(030)}$	$I_{(040)}$	Ratio $I_{(020)}:I_{(030)}:I_{(040)}$
$+\phi$	Y, 0.28	121	232	2470	1:1.9:20.5
	Y, 0.29	213	255	2194	1:1.2:10.3
	$\bar{Y}$, 0.25	102	115	862	1:1.1: 8.5
$-\phi$	$\bar{Y}$, 0.26	189	122	1197	1:0.6: 6.3
	Y, 0.28	125	103	2390	1:0.8:19.1
	Y, 0.29	220	113	2124	1:0.5: 9.6
$\pi + \phi$	—	—	—	—	—
$\pi - \phi$	Y, 0.28	123	526	2028	1:4.2:16.4
	Y, 0.29	217	577	1801	1:2.6: 8.2
Our data		110	100	1000	1:0.9: 9
Mann and Marrinan[17]		250	0	4500	1:0.0:18

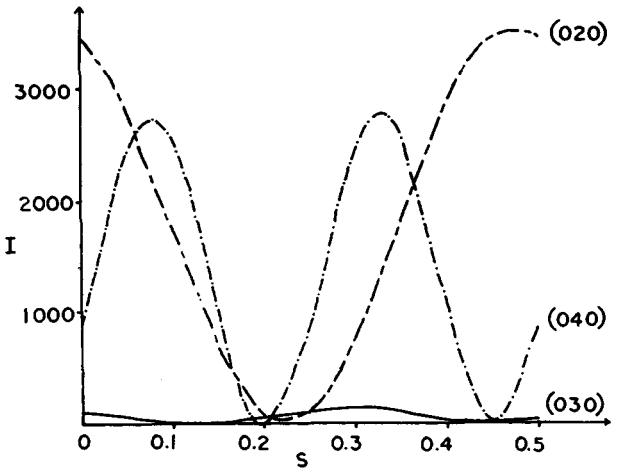

Fig. 6. Computed intensities of (020), (030), and (040) reflections plotted as a function of relative shift between antiparallel chains.

data on the closest fit between the observed and theoretical relative intensities of the first three observed (O*k*O) reflections. The data given by Mann and co-workers[22] on meridional reflections do not seem to agree with any of the theoretical values tabulated, especially on account of the fact that they believed the (030) reflection to be absent. A comparison of the intensities of the other two reflections would, however, seem to conform best to the combination of $-\phi$ rotation and parallel chains with a relative shift of 0.28. Taken together with their data on the equatorial reflections, $\pi + \phi$ rotation from the equatorial and $-\phi$ rotation from the meridional reflections would be the most appropriate. This ambiguity seems to confirm the remarks by Ellis and Warwicker[4] that "the list of structure factors derived by Mann et al. cannot be taken as a basis for comparison with the calculated structure factors."

On consideration of both sets of reflections, the best agreement between theory and experiment in the present study is obtained for the unique combination of $-\phi$ rotation and antiparallel chains with a relative shift of about 0.25. The $-\phi$ rotation indicates also that the helix is left-handed.

DISCUSSION

Orientation

The concept of helical structure gives an estimate of 7°51′ to the helical angle. This is only slightly lower than the value that can be assigned to native ramie for which an x-ray orientation factor of 0.970 was reported,[26] as compared to 0.968 obtained in the authors' laboratory[24] corresponding to 8°8′ and 8°21′, respectively, according to Hermans relation

$$f_x = 1 - \frac{3}{2}\overline{\sin^2 \beta}.$$

It must now be clarified that whereas the fiber axis is usually assumed to be inclined to the crystallites (consequently both to the crystallographic axis and to the axis of the molecular chains) in the helical structure, the fiber axis, in the best-oriented fibers such as ramie, is indeed parallel to the crystallographic axis, and it is only the molecular chain which spirals around the *b*-axis (or the fiber axis). In other words, for ramie, which is acknowledged to be the best-oriented naturally occurring cellulosic fiber, the orientation angle obtained by, say, the 50% x-ray angle seems to be none other than the angle of the helix suggested in this paper. Extending the same logic, it is possible to envisage that the x-ray orientation angle of 20° to 30° usually obtained for cottons is the resultant of (1) the helical angle of 7°51′ and (2) the spiral structure present in the agglomerates of microfibrils and fibrillar lamellae. DeLuca and Orr[27] have analyzed theoretically the intensity distribution of the (002) arc and arrived at an estimate of a spiral angle of 12° to 18° in cottons.

Chain Configuration in a Unit Cell

According to Jones,[8] the Meyer-Misch cell cannot be regarded as a sound approximation to the structure of crystalline cellulose I. The present study shows, however, that the Meyer-Misch model described with so much precision as early as 1937 still seems to hold its own. The only modification suggested now is that a sevenfold screw axis is more appropriate than the much debated twofold axis. Vainshtein[18] sees no reason why a fivefold or sevenfold axis should not exist. But the data given by Jones are quite exhaustive. His consideration of the ordered regions as assemblies of unit cells, each containing four anhydroglucose residues, led him to define a locus of possible position of the bridge oxygen between two glucose residues to be a circle of radius 1.97 Å, with the center at the midpoint of the line joining the two terminal oxygens O_1' and O_4. He assumed the glucose molecule to be 5.532 Å long and repeat unit along the *b*-axis of cellulose to be 10.34 Å long. His hypothesis, when extended to a cellulose chain, would mean: alternate bridge oxygens lie on the axis of a cylinder, the other set of alternate bridge oxygen atoms on the surface of the same cylinder. However, Jones pointed out that although the x-ray evidence is clearly against the existence of a helix of small pitch, no detailed calculations have been made for the case of a spiral having a very long period. The present work seems to fill in this gap. Regarding the relative shifts, Peirce[28] suggested a reversed chain structure with a relative *b*-axis shift of 0.36 for cellulose I. Frey-Wyssling[29] proposed central reversed and corner chains with a relative *b*-axis shift of $S = 0.25$, which is the same as in the present work.

Mechanism of Swelling

A reference to the recent work by Warwicker and co-workers[5] on the swelling behavior of cotton would not be out of place here. According to

them, the true fundamental unit in swelling reactions of cellulose is a sheet of chains and not a single chain. From Figure 7, which gives a projection of the cellobiose molecule on the xz plane, it is clear that the cellulose chains aligned parallel to the y-axis in the (101) planes have greater chances of making strong intermolecular hydrogen bonds than those aligned in the

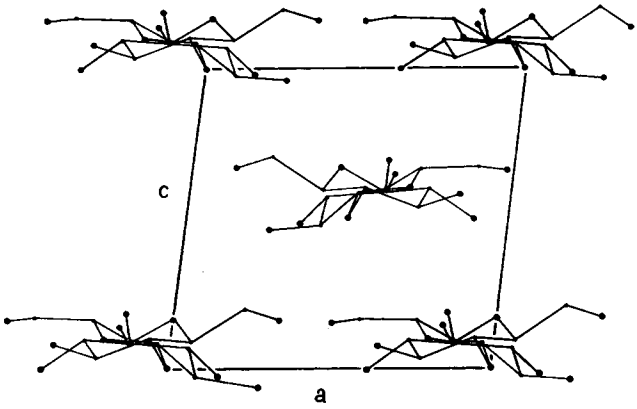

Fig. 7. Projection of the two cellobiose residues in a unit cell of cellulose I on the xz plane.

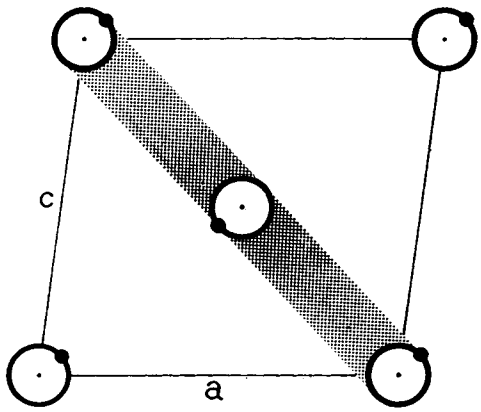

Fig. 8. Schematic representation of the sheet-like structure in (101) plane, with the helical cellulose molecules alternating in direction.

(10$\bar{1}$) planes. This effect will be much more pronounced if (1) the cellulose molecules assume a helical form and (2) the chains are alternating in direction, as seen in Figure 8. This would naturally support the view that (101) planes can very well be assumed to have a sheet-like structure in conformity with the strong intermolecular hydrogen bonding suggested by Ellefsen.[30]

SUMMARY

In view of the foregoing, it seems reasonable to assume that whatever be the nature of reversals in the agglomerates of molecular chains in a cotton fiber, the cellulose molecule itself seems to be endowed with a helical form, like human hair and other polypeptides. The parameters of such a helix are determined to be: radius, 1.5830 Å; helical angle, 7°51′; and pitch, 72.1 Å, corresponding to seven unit cells along the *b*-axis.

The x-ray orientation angle for the nearly ideally oriented fibers such as ramie seems then to give a direct measure of the helical angle. In cottons, the x-ray orientation angle would be a resultant of both this helical angle and the angle at which the lamellae (or crystallites) spiral around the fiber axis. The observed intensities are in best agreement with a structure where the adjacent helical molecules are alternating in direction, with a relative *b*-axis shift of about 0.25.

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