Mercerization of cellulose: 1. Determination of the structure of Mercerized cotton

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The structure of Mercerized cellulose II has been determined using the intensity data from Mercerized cotton fibres and rigid body least squares refinement techniques. The crystal structure consists of an array of antiparallel chain molecules essentially identical to that found for regenerated cellulose II. The unit cell is monoclinic with dimensions $a = 8.02$ Å, $b = 8.99$ Å, $c = 10.36$ Å (fibre axis), and $\gamma = 116.6°$; the space group is $P2_1$ and the cell contains sections of two cellulose chains which pass through the centre and corner of the *ab* projection. The final crystallographic *R* value was 0.263, based on intensity data for 30 observed and 11 unobserved non-meridional reflections. The $-CH_2OH$ groups of the corner chains are oriented near to the *gt* position while those of the centre chain are near to the *tg* position. The possibility of alternative side group orientations, most likely on the exterior of the cellulose II crystallites, has been demonstrated for both the Mercerized and regenerated structures. The percentage of these other orientations is small in the case of Fortisan (rayon) but substantial in the case of Mercerized cotton.

INTRODUCTION

Native cellulose (cellulose I) may be converted into the more stable cellulose II polymorph by two methods: regeneration and Mercerization. Regeneration involves dissolving cellulose in a derivative-forming solvent and then reprecipitating by dilution in water. This process is used to produce rayon fibres, and parallels recrystallization of most polymers from solution, except that cleavage of the derivative is a necessary first step. Mercerization is the name given to the conversion accomplished by swelling native cellulose fibres in concentrated sodium hydroxide solution. Although no dissolution occurs, the swelling allows for reorganization of the chains, and cellulose II results when the swelling agent is removed. This treatment leads to improvement in the properties of cotton yarns and fabrics, and the effects of the various processing parameters have been very well characterized[1]. However, the molecular mechanism of the conversion in the swollen state is largely unknown.

In the last 3 years the structures of native cellulose I[2,3] and regenerated cellulose II[4,5] have been determined by X-ray diffraction methods. The axial projections of these two structures are shown in *Figure 1*. Cellulose I consists of an array of parallel chains, i.e., all with the same sense, which are linked by intermolecular hydrogen bonds parallel to the *a*-axis in the 020 planes. In contrast, in regenerated cellulose II, adjacent chains are antiparallel, i.e., have alternating sense. The chains are linked by intermolecular

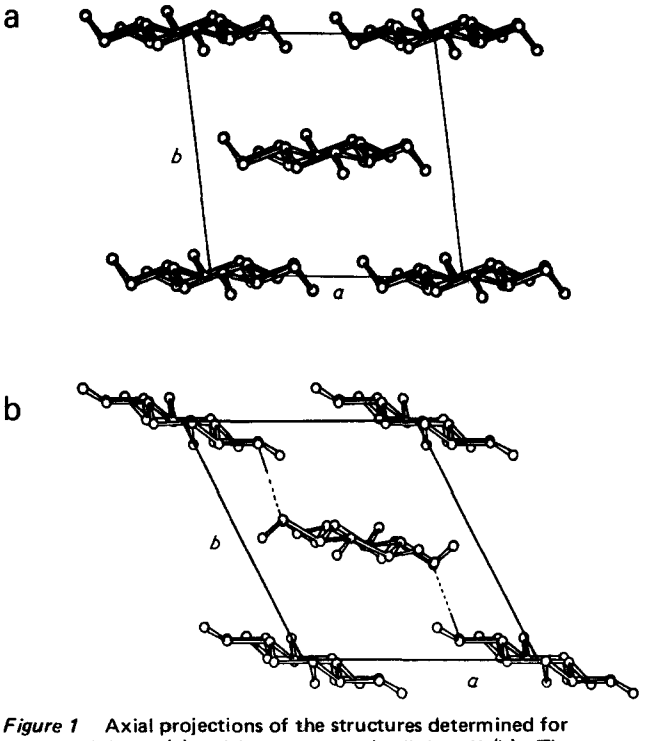

Figure 1 Axial projections of the structures determined for native cellulose I (a) and for regenerated cellulose II (b). The O2—H···O2' intermolecular bond in cellulose II between antiparallel chains in the 110 planes is shown in (b). Both structures also have intermolecular bonds between neighbouring chains along the *a* axis in the 020 planes: these are O6—H···O3 bonds in cellulose I and both O6—H···O3 and O6—H···O2 bonds in cellulose II (see refs 2 and 4)

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hydrogen bonds in the 020 planes and also in the 110 planes, i.e. along the long *ab* diagonal. This additional interchain bonding may account for the higher stability of the cellulose II polymorph.

Reversal of the polarity of the chains on conversion to cellulose II via the dissolution and reprecipitation process can be visualized without difficulty. However, this presents more of a problem for the mechanism of conversion via Mercerization, where the gross fibre structure is retained during the swelling. Thus it is first essential to examine the structure of Mercerized cellulose II in more detail, and to determine any differences between this material and regenerated specimens. Once the structure of the end product has been determined, then possible mechanisms of conversion can be postulated. This paper describes the determination of the structure of Mercerized cotton cellulose using refinement techniques similar to those used in our previous work on cellulose I[2] and regenerated cellulose II[4]. A subsequent paper will describe morphological studies of Mercerized cotton using the electron microscope[6].

EXPERIMENTAL

Materials and Methods

Native cotton of the *Hopi Acala* variety was received from Dr P. Ingram of the Camille Dreyfus Laboratory, North Carolina, USA and purified under moist conditions[7]. Specimens of native cotton were Mercerized both under slack and tensioned conditions. The slack specimens were treated in 22% aqueous sodium hydroxide for 4 h and then washed for 5 min successively with distilled water, dilute hydrochloric acid and distilled water; thereafter they were maintained under moist conditions. The process was repeated 6 times to achieve a high degree of conversion to cellulose II. Specimens of native cotton (cellulose I) and cotton Mercerized under slack conditions (cellulose II) were prepared for X-ray diffraction studies by bundling individual fibres in a parallel fashion. For the material Mercerized under tension, a parallel bundle of purified native cotton was glued to a sample holder (in a partly slack condition), which was then immersed in the alkali solution for the desired length of time (see below), rinsed successively with distilled water, dilute hydrochloric acid and distilled water, and allowed to air dry. To achieve a high degree of conversion, it was necessary to repeat this procedure 4 times.

X-ray diffraction patterns were recorded on Kodak No-Screen film using Ni-filtered CuKα radiation in an evacuated flat plate camera with pinhole collimation. Intensities for the X-ray structure refinement were obtained for 30 observed (non-meridional) reflections. Quantitative values for 19 of these reflections were obtained using a Photometrics EDP Scanning Microdensitometer[4]. The intensities of the remaining 11 (weak) reflections were estimated visually. In addition, there were 11 reflections that were predicted to fall within the limits of the observed X-ray data, but had intensities too weak to be detected. These unobserved reflections were considered prior to each cycle of least squares refinement and those which had calculated structure amplitudes higher than their respective estimated threshold values F(thres) were included in the data with assigned F(obs) equal to two thirds of F(thres).

X-ray diffraction studies of Mercerized cotton

Figure 2 shows the fibre diagrams of native cotton and

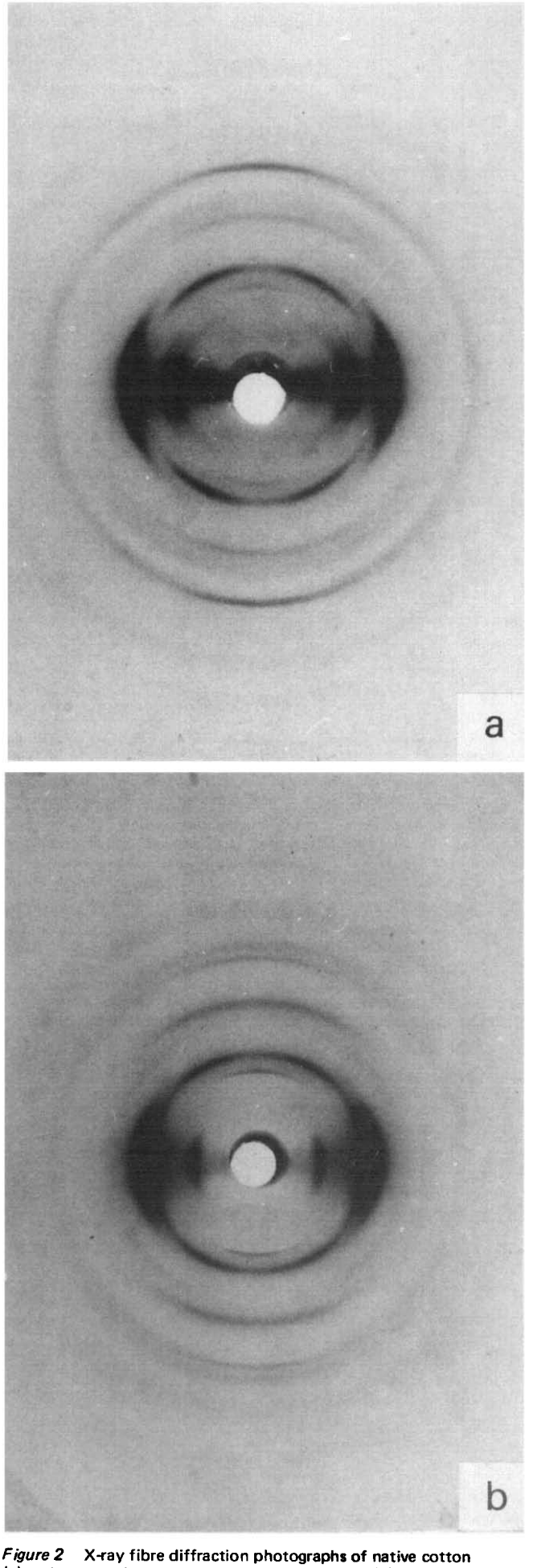

Figure 2 X-ray fibre diffraction photographs of native cotton (a) and cotton Mercerized under slack conditions (b)

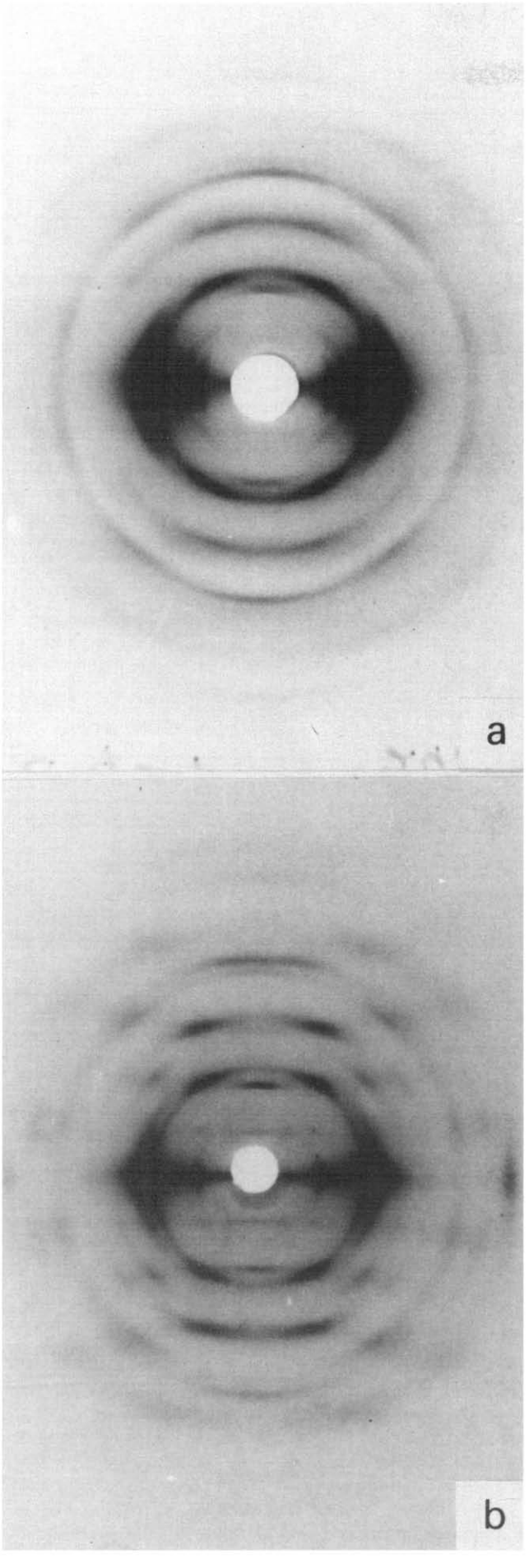

Figure 3 X-ray fibre diffraction photographs of tensioned Mercerized cotton: (a) low degree of conversion and (b) high degree of conversion

cotton Mercerized under slack conditions. For native cotton, the reflections are considerably arced, indicating a low degree of fibre orientation due to the spiral arrangement of crystallites in the macroscopic cotton hair. For Mercerization under slack conditions, essentially complete conversion to cellulose II is achieved with little change in orientation. At room temperature, slack fibres can be Mercerized with alkali concentration as low as ~9% and complete conversion to cellulose II occurs with concentrations >~16%[1,8–11]. When cellulose is Mercerized under tension, however, a higher alkali concentration is required to start conversion and complete removal of the cellulose I component appears to be impossible[11]. Variation of the alkali concentration used with tensioned samples served to determine the limiting conditions for Mercerization at ambient temperature. With 20% NaOH, Mercerization times as low as 1 min produced a substantial degree of conversion, while with 10% NaOH, Mercerization times of up to 10 min produced no noticeable change in the native fibre patterns. With ~17% NaOH, however, a rough correlation between degree of conversion and Mercerization time was found. *Figure 3a* shows the fibre patterns from a tensioned specimen following Mercerization for approximately 15 sec under the above conditions. Even this short exposure to alkali gives rise to substantial changes in the fibre pattern. In addition to the appearance of the cellulose II reflections, an increase in the degree of orientation can be seen. As the Mercerization time is increased, the extent of conversion to cellulose II increases as does the degree of orientation. The breadth of the equatorial reflections is larger for tension-Mercerized cotton than for the slack-Mercerized material, indicating a smaller crystallite size in the former. *Figure 3b* shows the fibre pattern of a tensioned specimen that has been Mercerized four times with 20% NaOH. Even in this pattern, weak $1\bar{1}0$ and 110 cellulose I reflections are present. Further treatment has little effect on the pattern, indicating that the conversion has progressed as far as possible under the conditions used.

As is well known, the layer line spacings and hence the chain backbone conformation do not change during Mercerization. However, there is a significant rearrangement of the cellulose molecules in the tensioned samples, as evidenced by the increase in the degree of orientation (as compared to the native structure) and the development of a weak small-angle maximum on the equator at $d = 14.0 \pm 0.3$ Å.

Structure determination of Mercerized cotton

Crystallographic data. Cotton which has been Mercerized several times under tension yields diffraction patterns of sufficient quality for a crystal structure determination using the rigid body techniques referred to earlier. The fibre pattern of the tension-Mercerized specimen from which the intensity data was collected is shown in *Figure 3b*. This particular specimen was prepared in the manner described earlier and Mercerized for one cycle of 19 h followed by three cycles of about 4 h each. The observed d-spacings could be indexed by a monoclinic unit cell with least squares refined dimensions: $a = 8.02 \pm 0.03$ Å, $b = 8.99 \pm 0.04$ Å, $c = 10.36 \pm 0.06$ Å, and $\gamma = 116.6° \pm 0.3°$. The observed and calculated d-spacings are compared in *Table 1*. Within experimental error, the unit cell is identical to that for rayon. The only systematic absences detected were the odd order $00l$ reflections and the space group was assumed to be $P2_1$. Under certain conditions, 001 and 003 reflections of varying intensity are observed, but these occur in patterns of very poor quality and are most likely due to imperfections in the sample.

Table 1 Crystallographic data for Mercerized cotton

d(obs)	*d*(cal)	*hkl*	*I*(obs) as measured	*I*(obs) minus cellulose I component	*d*(obs)	*d*(cal)	*hkl*	*I*(obs) as measured	*I*(obs) minus cellulose I component
Zero level:						2.35	$3\bar{1}2$		
7.29	7.18	$1\bar{1}0$	11.12	12.94	2.13	2.17	$3\bar{3}2$	0.07	0.08
	7.17	100				2.17	302		
4.44	4.46	$1\bar{2}0$	89.18	89.18					
	4.45	110							
4.03	4.02	020	100.00	100.00	Third level				
	4.01	$2\bar{1}0$			3.12	3.17	013	5.77	6.72
3.57	3.59	$2\bar{2}0$	0.35	0.40		3.11	$1\bar{1}3$		
	3.59	200				3.11	103		
2.98	2.99	$1\bar{3}0$	0.43	0.50	2.60	2.62	023	3.27	4.04
	2.98	120				2.62	$2\bar{1}3$		
2.58	2.68	030	0.45	0.52	2.48	2.49	$2\bar{2}3$	0.99	1.15
	2.64	$3\bar{2}0$				2.49	203		
	2.64	$3\bar{1}0$			2.22	2.26	$1\bar{3}3$	0.59	0.68
2.21	2.23	$2\bar{4}0$	1.66	1.93		2.26	123		
	2.23	220				2.19	$2\bar{3}3$		
	2.21	$1\bar{4}0$				2.19	213		
	2.21	130			2.12	2.12	033	0.66	0.76
						2.10	$3\bar{2}3$		
First level:						2.10	$3\bar{1}3$		
6.44	6.35	011	0.17	0.19					
—[a]	4.10	$1\bar{2}1$	—	—	Fourth level				
	4.09	111			2.59	2.59	004	Strong[b]	Strong[b]
—[a]	3.75	021	—	—	2.46	2.47	014	1.04	1.21
	3.74	$2\bar{1}1$				2.44	$1\bar{1}4$		
3.34	3.39	$2\bar{2}1$	0.17	0.20		2.44	104		
	3.39	201			2.20	2.24	$1\bar{2}4$	2.10	2.45
2.93	2.87	$1\bar{3}1$	0.18	0.20		2.24	114		
	2.87	121				2.18	024		
2.56	2.59	030	2.05	2.39		2.18	$2\bar{1}4$		
	2.56	$3\bar{2}1$			1.88	1.91	$2\bar{3}4$	0.39	0.46
	2.56	$3\bar{1}1$				1.91	214		
2.35	2.33	$3\bar{3}1$	1.05	1.22		1.86	034		
	2.33	301				1.85	$3\bar{2}4$		
2.19	2.18	$2\bar{4}1$	0.29	0.34		1.85	$3\bar{1}4$		
	2.18	221							
	2.16	$1\bar{4}1$			Fifth level:				
	2.16	131			2.00	2.01	015	Weak[b]	Weak[b]
						1.99	$1\bar{1}5$		
Second level:						1.99	105		
5.17	5.18	002	Medium[b]	Medium[b]	1.88	1.88	$1\bar{2}5$	0.41	0.48
4.37	4.35	012	8.18	8.28		1.88	115		
	4.20	$1\bar{1}2$				1.84	025		
	4.20	102				1.84	$2\bar{1}5$		
3.40	3.38	$1\bar{2}2$	2.43	2.82	1.67	1.70	$1\bar{3}5$	0.13	0.15
	3.38	112				1.70	125		
2.98	2.95	$2\bar{2}2$	0.91	1.06		1.67	$2\bar{3}5$		
	2.95	202				1.67	215		
2.58	2.59	$1\bar{3}2$	0.77	0.90		1.64	035		
	2.58	122				1.63	$3\bar{2}5$		
2.34	2.38	032	0.18	0.21		1.63	$3\bar{1}5$		
	2.35	$3\bar{2}2$							

[a] These reflections were obscured by the arcing of the 110 and 020 reflections and could not be measured accurately.
[b] Due to difficulties in applying corrections to reflections occurring outside the sphere of reflections, only an estimate of the intensity is given

The presence of weak $1\bar{1}0$ and 110 reflections for cellulose I indicate the presence of a residue of this form in the specimen. Thus Mercerized cellulose intensities occurring in the region of strong cellulose I intensities need to be corrected for the contribution of the latter. Specifically, equatorials at d = 4.44 and 4.03 Å and the second layer line reflection at d = 4.37 Å for Mercerized cellulose need to be corrected for contributions of the equivalent cellulose I reflections at d = 3.93 and 4.33 Å respectively. The cellulose I contributions were computed based on the intensities of the $1\bar{1}0$ and 110 reflections (for cellulose I) and subtracted from the measured intensities to yield the corrected values for Mercerized cellulose. The measured and subtracted intensity data (corrected for Lorentz and polarization effects) are given in *Table 1*. In both cases, the strongest reflection is assigned an intensity of 100 and the remaining reflections are scaled accordingly.

Molecular model and chain packing. Consistent with the $P2_1$ symmetry, a model for the cellulose chain was constructed as a two-fold helix repeating in 10.36 Å. Standard bond distances and bond angles[12] were used, and the molecular model incorporated an O3–H · · · O5′ intramolecular

Table 2 Refinement results for the Mercerized cotton structure

	Observed data				Full data			
	p_1	p_2	a_1	a_2	p_1	p_2	a_1	a_2
χ	169.1°	147.6°	−178.4°	178.5°	147.4°	145.2°	158.8°	174.8°
χ′	68.1°	84.9°	138.9°	90.8°	53.0°	87.7°	149.6°	121.5°
PHI	18.0°	66.4°	14.0°	17.4°	11.1°	66.3°	16.4°	17.2°
PHI′	10.2°	63.8°	67.7°	63.4°	16.7°	63.7°	62.4°	63.6°
SHIFT	0.253*c*	0.206*c*	−0.104*c*	0.233*c*	0.272*c*	0.195*c*	−0.108*c*	0.241*c*
K	0.59	0.58	0.58	0.58	0.59	0.58	0.58	0.58
B	31.3	32.0	31.4	32.4	31.9	32.4	32.0	32.6
R	0.231	0.148	0.154	0.160	0.280	0.192	0.222	0.188
R′	0.231	0.148	0.154	0.160	0.265	0.180	0.203	0.180
R″	0.158	0.111	0.114	0.116	0.172	0.125	0.143	0.126
Bad contacts								
C···O (Å)	–	2.48	2.41	–	–	2.46	2.00	–
O···O (Å)	2.49	2.46	2.15	2.45	2.42	2.56	2.18	2.59
		2.58	2.57	2.54	2.52	2.45		2.50
					2.59			2.48

hydrogen bond[4]. The disaccharide residue has a glycosidic bond angle of 114.8° and glycosidic torsion angles of ϕ = 24.7°, ψ = −26.2° (using the convention followed by Sundararajan and Rao[13]). The chain is completely rigid except for the allowed rotation of the $-CH_2OH$ group about the C5–C6 bond. This rotation is described by the dihedral angle χ, where χ has a value of zero when the C6–O6 bond is *cis* to the C4–C5 bond. Counterclockwise rotation of the group when looking down the C5–C6 bond represents positive rotation. The $-CH_2OH$ orientation is also described in terms of its orientation relative to the C4–C5 and C5–O5 bonds: *gg, gauche* to C5–O5 and *gauche* to C4–C5 (χ = −60°); *gt, gauche* to C5–O5 and *trans* to C4–C5 (χ = 180°); and *tg, trans* to C5–O5 and *gauche* to C4–C5 (χ = 60°)[14].

The positions of the two cellulose chains in the unit cell are defined by three packing parameters, whether they have the same or opposite sense. These parameters are the shift of one chain (along *c*) with respect to the other chain, and two parameters defining the orientation of the two chains (about their helix axes). The relative intensities of the 002 (medium) and 004 (strong) indicate an approximate *c*/4 stagger of the chains, and hence four basic models need to be considered, as was the cause for the native structure[2]. In each case the first chain through (0, 0, *z*) has the glycosidic oxygen O1′ at *z* = 0, and 'shift' describes the *c*-axis displacement of O1′ in the second chain through (1/2, 1/2, *z*); the chain sense is defined as 'up' when $z_{O5} > z_{C5}$. The four models are the following: p_1, parallel chains oriented up with a shift of +*c*/4 for the second chain; p_2, parallel chains oriented down with a shift of +*c*/4 for the second chain; a_1, antiparallel chains with an up chain at the origin and a down chain at (1/2, 1/2, *z*), with a shift of −*c*/4; a_2, antiparallel chains as in a_1, except with a shift of +*c*/4 for the second chain.

Thus, for each of the four possible models there are seven refineable parameters.

Three packing parameters:

(1) *SHIFT*, the stagger of the centre chain along its helix axis with respect to that at the origin;

(2) *PHI*, the rotation of the origin chain about its helix axis;

(3) *PHI′*, the rotation of the centre chain about its helix axis.

Two molecular parameters:

(4) the dihedral angle χ, which determines the orientation of the $-CH_2OH$ group in the origin chain;

(5) the dihedral angle χ′, which determines the orientation of the $-CH_2OH$ group in the centre chain.

Two crystallographic parameters:

(6) *K*, the scale factor;

(7) *B*, the average isotropic temperature factor.

The possible structural models for cellulose were refined by adjusting the above parameters using a least squares process[15] to provide the best fit between observed and calculated structure factor amplitudes. The agreement is measured in terms of the usual crystallographic residuals *R*, *R′*, and *R″*, which are in terms of *F*, weighted *F* and weighted F^2 respectively[2,4]. Observed reflections were given a weight of one and unobserved a weight of one half in the calculation of *R′* and *R″*.

RESULTS AND DISCUSSION

Structure determination

The final values of the refineable parameters for the four models following refinement against the observed data and against the observed and unobserved (full) data are given in *Table 2*. The values of *PHI* and *PHI′* are similar to those reported for rayon[4] in that the planes of the sugar rings are refined approximately parallel to the *ac* unit cell face. The chain stagger, *SHIFT*, is ~1/4*c* for all models except a_1. The refined value for the isotropic temperature factor is ~32.0 Å^2 in all cases, which is 60% higher than that found for rayon[4], and reflects the higher disorder for Mercerized cellulose. As a result, the parameters χ and χ′ are not very sensitive to the data and several unacceptable stereochemical contacts exist for the $-CH_2OH$ groups in all four models. Non-bonded constraints were introduced in an effort to eliminate these bad contacts. In those situations where a potential hydrogen bond existed, the model was constrained to form that hydrogen bond.

A stereochemically acceptable structure was found for model a_2 with (χ, χ′) near (*gt, tg*), as was found for regenerated cellulose[4]. This final model has residuals *R* = 0.263, *R′* = 0.248 and *R″* = 0.168 for the full data. For models p_1, p_2 and a_1, removal of the unacceptable contacts could only be accomplished by changing the packing parameters in addition to χ and χ′. In all three cases, the *R″* values were sufficiently high that models p_1, p_2 and a_1 can be eliminated in favour of model a_2 at significance levels of better than 1%[16].

Table 3 Calculated structure factor amplitudes for final Mercerized cellulose model a_2

hkl	*F*(obs)	*F*(cal)	*hkl*	*F*(obs)	*F*(cal)
Zero level:			032	9.13	14.85
010	(12.0)[a]	14.59	$3\bar{2}2$		
$1\bar{1}0$	71.93	84.95	$3\bar{1}2$		
$1\bar{2}0$	188.82	200.62	$3\bar{3}2$	5.73	5.78
110			302		
020	199.95	175.54			
$2\bar{1}0$			Third level:		
$2\bar{2}0$	12.70	14.61	003	–	0.0
200			013	51.83	42.60
$1\bar{3}0$	14.13	24.64	$1\bar{1}3$		
120			103		
$2\bar{3}0$	(12.0)	5.69	$1\bar{2}3$	(12.0)	6.06
210			113		
030	14.47	22.90	023	40.18	26.91
$3\bar{2}0$			$2\bar{1}3$		
$3\bar{1}0$			$2\bar{2}3$	21.48	21.06
$3\bar{3}0$	(12.0)	4.38	203		
300			$1\bar{3}3$	16.51	23.31
$2\bar{4}0$	27.78	39.41	123		
220			$2\bar{3}3$		
$1\bar{4}0$			213		
130			033	17.49	17.88
			$3\bar{2}3$		
First level:			$3\bar{1}3$		
001	–	0.0			
011	8.78	15.21	Fourth level:		
$1\bar{1}1$	(8.0)	18.53	004	Strong[c]	22.06
101			014	21.98	17.28
$1\bar{2}1$	–[b]	42.60	$1\bar{1}4$		
111			104		
021	–[b]	12.25	$1\bar{2}4$	31.30	21.16
$2\bar{1}1$			114		
$2\bar{2}1$	9.00	20.23	024		
201			$2\bar{1}4$		
$1\bar{3}1$	9.05	21.55	$2\bar{2}4$	(12.0)	3.84
121			204		
$2\bar{3}1$	(8.0)	15.51	$1\bar{3}4$	(12.0)	3.88
211			124		
031	30.92	30.11	$2\bar{3}4$	13.49	8.07
$3\bar{2}1$			214		
$3\bar{1}1$			034		
$3\bar{3}1$	22.06	25.99	$3\bar{2}4$		
301			$3\bar{1}4$		
$2\bar{4}1$	11.61	15.32			
221			Fifth level:		
$1\bar{4}1$			005	–	0.0
131			015	Medium[c]	8.30
			$1\bar{1}5$		
Second level:			105		
002	Medium[c]	21.94	$1\bar{2}5$	13.83	7.63
012	57.52	47.20	115		
$1\bar{1}2$			025		
102			$2\bar{1}5$		
$1\bar{2}2$	33.60	27.15	$2\bar{2}5$	(8.0)	2.61
112			205		
022	(10.0)	26.70	$1\bar{3}5$	7.78	5.47
$2\bar{1}2$			125		
$2\bar{2}2$	20.59	15.68	$2\bar{3}5$		
202			215		
$1\bar{3}2$	18.95	23.18	035		
122			$3\bar{2}5$		
$2\bar{3}2$	(8.0)	15.86	$3\bar{1}5$		
212					

[a] Numbers in parentheses are estimated threshold values for unobserved reflections

[b] Reflections obscured by arcing of equatorial reflections

[c] Reflections occurring outside the sphere of reflection but observed due to imperfect specimen orientation. The *F*'s are calculated for a qualitative comparison with the observed intensity

Table 4 Fractional atomic coordinates for one glucose residue of each chain: model a_2 with (χ, χ') in (*gt*, *tg*)[a]

Atom	x/a	y/b	z/c
Origin chain			
C1	–0.043	0.006	0.386
C2	–0.114	0.092	0.230
C3	–0.142	0.009	0.158
C4	0.034	0.000	0.115
C5	0.101	–0.080	0.220
C6	0.285	–0.079	0.188
O1′	0.001	–0.097	0.000
O2	–0.283	0.087	0.336
O3	–0.190	0.102	0.066
O5	0.127	0.010	0.339
O6	0.352	–0.142	0.292
Centre chain			
C1	0.468	0.519	–0.159
C2	0.318	0.505	–0.062
C3	0.404	0.569	0.070
C4	0.520	0.482	0.112
C5	0.659	0.495	0.007
C6	0.767	0.398	0.040
O1′	0.621	0.557	0.227
O2	0.224	0.596	–0.109
O3	0.260	0.539	0.162
O5	0.563	0.428	–0.112
O6	0.896	0.474	0.143

[a] Complementary half of the unit cell can be generated by the symmetry operation $-x, -y, z+0.5$

The refined values for the packing parameters in model a_2 are: $PHI = 22.0°$ ($\sigma_{PHI} = 2.7°$), $PHI' = 62.7°$ ($\sigma_{PHI'} = 2.2°$) and $SHIFT = 0.227c$ ($\sigma_{SHIFT} = 0.025c$). For the side groups, $\chi = -175.1°$ ($\sigma_\chi = 20.5°$), placing the $-CH_2OH$ group of the origin chain within ~5° of the *gt* position; and $\chi' = 69.9°$ ($\sigma_{\chi'} = 15.9°$), which positions the $-CH_2OH$ group of the centre chain within ~10° of the *tg* position. The refined isotropic temperature factor is $B = 32.38$ Å^2 ($\sigma_B = 3.39$ Å^2). The observed and calculated structure factor amplitudes for this model are compared in *Table 3*, and the fractional atomic coordinates are given in *Table 4*. The *ac* projection of the proposed structure is shown in *Figure 4*; the structure is almost the same as that we have determined for rayon[4], and the *ab* projection is not significantly different from that shown in *Figure 1b*.

The hydrogen bonding network in Mercerized cotton is identical to that in rayon and need only be summarized briefly. Each chain possesses an intramolecular O3–H···O5′ hydrogen bond as defined in the model. With the $-CH_2OH$ group near *tg* to the position, the centre 'down' chains contain an additional O2′–H···O6 intramolecular hydrogen bond. Intermolecular hydrogen bonds are formed between adjacent chains in the 020 plane: an O6–H···O2 hydrogen for the corner chains and an O6–H···O3 hydrogen bond for the centre chains. Finally, additional intermolecular hydrogen bonding occurs between the antiparallel sheets of cellulose chains, in which the O2–H of a corner chain is bonded to the O2′ of the centre chain along the 110 diagonal. The bond lengths and angles for the hydrogen bonds are given in *Table 5*.

Alternative side group orientation in cellulose II

The structures of regenerated and Mercerized cellulose have been shown to be essentially identical, and thus the structure of form II is independent of the means of conversion from form I. The major difference is the much larger isotropic temperature factor for Mercerized cellulose, which reflects a higher degree of disorder in this form than in the regenerated cellulose. Possible sources of this disorder are imperfections within the cellulose II crystallites, such as incorrect chain polarity at a lattice position or alternative orientations for the $-CH_2OH$ side groups. The confidence with which alternative packing models can be excluded in favour of the proposed structure precludes any significant percentage of chains with incorrect polarity. However, the high standard deviations in the refined values of χ and χ' suggest that alternative side group orientations may well occur.

As confirmed by potential energy calculations[17], the $-CH_2OH$ groups in cellulose can be expected to adopt one of three staggered rotational conformations, designated *gt*, *tg* and *gg*; these would be likely candidates for alternative conformations in the structure. However, since packing considerations can alter conformational preferences, intermediate values need to be checked as well. With the positions of the chains fixed by the parameters for the a_2 model, the $-CH_2OH$ conformations χ and χ' were varied in increments of 30° and the residual calculated for each combination. These results were then used to produce a

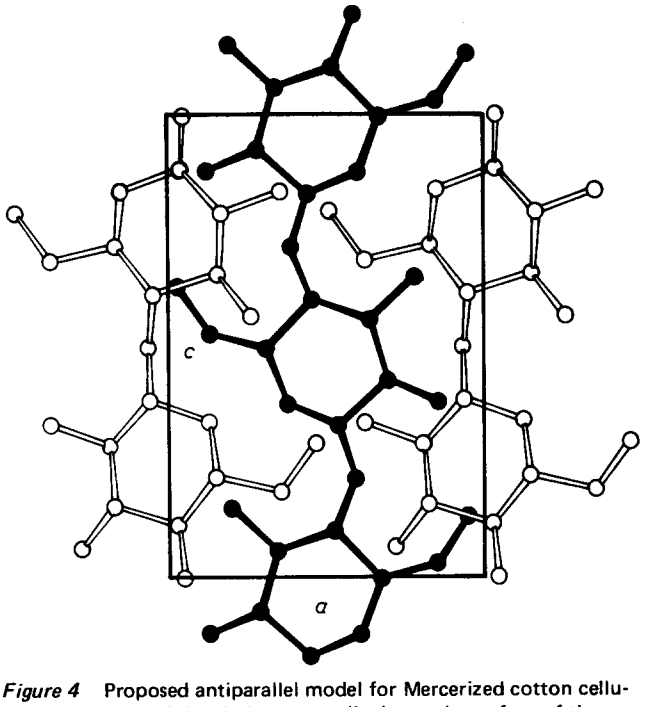

Figure 4 Proposed antiparallel model for Mercerized cotton cellulose; projection of the chains perpendicular to the *ac* face of the unit cell

Table 5 Summary of hydrogen bonding. Network for final model a_2

Hydrogen bond[a]	Bond length (Å)	Bond angle (degree)
C3–O3···O5′	2.69	102.6
C6–O6···O2a	2.76	107.1
C2*′–O2*′···O6*	2.72	114.3
C6*–O6*···O3*a	2.72	129.4
C2a–O2a···O2*′	2.73	108.8

[a] The symbols used are the following: * denotes an atom on the centre 'down' chain; ′ denotes an atom on the next residue up from the asymmetric residue and (a) denotes an atom on the next chain along the positive *a*-axis

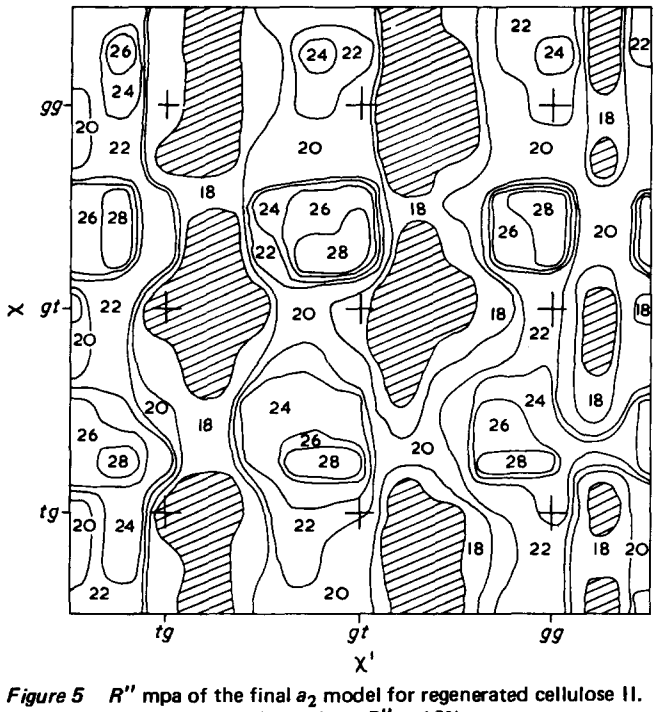

Figure 5 R'' mpa of the final a_2 model for regenerated cellulose II. The lined areas indicate regions where $R'' < 18\%$

two dimensional map of R'' contours for χ against χ'. The calculations were performed using both the regenerated cellulose and Mercerized cellulose intensity data; the results are shown in *Figures 5* and *6* respectively. In each case the scale and isotropic temperature factors used were those of the refined structure. In addition, the possibility of stereochemically bad contacts was checked for each (χ, χ') position.

Regenerated cellulose had the lower isotropic temperature factor, and the work for this structure is considered first. The R'' map in *Figure 5* shows a number of minima, which occur near the nine combinations of the preferred orientations for χ and χ'. A check of the stereochemistry reveals that six of these: (*tg, tg*), (*tg, gt*), (*tg, gg*), (*gt, gg*), (*gg, gg*) and (*gt, gt*), contain unacceptable C···O and O···O non-bonded contacts and can be eliminated from consideration. In the remaining three models, all C···O and O···O non-bonded contacts are acceptable. However, if pendant hydrogen atoms are placed on the glucose ring with appropriate stereochemistry, an unacceptable H···O contact is found when χ is near *gg*, thus eliminating the combinations (*gg, tg*) and (*gg, gt*). Therefore, the only stereochemically acceptable model is (*gt, tg*), which is the result from the X-ray refinement[4]. All of the alternative combinations except (*gg, tg*) could be eliminated in favour of (*gt, tg*) at a significance level of better than 5%. For (*gg, tg*) the significance level is somewhat lower.

In addition, the proposed model is the only one completely consistent with the infra-red evidence. In the O–H stretching region of the cellulose II spectrum, two of the five observed bands show parallel dichroism and the remaining three perpendicular dichroism[18]. One parallel band is expected from the O3···O5′ intramolecular hydrogen bond. Examination of possible hydrogen bonding schemes for the various combinations revealed that only when χ or χ' is near *tg* and an O6···O2′ intramolecular hydrogen bond formed will another parallel band be expected. Therefore, those (χ, χ') combinations with neither $-CH_2OH$ group near *tg* are inconsistent with the infra-red dichroism in the hydroxyl stretching region. Also the dichroisms of the CH_2 symmetric and antisymmetric stretching bands are consistent with *gt* and/or *tg* for the $-CH_2OH$ group, but rule out the *gg* conformation[19]. In summary, taking into account the X-ray agreement, stereochemical criteria and infra-red evidence, only the a_2 model with the $-CH_2OH$ groups in the (*gt, tg*) conformations is fully satisfactory.

In contrast to the results for regenerated cellulose, the R'' map for Mercerized cotton (*Figure 6*) contains a single large minimum which contains four of the nine preferred (χ, χ') combinations: (*gt, tg*), (*gg, tg*), (*gg, gt*) and (*gt, gt*). The five remaining combinations and (*gt, gt*) have R'' values of sufficient magnitude to be ruled out in favour of either (*gt, tg*), (*gg, tg*) or (*gg, gt*); but, on the basis of the Hamilton[16] statistics alone, either (*gg, tg*) or (*gg, gt*) is as good a model for the data as (*gt, tg*). However, since the refined values of the packing parameters are similar for both regenerated and Mercerized cellulose II, similar contact criteria hold for the Mercerized cotton structure, and all combinations except (*gt, tg*) can be ruled out on this basis. Thus in the case of Mercerized cotton, stereochemical contact criteria are the deciding factors in the choice of a model.

The existence of the additional R'' minima for regenerated cellulose suggests that a percentage of the cellulose chains have their pendant groups in conformations other than (*gt, tg*). These conformations most likely occur on the periphery of the crystallites where the unit cell contact criteria may not apply. Electron microscopy[20] shows that regenerated cellulose (Fortisan rayon) consists of fibrillar crystallites with widths in the range 20–40 Å. Thus an estimated 20–30% of the $-CH_2OH$ groups are located on the surface of the crystallites, where considerations other than crystal packing would allow the hydroxymethyl groups to assume a number of conformations. Morphological investigation of cotton Mercerized under slack conditions (see following paper[6]) shows that the crystallites have widths similar to those in regenerated cellulose. X-ray line broadening indicates equivalent or smaller crystallites for cotton Mercerized under tension and thus a similar propor-

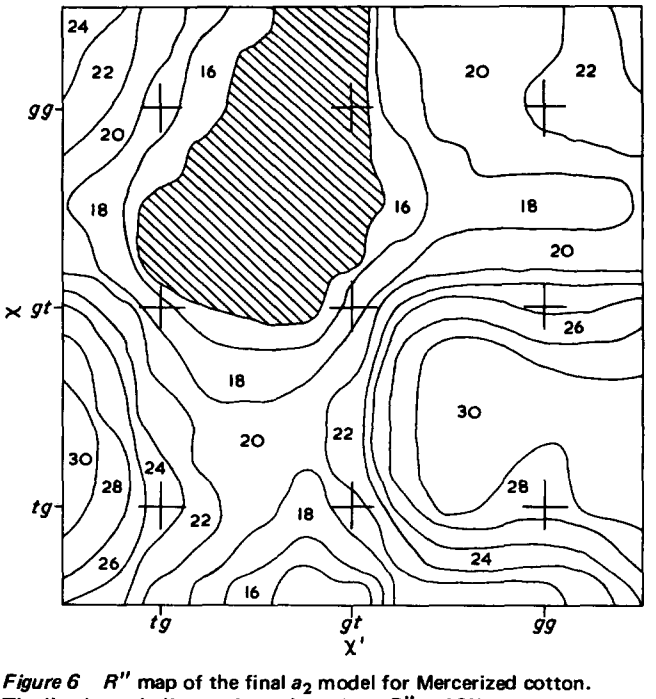

Figure 6 R'' map of the final a_2 model for Mercerized cotton. The lined area indicates the region where $R'' < 16\%$

tion of the $-CH_2OH$ groups are on the exterior of the Mercerized cotton crystallites. However, the single minimum in the R'' map for Mercerized cotton excludes the *tg* conformation for the 'up' chains and the *gg* conformation for the 'down' chains. This suggests that the $-CH_2OH$ groups on the surface of the Mercerized crystallites do not have the same conformational freedom as in regenerated cellulose.

CONCLUSIONS

In spite of the uncertainty about the $-CH_2OH$ group orientations, the presence of antiparallel chains in Mercerized cotton has been demonstrated. The stereochemically acceptable a_2 model is essentially identical to that determined for regenerated cellulose[4]. The Mercerized cellulose structure is an array of antiparallel sheets of chains, which are stabilized by both intrasheet and intersheet hydrogen bonding. There is less crystalline perfection in Mercerized cellulose than in regenerated cellulose, as evidenced by the substantially larger isotropic temperature factor, and the lower sensitivity of the intensity data to the position of the $-CH_2OH$ groups for the former.

For regenerated cellulose, additional minima occur in the R'' map corresponding conformations of the CH_2OH group other than the *gt, tg* combination required in the crystal structure. Thus the X-ray agreement for these conformations is reasonably good, but they are eliminated by stereochemical criteria. However, up to half the chains are on the edges of the crystallites, where the packing requirements are partially relaxed, and where other CH_2OH conformations will be allowed. The existence of the nine minima in the R'' map suggests that all possible combinations of *gt, tg* and *gg* do in fact occur for regenerated cellulose. In contrast, the single large minimum for Mercerized cotton suggests that not all orientations are available to the CH_2OH groups. From this it can be argued that the $-CH_2OH$ groups could have limited rotational freedom during the conversion process, and hence not all conformations can be adopted after the swelling agent is removed. The substantially higher degree of disorder in Mercerized cotton as compared with regenerated cellulose suggests that the defects caused by alternative $-CH_2OH$ orientations may occur within the crystallites as well as on the periphery.

The refined structure requires a change from parallel to antiparallel chain polarity during Mercerization. Since the cellulose chains are not dissolved in this process, the swelling of the fibres by the alkali medium must provide the necessary freedom for chain rearrangement. The intersheet hydrogen bonding found in cellulose II is one of the most significant differences between this structure and the native form. This feature of the structure almost certainly provides a driving force for the cellulose chains to adopt the cellulose II lattice once the swelling medium is removed. Changes which occur in the degree of orientation and crystallite size after even low degrees of conversion indicate that substantial morphological rearrangement is taking place upon Mercerization. A further investigation of these morphological changes is reported in the following paper[6].

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