

X-Ray Diffraction Pattern of Native Cellulose

By

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Abstract

The form of the crystallographic unit cell of native cellulose was examined by X-rays. The diffraction spots A_3 and A_1 on the equatorial layer line were discarded as not being of $K\alpha$ origin, the former spot being taken as of $K\beta$ origin and the latter as due to the critical absorption edge of bromine contained in the sensitive film of the photographic plate as silver bromide. The lattice form was taken to be tetragonal, having the edges $a=b=7.79$ A. U., and $c=10.26$ A. U.; and 4 $C_6H_{10}O_5$ -groups are supposed to be contained in a unit cell.

The crystalline structure of cellulose is a subject which has been discussed already by many authors. The form of the crystallographic unit cell of native cellulose, as revealed by X-ray diffraction, is considered to be orthorhombic by Polanyi¹ and Herzog², and also to be an orthorhombic structure of different size by O. L. Sponsler³. A refinement of the orthorhombic structure suggested by Polanyi and Herzog, a monoclinic structure, which is only a little different from the orthorhombic one, was proposed by Mark and Meyer⁴, and worked out thoroughly by Andress⁵. Many authors agree in saying that the identity period c , that is the length of the crystallographic axis of the unit cell of the crystallite in the direction parallel to the axis of the fibre of the native cellulose, is about 10.3 A. U., this having been

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1. M. Polanyi: *Naturwiss.*, **9**, 228 (1921)
 2. R. O. Herzog: *J. Physic. Chem.*, **30**, 457 (1926)
 3. O. L. Sponsler: *J. General Physiol.*, **9**, 677 (1926)
 4. H. Mark and K. H. Meyer: *Ber. D. Chem. Gesells.*, **61**, 593 (1928); *Z. s. physik. Chem.*, **2**, 115 (1929)
 5. K. R. Andress: *Z. s. physik. Chem.*, **136**, 279 (1928); and **2**, 380 (1929)

determined from the distribution on the photographic plate of the layer lines which are obtained by sending the monochromatic X-ray beam perpendicularly to the axis of the fibre. If the lengths of the two crystallographic axes of the unit cell which are both perpendicular to the c axis mentioned above, are represented by a and b , there is a great discrepancy in opinion among many authors as to the magnitudes of the a and b axes and the angle between these two axes. With regard to these points, the positions and the distribution of the diffraction spots belonging to the equatorial layer line on the photograph have the prime importance, and they have been examined very closely by many authors. According to O. I. Sponsler¹, K. R. Andress² and H. Mark and H. Meyer³ the diffraction spot A_3 , as it was designated by Herzog, is of K_3 origin, and not due to the K_2 line of the copper target they used. This point was also confirmed by the writers by filtering off as far as possible the K_3 line of copper with a thin nickel foil, as is shown by the photograph reproduced in Fig. 1 of the annexed Plate, which was taken with native ramie fibre. Thus, as this spot has no bearing on the determination of the lattice form of native cellulose, it was omitted in the following.

When we use the X-rays coming from a copper target, the diffuse spots A_1 and A_2 overlap each other considerably as is illustrated in Fig. 2 of the annexed Plate, which was taken with native ramie fibre, so that it is usually difficult to measure their positions accurately. However, when the photograph is taken with the X-rays coming from an iron target, these two spots are separated clearly as shown in Fig. 3 of the annexed Plate. The results obtained with the photographs taken by using the X-rays coming from the copper and the iron target are tabulated in Table I. In this table, the values of $\sin\theta$ obtained with the copper and the iron target are given in the second and the third column respectively for the spots A_1 , A_2 , A_3 and A_4 , where θ is the glancing angle of the X-rays to an atomic plane in the crystallite. For comparison, the values obtained by Herzog and Andress are tabulated in the fifth and the sixth column respectively. In the fourth column is given the ratio of the $\sin\theta$ obtained with the iron target to that obtained with the copper target. For the spots A_2 , A_3 and A_4 this ratio is nearly equal to 1.26, which is the ratio of the wave-

1. loc. cit.
2. loc. cit.
3. loc. cit.

lengths of the K-radiations from iron and copper. But for the spot A_1 it is different, and takes the value of 0.951, which may be looked upon as unity within the limit of experimental errors. If we disregard the spot A_3 which is of K_α origin due to the same atomic plane as the spot A_1 , then we may say clearly that the spots A_2 and A_4 are

Table I

Spot	With Cu Target, $\sin \theta_{Cu}$	With Fe Target, $\sin \theta_{Fe}$	$\frac{\sin \theta_{Fe}}{\sin \theta_{Cu}}$	$\sin \theta_{Cu}$ (Herzog)	$\sin \theta_{Cu}$ (Address)
A_1	.123	.117	.951	.1294	.1297
A_2	.143	.175	1.22	.1451	.1436
A_3	.186	.230	1.24	.1791	—
A_4	.202	.255	1.26	.1981	.1979

$$\lambda_{K\alpha} \begin{cases} \text{Fe} \dots 1.934 \text{ A. U.}, \\ \text{Cu} \dots 1.54 \text{ A. U.}, \end{cases} \quad \frac{1.934}{1.54} = 1.256$$

$$\lambda_{K\beta} \begin{cases} \text{Fe} \dots 1.753 \text{ A. U.}, \\ \text{Cu} \dots 1.389 \text{ A. U.}, \end{cases} \quad \frac{1.753}{1.389} = 1.263$$

caused by the reflection of the K_α radiation from the two sets of atomic planes of the crystallite which have different spacings. In the case of the spot A_1 , the circumstances are different, and its position on the photograph remains unaltered though the cellulose is illuminated with the X-rays coming from the iron and the copper target. This peculiarity of the spot A_1 suggests that it may be due to the sudden increase in the photographic sensitivity at the wave-length corresponding to the critical absorption edge of bromine, which is contained as silver bromide in the sensitive film of the photographic plate. As will be stated later, it seems to be quite reasonable to consider that the strongest spot A_1 is due to the second order reflection from the atomic planes having the spacing 7.79 A. U., between two successive atomic planes. As the crystallites are arranged fibrously, in our case, with a certain direction parallel to the atomic planes above mentioned as their common axis, the X-rays coming from the target are resolved and impressed on the photographic plate as their spectrum. The wave-length of the critical absorption edge of bromine is 0.918 A. U. Thus if we assume that the X-rays having this wave-length are subjected to the second order reflection from the atomic planes having eth

spacing value 7.79 A. U., then the value of $\sin\theta$ becomes 0.118, by Bragg's formula. This is in fair agreement with the value 0.117 obtained with the iron target, and also with 0.123 obtained with the copper target by the writers. The values observed by Herzog and Andress with a copper target deviate from the calculated one by about 10%. But the spot A_1 is very diffuse and overlaps the spot A_2 considerably with copper radiation, as was stated before. Moreover the spot A_1 is the nearest to the central spot caused by the direct X-ray beam. As these circumstances considerably hinder the accurate measurement of the position of this spot, a discrepancy of about 10% must be allowed for as the experimental error. The wave-length of the critical absorption edge of bromine corresponds to 13.5 K. V. s by the quantum relation. So if the X-ray tube is excited with a voltage higher than this critical value, we must always expect to get the impression of this critical absorption edge on the photograph, even if the K_β line is excluded by proper filtering. Figs. 2 and 3 in the annexed Plate were taken with copper and iron targets respectively, which were bombarded with about 25 K. V. cathode rays. In these figures we can detect that the weak continuous spectrum of X-rays runs from the spot A_1 to the very diffuse central spot.

If the consideration stated above, that the origin of the spot A_1 is the critical absorption edge of bromine, be correct, this spot must disappear when the X-ray tube is excited with a voltage lower than 13.5 K. V. s. This point was actually tested by exciting the tube, provided with a copper target, with a peak voltage of about 14 K. V. s. The presence of the A_1 spot and the continuous spectrum running from it to the central spot was scarcely perceptible in this case.

The appearance of the spot A_1 is very diffuse as was stated before. This is very different from the sharp image of the critical absorption edge in an ordinary spectrum obtained with a crystal of tolerable size. But if we consider that the crystals are very small in our case, as is revealed by the haziness of all the diffraction spots, it seems not to be altogether unnatural to regard the origin of the diffuse spot A_1 as the critical absorption edge of bromine.

Thus considering, the writers discarded the spot A_1 , together with the spot A_3 , in considering the lattice form of the native cellulose and it was found that the lattice form of the unit cell was very well expressed by a tetragonal form having the size:—

$$a=b=7.79 \text{ A. U.}, \text{ and } c=10.26 \text{ A. U.}$$

With this size of unit cell the quadratic equation becomes

$$\frac{4 \sin^2 \theta}{\lambda^2} = 0.0165(p^2 + q^2) + 0.0095 r^2,$$

where λ is the wave-length of the X-rays employed expressed by the unit A. U., and p, q, r are the indices of the atomic planes. The values of $\frac{4}{\lambda^2} \sin^2 \theta$ calculated and observed by the writers, by Andress and by Herzog are tabulated in Table II. The agreement between the observed and the calculated values seems to be within the limit of experimental errors, excepting a few spots of weak intensity. For the spots of poor agreement the mark (?) is attached to the respective spots in the first column.

The spot A_6 is only observed by Andress. Though the observed value is somewhat larger than that calculated, it seems not to be quite unreasonable to ascribe this discrepancy to experimental error, because this spot is stated to be very weak by Andress.

The spot I_4 is very diffuse. Thus this spot is considered to be caused by the overlapping of the two spots due to the (311) and (321) planes.

The very weak spot II_6 is only observed by Herzog, and its origin is ascribed to the overlapping of the two spots due to the (312) and (322) planes.

The observed values tabulated in Table II, which were obtained by the writers, are the mean values measured on several photographs, which are taken with the K_α line of copper and iron. As an example, a photograph taken with the unfiltered K radiation of copper is reproduced in Fig. 4 of the annexed Plate, which was taken with native ramie fibre.

From the numbers given in Table II, the discrepancy between the observation and the calculation can not necessarily be said to be very small. But if we consider the circumstance that by the squaring of the observed values of $\sin \theta$, the percentage error in Table II is double that of the direct observation, a discrepancy of such extent as is seen in the table seems to be permissible as experimental error for the present case, where the diffraction spots come out pretty diffused on the photographic plate.

By assuming the form and the size of the unit cell of cellulose to be as stated before, the writers calculated the number of the $C_6H_{10}O_6$ -groups contained in a unit cell. The volume of a unit cell is equal to

Table II

Spots	Indices	$-\frac{4}{\lambda^2} \sin^2 \theta$				Intensity
		calc.	observed by the writers	observed by Andress	observed by Herzog	
A_2	100	0.0165				
	110	0.0330	0.0338	0.0348	0.0356	str.
A_4	200	0.0660	0.0693	0.0660	0.0662	v. str.
	210	0.0825				
A_5	220	0.1320				
	300	0.1485		0.149		w.
$A_6(?)$	310	0.1650				
	320	0.2145		0.240		v. w.
A_7	400	0.2640	0.267	0.264	0.270	m.
	410	0.2805				
	330	0.2970				
I_1	001	0.0095				
	101	0.0260		0.0245	0.0293	w.
I_2	111	0.0425		0.0446		v. v. w.
	201	0.0755				
I_3	211	0.0920				
	221	0.1415				
$I_4(?)$	301	0.1580	0.156	0.149	0.149	m.
	311	0.1745	0.194	0.190	0.1936	w.
321	0.2240					
II_1	002	0.0380		0.0384		w.
	102	0.0545	0.0565	0.0540	0.0549	str.
II_2	112	0.0710				
	202	0.1040	0.111	0.106	0.1092	str.
II_3	212	0.1205	0.125	0.122	0.1210	str.
	222	0.1700		0.176		v. v. w.
II_4	302	0.1865				
	312	0.2030			0.2252	v. w.
322	0.2525					
$II_5(?)$	402	0.3020			0.284	v. w.
	332	0.3350				
III_1	003	0.0855				
	103	0.1020	0.103	0.100	0.1018	m.
III_2	113	0.1185	0.121	0.116	0.1163	m.
	203	0.1515	0.154	0.145	0.1507	str.
III_3	213	0.1680	0.174	0.150		w.
	223	0.2175				
III_4	303	0.2340	0.230		0.225	w.
	313	0.2505	0.252		0.2455	w.
IV_1	004	0.1520	0.155	0.151		str.
	104	0.1685				
IV_2	114	0.1850	0.190	0.184	0.186	w.
	204	0.2180	0.222	0.214	0.2185	str.
IV_3	214	0.2345				
	224	0.2840			0.2882	w.
IV_4	304	0.3005	0.295			w.
V_1	005	0.2375				
	105	0.2540	0.259			w.
V_2	115	0.2705				
	205	0.3035				
V_3	215	0.3200	0.321			w.
	225	0.3695				
V_4	305	0.3860				
VI_1	006	0.3420		0.340		m.

$$a^3 \cdot c = (7.79 \times 10^{-8})^2 \times 10.26 \times 10^{-8} = 624 \times 10^{-24} \text{ c.c.}$$

By taking the density of cellulose to be 1.59, after Andress¹, the mass of a unit cell becomes

$$1.59 \times 624 \times 10^{-24} = 9.92 \times 10^{-22} \text{ gms.}$$

As the mass of a $C_6H_{10}O_5$ -group is equal to

$$\frac{162}{6.06 \times 10^{23}} = 2.675 \times 10^{-22} \text{ gms.,}$$

the number of $C_6H_{10}O_5$ -groups contained in a unit cell becomes

$$\frac{9.92 \times 10^{-22}}{2.675 \times 10^{-22}} = 3.71.$$

This is not a whole number. But when we consider the circumstances that the accurate determination of the density of native cellulose is very difficult, and moreover that there is reason to take the net density of native cellulose somewhat higher than the value observed actually, then it seems to be quite legitimate to take the number of $C_6H_{10}O_5$ -groups contained in a unit cell of native cellulose to be four.

In conclusion, the writers' sincere thanks are due to Prof. G. Kita of the laboratory of industrial chemistry in the Kyoto Imperial University for his kind advice.

1. K. R. Andress: *Z. s. physik. Chem.*, **136**, 279 (1928)

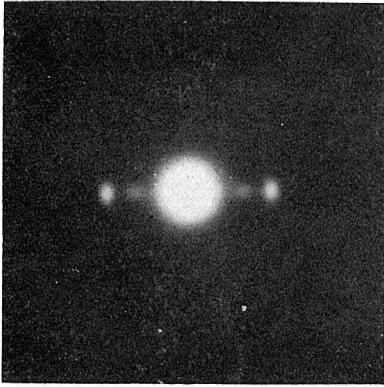


Fig. 1

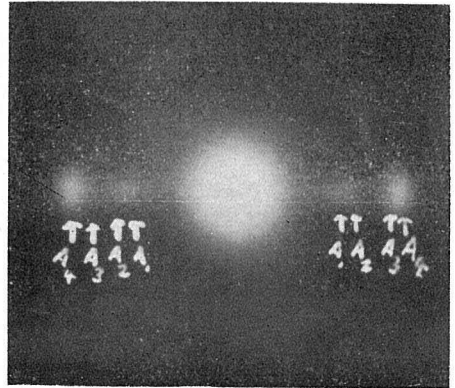


Fig. 2

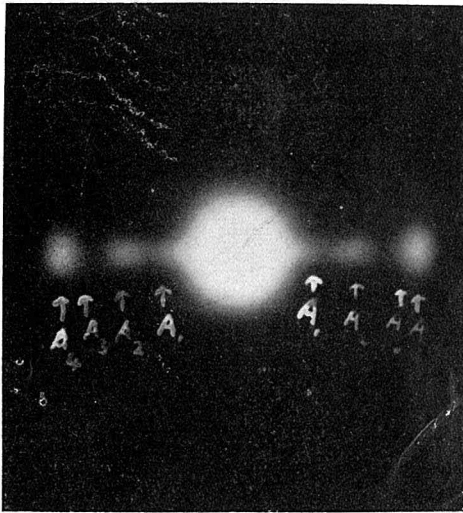


Fig. 3

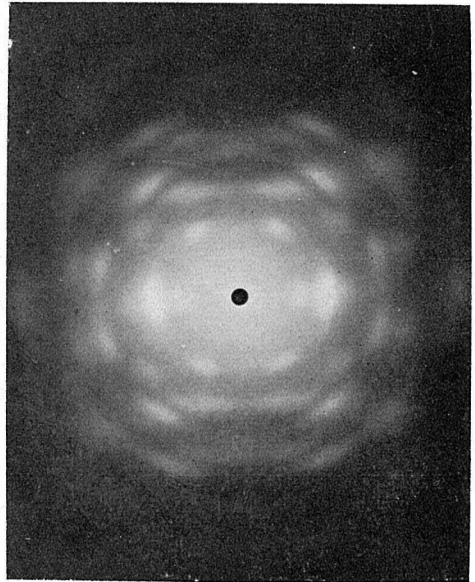


Fig. 4