Further Investigation on the X-Ray Diffraction Pattern of Native Cellulose

By

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Abstract

It was confirmed that the lattice form of the crystallographic unit cell of native cellulose is monoclinic. With a Cr target the writers found a spot which might be caused by either one of the atomic planes 100 and 001 or by both of them. With the values of the dimension of the unit cell taken by the writers (a=8.22 A. U., b=10.33 A. U., c=7.84 A. U., β=84°) and the most reliable net density ρ=1.614 of ramie cellulose, the writers got the number 4.01 of the ($C_6H_{10}O_5$)-groups contained in a unit cell. This number is exactly whole within the limit of experimental errors.

In a paper published in 1931,[1] one of the writers and N. Matsumoto suggested that the form of the crystallographic unit cell of native cellulose is tetragonal, which is different from the forms suggested by Herzog[2], Andress, Meyer and Mark[3], and the others.

In the determination of the form of the crystallographic unit cell of native cellulose, the prime importance is the examination of the positions and the distribution of the diffraction spots belonging to the equatorial layer line on the photograph. Thus, in this experiment the writers have chiefly examined the distribution of the spots on the equatorial layer line.

According to O. L. Sponsler[4], K. R. Andress, and K. H. Meyer and H. Mark, the diffraction spot A_3 in fig. 1 in the annexed Plate

1. U. Yoshida and N. Matsumoto: These Memoirs, **14**, 115 (1931).
2. R. O. Herzog: J. physic. Chem., **30**, 457 (1926).
3. K. H. Meyer and H. Mark: Ber. D. chem. Gesells., **61**, 593 (1928); Z. S. physik. Chem., 2B, 115 (1929).
4. O. L. Sponsler: J. General Phisiol., **9**, 677 (1926).

I, as it was designated by Herzog, is of K_β origin and not due to the K_α line of the copper target they used. This point was also confirmed by one of the writers and N. Matsumoto. Thus, as this spot has no bearing on the determination of the lattice form of native cellulose, it was omitted in the following.

According to the former investigation[1] made by one of the writers and N. Matsumoto, it is clear that the spot A_1 is due to the critical absorption edge of bromine contained as silver bromide in the sensitive film of the photographic plate. Thus, this spot was also omitted in the following.

If we disregard the spots A_1 and A_3, and assume that the spots on the equatorial layer line which are caused by the reflection of the K_α radiation from the atomic planes of the crystallites which have different spacings are A_2 and A_4 only in the vicinity of the central spot, then it is legitimate to take the lattice form of the unit cell of the native cellulose as a tetragonal one as was suggested by one of the writers and N. Matsumoto. But if there exists still another spot which overlaps the spot A_2, which is very broad even with the X-rays coming from an iron target, the assumption that the lattice form of native cellulose is tetragonal may be incorrect.

Thus considering this point seems to be very important, and the writers attempted to resolve the spot A_2 as far as possible. For this purpose the writers used a thin sheet of native ramie cellulose as the specimen; and a long very narrow slit was employed for the illumination of the specimen with the X-rays coming from an iron target, by setting the slit parallel to the direction of the fibre of the specimen. In such a way the writers succeeded in separating the spot A_2 into two as shown by the fig. 2 in the annexed Plate I. In this figure the inner component of the spot A_2 is denoted by A_{21} and the other one by A_{22}. It was confirmed, from the positions of these two components, that the spots A_{21} and A_{22} were respectively the same as A_1 and A_2 observed by Herzog, Andress, and the others. As to the intensities of the spots A_{21} and A_{22} they came out to be nearly the same in the present case. But according to Herzog, Andress[2], and Meyer and Mark, they are different, and the inner one A_{21} is stronger than A_{22}. In the case of Herzog, Andress, and Meyer and Mark, the

1. U. Yoshida and N. Matsumoto: Loc. cit.
2. K. R. Andress: Z. S. physik. Chem., **136**, 279 (1928); and 2B, 380 (1929)

X-rays coming from a copper target were used, and the overlapping of the spot A_{21} to the critical absorption edge of bromine contained as silver bromide in the sensitive film of the photographic plate was inevitable, resulting in a false estimation of the relative intensities of the two spots.

When we accept the real existence of the spots A_{21} and A_{22}, all the diffraction spots are well designated by taking the lattice form of a unit cell of native cellulose to be monoclinic, as was suggested by Meyer and Mark.

Next, to increase the separation of the spots appearing in the vicinity of the direct spot, the writers used the X-rays coming from a Cr target. With this target a new diffuse spot was found on the equatorial layer line in a position nearer to the central image than the spot A_{21}, as shown by A_{11} in fig. 3 in the annexed Plate I. This diffuse spot A_{11} may be due to either one of the atomic planes 100 and 001 or to both of them. To make this point clear we must consider that 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, occurs somewhere on the photographic plate. With the Cr target used in the present experiment, we must of course expect the presence of continuous X-rays besides the K lines of Cr. When these X-rays are resolved as their spectrum on the photographic plate by the atomic planes which caused the strongest spot A_4, the X-rays having the wave length (0.918 A. U.) which corresponds to the critical absorption edge of bromine attack the photographic plate just at the position occupied by the diffuse spot A_{11}. These circumstances unhappily hinder the determination of the origin of the spot in question.

From the experimental data obtained by the writers and the former experiment[1] the following quadratic equation was obtained:

$$\frac{4\sin^2\theta}{\lambda^2}=0.0151h^2+0.0095k^2+0.0164l^2-0.0033hl,$$

where λ is the wave length of the X-rays employed expressed by the unit of A. U., and h, k, l are the indices of the atomic planes, by taking the dimension of a unit cell of native cellulose as

$$a=8.22 \text{ A. U.}, \quad b=10.33 \text{ A. U.}, \quad c=7.84 \text{ A. U.}, \quad \beta=84^\circ.$$

The values of $\frac{4\sin^2\theta}{\lambda^2}$ calculated and observed are tabulated in Table

1. U. Yoshida and N. Matsumoto: Loc. cit.

Table I

Spots	Indices	$\frac{4}{\lambda^2}\sin^2\theta$ calculated	$\frac{4}{\lambda^2}\sin^2\theta$ observed	Intensities	Remarks
	100 001	0.0151 0.0164	0.0175	m. st.*	*We can not say exactly whether this spot is due to either one of the 100 and 001 planes or to both of them.
A_{21}	101	0.0282	0.0284	st.	
A_{22}	$10\bar{1}$	0.0348	0.0349	st.	
A_4	002	0.0656	0.0667	v. st.	
A_5	004	0.2624	0.2672	m.	
I_1	310	0.1454	0.156	m.	
I_2	213	0.1977	0.194	w.	
II_1	021	0.0544	0.0565	st.	
II_2	221	0.1082	0.111	st.	
II_3	$22\bar{1}$	0.1214	0.125	st.	
III_1	031	0.1019	0.103	m.	
III_2	131	0.1137	0.121	m.	
III_3	230 032	0.1459 0.1511	0.154	st.	
III_4	$13\bar{2}$	0.1728	0.174	w.	
III_5	$23\bar{2}$ 033	0.2247 0.2331	0.230	w.	
III_6	$33\bar{1}$	0.2477	0.252	w.	
IV_1	040	0.1520	0.155	st.	
IV_2	$14\bar{1}$	0.1868	0.190	w.	
IV_3	240 042	0.2124 0.2176	0.222	st.	
IV_4	143	0.3048	0.295	w.	
V_1	051 150	0.2539 0.2526	0.259	w.	
V_2	251 $15\bar{2}$	0.3077 0.3248	0.321	w.	

I. The observed values given in the fourth column are those obtained by the writers and by the previous experiment already referred to.

By assuming the form and the size of the unit cell of native cellulose to be as stated before, the writers calculated the number of the $(C_6H_{10}O_5)$-groups contained in a unit cell. The volume of a unit cell is equal to

$$V_c = a \cdot b \cdot c \cdot \sin\beta$$
$$= 8.22 \times 10.33 \times 7.84 \times 10^{-24} \times 0.9945$$
$$= 662.1 \times 10^{-24} \text{ C. C.}.$$

By taking the net density of native cellulose to be 1.614[1] the mass of a unit cell becomes

1. U. Yoshida and B. Takei: These Memoirs, **15**, 1 (1932).

$$M_c = \rho \cdot V$$
$$= 1.614 \times 662.1 \times 10^{-24} \text{ gr.}$$
$$= 10.7 \times 10^{-22} \text{ gr.}$$

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

$$M_m = \frac{162}{6.06 \times 10^{23}}$$
$$= 2.67 \times 10^{-22} \text{ gr.},$$

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

$$N = \frac{M_c}{M_m}$$
$$= \frac{10.7 \times 10^{-22} \text{ gr.}}{2.67 \times 20^{-22} \text{ gr.}}$$
$$= 4.01.$$

This number is very close to four.

Thus it may be concluded clearly that with the most reliable value of the net density of ramie cellulose this number became exactly a whole number within the limit of experimental errors. This fact is nothing but the justification of the correctness of the size and the shape of the unit cell of ramie cellulose, which are proposed by the writers.

The values of the dimension of a unit cell as given above, $a=8.22$ A. U., $b=10.33$ A. U., $c=7.84$ A. U., $\beta=84^\circ$ are a little smaller than those given by Meyer and Mark, $a=8.3$ A. U., $b=10.3$ A. U., $c=7.9$ A. U., $\beta=84^\circ$.

Plate I

Fig. 1

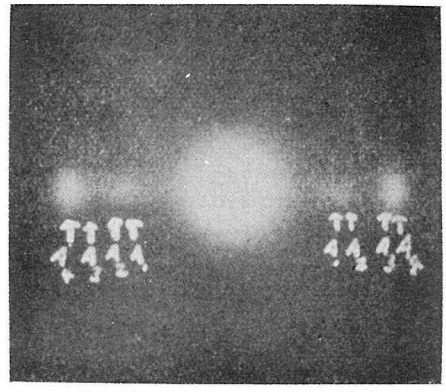

Fig. 2

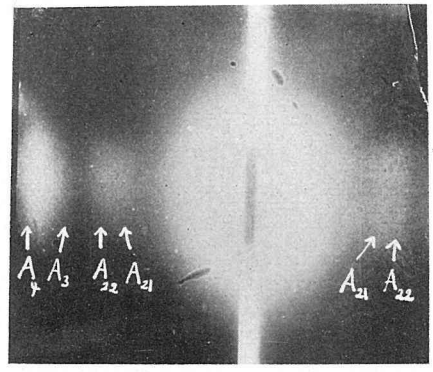

Fig. 3