On the crystal structure of cellulose I

In the crystal lattice of cellulose, the plane (002) plays the predominant role, because it contains the flat pyranose rings of the chain molecules. MEYER AND MISCH[1] placed into this plane not only the bonds between the six carbon atoms and the two secondary hydroxyl groups (with the necessary deviations due to the valency angles and the space constellation of the pyranose ring), but also as far as possible the $CH_2 \cdot OH$ bond to the primary hydroxyl group (Fig. 1a). As a consequence, the hydroxyl groups of neighbouring cellulose chains are at a distance of only 2.6 Å from each other so that the hydrogen bonds of the cellulose lattice[2] ought to be formed in the (002) plane of the lattice (Fig. 1b).

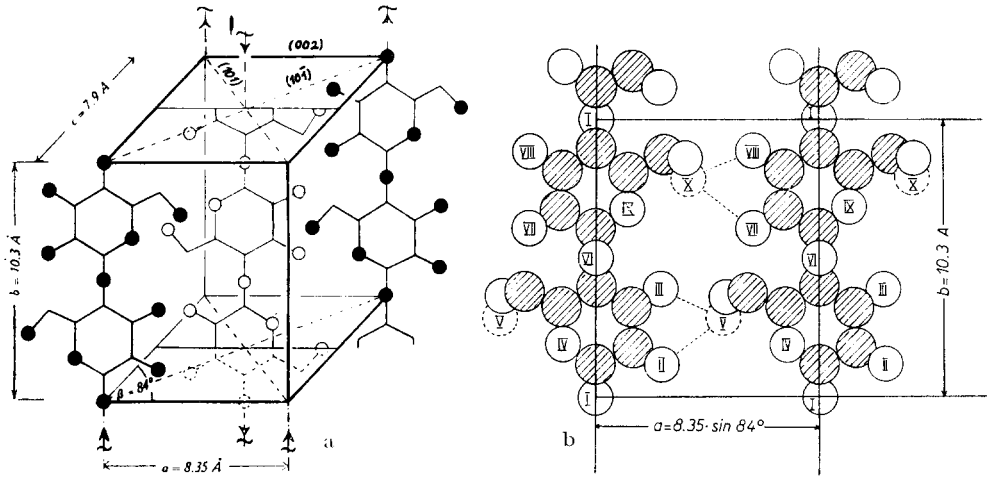

Fig. 1. Cellulose I according to MEYER AND MISCH[1]. 1a. Space lattice; 1b. hydrogen bonds tie together the cellulose chains of the plane (002). O_Y and O_X in dotted lines, before the suggested rotation; in full lines, after.

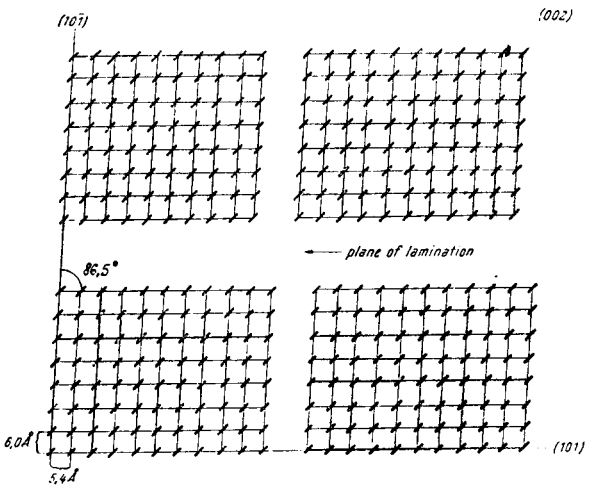

Fig. 2. Orientation of the cellulose crystallites in the plant cell wall. Section ⊥ to the axis of the chain lattice. The plane (101) lies parallel to the cell surface; it is the plane of lamination and growth in area.

In silk fibroin, MARSH, COREY AND PAULING[3] found the orientation of the hydrogen bonds to govern the shape and the growth of the microfibrils visible in the electron microscope, since these microfibrils represent flat ribbons[4] whose surface corresponds to the direction of the hydrogen bonds. By analogy, the lattice plane (002) ought to control the submicroscopic morphology of the cellulose microfibrils. But this is not the case. Morphologically the plane (101) seems to be much more important than (002): According to X-ray diffraction evidence, in plant cell walls the submicroscopic crystallites have the plane (101) oriented parallel to the surface of the cytoplasm by which they are produced[5]; at the same time it is the plane of lamination of the membranes thickening by apposition[6]. In some special cases the microfibrils display even beautiful aggregations and fasciations in that plane[7]. Further, microfibrils suspended in water and produced by mechanical or chemical disintegration of native textile fibres are deposited on their (101) plane[8]. These facts prove that (101) is the principal plane of growth of the cellulose crystallites (Fig. 2). Therefore, it is likely that the hydrogen bonds are more active in (101) than in any other lattice plane.

The mass predominance of (002) in the crystal structure of cellulose I must not necessarily induce the strongest lateral cohesion in this very plane. MEYER AND MISCH[1] mention that the true position of the primary hydroxyl is uncertain so that the chosen disposition (Fig. 1) is just one of many possibilities. As a matter of fact the primary hydroxyl of the angled group $>C_{VI}H—C_{VI}H_2\diagdown OH$ can freely rotate around the axis $C_V—C_{VI}$.

If such rotation is allowed so that the primary hydroxyl is moved out of the plane (002) (Fig. 1) and brought as near as possible to the oxygen bridge of the nearest antiparallel cellulose chain which is shifted by ¼ of the fibre period along the *b* axis of the chain lattice, the following configuration results (Figs. 3 and 4).

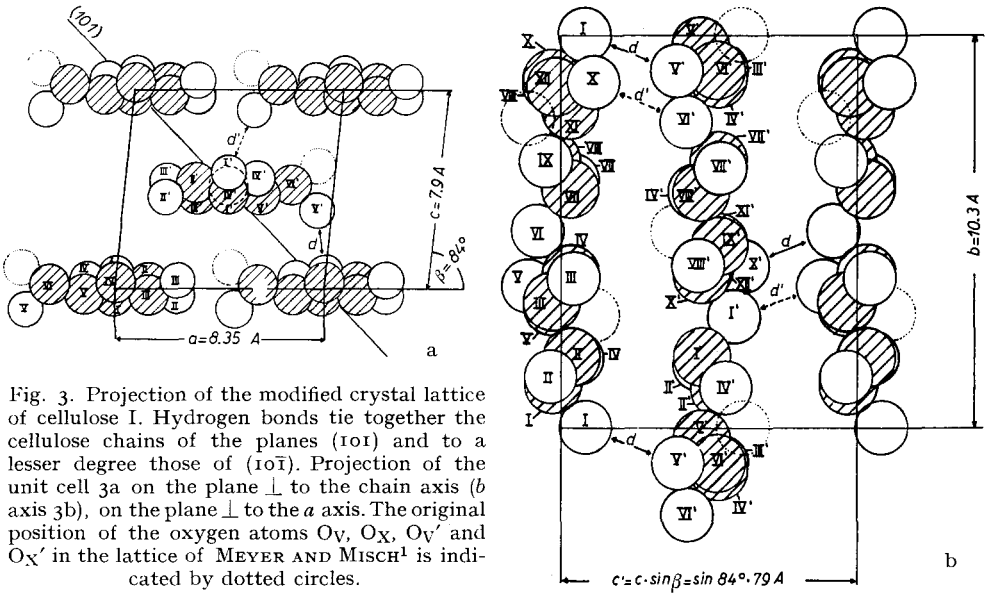

Fig. 3. Projection of the modified crystal lattice of cellulose I. Hydrogen bonds tie together the cellulose chains of the planes (101) and to a lesser degree those of (10$\bar{1}$). Projection of the unit cell 3a on the plane ⊥ to the chain axis (*b* axis 3b), on the plane ⊥ to the *a* axis. The original position of the oxygen atoms O_V, O_X, O_V' and O_X' in the lattice of MEYER AND MISCH[1] is indicated by dotted circles.

The smallest distance between oxygen atoms of parallel cellulose chains is located between O_V' and O_I (indicated by a full line in Fig. 3). It measures d = 2.5_4 A, whilst that of $O_V—O_I'$ amounts to 2.8_0 A (indicated by a dotted line). The distance between the hydroxyls $O_V\cdots O_{III}$ and $O_V'\cdots O_{III}$ has an intermediate value of 2.6_5 A and that between $O_V\cdots O_{II}$ and $O_V'\cdots O_{II}'$ 3.4_2 A. Since $O_V'\cdots O_I$ is shorter than $O_V'\cdots O_{III}'$ the conditions for the formation of hydrogen bonds is most favourable between chains lying in the plane (101). If those bonds are formed, the bond $O_V'\cdots O_{III}'$ cannot exist at the same time. So the next possible distance for the formation of hydrogen bonds is $O_V—O_I'$, by which the cellulose chains are linked together along the plane (10$\bar{1}$).

The distances have been found graphically by using the parameters of the atoms in the crystal lattice given by MEYER AND MISCH[1], the bond distances C—C = 1.54 A, C—O = 1.45 A and the valency angle 109°40'. O_V' has been rotated around the axis $C_V'—C_{VI}'$ into the plane $C_V'C_{VI}'O_I$ and O_V around the axis $C_V—C_{VI}$ into the plane $C_VC_{VI}O_I'$. The new parameters of O_V, O_X, O_V' and O_X' as compared with those of MEYER AND MISCH[1] are:

parameters of	MEYER AND MISCH			*new position*		
	a	*b*	*c*	*a*	*b*	*c*
O_V	0.57	0.29	0.11	0.59	0.37	0.89
O_X	0.43	0.79	0.89	0.41	0.87	0.11
O_V'	0.91	0.00	0.61	0.93	0.91	0.39
O_X'	0.09	0.50	0.39	0.07	0.41	0.61

The *a* parameter of the rotated primary hydroxyl groups has not changed appreciably, but referred to the *b* axis O_V and O_X appear considerably raised and O_V' and O_X' correspondingly lowered. Incidentally the parameters of O_V and O_X or O_V' and O_X' are interchanged. The parameters do not essentially change if the new dimensions of the unit cell of LEGRAND[9], TRILLAT AND LEGRAND[10] and KIESSIG[11] are considered:

MEYER AND MISCH[1]	a = 8.35 Å,	b = 10.3 Å,	c = 7.9 Å,	β = 84
LEGRAND[9]	8.16	10.28	7.83	84 20′
KIESSIG[11]	8.17	10.31	7.84	84 5′

The proposed change cannot appreciably alter the intensity of the (002) spot on the X-ray diffraction diagram so that the qualitative evaluation of the intensities of the X-ray interferences by MEYER AND MISCH[1] does not exclude such a possibility. It yields a crystal lattice of cellulose I which is in better accord with the morphology of the microfibrils observed in the electron microscope than the classical model. The lattice of K. H. MEYER would demand a pronounced lamination of the native cellulose parallel to the plane (002), and the cohesion of the lattice perpendicular to it would be so weak that (002) ought to be a plane of cleavage. Further, (002) would not only be a plane of lamination, but also a plane of preferred growth so that a foliar lattice would result. None of these expectations proves to be correct. On the contrary, the diagonal plane (101) is the plane of growth, lamination and cleavage. Whilst in the old model all hydrogen bonds were concentrated in one plane demanding a pronounced sheet-like habit, in the new crystal lattice these bonds work in such a way that the chains are tied together in the two planes (101) and (10$\bar{1}$), producing a fibrillar and not a foliar habit. However, the strength of the bonds in the (101) plane is appreciably stronger than in the (10$\bar{1}$) plane, according to the distance of the oxygen atoms yielding hydrogen bonds, which is 11 % less in the (101) than in the (10$\bar{1}$) plane. As a result there is a certain tendency to form ribbon-shaped fibrils.

A. FREY-WYSSLING

Laboratory of General Botany, Swiss Federal Institute of Technology, Zurich (Switzerland)

1 K. H. MEYER AND L. MISCH, *Helv. Chim. Acta*, 20 (1937) 232.
2 E. J. AMBROSE, *The Stereochemistry of Compounds of High Molecular Weight*, in W. KLYNE, *Progress in Stereochemistry*, London, 1954, p. 280.
3 R. E. MARSH, R. B. COREY AND L. PAULING, *Biochim. Biophys. Acta*, 16 (1955) 1.
4 R. HEGETSCHWEILER, *Über den Feinbau des Seidenfibroins*, Thesis, Swiss Federal Inst. Techn., Zurich, 1949, and *Makromol. Chem.*, 4 (1949) 156.
5 O. L. SPONSLER, *Protoplasma*, 12 (1931) 241.
6 A. FREY-WYSSLING AND K. MÜHLETHALER, *Fortschr. Chemie org. Naturstoffe*, 8 (1951) 1.
7 A. FREY-WYSSLING, *Holz*, 9 (1951) 333.
8 S. M. MUKHERJEE, J. SIKORSKI AND H. J. WOODS, *Nature*, 167 (1951) 821.
9 C. LEGRAND, *Bull. soc. chim. Belges*, 57 (1948) 113.
10 J. J. TRILLAT AND C. LEGRAND, *Bull. soc. franç. minéral. et cryst.*, 77 (1954) 302.
11 H. KIESSIG, *Z. Elektrochem.*, 54 (1950) 320.

Received June 15th, 1955

A powerful reactivator of alkylphosphate-inhibited acetylcholinesterase*

Certain phosphate esters such as tetraalkylpyrophosphates, dialkyl-*p*-nitrophenyl phosphates, and dialkyl fluorophosphates are potent irreversible inhibitors of acetylcholinesterase and esterases in general. The reactivation of alkylphosphate-inhibited acetylcholinesterase is of both practical and theoretical importance. It is of practical interest because the most potent chemical warfare gases and some powerful insecticides are alkylphosphates and their lethal action is due to the inhibition of acetylcholinesterase. It is of theoretical interest because the mechanism of inhibition and of reactivation is very closely related to the mechanism of enzymic hydrolysis[1]. This enzyme contains two sites, (i) an anionic site which contributes to the catalytic activity by binding and orienting molecules containing substituted ammonium structures, and (ii) an esteratic site which interacts with the ester function and is primarily responsible for the hydrolytic activity. During the hydrolysis of a carboxylic ester a basic group in the esteratic site is acylated to form an acyl-enzyme as intermediate. Acetyl-enzyme (from acetate-esters or anhydrides)

* This work was supported in part by the Medical Research and Development Board, Department of the Army, Office of the Surgeon General, Contract No. DA-49-007-MD-37, and in part by the Division of Research Grants and Fellowships of the National Institutes of Health, Grant B-573, United States Public Health Service.