

prising indeed if these principles and these compounds with their congeners do not yield new means for cancer control in man within the foreseeable future.

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The Fine Structure of Cellulose Microfibrils

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THE microfibrils detected in native cellulose with the electron microscope (1, 2) can be further disintegrated by means of ultrasonics (3), hydrolysis (4), or oxidation (5). Whereas the microfibrils show diameters of 150–250 Å, the resulting elementary fibrils (or micellar strands) grade down to 90–70 Å. Vogel (6) has found that these elementary fibrils are flat filaments, sometimes only 30 Å thick. These ribbons anastomose laterally with each other. Their lateral aggregation is visible when ultrathin sections of ramie fibers are disintegrated in a blender. The plane of the ribbon must correspond to the (101) plane of the cellulose crystal lattice, since Mukherjee and Woods (7) find by x-ray analysis that cellulose particles of ramie and cotton produced by H_2SO_4 hydrolysis sediment are parallel to that plane.

Based on these facts, the amicroscopic¹ structure of a microfibril can be described by Fig. 1. It represents the cross section of a thin microfibril which is composed of several aggregated elementary fibrils (micellar strands).

The elementary fibrils consist of a crystalline core that is flattened parallel to the (101) lattice plane. This shape is due to a faster growth of the (101) plane, which is more hydrophilic (8) than the more slowly growing (10 $\bar{1}$) plane. Therefore, more energy

¹ Amicroscopic, particles less than 50 Å, not visible in even the electron microscope.

is needed to remove the hydration water from the (101) plane when adding a new layer of chain molecules. The crystalline core of the microfibrils is embedded in a cortex of paracrystalline cellulose (9). The insufficient order of the chain molecules in this cortex may be caused by the escaping water released on the occasion of the polymerization of glucose and the crystallization of the resulting chain molecules.

The paracrystalline cellulose is responsible for the aggregation of the elementary fibrils to form microfibrils. The tendency toward aggregation in the (101) plane is greater than perpendicular to it. As a result,

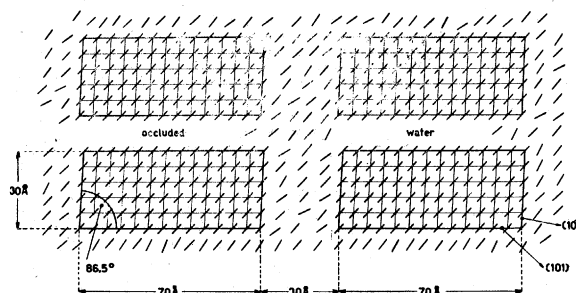


FIG. 1. Section across a microfibril of native cellulose composed of four elementary fibrils or micellar strands. A core of crystalline cellulose chains, seen in cross section, is embedded in paracrystalline cellulose. (101) and (10 $\bar{1}$) planes of crystal lattice.

water may be occluded between (101) planes. Therefore, the microfibrils are laminated and easily split parallel to the (101) plane, whereas the micellar strands adhere laterally to each other. In this way, broad aggregated ribbons can be formed, as demonstrated in the electron microscope (10).

The paracrystalline cellulose and the clefts parallel to the (101) plane are the places where water is adsorbed when cellulose fibers swell. Also, iodine may penetrate between the layers of the microfibrils.

It has been shown (11) that, besides these amicroscopic inhomogeneities, there are much coarser submicroscopic capillaries in cellulose fibers which are accessible to colloidal dyestuffs. Those spaces are situated between the microfibrils. They may contain other cell-wall substances and must be considered as channels by which the living cytoplasm receded after the formation of the microfibrils.

The model presented in Fig. 1 is in accordance with the following physical data measured on cellulose fibers. The x-ray analysis of the diameter of the cellulose crystallites yields about 50 Å (11). Since the cross section of the crystalline area is not isodiametric but is a flat rectangle of about $30 \times 70 \text{ Å}^2$, the value 50 Å represents a mean value. This mean results from the circular arrangement of the flat elementary fibrils, which have their (101) plane oriented parallel to the lumen of the fiber cell.

The density of crystalline cellulose is 1.59, whereas that of pure fiber cellulose reaches only 1.55 (12). Since the void of the submicroscopic capillaries in the fiber cell wall is eliminated when the density is measured, this difference of 0.04 must be due to unorderly crystallized (paracrystalline) cellulose.

Hermans and Weidinger (13) find that the so-called crystallinity derived from x-ray scattering is only 70 percent in native fibers, while 30 percent of the cellulose is said to be "amorphous." Since in the electron microscope no such amorphous cellulose can be detected, but only microfibrils and elementary fibrils, the amorphous cellulose must be located inside the microfibrils and therefore be identical with our paracrystalline cellulose. Our model shows that at least a third of the cellulose chains must be paracrystalline when the surface of the elementary fibrils is covered by slightly disordered chain molecules. If the crystallinity is derived from the resistance to hydrolysis (hydrolysis velocity), at least 80 percent is found (14). From our figure, it is evident that paracrystalline cellulose chains at the very surface of the crystalline area, although they contribute to the diffuse diffraction of x-rays, are better protected against hydrolysis than more distant ones. Therefore, the hydrolysis method must yield higher values for the crystallinity than the x-ray diffraction.

In primary cell walls (1) and plant slimes (15), the microfibrils are clearly individualized, whereas in secondary cell walls, due to the paracrystalline cortex, they aggregate to form coarser bands (10), as indicated above. It was open to discussion whether the individuality in the first case is caused by a more com-

pact surface of the microfibrils or only by their considerable distance, since the cellulose component represents but a small fraction in growing cell walls and slimes.

Figure 2 shows how distantly the cellulose micro-

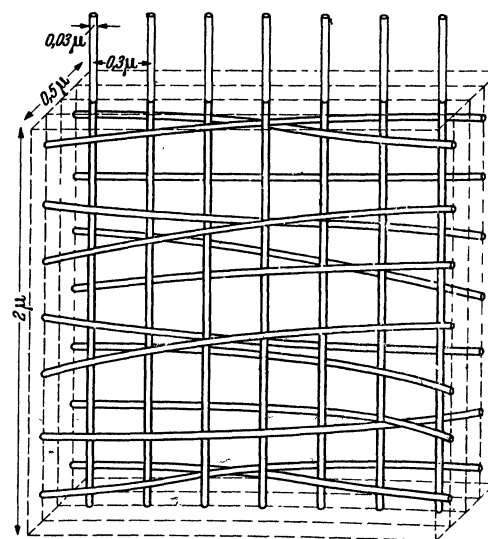


FIG. 2. Texture of the cellulose microfibrils in the growing primary cell wall.

fibrils are situated in a growing primary cell wall before it is freed of all wall substances other than cellulose and dehydrated for examination in the electron microscope. It was of interest to know whether the macromolecular properties of this cellulose in primary cell walls differ from those of the cellulose in such secondary walls of cotton, ramie, and wood. G. V. Schulz and M. Marx in Mainz, and P. H. Hermans and A. Weidinger in Utrecht, were kind enough to determine the degree of polymerization and the crystallinity in cellulose prepared from growing root tips and coleoptiles of corn. The results are shown in Table 1.

TABLE 1. Cellulose of primary (I) cell walls of *Zea mays* and secondary (II) cell walls of ramie.

	Root tip (I)	Coleop- tile (I)	Cellu- lose fibers (II)
Chemical composition*			
Lipid extract	3.4%	5.3%	—
Alkali extract†	84.5%	89.5%	10%
α-Cellulose	12.1%	5.2%	90%
Degree of polymerization (DP)*	1050	867	> 3000
Crystallinity‡			
Prep. for electron microscopy	57%	59%	
Prep. for DP determination	34%	37%	70%

* By courtesy of G. V. Schulz and M. Marx, Mainz.

† These figures include the protoplasmic contents of the growing cells.

‡ By courtesy of P. H. Hermans and A. Weidinger, Utrecht.

The degree of polymerization of primary wall cellulose seems to be considerably less than that of secondary walls. But it is still good α -cellulose. On the other hand, the crystallinity is astonishingly poor. Dr. Hermans has informed me that only extracellular cellulose of *Bacterium xylinum* has as low a crystallinity as these preparations. According to our model of Fig. 1, the elementary fibrils of such cellulose must have a broader cortex of paracrystalline chains. This insufficient order of the surface layers in the primary wall is probably caused by the large amount of hemicelluloses and pectins, which may hinder an orderly crystallization. The fact that only one-third of its cellulose is really crystalline rules out the possibility that the observed individuality of the microfibrils is due to a better surface delimitation. Therefore, the lack of lateral aggregation of the cellulose microfibrils in the primary wall must be caused by their considerable distance apart (Fig. 2).

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News and Notes

Symposium on the Utilization of Solar Energy

A Symposium on the Utilization of Solar Energy was held at the University of Wisconsin Sept. 12-14. It was sponsored jointly by the National Science Foundation and the University of Wisconsin, with Professor Farrington Daniels acting as Chairman. Attendance was limited to an invited list of 40 people in order that the discussions and exchange of information could be as free as possible; no formal papers were presented.

The general purpose of the symposium was to assess the present knowledge of solar energy and to consider its future. It was hoped that to point out unexplored areas would arouse the attention of those who might be interested in conducting research.

Palmer Putnam opened the conference with a statement concerning the long-range inadequacy of the world's resources of coal, gas, oil, and uranium. At the present rate of fuel consumption, and including the projected increase over the near future, it was estimated that the supply of easily obtainable (i.e., at a cost not more than twice present prices) coal, oil, and gas would be exhausted in less than 100 years. The nuclear fuels would only last another 150 to 200 years. Therefore, it was felt that this generation would be negligent in its duty to posterity if research in the utilization of solar energy were not quickly accelerated.

The first general discussion on solar energy at the conference centered around its storage and utilization for house heating, water heating, and cooking. This discussion indicated that knowledge of absorbents of solar energy was well advanced, but that consider-

able improvement was still necessary before house heating with solar energy could be achieved without the use of auxiliary fossil fuels. One of the major problems is the storage of energy through the night and during long periods of overcast or stormy weather. Collection and storage are interrelated and will require much more research, but substantial progress is to be expected in the near future. Improvements in house design would make possible better use of the sun's heat in both winter and summer.

The next question considered was that of solar power. Present knowledge indicated that solar power in small units might be produced in certain parts of the world, including the southwestern part of the United States, at from two to three times the current cost of power production from coal and oil. The chief disadvantage is that the power would be intermittent because it can be produced only during the hours of sunlight. There was some discussion of the possibility of deriving power from engines with water vapor at low pressures, making use of low temperatures. This method seemed farther away than the absorption of solar energy to produce steam, and there were arguments concerning the relative merits of focusing mirrors and black collectors with multiple glass plates.

Closely allied to the power problem is the solar evaporation of sea water. Some progress in this regard has been made by putting dyes in the water in order to improve the absorption of energy. One part per million of dye may increase absorption by as much as thirty percent in the evaporation of water to yield salt.

The question of the production of conventional fuels from agricultural and algal sources was considered briefly. The consensus was that this would be an in-