STRUCTURE OF THE CELL WALL OF WOOD

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STRUCTURE OF THE CELL WALL OF WOOD FIBERS[1]

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Introduction

Records of observations made by early research workers on the cell-wall structure are an inspiration to present-day workers. Although at that time the microscopes were less refined than they are today, yet in the hands of careful observers amazingly fine structures of the cell wall were reported. The discovery of the fibrils was reported by Meyer as early as in 1838.[2] Stratifications in cross sections of fibers and striations on the lateral surfaces of fibers were reported in 1877[3] and in 1882.[4] In 1892, Wiesner,[5] on treating fibers with acid at elevated temperatures, obtained a fine dust-like residue, the particles of which he named dermatosomes. Submicroscopic structural units were postulated in 1877 by Nageli[3] in his micelle theory which is still fundamentally sound.

During the last 12 years several investigators have developed methods for locating the chemical constituents in the cell wall. Wood sections are treated with reagents for dissolving a given component and with the aid of a microscope the location of the remaining components in the wood residue is noted. Preliminary studies by König and Rump[6] and by Abrams[7] in this field showed the possibilities of obtaining fundamental data on the cell-wall structure. A series of papers by the Forest Products Laboratory, Lüdtke, Scarth, Harlow, Von Iterson, Trogus, Krüger, and others has furnished many confirmatory data interspersed with some of a contradictory nature.

This paper deals with (1) the distribution of the lignin in the cell wall of wood fibers; (2) the distribution of carbohydrates in the cell wall; and (3) the microstructure of the cell wall.

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[1] Presented before the annual meeting of the American Chemical Society, Chicago, Ill., Sept. 12, 1933, and published in The Paper Industry June 1934. Vol. 16, p. 178 .

[2] Lüdtke, M. Liebig's Ann. 466:44 (1928).

[3] Nageli, C. V. Das Mikroskop, Leipzig, 1877.

[4] Strassburger, E. Ueber den Bau und das Wachstrum der Zellhauete, Jena, 1882.

[5] Wiesner, J. Die Elementarstructur, Wien (1892).

[6] König, J. and Rump E. Nahr Genussm. 28:4 (1914).

[7] Abrams, A. Ind. Eng. Chem. 13:786 (1921).

Distribution of Lignin in the Cell Wall

The major portion of the lignin in wood is located in the middle lamella; the remaining portion is in the cell wall (Plate 1). The lignin in the middle lamella forms a continuous, thin-walled medium which resembles honeycomb and which serves as a cementing substance between the wood fibers. These thin walls are characterized by thickened areas, known as tori and bars of Sanio, and thinned areas, termed pit membranes.

Lignin from the cell wall has been isolated at the Forest Products Laboratory as a finely divided amorphous material by means of 72 percent sulphuric acid.[8] Freudenberg[9] and Harlow,[10] on the other hand, have isolated lignin from the cell wall as a fragile porous structure. They state that on drying, the lignin residue of the cell wall shrinks against the middle-lamella lignin. This concept of the structure of the cell-wall lignin seems plausible. It is possible that the treatments used for isolating the lignin at the Forest Products Laboratory were too drastic for the fragile structure to withstand. As a result, the cell-wall lignin was obtained in a finely crumbled state.

The lignin content of the cell walls of hardwoods is less than that of softwoods. As a result, during chemical and mechanical treatments, the cell-wall lignin in the hardwoods crumbles into a finely divided amorphous material more easily than that in the softwoods. After crumbling it can be removed by careful washing leaving the middle-lamella lignin with no sharp lateral projections (Plate 2). The absence of sharp projections on the middle-lamella lignin would indicate that the two types of lignin are not joined in structure as suggested by Freudenberg.[9]

When sulphuric acid is used, the amorphous lignin is mixed with partly decomposed carbohydrates since 72 percent sulphuric acid at temperatures from 20° to 35° converts hemicellulose into a material having some properties similar to those of lignin.[11] The early isolations of lignin at the Forest Products Laboratory were made without close temperature control. Consequently, the yields of cell-wall lignin as reported[8] are too high. Formation of partially charred carbohydrates can be reduced to a minimum by temperature control, but there is still no reliable method for quantitatively separating the cell-wall lignin from the middle-lamella lignin. Until such a method is developed the ratio of the two types of lignin in wood will remain unknown.

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[8] Ritter, Geo. J. Ind. Eng. Chem. 17:1194-99 (1925).

[9] Freudenberg, K. Ber. Deut. Geselft. 62:1814 (1929).

[10] Harlow, W. M. Am. J. Bot. 19:729 (1932).

[11] Ritter, Geo. J. Ind. Eng. Chem. (anal. ed.) 4:202 (1932).

Distribution of Carbohydrates

Cross and Bevan cellulose (Plates 3 and 4), which constitutes the bulk of the cell wall, is obtained through repeated alternate treatments of wood with chlorine gas and sulphite solution. Some of the hemicelluloses that are dissolved by this procedure seem to be located with the lignin/the middle lamella since wood fibers still cling together in a total carbohydrate residue, even though the lignin has been removed.[12]

Microstructure of Cell Wall

The cell wall has been dissected into layers, fibrils, fusiform bodies, and spherical units.

Layers

Wood fibers are composed of concentric sleeve-like layers[13], [14] which cling together. This clinging of the layers is partly accounted for by their molecular adhesion and is further augmented by a cementing substance. It is plausible to consider such a cementing material as consisting of ligneous and hemicellulosic materials present in the aqueous protoplasmic solution from which the polysaccharides of the consecutive cellulosic layers crystallize. Thus between the cellulosic layers of the cell wall there would remain an aqueous protoplasmic film of hemicelluloses or other materials which would eventually solidify to form a binding substance in any interstices between successively developed cellulosic layers.

Similarly, a cementing substance appears to be present in the interstices between fibrils. The Forest Products Laboratory has no experimental evidence that a cementing material is located between the microstructural units smaller than the fibrils; neither has it any evidence to the contrary.

The layers of delignified fibers can be loosened by either alkaline or acid treatments (Plate 5) and if short fiber sections having open ends are employed the concentric layers can be separated[12] by slipping them fron one another endwise (Plate 6).

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[12] Ritter, Geo. J. and Kurth, E. F. Holocellulose, Total Carbohydrates of Extractive-free Wood: Its Isolation and Properties. Ind. Eng. Chem. 25:1250-53 (1933).

[13] Ritter, Geo. J. Ind. Eng. Chem. 20:941 (1928).

[14] Scarth, F. W. Trans. Roy. Soc. Can. 23, Pt. 2, 288 (1929).

Except for the numerous pit apertures, the outer layer before being subjected to dissecting agents, appears as a smooth homogeneous capsule that is slender and pointed. After the chemical dissecting agents are applied, however, transverse striations appear (Plate 7). Continued treatment discloses that the layer is actually composed of fine cellulosic strands,[15] termed fibrils, which are wrapped around the inner concentric layers almost at right angles to the fiber axis (Plate 8).

As will be discussed later, the outer layer helps to retain the shape of the fiber by restraining swelling beyond certain limits transversely.[16] This function is manifested by the beadlike appearance which fibers develop when treated with acid and alkaline swelling agents that dissolve the outer layer from restricted areas of the fiber (Plate 9). The areas over which the outer layer is intact appear as constrictions between the swollen beadlike structures.

The inner layers that have been loosened from one another can be distinguished under high magnification (Plate 10) both in the beadlike structures and in the constrictions, but the outer layer is recognizable only about the constrictions.

It is apparent from the foregoing plates that the outer or primary layer consists of fibrils helically wrapped about the secondary cell wall to form, in conjunction with interfibrillar cementing material, a smooth-surfaced capsule. It is recognized, on the other hand, that a striated appearance resembling fibril windings could also result if the primary layer were a homogeneous envelope as suggested by Trogus.[17] Rupturing of such an envelope by swelling agents would allow the secondary walls to form beadlike structures which would force the primary layer to fold, forming transverse striations (Plate 11). It is improbable, however, that the uniformity in the transverse striations as shown in Plates 8 and 9 would obtain under such conditions. It is further inconceivable to procure with such a suggested structure a helical winding as disclosed in Plate 12, which shows the fibril windings of the isolated primary layer slightly stretched.

The structural arrangement of the outer layer differs from that of the inner layers. The inner layers are composed of fibrils oriented more nearly parallel (10° to 30°) to the long axis of the wood fiber than those in the outer layer (Plate 13). The helical arrangement of the fibrils varies in adjoining layers of the cell wall of the same fiber; in normal fibers the variation ranges from 5° to 30°; in compression fibers from 30° to 45°. The windings were either all clockwise or all counterclockwise in the fibers which were examined. This finding is contrary to that of Lüdtke[18] who states

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[15] Ritter, Geo. J. Jour. of Forestry 28:533 (1930).

[16] Ritter, Geo. J. and Chidester, G. H. Paper Trade J. 83:131 (1928).

[17] Trogus, C. Beziehung zwischen quellung salzbildung und feinbau bei der cellulosefaser. Papierfabr. 27(4):55-60 (1929).

[18] Lüdtke, M. Milliand Textile Monthly 4:259-62 (1933).

that the windings alternate from clock to counterclockwise in adjoining layers of the same fiber. The alternate markings shown in Plate 13 are on the opposite walls of the collapsed fiber and not on successive layers in the wall.

Fibrils

As already mentioned, the outer layer of the wall restrains transverse swelling of the wood fibers. In contrast, the several inner layers of the cell wall restrain longitudinal swelling of the wood fibers. These two restraints can be explained on the basis of the cellulose micelle arrangement in the fibrils of the layers. These micelles are oriented parallel with the fibril axis. Swelling them with water increases their longitudinal dimensions very little, but it increases their transverse dimensions 20 percent.[19] The arrangement of the micelles (transverse to fiber) in the outer layer would, therefore, induce longitudinal swelling but restrain transverse swelling of the wood fiber. In contrast the arrangement of the micelles (parallel with the fiber axis) in the several inner layers would induce transverse swelling but restrain longitudinal swelling of the wood fiber. Since the cellulose micelles of the inner layer fibrils constitute the major portion of the fiber wall, they confine any change in fiber length within exceedingly narrow limits when water is employed as the swelling agent.

Wood fibers from which the lignin and the hemicelluloses have been removed can be easily dissected into their fibrils (Plate 14), provided they are not allowed to dry before the acid or alkaline dissecting agents are applied. Once these structural units of the more stable cellulosic materials shrink together through dehydration, extreme difficulty is experienced in dissecting them from one another. This increased resistance of the cell wall to dissection is likely due to traces of hemicelluloses dispersed into fine particles which form during the alkaline or acid treatment for removing the carbohydrates and which become a horny-like substance on subsequent drying. The result is a more resistant cementing substance between the fibrils and also the layers than was present in the original fibers. It is recognized that the increased resistance of dehydrated fibers to dissection may also be explained on another basis. In case no interfibrillar cementing material were present in the chemically treated fibers, dehydration of those fibers would shrink their fibrils together to form between them (fibrils) molecular adhesive forces which would retard the re-entrance of chemical dissecting agents. Fibrils separated from the inner layers are long, slender, cellulosic filaments which appear extremely flexible when suspended in an aqueous medium.

In connection with the length of fibrils, Lüdtke[20] introduces new structural elements. He believes that these elements differ chemically from both the lignin and the carbohydrates and has described them as being composed of a Fremdsubstanz. According to his conception the fibers are limited in length

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[19] Frey, A. and Jaccard, P. Jahrbucher fur Wissenschaftliche Botanik 69:549, Leipzig (1928).

[20] Lüdtke, M. Biochem. Zeitschr. 233:1 (1931).

by transverse elements intersecting them at fairly uniform intervals corresponding to the constrictions between the beadlike swelling shown in Plate 9. Definite contrast observed at the Forest Products Laboratory between the optical properties of the outer layer and the remainder of the cell wall indicates the only transverse structural arrangement of the constrictions is the outer layer. This contrast is observed if the fiber constrictions are viewed with the aid of crossed Nicol prisms between which a quartz plate has been inserted. When the windings of the outer layer appear blue, the remainder of the cell wall appears yellow. This indicates that the crystalline elements of the outer layer are at approximately right angles to the corresponding ones in the remainder of the cell wall. Further evidence that the fibrils of the inner layers extend longitudinally through the constrictions without being intersected by transverse elements is furnished in Plate 10. When the outer layer is removed, the constricted sections separate into longitudinal fibrils.

Still other additional evidence that disproves the presence of transverse walls in wood fibers is furnished by the isolation of fibrils and bundles of fibrils more than 40 to 60 microns in length, the distance between the cross walls as given by Ludtke. Fibrils and bundles of fibrils approximately 230 microns long have been isolated from sections of fibers as shown in Plate 15.

Under certain conditions wood fibers fracture rather abruptly in the crosswise direction. This fact has been used by Lüdtke[20] as an argument for the presence of transverse elements. Abrupt transverse fracturing is especially noticeable in the residue remaining after the fibrous material has been heated in boiling 12 percent hydrochloric for the conversion of the pentosans to furfural. Similarly, following prolonged alkaline and acid treatments fibers become brash and break abruptly. Such treatments dissolve the cementing substance from between the layers and the fibrils and also swell the residue beyond its green volume, thereby weakening the valence bonds between the cellulose micelles. These modifications, then, weaken the fiber structure both longitudinally and transversely, but the anatomy of the fiber is such as to induce transverse rather than longitudinal fractures. The seemingly abrupt transverse fractures of the cell wall generally occur in the slip planes, in the weak areas of the pits, and in the thin areas which compensate in the wall structure for the bars of Sanio in the middle lamella.

Lüdtke[20] contends that the Fremdsubstanz, which constitutes the transverse elements just discussed, forms an elaborate structure known as a skin system, "Das Hautsystem." This skin system includes the transverse elements, the primary or outer layer of the cell wall, and sheaths around each of the layers of the secondary cell wall, each of the fibrils, and each of any smaller structural units. According to such a concept the carbohydrate units are each in a compartment whose walls are a part of the skin system.

Lüdtke[20] determines the amount of skin system in the cell wall by first oxidizing fibers to form carboxyl groups which are assumed to develop on the skin substance. These carboxyl groups are then neutralized with a standard solution of alkali. The amount of alkali consumed is a measure of the carboxyl groups. Assuming the molecular weight to be 200 and each molecule

having one carboxyl group, he finds the content of skin substance in the wood fibers to average about 2.8 percent. This value approximates the polyuronide content of maple Cross and Bevan cellulose as determined at the Forest Products Laboratory.

As has been previously stated, observations at the Forest Products Laboratory indicate that a hemicellulosic cementing material occupies the interstices between the cell wall layers and between the fibrils. Such a cementing substance often appears as flakes when fibrils are torn apart mechanically after they have been partly loosened by chemical means. It is difficult to distinguish optically between the cementing material and the layers or the fibrils of untreated fibers. This may be explained on the basis of very thin films of the cementing material in comparison with the layers and fibrils. It may also be explained on the basis of close agreement between the indices of refraction of the cementing substance and that of the polysaccharides in the layers and the fibrils. After the cementing material is dissolved and the layers or the fibrils are loosened, stratifications and striations become prominent. This change in optical properties occurs because a dissolving medium having an index of refraction different from that of microstructural units has been introduced into the interstices previously occupied by the binding substance.

The foregoing conception concerning hemicellulosic cementing substances accounts for only a small part of the hemicelluloses in delignified wood fibers. The remaining portion is intimately associated with the cellulose in the fibrils, the fusiform bodies, and the spherical units.

Fusiform Bodies

Wood fibrils can be dissected[21] into small, spindle-shaped units, termed fusiform bodies (Plate 16). These microstructural units of the fibrils may be cemented together similarly to the fibrils and the layers, for it requires dissolution of some carbohydrate material before the fusiform bodies can be separated from one another. Wiesner[22] states that fibers after prolonged treatment with hydrochloric acid and subsequent heating from 50° to 60° will carbonize, leaving a fine dustlike residue called dermatosomes. However, the described structure of the particles in that residue is not comparable to the uniformly shaped fusiform bodies.

Spherical Units

Fusiform bodies can be divided by means of phosphoric and sulphuric acids into still smaller, characteristically shaped subdivisions[23] called spherical units (Plate 17). Since spherical units have not been observed in the

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[21] Ritter, George J. Ind. Eng. Chem. 21:289 (1929).

[22] Wiesner, J. Phys. Plant Anatomy, Haberlandt, p. 46 (1914).

[23] Ritter, Geo. J. and Seborg, R. M. Ind. Eng. Chem. 22:1339 (1930).

fusiform bodies their original structure is unknown, but some shape other than spherical is suggested by a contrast of their optical properties with those of the fusiform bodies.

Between crossed Nicol prisms, fusiform bodies manifest a sharp angle in changing from the minimum luminosity (parallel to Nichols) and the maximum luminosity (45° to Nicols). Such phenomena indicate parallelism of cellulose crystallites in the fusiform bodies. Since the fusiform bodies manifest parallel arrangement in their crystalline structure then their smaller composites must also have parallel crystalline structure, for otherwise the sharp angle in minimum and maximum luminosity would not obtain. Isolated spherical units, however, when viewed between crossed Nicol prisms are luminous in all positions, indicating random arrangement of their crystallites. Such an arrangement of the crystallites would result during the deformation of an angular oblong body to a spherical one by means of extreme swelling.

Some Swelling Properties Due to Fiber Structure

Due to their structure and their property to absorb swelling agents, isolated wood fibers are prone to change their cross-sectional area from an angular to a circular shape.

This tendency of fibers to assume shapes having the least possible external surface when swollen with alkaline solutions manifests itself especially when the outer layer is intact. For example, if short cross sections of delignified fibers are treated with dilute alkaline solutions their angular perimeters become gradually curves (Plates 3 and 4); if the swelling is increased by means of a stronger alkali, the cross section of the angular tubes becomes one of a circular rod (Plate 18). When the outer layer is removed fibrillation develops rapidly. Moreover, retention of the outer layer at the middle of short sections produces neatly wrapped bundles having broomed ends (Plate 19).

Cell Wall Structure as Observed Through a Spierer Lens

Siefriz[24] and Thiesen[25] with the aid of a Spierer lens attached to a microscope, have photographed what they call the cellulose micelles. Their photographs show white parallel striations on a dark background. At short intervals indentations appear to separate the striations into slender rods aligned end to end. In a cross section of wood the white striations appear in the

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[23] Ritter, Geo. J. and Seborg, R. M. Ind. Eng. Chem. 22:1339 (1930).

[24] Siefriz, W. J. Phys. Chem. 35:118-29 (1931).

[25] Thiesen, R. Ind. Eng. Chem. 24:1032-41 (1932).

cell wall, paralleling the perimeters of the cell wall and the lumen. In longitudinal wood sections the white lines are arranged parallel with inner and outer edge of vertical parts of the cell wall and parallel with the fibrils in the horizontal parts of the wall.

While the phenomenon just described is more clearly shown by means of the Spierer lens, the same optical effect can also be seen with the aid of a petrographic microscope when the Nicol prisms are crossed at 90°. To see it requires an arrangement of the lighting systems so as to increase to the possible maximum the amount of oblique light passing from the specimen into the microscope lens. The phenomenon as observed with a petrographic microscope is considered at the Forest Products Laboratory as an extreme case of diffraction bands.

Thiesen[25] found the white parallel striations to average 0.83 microns in width and he uses that figure as the width of the cellulose micelle. This dimension of the cellulose micelle, however, cannot be reconciled with the cellulose micelle conceived from X-ray measurements,[26] which approximates only 50 A.U. in width. Further, the width of the cellulose micelle as conceived from X-ray patterns is far below the resolving power of the microscope.

Summary

The major portion of the lignin is located in the middle lamella; the remaining portion is in the cell wall. Cellulose and hemicellulose form the major part of the cell wall, which is composed of several thin layers arranged as concentric sleeves that can be loosened chemically and separated mechanically by slipping them off from one another endwise.

Layers of the cell wall can be separated into fibrils by chemical and mechanical means. The fibrils of the outer layer are oriented at approximately 90° to the fiber's long axis, whereas those in the remaining layers are oriented anywhere from zero to 30° to the fiber's axis.

Fibrils can be separated into fusiform bodies that are uniformly spindle-shaped.

Fusiform bodies can be separated into smaller subdivisions which are spherical in shape when separated and have accordingly been named spherical units.

A cementing material of hemicellulosic nature is believed to exist between the layers and the fibrils of the cell wall of delignified fibers. When the material is removed by means of hemicellulosic solvents, the layers and the fibrils of the cell wall can be separated by mechanical means. The conception of Lüdtke regarding the Fremdsubstanz, or cementing material in the cell wall, is discussed.

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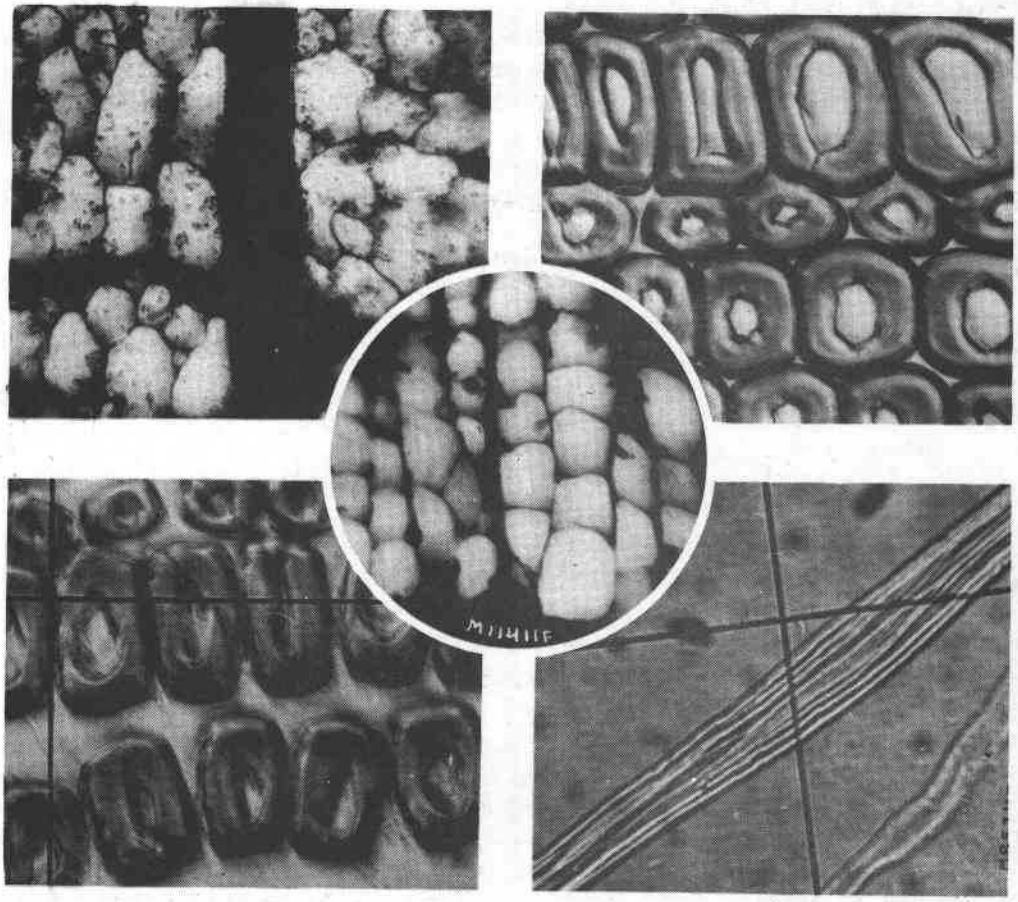
[26] Clark, G. L. Ind. Eng. Chem. 22:474 (1930).



Pl. 1—The middle-lamella lignin and the cell-wall lignin of red alder

Pl. 2—The middle lamella lignin of ponderosa pine

Pl. 3—Cross section of ponderosa pine showing carbohydrates (Cross and Bevan cellulose) partially delignified

Pl. 4—Cross section of ponderosa pine showing delignified Cross and Bevan cellulose

Pl. 5—A delignified elm wood fiber the layers of which have been loosened

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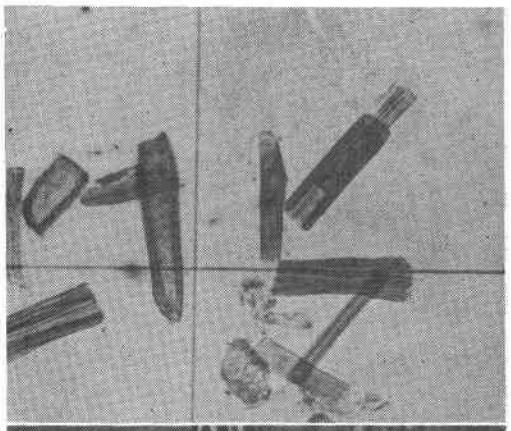

Pl. 6—Short sections of delignified elm wood fibers the cell-wall layers of which have been loosened and partially separated by slipping them endwise

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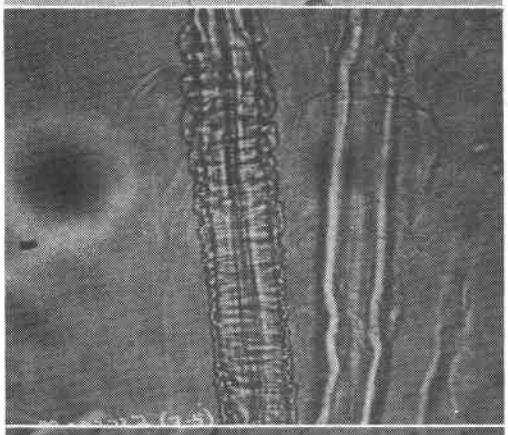

Pl. 7—Transverse striated appearance of wood fiber observed when the fibrils of the outer layer begin to loosen

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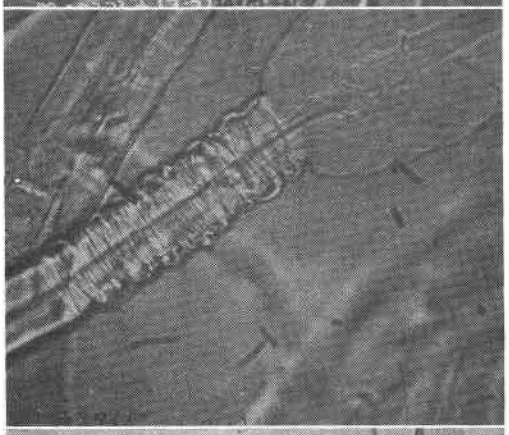

Pl. 8—Windings of the fibrils of the outer layer of a wood fiber and the extreme transverse swelling of the inner layers from which the outer layer has been dissolved

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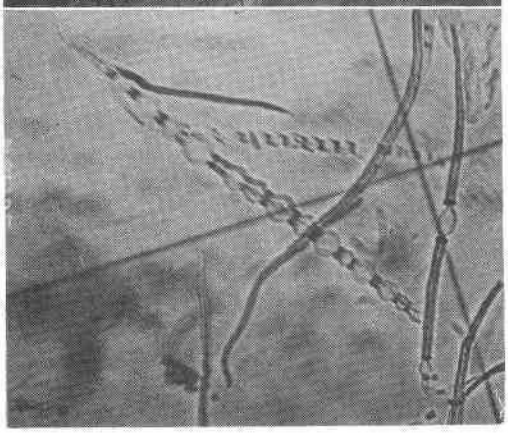

Pl. 9—Transverse swelling of inner layers in places at which outer layer has been dissolved

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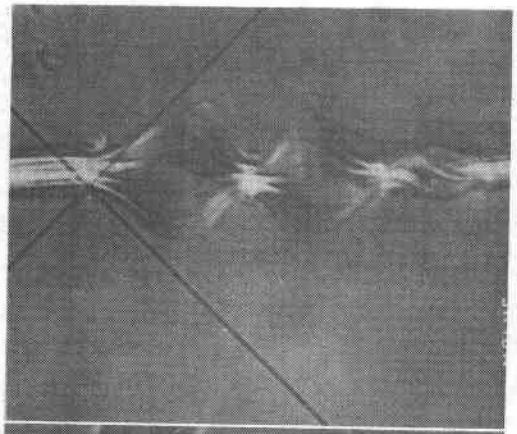
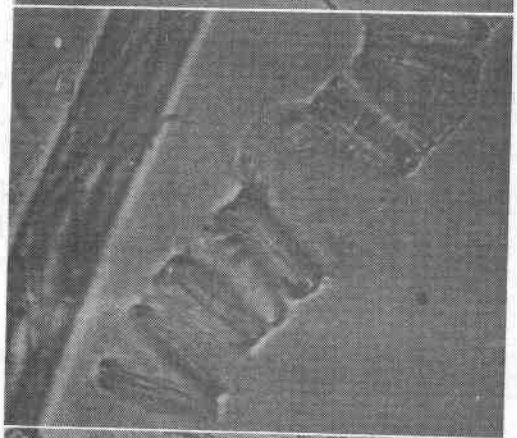
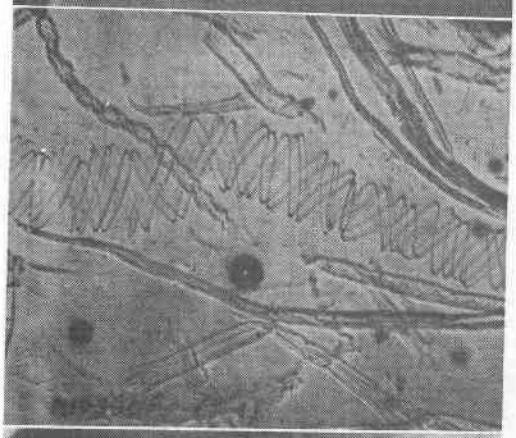


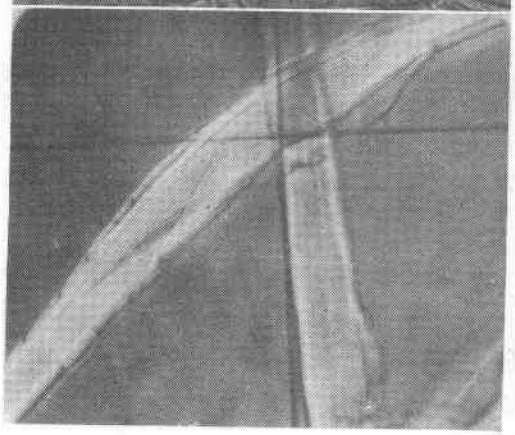
Pl. 10—Continuous longitudinal structure of inner layers of the cell wall can be distinguished in both the swollen and the constricted parts; the outer is recognizable at the sides of the constriction only



Pl. 11—Windings of the outer layer pushed apart by the extreme swelling of the inner layers



Pl. 12—Outer layer removed from the delignified spruce fiber and stretched slightly endwise



Pl. 13—Partially loosened fibrils of the inner layers of a delignified elm fiber

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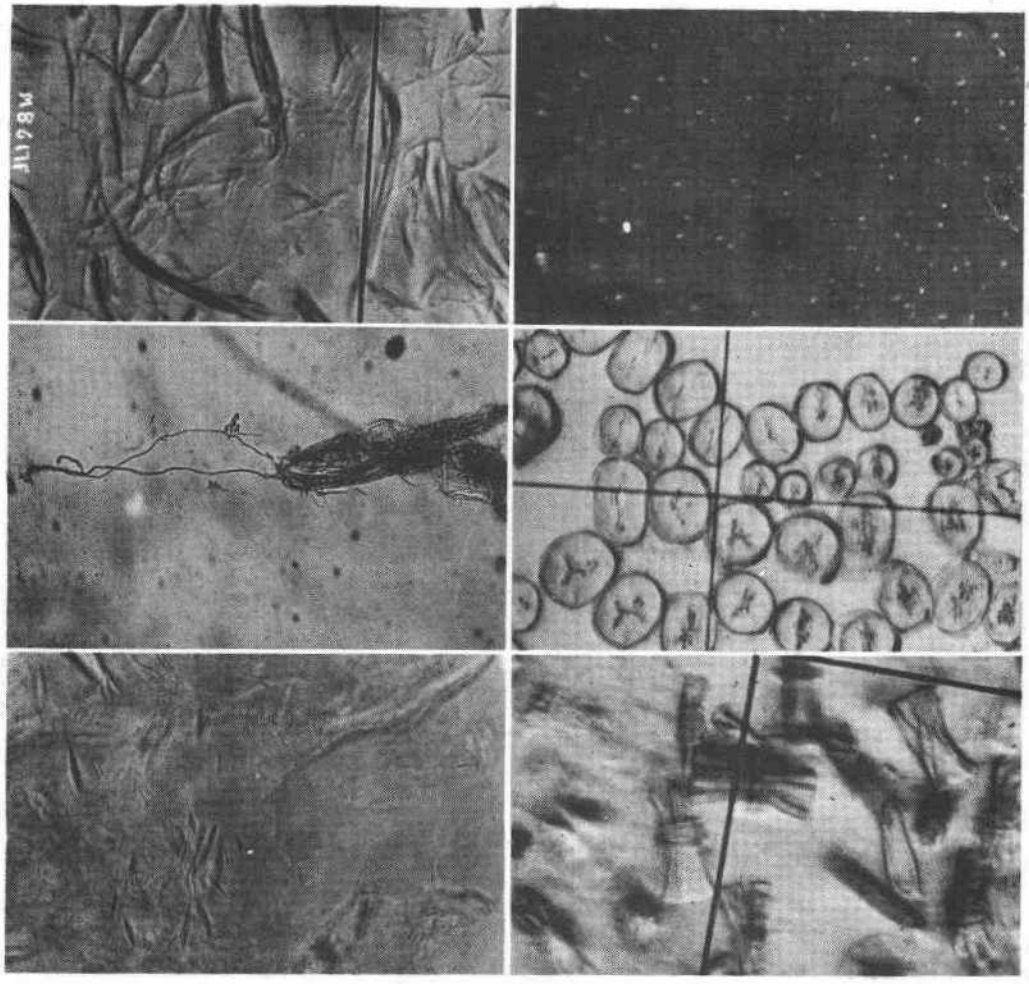

Pl. 14—Isolated fibrils and bundles of fibrils from a delignified elm fiber

Pl. 15—Fibrils isolated from a delignified section of a spruce fiber

Pl. 16—Fusiform bodies from an elm fiber

Pl. 17—Spherical units isolated from spruce fibers

Pl. 18—Cross sections of delignified spruce fibers after swelling with sodium hydroxide solution

Pl. 19—Short sections of delignified elm fibers showing bundle-like residue when the dissolving action of the phosphoric acid is arrested before the outer layer is completely removed