MODERN MATERIALS

ADVANCES IN DEVELOPMENT AND APPLICATIONS

EDITED BY

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PREFACE

Knowledge of materials has increased so rapidly in recent years that it was felt that the introduction of a series of volumes on *Modern Materials: Advances in Development and Applications* would be welcomed by workers in many fields. These volumes will serve as a valuable source of information for the engineer with broad interests, for the specialist who wants information beyond his field of specialization, and for others particularly interested in materials—executives, research and development engineers, pioneers of new materials, and students.

For many years the general trend in engineering education has been toward specialization. Even in college the prospective engineer who is especially interested in materials has been more or less required to become a specialist in chemical engineering, or metallurgy, or ceramics, and has hardly become acquainted with many important materials outside of his special field. Today there is a change of thought in this respect, although there is not yet a change in the engineering college curriculum, and engineers in general are more material-minded than they were years ago.

For example, to satisfy adequately the demands of his profession the nuclear reactor materials engineer has to know about many different liquids and solids; about metals, ceramics, and plastics; about the effects of irradiation and corrosion on a wide variety of materials. The same is true of the electronics engineer and the engineer working on the development of rockets, jet engines, and other high temperature engines. A further example of the development of diversity in our engineering thinking is that in one of our leading electronics research laboratories a metallurgist is in charge of the development of ceramic materials, electrical engineers work on the development of metallic materials, and plastics engineers are studying the principles of metallurgy. Failures in electronic devices are usually due to the unforeseen behavior of a particular component, and the component may be of metallic, semiconducting, or ceramic nature; even the behavior of an insulating paper could be the cause of failure. The electronics engineer, therefore, must be well acquainted with a variety of materials.

This first volume of *Modern Materials: Advances in Development and Applications* covers a variety of materials and the recent developments in connection with them—zirconium and the semiconductors germanium and silicon—ceramic engineering materials and their increasingly wider applications—insulating papers for high voltages—glasses required to withstand strong irradiation in nuclear engineering—synthetic rubbers for special purposes—new uses of wood as a structural material—organic and inorganic fiber materials. All of the contributions have been prepared by well-known experts, who discuss the results of their own experience for the benefit of nonspecialists. The chapters are written in scientific engineering language, but the use of mathematics has been kept to a minimum so that the engineer with the usual college background will easily be able to follow the thoughts of the authors.

The technology of our time requires the development of more and more types of materials for entirely new engineering applications. Not the specialist, but the engineer with a broad knowledge of various materials will contribute most substantially to the development of materials suitable for these new applications.

The editor expresses his gratitude to the members of his Advisory Board, to the authors for their understanding of the general disposition of this series and for their contributions, to Academic Press for helpful cooperation and discussions on material problems, and especially to Mrs. Helen Friedemann for her patience and invaluable help in the editorial tasks.

May, 1958 HENRY H. HAUSNER

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SOME NEW DEVELOPMENTS IN WOOD AS A MATERIAL

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I. Introduction and General Concepts

Wood is one of the most ancient structural materials known to man and, paradoxically, it is at the same time one of the newest and most promising of the polymer family. Centuries of use on an empiric basis, coupled with a truly amazing complex of interlocking technical properties have combined to thwart studies which would reveal the nature of the material and the governing laws for its behavior. The history of biology shows that as early as 1682, Nehemiah Grew first published information on the gross structure of woody tissue, but it has been only late in the present century that tools have been developed to allow man to actually study more than the features visible under a light microscope. Paralleling this, the entire field of physical properties of wood was the subject of early work which indicated the complexity of the interrelated factors. For example, mechanical tests began as early as 1707 and critical studies of elasticity date back to Savart in 1830 and Wheatstone in 1833. Unfortunately, these fine starts produced no more than a clear indication of the extremely complicated system involved and for many years no really important work was done on wood except to carry out extensive mechanical tests. Advances in chemistry and physics have developed new tools and concepts which have enabled a tremendous expansion in the knowledge of wood in the past thirty years. Consequently, there are many recent studies which are important to an understanding of the structural nature of wood. In order to keep this material within reasonable bounds, this chapter is organized so that certain important phases of the behavior of wood are grouped and the papers which bear on a given facet are discussed in connection with the topic. Roughly, these can be summarized as the submicroscopic organization of the materials from which wood is formed; the anisotropy of wood, with some of the factors which may serve to control the swelling and shrinking, and the little which is known of the evaluation of the mechanical relations involved; the bare outlines of the rheological properties and the viscoelastic behavior of wood; and lastly, an indication of the start which is being made towards a biological control of certain of the growth factors affecting the physical properties.

While there is no space in this present work to give any detailed discussion of the botanical structure of wood and the growth systems by which it is produced, it is felt necessary to include a brief résumé. Complete presentations of this material can be found in Brown *et al.* (*1*). In a vastly oversimplified way, one can say that wood is a naturally formed material composed 50% to 60% of a highly polymerized carbohydrate called cellulose which determines most of its mechanical properties. A complex material known as lignin, which is still very imperfectly known, constitutes about 25%. The remainder of the volume of solids is composed of some 24% of material of a mixed nature, such as water-soluble carbohydrates, gums, resins, and so on—with an additional 1% ash. All of these chemical components vary with the kind of tree and, to a certain extent, the growing conditions. These raw materials are organized in a complex manner into oriented walls of tubular structures called cells. These cells differ in shape and structure according to function and are in turn systematically ordered into tissues which are laid down in a generally cylindrical sheet about the surface of the tree stem. This latter is an approximation of a cubical paraboloid and gives the trunk the properties of a beam of constant strength. The entire organization produces a mass which has radial symmetry; three axes of major orientation with respect to the stem axis, i.e., longitudinal, radial, and tangential; complex anisotropy traceable to the varied orientation of elongated polymer molecules of the cellulose; and an overall variability which is produced by the uncontrolled growth factors. This "sponge" sorbs water, dependent on the surrounding atmospheric conditions, and changes dimensions accord-

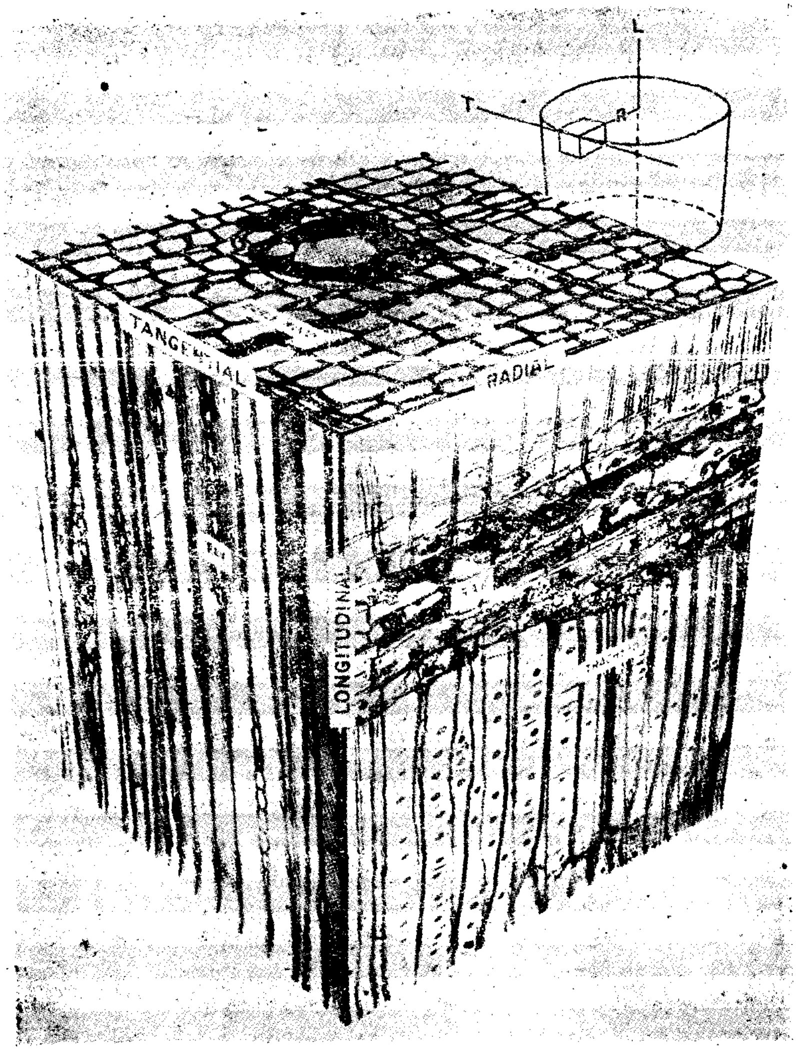

Fig. 1. A cube of Eastern white pine (*Pinus strobus* L.) magnified approximately 200 times. The three axes of symmetry of the block are shown in relation to the phantom diagram for the radial symmetry of the stem. Only those anatomical features of interest for physical considerations are labeled. (Photograph by W. A. Coté, Jr.)

ingly. All factors unite to give wood a wonderful ratio of weight to strength which is especially apparent in the inherent stiffness.

II. The Nature of Wood as a Material

A. The Woody Cell Wall

As has been noted previously, cellulose is the one component of the woody cell wall which is of importance from the standpoint of strength and elasticity. It is probably the most important natural, structural polymer known, as can be easily substantiated on the basis of its wide distribution in nature (it occurs in the higher seed plants, algae, mosses, bacteria, and certain animals such as the Tunicates), and the enormous volume of the material produced. In recent years, several new techniques have been developed which have led to a significant advance in knowledge of the structure of cellulose and its organization in the plant.

1. Structure of the Cellulose Molecule

Present evidence is unanimous that cellulose is a carbohydrate composed of macromolecules with remarkably uniform structure regardless of the source. These are chains which can be hydrolyzed and reduced to ultimate units of β-D-glucose (β-glucopyranose residues). However, the smallest fraction with any of the characteristics of the parent compound is cellobiose and it consists of two of these glucose residues joined end-to-end through 4-β-glucosidic linkages. The generally accepted configuration of the molecular chain, which has been formulated from a beautiful series of studies, is that given by Haworth (*2*) and illustrated by Fig. 2.

Such a plane figure cannot afford a true indication of the spatial configuration of the glucose unit. Figure 3 is a representation of the three-dimensional nature of this structure. It should be especially noted that the fixed angular spacing of the primary valence bonds of the carbon atoms predetermines the relative positions of the skeletal members. Purves (*3*) has summarized these spatial characteristics of the chain molecule of cellulose and states in part: the hydroxyl and glucosidic groups attached to carbons one to five are completely *trans* (i.e., alternately above and below the plane of the paper); end linkages of the glucopyranose residues are of the 4-β-glucosidic type, and this is supported by polarimetric and kinetic proofs which agree so closely that it must be concluded that at least 99% of the glucosidic bonds are equivalent and of the type indicated; lastly, the glucopyranose units must alternate with respect to the side which is uppermost, and the possibility of some rotation about the glucosidic bonds allows the chain to extend in either a straight line or in large loops and coils.

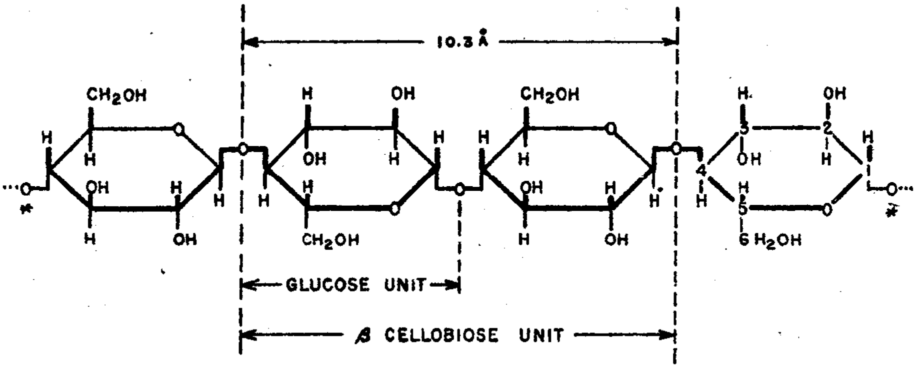

Fig. 2. Diagram of a segment of the molecular chain of cellulose, according to Haworth. The glucose units are in perspective with the heavy lines representing the top faces and the near edges. The numbers in the glucose unit at the right-hand end indicate the conventional order for the carbon atoms. The asterisks mark the positions for further extension of the chain.

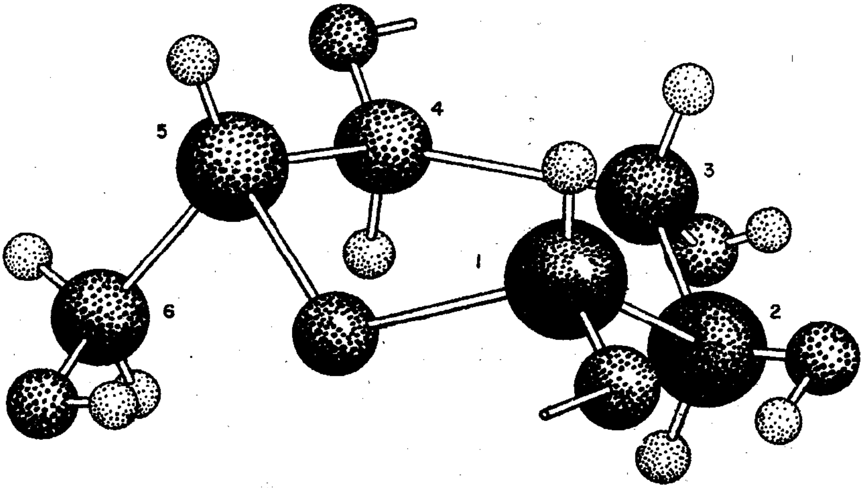

Fig. 3. Model of a glucose unit seen in perspective approximately along the axis which it would occupy in the cellulose chain. The large, numbered, dark spheres represent the carbon atoms. The middle-sized dark balls are the oxygen atoms and the small, light ones are hydrogen. The β-linkage positions are shown on carbons 1 and 4.

Up to this point nothing particularly new has been indicated and the principal purpose of the summary is to give the generally accepted picture of the basic units of the molecule. It can be readily seen that in a chain molecule such as cellulose it is at least theoretically possible for the chain length to be infinite. However, this is apparently not the case. Determination of chain length is made by studies of cellulose in solution. Now this presents a difficulty at the very start since cellulose is naturally soluble in only a few liquids, and it is possible that some reduction in length or primary cleavage may occur simply by the solvation. Regardless of this difficulty, most of the measurements which are available for the length of the molecule are based on determinations of the degree of polymerization (D.P.) from viscosity, ultracentrifuge sedimentation, and osmotic pressure methods; and these show chain lengths in the order of 10,000 to 50,000 angstrom units (Å)[1] (0.001–0.005 mm). An indication of support for these data is found in work by Dolmetsch (*4*, *5*). Observations on fibers swollen in various ways using phase-contrast microscopy show cross-striations in the structure of the cellulose fibers at distances of 1 to 2 microns (μ) for the most part, and up to 5 μ. Dolmetsch interprets these discontinuities to correspond with molecular chain lengths. Furthermore, he has shown by electron micrographs that constrictions occur at these zones, and he states that degradation reactions begin at the zones to reduce fibrils to shorter lengths. It seems possible that such zonation might occur if the formation of cellulose molecules by the cytoplasm is in any way directed, and certain indications are that some structures in the cell wall are related to cytoplasmic orientation [Wardrop and Dadswell (*6*)].

The determination of the length of the molecule for wood cellulose is however not settled completely because so much of the work is based on material in solution, and very little direct evidence is available for cellulose *in situ*. Also there are reports based on viscosity methods which do not give agreement with the figures generally accepted. An example is the work of Schulz and Marx (*7*) who used viscosity in acetone and showed that fiber celluloses such as cotton, ramie, and flax consist of chains with a D.P. of 6500 to 9000. The higher fractions of wood pulps which have been carefully prepared have about the same D.P. as the fiber cellulose. This indicates a chain length of 68,000 to 94,000 Å (0.0068 to 0.0094 mm), which is well above the upper limit of the previous figure and was determined for material which had been possibly degraded by the pulping process.

When one adds up the possibilities, it might seem reasonable that the cellulose chain in undisturbed wood is continuous with zones at which there is preferential attack, as indicated by Dolmetsch, and the measured chain lengths are due to the cleavage of the cellulose as it passes into solution.

2. *Formation of Cellulose by the Plant*

Recent work has shown by radioactive carbon tracer experiments that D-glucose is synthesized into cellulose in plants, thus indicating in

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[1] Angstrom unit (Å) = 1/100,000,000 cm.

two ways that this constitutes the smallest unit of the cellulose chain. The conclusion was reached by experiments using tagged nutrients as substrates for the vinegar bacterium (*Acetobacter xylinum*) which forms an extracellular cellulose first reported in 1886 by Brown (*8*). The cellulose formed by this bacterium is identical with that formed by higher plants on the basis of X-ray analysis, chemical analysis, and electron microscope and infrared spectral techniques [Minor *et al.* (*9*)]. Additional studies of the biosynthesis of cellulose specifically labeled with C^{14} have shown that the same thing holds true for cotton fibers [Greathouse (*10*)], and also for cellulose in the wheat plant [Brown and Neish (*11*)].

The same series of studies have revealed some of the process by which the cellulose is synthesized. It appears certain now that the polymerization depends on the action of enzymes, as has been shown by Hestrin (*12*) in a study of the formation of cellulose from glucose using nonviable, active, dried cells of *Acetobacter xylinum* and oxygen as the electron acceptor. More recently, Greathouse (*10*), has reported similar work with cell-free extracts. Whether the chain is formed as a complete unit and moves into place or is built up by end addition in the wall, is not clear at this time. Regardless of the matters still remaining for investigation, the possibilities of controlled formation of chemically pure cellulose or the recombination of cellulose which has been degraded by processing in order to improve the technical properties, are very intriguing.

3. Organization of Molecular Aggregates

The cellulose molecules in the cell wall show a relationship to each other on the submicroscopic level which has been extensively investigated since the middle of the last century. The literature is confusing because of the variety of terms employed for the same structures and also because so much of the early work was pure speculation. In recent years, the advent of X-ray analysis, and more lately still, the electron microscope have reactivated the work in this field and produced some notable advances and unification of ideas.

Based on evidence from many previous studies, Frey-Wyssling (*13*) has organized a consistent concept of the arrangement of cellulose on the submicroscopic level. In summary, he states that the cellulose molecules are ordered into biological units termed microfibrils which measure about 200 Å in width, are less than 100 Å thick, are indefinitely long, and branch laterally in an anastomosing pattern. The internal structure of the microfibril consists of regions in which the molecular orientation varies from partial to nearly perfect order. Those portions with higher orientation he calls micelles, following the older botanical terminology. This corresponds to the term crystallites which is very commonly employed. Each of these crystallites is a flat rectangle approximately 30 × 70 Å. The zones between the micellar strands consist of a paracrystalline phase of cellulose, i.e., the molecules are in regular order only lengthwise of the microfibril. An aggregation of microfibrils, plus other constituents, then form the cell wall.

The zones of crystallinity which Frey-Wyssling proposes are in most respects substantiated by X-ray data from many sources. These papers have built up proof of a crystalline lattice whose dimensions are those shown in Fig. 4. One of the first things noted about these values was that the length 10.3 Å corresponds to the strainless configuration of β-cellobiose as proposed by Haworth, and it is agreed that the cellulose chains lie parallel to this direction. Geometrically, the diagram in Fig. 4 allows two possibilities for a unit cell. The first places chains with similar orientation at the corners ABCD. The cell is completed by a chain at the center (point E) which is offset one-half unit and whose orientation is reversed with respect to the corner chains; this is the generally accepted unit cell of Meyer and Misch (*14*), as is illustrated by Fig. 5. The other configuration employs the points ECFD as corners and is essentially the unit cell proposed by Sponsler and Dore (*15*). The reversed and offset

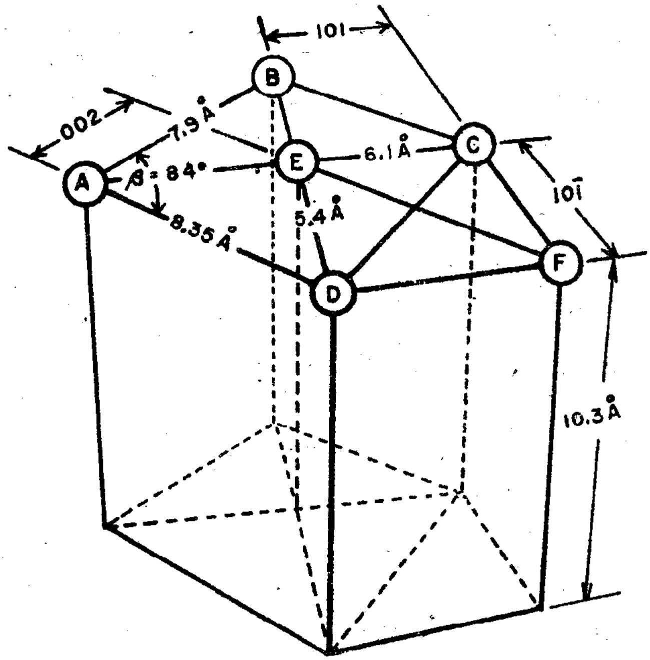

FIG. 4. Diagram of a portion of the crystalline lattice for native cellulose. The dimensions are according to S. T. Gross and G. L. Clark, *Z. Krist.* **A99**, 357 (1938).

central chain in the Meyer and Misch model is postulated on studies of coagulated viscose solutions and is subject to some doubt as representing the true situation for native cellulose, as noted by Preston (*16*).

Frey-Wyssling (*13*) states that flat filaments result when the microfibrils are disintegrated by ultrasonic vibrations, hydrolysis, or oxidation.

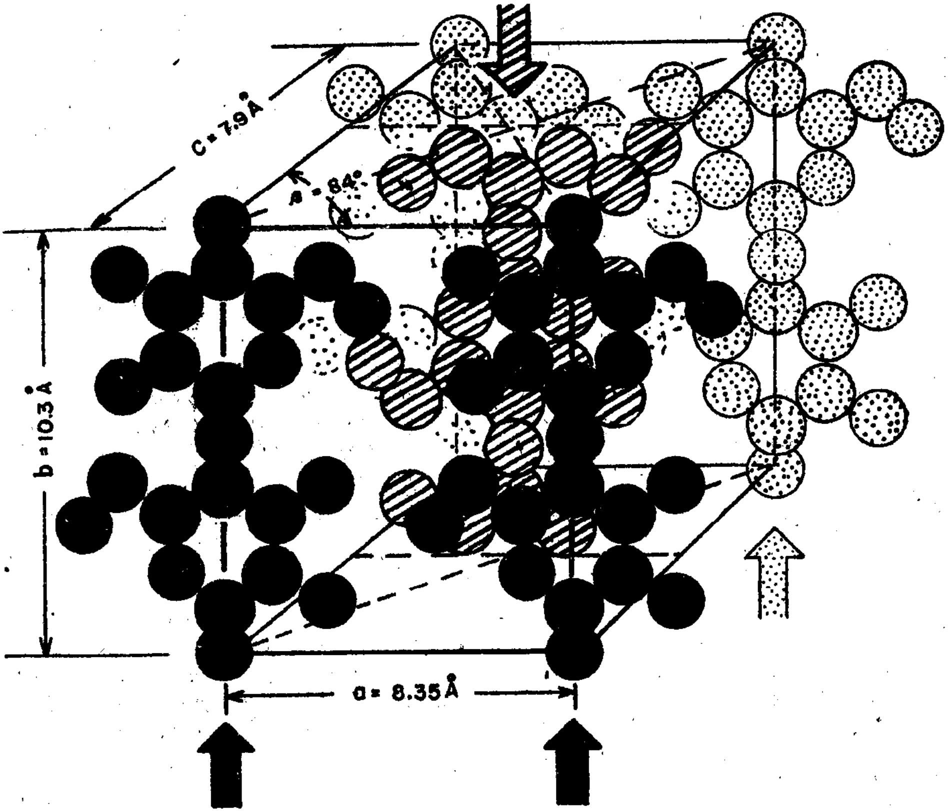

FIG. 5. The unit cell of crystalline cellulose, according to Meyer and Misch. The chain occupying the central position in the cell runs in the opposite direction to the chains at the corners, as shown by the direction of the arrows, and is offset one-half unit.

These ribbons range from 90 down to 70 Å generally, and may be as thin as 30 Å; they also show lateral anastomosing. A paper by Kratky and Sembach (*17*) definitely supports this structure with cross-sectional dimensions for a ribbon structure of 32 × 93 Å in native cellulose. From evidence in work by Mukherjee and Woods (*18*), the plane of the ribbon must be that of the (101) plane of the crystal lattice, since the flat particles produced by acid hydrolysis of ramie and cotton are naturally