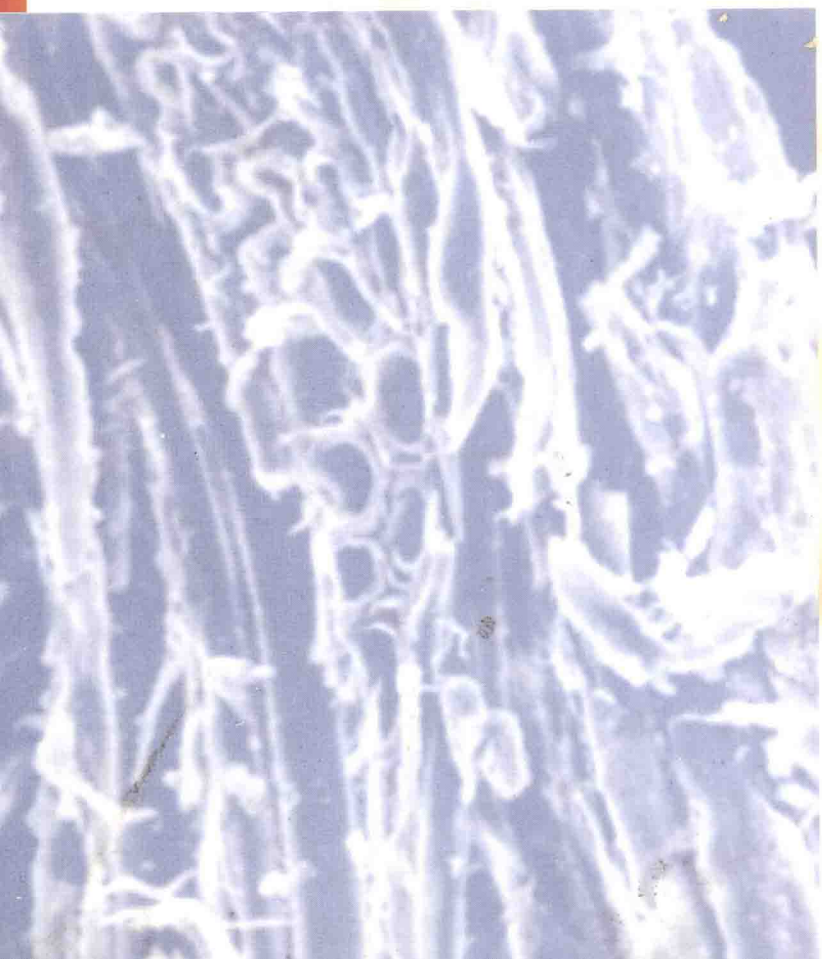
WOOD AND CELLULOSIC CHEMISTRY

second edition, revised and expanded



edited by
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Preface

Life and its surroundings are constantly changing within our dynamic world. As we stride into the new millennium, information technology and biotechnology continue to flourish. Rapid economic expansion, social development, and high demands for shelter, clothing, energy, and food for our overpopulated world have resulted in a desperate need for new and yet functional materials to support society's infrastructure.

Wood or lignocellulosic-based materials have made a significant contribution to the quality of living for human beings. With new developments in wood chemistry, scientists are confident that wood will continue to play an important role in fulfilling the needs of human beings.

Over the past decade, the trend of emphasizing bio-based technologies has been observed worldwide. In February 1998, a long-term development project, Plant/Crop-based Renewable Resources 2020, was implemented among the U.S. Department of Agriculture, U.S. Department of Energy, and many U.S. companies, agricultural associations, and universities. The aim of the project was to obtain novel chemicals from plant- and crop-based renewable resources in order to widen the usage of crops, the yield of which has been significantly increased through bio-technological advancements. The recent movement of producing foods by means of genetically manipulated seeds should enhance the effectiveness of this project. Before the start of this project—which is considered the future of the petrochemical industry—major chemical companies in the United States, such as Dow Chemical, Dupont, and Monsanto, have been changing their strategies in research and development. They have strengthened their bio-based research field, trying to yield as many chemicals as possible from biomass. They are developing production technologies for ethanol, sorbitol, lysine, tryptophane, citric acid, lactic acid, poly(lactic acid), erythritol, 1,3-propanediol, etc., from biomass. Furthermore, in August of 1998 President Clinton issued an executive order, "Developing and Promoting Biobased Products and Bioenergy," to further the development of a comprehensive national strategy that includes research, development, and private sector incentives to stimulate the creation and early adoption of technology needed to make bio-based products and bio-energy cost-competitive in national and international markets. Also, there has been research in so-called "green chemistry." In this new methodology, biomass is the recommended raw material. The importance of wood and cellulose research is thus recognized.

Since the publication of the first edition of this book, considerable advancement in various fields of wood chemistry has been made, as can be attested by many scientific publications in addition to well-attended international conferences. We contacted the contributors to the first edition, soliciting their opinions on revising and updating the book, and we received tremendous support from them as well as the publisher. Unfortunately, and inevitably, several authors were unable to participate, but they recommended their successors.

Although most of the chapters in this new edition carry the same titles as those in the previous edition, they have all been extensively revised and updated. In addition, this edition includes several new chapters representing important threads in the total fabric of wood chemistry. These new chapters cover the subjects of chemical synthesis of cellulose, preservation of wood, preservation of waterlogged wood, biodegradable polymers from lignocellulosics, recycling of wood and fiber products, and pulping chemistry.

As editors, we feel fortunate to have been able to recruit some of the best talent in the field to this endeavor. We thank the contributors for their efforts. Any praise for the content should be addressed to them, and comments and criticisms to us will be welcome.

David N.-S. Hon
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Ultrastructure and Formation of Wood Cell Wall

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I. GENERAL STRUCTURE OF WOOD AND WOOD CELLS

A. Wood

1. Softwood and Hardwood

In introduction it should be understood that the term "wood" refers to the secondary xylem formed by cell division in the vascular cambium of both gymnosperms (softwoods) and angiosperms (hardwoods), and especially in *Ginkgo*. Similar secondary xylem may be produced by plants of different form and structure, such as vines and shrubs, the xylem of which may be an important resource of pulping material. The structure and formation of the secondary xylem are discussed in this chapter.

Both softwoods and hardwoods are widely distributed on earth, from tropical to arctic regions. The xylem of those species present in moderate-temperate to arctic regions is characterized by distinct growth rings, in which some anatomical differences can be noted. In the softwoods consisting mainly of tracheids (approximately 90% of wood volume), the latewood (summer wood) can be distinguished from the earlywood (spring wood) by its smaller radial dimensions and thicker cells walls. These anatomical differences are reflected in the higher density of the latewood compared with the earlywood. In softwoods growing in tropical or warm areas, growth rings cannot be distinguished due to the indistinct boundary between earlywood and latewood.

As with the softwoods, hardwoods are also present in tropical to arctic regions. In colder regions, hardwood species are deciduous, whereas in tropical regions, they are predominantly evergreen and their growth rings are difficult to recognize. The macroscopic characteristics of hardwoods are reflected in the distribution and number of different cell types such as vessels (pores), parenchyma, and fibers. Although fibers may account for only 25% of wood volume, in some cases, for hardwood, it may be as high as 50–70%. In contrast to the tracheid as the main cell in softwoods, hardwoods have a variety of cells.

Some deciduous hardwoods such as oak or elm have very large vessels concentrated at the beginning of annual rings. Such woods are called "ring porous wood," whereas other deciduous species and almost all evergreen hardwoods in which the vessels are evenly dispersed over the annual ring are called "diffuse porous wood." The above dis-

tinctions represent extremes and there are many intermediate arrangements of the vessels. Variations in arrangements of these vessels with other xylem tissues such as parenchyma are reflected in the "figure" and "grain" of the wood itself when it is cut from the tree. The physical properties of wood such as density also result from such arrangements of the cells.

2. Sapwood and Heartwood

When a tree stem is cut transversely, a portion of "heartwood" can be seen frequently as a dark-colored zone near the center of the stem. This portion is surrounded by a light-colored peripheral zone called "sapwood." The sapwood or at least the outer part of the stem conducts water through the tissue where the water is transpired, and mineral nutrients are also carried with water from the roots into the wood. In addition, the sapwood has living parenchyma tissue, which often plays some physiological role such as the storage of starch or fat. From this point of view, the sapwood is considered an active xylem tissue.

In contrast to sapwood, heartwood is dead xylem. As the tree matures, all parenchyma cells of the sapwood die, and other types of cells such as tracheids or fibers become occluded with pigment composed of polyphenols and flavanoids supplied mainly from the ray parenchyma. The bordered pits of gymnosperms become aspirated, whereas the vessels are blocked by tyloses or gum in angiosperms. Thus, heartwood does not participate in water conduction. Although the conducting and physiological functions are lost in heartwood, the durability of wood against rot or insect decay is remarkably improved due to an addition of such pigments. Moreover, these pigments confer a variety of beautiful colors on wood.

3. Reaction Wood

Reaction woods that appear on branches or a leaning stem by any force such as a landslide or snowfall have a peculiar nature. Once reaction wood is formed as a biological response, the living tree tries to preserve the original position of its stem or branches. For the practical use of woods, the reaction woods have not been appreciated very much because of their different characteristics from normal wood in both a physical and a chemical sense.

The occurrence and nature of reaction woods contrast quite a bit between softwood and hardwood. In softwood trees, the reaction wood forms at the lower side of a leaning stem or branches, where the compression stress reacts on the xylem. Therefore, this reaction wood is generally called "compression wood." Compression wood is heavy and appears dark brown on account of its highly lignified tracheid walls (see Section II), which seem to adapt to compression stress. Thus, compression wood is easily distinguished from normal wood by its dark color. The cambial activity at the lower position of a leaning stem or branch accelerates very quickly and develops a wider compression area than normal wood on the opposite side. Through the accumulation of compression wood tracheids over many years, a leaning stem will return gradually to the vertical position. The annual rings of such a stem, however, are conspicuously eccentric.

On the contrary, reaction wood in many species of hardwoods is formed at the upper side of a leaning stem or branches where the xylem loads the tensile stress. Therefore, such reaction woods are called "tension wood." Fibers of tension wood have a slightly lignified cell wall (see Section II) that is adapted to the tensile stress just like a bowstring. It is not so easy to distinguish this area from a normal one on account of its slightly pale tone, in comparison to the case of compression wood.

In fact, the occurrence of both reaction woods is a very troublesome problem in wood utilization. These reaction woods, however, are interesting material for the examination of wood structure and formation, as will be noted often in the following sections.

B. Wood Cells

Wood cells are produced in the vascular cambium from two types of meristematic cells: the fusiform initial and the ray initial (Fig. 1). Since cells derived from the fusiform initials that are upright in the stem occupy a major part of xylem, woods show remarkable anisotropism. The principal functions of xylem tissue are water conduction from roots to shoots, the mechanical support of a huge tree body, and a physiological role such as the storage of starch. Although these functions are common in both softwoods and hardwoods, the xylem of the latter is more evolved than that of the former, being adapted to each function.

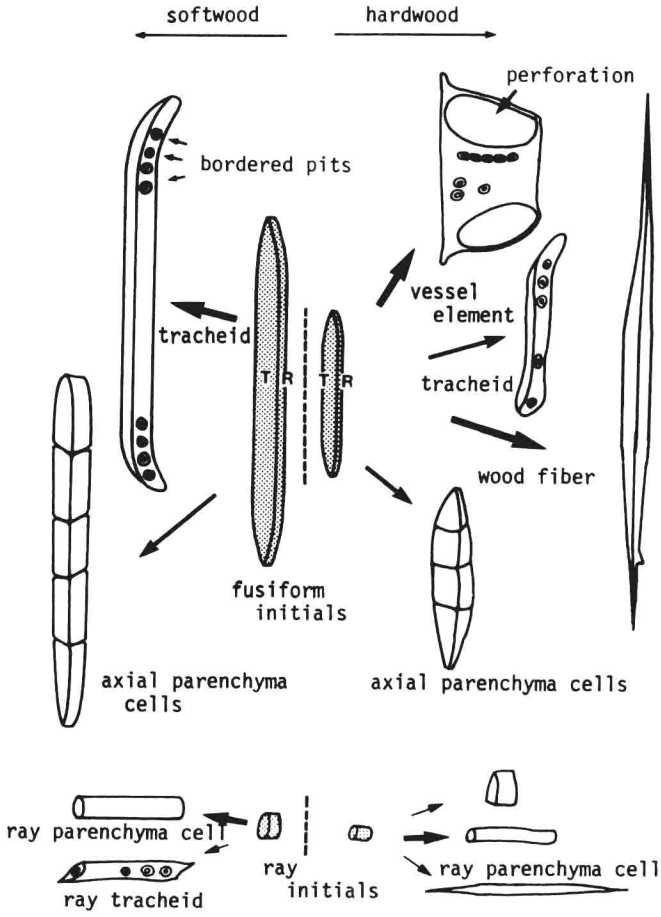

FIGURE 1 Shapes of major wood cells from the fusiform and ray initials in softwood and hardwood.

In softwoods and *Ginkgo*, tracheids, being major cells of xylem, are considered relatively underevolved because they have both conductive and mechanical properties. Bordered pits, the occurrence of which define a cell as a tracheid, are very important to the regulation of water flow. On the other hand, cell wall thickness is related directly to the strength of tracheids. The earlywood tracheids, therefore, seem to be well adapted to the conducting function whereas the latewood tracheids are loaded with the mechanical property, judging from their peculiar shapes. On the earlywood tracheids, well-developed pit pairs are distributed abundantly between the neighboring tracheids, and the cell walls of latewood tracheids are very thick.

Only a small number of fusiform cells are subdivided into strand cells by horizontal partitions and compose an axial parenchyma. These parenchymatous cells survive in the sapwood for many years, being different from the tracheid, in which the protoplast is lost soon after differentiation (see Section III), and are part of some physiological functions. In some genera of Pinaceae, axial resin canals surrounded by epitherial cells are constructed. The occurrence and structure of resin canals are often used in the identification of softwoods, although the volume of such resin canals is very slight in wood.

Ray cells are derived from the ray initials and elongated radially. A series of these ray cells make a ray parenchyma. Needless to say, these parenchyma cells are alive in the sapwood and are tied to the storage of nutrients such as starch or fat and also the transportation of some metabolites between the phloem and the heartwood. As a result, they must be related to the secretion of heartwood substance into the tracheids. Also, in some genera of Pinaceae, radial resin canals surrounded by epitherial cells are formed in many ray tissues, and more ray tracheids occur in the ray tissues.

Hardwood xylem can be characterized by the development of vessel elements and wood fibers specialized for water conduction and the mechanical property, respectively. The vessel elements construct a very long and thick tube, namely, a vessel, being joined vertically with one another by a perforation that has a more developed style compared with the bordered pit pairs between tracheids. The occurrence of perforation distinguishes the vessel elements from the tracheids. Wood fibers elongate remarkably and possess very thick cell walls. The most developed type of cell, having simple pits (see Section II), is called libriform wood fiber. On the other hand, there are some intermediating cells from the tracheids to the vessel elements or wood fibers, i.e., vascular tracheids, vascentric tracheids, and fiber tracheids. The fiber tracheids are often included in the category of wood fibers, because there is no need to separate them from the libriform wood fibers in the practical use of wood. Vessel elements, wood fibers, and various types of tracheids in the hardwoods lose their protoplast just after the development of their secondary wall. However, in some hardwood species specialized wood fibers that remain alive for several years and often store starch grains are formed; they are called "living wood fibers."

Axial parenchyma cells, which are dispersed on the transverse section of softwoods, are clustered at the vessel periphery or form a group that is often linked tangentially. Resin canals that are surrounded by epitherial cells are formed in many genera of Dipterocarpaceae and a few Leguminosae.

Ray parenchyma cells sometimes aggregate and develop a so-called broad ray. The broad rays make a peculiar figure on a board, especially on the radial surface, as observed in oak or beech. Cells contained in the ray also vary in their anatomical features. Some of them are upright or square at the marginal position. These variations are used for the identification of hardwoods [1]. Both axial and ray parenchyma cells are apparently concerned with physiological functions—for instance, the storage of nutrients or heartwood

formation. Radial resin canals or latex tubes are formed in the ray tissue of some tropical hardwoods.

II. ULTRASTRUCTURE OF WOOD CELL WALL

Wood is a natural composite material and a chemical complex of cellulose, lignin, hemicelluloses, and extractives [2]. Cellulose is the framework substance, comprising 40–50% of wood in the form of cellulose microfibrils, whereas hemicelluloses are the matrix substances present between cellulose microfibrils. Lignin, on the other hand, is the encrusting substance solidifying the cell wall associated with the matrix substances. The significance of lignin as the encrusting substance can be demonstrated by examination of the lignin skeleton created by the acid removal of carbohydrates (Fig. 2).

The roles of these three chemical substances in the cell wall are compared to those of the constructing materials in the structures made from the reinforced concrete in which cellulose, lignin, and hemicelluloses correspond, respectively, to the iron core, cement, and buffering material to improve their bonding.

A. Cellulose Microfibrils

The crystalline nature of cellulose in wood has been demonstrated by studies with X-ray diffractometry and polarization microscopy. This crystalline nature was also confirmed by the electron diffraction patterns of the secondary walls of wood cells in selected areas [3]. Figure 3a is a transmission electron micrograph of a longitudinal section of latewood tracheids of *Pinus densiflora*, showing the intercellular layer (I), and the S_1 and S_2 layers. The electron diffraction diagram is of a selected area in S_2 (Fig. 3b), which is represented by a small circle. The (101), (10$\bar{1}$), and (002) of the equatorial reflections and (040) of

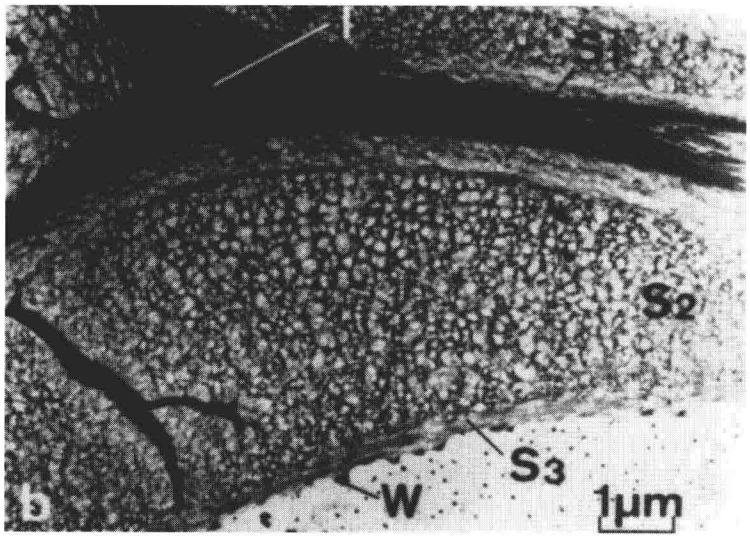

FIGURE 2 Electron micrograph of ultrathin transverse section of earlywood tracheids from *Pinus densiflora*, showing the distribution of lignin in the cell wall, which was skeletonized using the hydrofluoric acid technique.

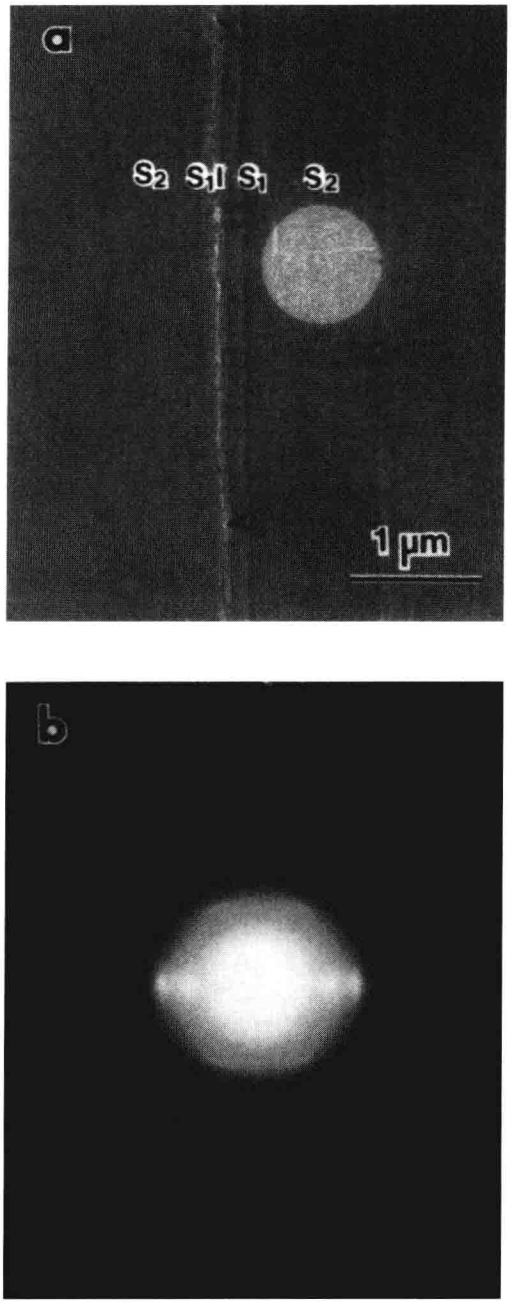

FIGURE 3 (a) Electron micrograph of ultrathin longitudinal section of tension wood fibers from *Pinus densiflora*. (b) The corresponding diffraction diagram taken from the encircled area.

the meridional reflection can be seen. It should be noted that crystallographic planes are based on the Meyer and Misch (1937) model of the unit cell of cellulose I, in which the *b* axis (the fiber axis) is vertical.

It is well known that in the wood cell wall, cellulose exists in the form of thin threads with an indefinite length. Such threads are called cellulose microfibrils, and they play an important role in the chemical, physical, and mechanical properties of the wood.

The green alga, *Valonia*, which is one form of Chlorophyceae, has been studied intensively by microscopists and crystallographers as an excellent material for the ultrastructural study of cellulose microfibril. Why then is *Valonia* used for the study of the cellulose microfibril of the wood cell wall? Because the cell walls of *Valonia* are unlignified, their microfibrils are readily isolated. Furthermore, as described later, *Valonia* microfibrils are approximately 20 nm in width, which is about five times larger than those of wood, and they are highly crystallized. However, the difference between algal microfibrils such as those of *Valonia* and ordinary ones produced by the higher plants also must be stressed. One of the differences is the selectively uniplaner orientation of algal microfibrils, that is, the (101) plane facing the cell surface, while cellulose microfibrils of higher plants are randomly oriented, although both microfibrils are laid along the cell surface in their longitudinal direction [3,4]. The other is the crystallographic heterogeneity in algal microfibrils as detected by NMR [5], and a triclinic system mixed with an ordinary monoclinic system was detected by electron diffraction [6]. The interface between these systems is not yet shown, although the former amounts to about 50%.

1. Dimensions of the Cellulose Microfibril

As described above, it is clearly demonstrated through electron microscopy that the cellulose molecular chains are organized into strands as cellulose microfibrils. Figure 4 shows transmission electron micrographs of disintegrated cellulose microfibrils negatively stained with uranyl acetate. Figures 4a and 4b, respectively, show the microfibrils of *Valonia macrophysa* cell wall and the holocellulose of *Pinus densiflora*.

A discrepancy in the size of the crystalline region of cellulose, obtained by X-ray diffractometry and electron microscopy, led to differing concepts as to the molecular organization of microfibrils. Frey-Wyssling [7] regarded the microfibril itself as being made up of a number of crystallites, each of which was separated by a paracrystalline region and later termed "elementary fibril" by Frey-Wyssling and Mühlethaler [8]. The term "elementary fibril" is therefore applied to the smallest cellulosic strand. Mühlethaler [10,11] applied this term to the cellulose fibril with a diameter of approximately 3.5 nm, using the negative-contrast preparation technique for electron microscopy. Preston and Cronshaw [9], on the other hand, considered the microfibril to have a single core of cellulose crystallite surrounded by a paracrystalline region.

The width of cellulose microfibrils is reported to vary in different cellulose materials [12]. For instance, as shown in Fig. 4, *Valonia* cellulose microfibrils, being about 20 nm wide, are much larger than those of wood holocellulose.

Shown in Table 1 are the crystallite size and microfibril width for several cellulose materials [13]. The crystallite size was estimated with Scherrer's equation at the reflection (002) or (101) of X-ray diffractometry, whereas the microfibril widths were measured directly from the electron micrographs. The width range and mode width are also included in this table. It should be noted that the size of crystallites varies in different sources of cellulose materials, for results from both X-ray diffractometry and electron microscopy.

According to Heyn [14], the negative stain can penetrate only the regions accessible to water. Thus, the translucent parts seen on the electron micrographs correspond to the

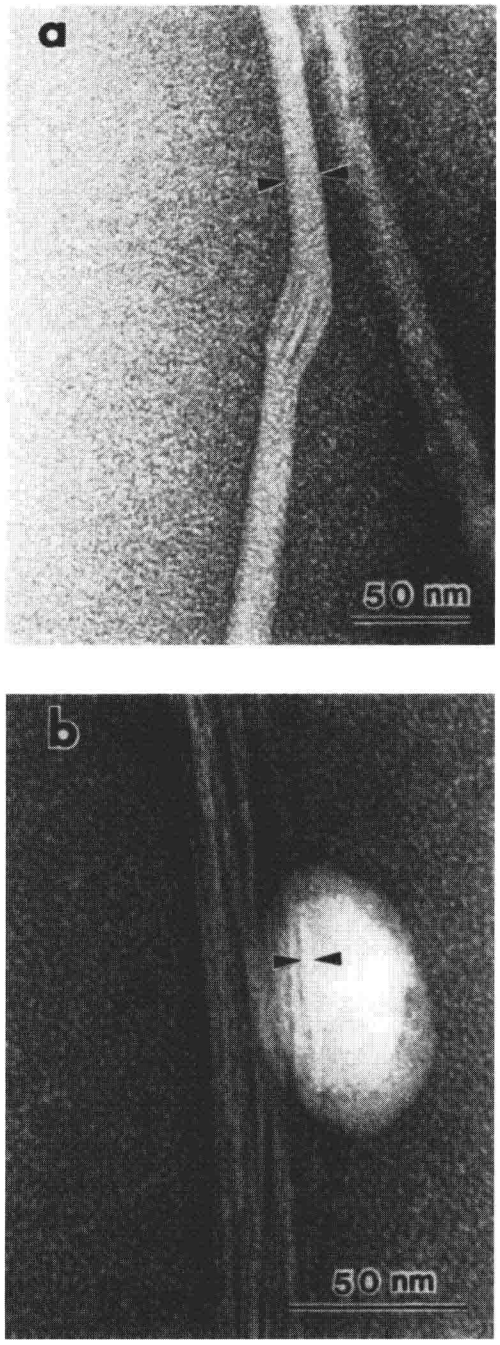

FIGURE 4 Electron micrographs of the cellulose microfibrils of *Valonia macrophysa* (a) and of *Pinus densiflora* holocellulose (b) (disintegration, negatively stained with uranyl acetate), showing the difference of cellulose microfibril width between wood and *Valonia*.