THE INFLUENCE OF SAPWOOD-HEARTWOOD CONVERSION OF BORDERED PIT TORI IN WESTERN HEMLOCK ON BISULFITE PULPING[1]

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ABSTRACT

In an effort to determine why heartwood of western Hemlock [*Tsuga heterophylla* (Raf.) Sarg.] is difficult to pulp by sulfite technology, ultraviolet (UV) and scanning electron microscopy were used to examine hemlock heartwood and sapwood before and after acid-bisulfite pulping. Resulting data showed that UV-absorbing material that is located in the intertracheid bordered-pit membranes and that is solvent-extractable in the sapwood is suggested to be low molecular weight procyanidins that polymerize into unextractable polymers during heartwood formation. Condensation of these polymers occurs under the strongly acidic conditions of acid bisulfite pulping, reducing wood permeability to cooking liquor.

Keywords: Western hemlock, bordered pits, bisulfite pulping, sapwood-heartwood tori.

INTRODUCTION

The heartwood of certain species of wood is resistant to chemical pulping by the acid bisulfite process. In the case of southern pine, for example, the presence of substituted stilbene and flavonoid derivatives is partly responsible for this phenomenon (Rickey and Hergert 1974). Western hemlock [*Tsuga heterophylla* (Raf.) Sarg.] is not reported to contain extractives that inhibit pulping, yet a series of chemical pulping studies on this important pulpwood in our laboratory showed that the heartwood consistently yielded pulp with a higher permanganate or K Number (lignin content) and higher screenings than sapwood from the same tree. Investigation of the reasons for this behavior showed that it was related to the presence of compression wood at the center of the tree, which is high in lignin content, and to certain chemical and physical changes associated with sapwood-heartwood conversion, which inhibit pulping liquor penetration (Hergert et al. 1979).

It has long been recognized that fluid movement between adjacent conifer tra-

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cheids takes place through the bordered-pit pairs. It has also been shown that pit closure during heartwood formation contributes significantly to reduced liquid permeability in heartwood (Côté 1963; Krahmer and Côté 1963). The reduction in heartwood permeability has been attributed to either pit aspiration, to deposition of extraneous materials in the fine structure of the heartwood pit perforations, or to a combination of these factors (Krahmer and Côté 1963).

The actual presence or absence of lignin in the heartwood bordered-pit tori of conifers appears to be a point of controversy when one reviews the literature. One side concludes that polyphenols were present in the sapwood tori of several conifer species studied but lignin was absent, and that during heartwood formation, in addition to the aromatic substances already present, lignin is synthesized and added to the pit membrane (Bauch and Berndt 1973; Bauch et al. 1974). The contrasting side agrees that lignin is absent in sapwood tori but argues that during heartwood formation additional polyphenols, not lignin, produced by dying parenchyma cells, diffuse into adjacent tracheids and are deposited within the pit tori (Thomas 1976). If the latter view is correct, these polyphenols could also inhibit the flow of liquid through the heartwood and thereby interfere with the normal course of the pulping process.

The purpose of this study was not to solve this controversy, but to further clarify the chemical and physical changes associated with western hemlock during sapwood-heartwood conversion that inhibit pulping.

Lignin is defined for this study as a polymeric natural product arising from an enzyme-initiated dehydrogenative polymerization of three primary procursors: trans-coniferyl, trans-sinapyl, and trans-p-caumaryl alcohols. In the case of conifers trans-coniferyl alcohol is the main precursor (Sarkanen and Ludwig 1971; Thomas 1976).

METHODS AND MATERIALS

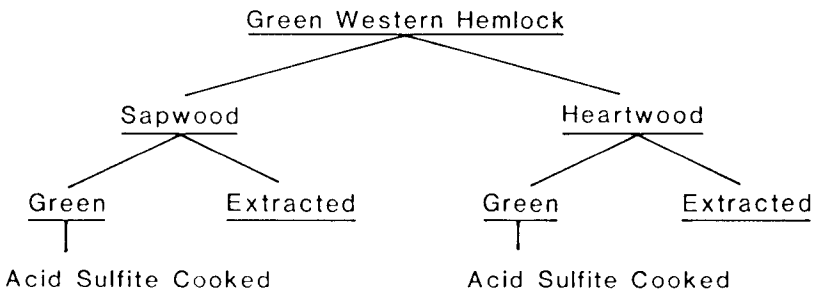
The use of ultraviolet (UV) microscopy to study quantitatively lignin concentrations in ultrathin cross sections of wood cellular elements has been successfully employed in past research (Bauch and Berndt 1973; Boutelje and Jonsson 1980; Imagawa and Fukazawa 1978; Scott et al. 1969). Lignin possesses a characteristic UV absorption spectrum with absorption maxima around 212 nm and 280 nm. Fortunately for wood research, no other major component of the mature wood cell wall displays UV absorption properties in the same spectral region. The intensity of the UV absorption is proportional to the lignin concentration in the microscopic detail under observation if the absorptivity of lignin for UV light is the same in different morphological regions. This means the higher the lignin concentration the darker the microscopic image. However, it has been carefully noted that there are certain precautions to be taken when using this technique and when interpreting results (Boutelje and Jonsson 1980; Scott and Goring 1970). For instance, there is evidence in the literature that certain other phenolic compounds (extractives) in wood absorb strongly in ultraviolet light and may interfere with an accurate lignin determination (Imagawa and Fukazawa 1978). Interference from this source can, of course, be minimized by pre-extraction of wood samples prior to microscopic studies.

The UV absorbance attributable to lignin can be measured in two different ways, either by density evaluation of negatives from photomicrography (micro

densitometry), or directly in the microscope by recording the light intensities with photomultiplier equipment (microphotometry). This latter method, which is more direct and faster, was adapted for this study.

Samples

The tree used for this study was a 51-year-old western hemlock from Grays Harbor County in Western Washington. Freshly cut (green) cross-sectional disks were subdivided into sapwood and heartwood chips and processed according to the scheme shown below. Extracted chips represent thirty hours of soxhlet extraction with acetone. Representatives samples of each treatment conditions were prepared for UV microscopy and scanning electron microscopy (SEM) examination.



UV microscopy

Ultrathin sections were prepared from solvent-dried, Epon embedded specimens, and from frozen specimens. For Epon-embedding, wood chips representative of each treatment condition (1 mm^2 × 6 mm) were solvent-exchanged from the water-swollen state to absolute ethanol followed by propylene oxide; they were then embedded in Epon 812. The ultrathin sections were cut with a diamond knife and collected on a flotation liquid consisting of 10% acetone in water.

For freeze-sectioning, the wood chips were frozen in their water-swollen state in O.C.T. compound (Ames) and sectioned with a diamond knife at a temperature of −50 C. The ultrathin sections were collected on a flotation liquid consisting of a 1:1 mixture of dimethylsulfoxide and water.

Ultrathin sections of nominal thickness of about 0.7 μm were transferred to a quartz slide and examined with a Leitz UV-microscope. The transmittance at 280 nm was measured with a photomultiplier tube directly above the objective. Photomicrographs of representative areas of the specimen were also taken.

The morphological elements studied include the bordered-pit torus (T), the pit border or secondary wall near the torus (S_T), the normal secondary wall (S), and an adjacent ray paraenchyma cell (R).

Five sections from each sample were examined. Two measurements of each element were made on each section and the resulting ten measurements were averaged to give the absorbance.

TABLE 1. *UV absorbance at 280 nm.*

	T	S_T	S	R
Samples: Freeze-sectioned				
Unextracted sapwood	0.634	0.302	0.298	0.556
Extracted sapwood	0.201	0.220	0.228	0.439
Unextracted heartwood	0.670	0.229	0.231	0.396
Extracted heartwood	0.711	0.262	0.265	0.524
Samples: Epon-embedded				
Unextracted sapwood	0.534	0.215	0.215	0.366
Extracted sapwood	0.233	0.226	0.220	0.344
Unextracted heartwood	0.628	0.220	0.219	0.341
Extracted heartwood	0.575	0.208	0.205	0.341

SEM microscopy

Representative specimens from each treatment condition were gradually solvent-exchanged from their water-swollen state to absolute ethanol. To preserve water-swollen structure, the samples were critical-point-dried in a Bomar SPC-900/EX critical-point dryer. Following drying, individual samples were fractured longitudinally to expose the bordered-pit membranes and then lightly metalized with a 60:40 coating of gold/palladium before examination in a JEOL 35C SEM.

RESULTS AND DISCUSSION

UV microscopy

The absorbances of the various morphological regions of the wood (green and acetone-extracted) in the sections prepared by freeze sectioning are shown in Table 1. It is likely that both the concentration and absorptivity of the lignin in the secondary wall of the tracheid are equal for sapwood and heartwood and, also, are unchanged by solvent extraction. The variations seen in the values for (S) given in Table 1 are probably due to variations in the thicknesses of the

TABLE 2. *UV absorbance at 280 nm relative to the absorbance of the secondary wall.*

	T	S_T	S	R
Samples: Freeze-sectioned				
Unextracted sapwood	2.1	1.01	1.00	1.9
Extracted sapwood	0.9	0.97	1.00	1.9
Unextracted heartwood	2.9	0.99	1.00	1.7
Extracted heartwood	2.7	0.99	1.00	2.0
Samples: Epon-embedded				
Unextracted sapwood	2.5	1.00	1.00	1.7
Extracted sapwood	1.1	1.03	1.00	1.6
Unextracted heartwood	2.9	1.00	1.00	1.6
Extracted heartwood	2.8	1.01	1.00	1.7

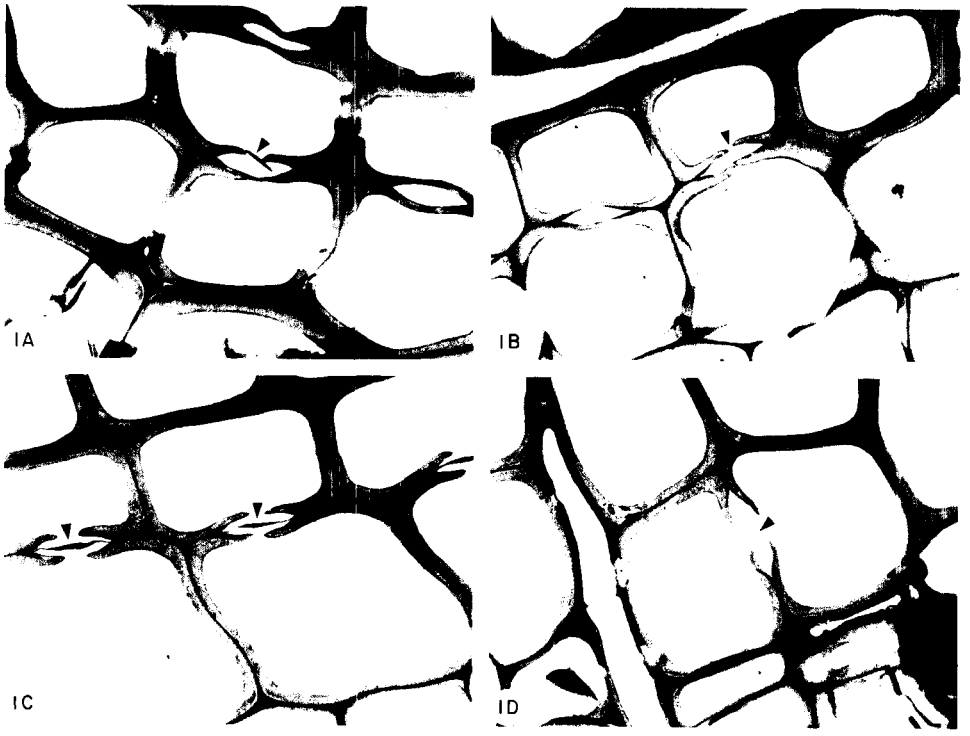


FIG. 1. A. Unextracted sapwood cross section. Note torus (arrow). Freeze-sectioned. UV micrograph. Width of micrograph (wm) = 90 μm. B. Extracted sapwood cross section. Torus (arrow). Freeze-sectioned. UV micrograph. wm = 90 μm. C. Unextracted sapwood cross section. Tori (arrows). Epon embedded. UV micrograph. wm = 90 μm. D. Extracted sapwood cross section. Torus (arrow). Epon embedded. UV micrograph. wm = 90 μm.

sections. A more accurate measure of the absorbance may be obtained by calculating a relative absorbance from:

$$\text{Relative Absorbance} = \frac{\text{Measured Absorbance}}{\text{Absorbance of S Measured on the Same Section}}$$

Values of relative absorbance for the tissue elements studied are given in Table 2. The results show quite clearly that the relative absorbance for the secondary wall near the torus (S_T) and the ray cell wall (R) are the same for sapwood and heartwood and remain unchanged on solvent extraction. Note that a small overall increase in lignin concentration in the heartwood would not be detected since the relative absorbances in Table 2 are based on the assumption that lignin concentration and absorptivity in the secondary wall are unchanged by the sapwood-heartwood transformation.

With the bordered-pit torus (T), the picture is different. The data in Table 2 indicate that the UV absorbance (and thus the concentration of UV-absorbing material in the sapwood torus) is reduced by a factor of two on solvent extraction. This material is probably a mixture of Brauns' Native Lignin and procyanidins (Goldschmid and Hergert 1961; Hergert 1977), which condenses into an insoluble

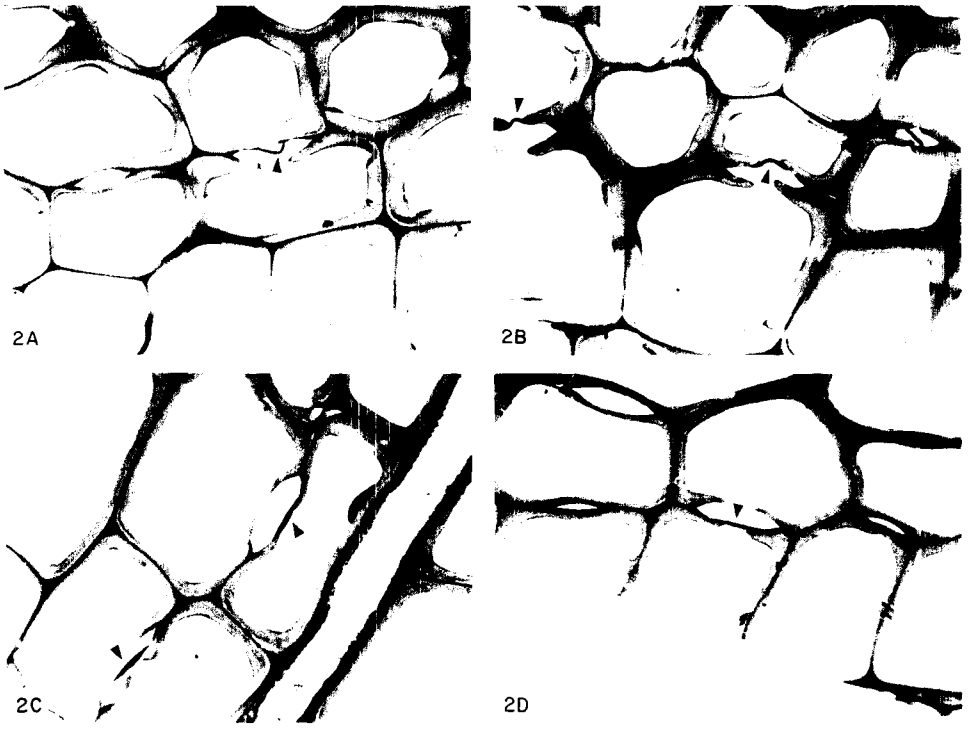


FIG. 2. A. Unextracted heartwood cross section. Torus (arrows). Freeze-sectioned. UV micrograph. wm = 90 μm. B. Extracted heartwood cross section. Tori (arrows). Freeze-sectioned. UV micrograph. wm = 90 μm. C. Unextracted heartwood cross section. Tori (arrows). Epon embedded. UV micrograph. wm = 90 μm. D. Extracted heartwood cross section. Torus (arrow). Epon embedded. UV micrograph. wm = 90 μm.

state in the heartwood. Note also that the absorbance in the heartwood is higher than that of the sapwood torus. This strongly suggests that the concentration of UV-absorbing material is increased in the heartwood torus, e.g., nonextractable phenolic polymers are deposited in the torus during heartwood formation.

The results obtained with Epon-embedded sections (Tables 1 and 2) agree fairly well with the freezed-sectioned data, thereby confirming the reality of the effects observed.

Although information obtained from photographic evidence is qualitative, it does generally support the UV-absorption data. Figures 1 and 2 are representative UV photomicrographs of unextracted and extracted heartwood and sapwood cross sections illustrating the lignin or UV-absorbing material (black) in the middle lamella region, bordered-pit tori, and ray cell walls. In those sapwood sections prepared by freeze sectioning, the concentration of lignin in the middle lamella region does not appear to be changed by solvent extraction. The bordered-pit tori, however, appear significantly lighter following extractions, indicating a decrease in concentration of UV-absorbing material (Figs. 1A and 1B). This same trend was evident in a similar set of samples prepared by Epon-embedding (Figs. 1C and 1D).

TABLE 3. *UV absorbance at 280 nm.*

	T	S_T	S	R
Samples: Freeze-sectioned				
Unextracted sapwood	0.634	0.302	0.298	0.556
Cooked sapwood	0.616	0.016	0.016	0.016
Unextracted heartwood	0.670	0.229	0.231	0.396
Cooked heartwood	0.570	0.014	0.015	0.049
Samples: Epon-embedded				
Unextracted sapwood	0.534	0.215	0.215	0.366
Cooked sapwood	0.426	0.014	0.014	0.116
Unextracted heartwood	0.628	0.220	0.219	0.341
Cooked heartwood	0.632	0.012	0.011	0.105

The UV-absorbance data (Tables 1 and 2) revealed a higher concentration of UV-absorbing material in heartwood tori as compared to sapwood tori; however, this increase could not be detected from the photomicrographs of cross sections prepared by freeze sectioning (Figs. 2A and 2B) or Epon-embedding (Figs. 2C and 2D).

Absorbance data indicated no significant difference in lignin concentration in ray cell walls of either sapwood or heartwood, unextracted or extracted. This was also evident from the photomicrographs of Figs. 1 and 2.

The UV absorbances of the various morphological regions for sulfite-cooked sapwood and heartwood are shown in Table 3. Also included for comparison are the absorbances for the unextracted sapwood and heartwood given in Table 1. From the data obtained on freeze-sectioned specimens, it is clear that the delignification by sulfite has produced a marked decrease in the lignin concentration of the secondary wall. Less expected was the negligible change in the UV absorbance of the tori during the cook. This suggests that the UV-absorbing material in the tori was not removed by sulfite pulping. This was true even in the sapwood from which much of the UV-absorbing material can be removed by solvent extraction, as discussed earlier.

The most probable explanation for the above finding is that the tori contain a mixture of lignin-like and procyanidin polymers which, in acid conditions, have

TABLE 4. *UV absorbance at 280 nm relative to the absorbance of the secondary wall.*

	T	S_T	S	R
Samples: Freeze-sectioned				
Unextracted sapwood	2.1	1.01	1.00	1.9
Cooked sapwood	39.0	0.99	1.00	1.0
Unextracted heartwood	2.9	0.99	1.00	1.7
Cooked heartwood	38.0	0.93	1.00	3.3
Samples: Epon-embedded				
Unextracted sapwood	2.5	1.00	1.00	1.7
Cooked sapwood	30.0	1.00	1.00	8.3
Unextracted heartwood	2.9	1.00	1.00	1.6
Cooked heartwood	55.0	1.09	1.00	9.5

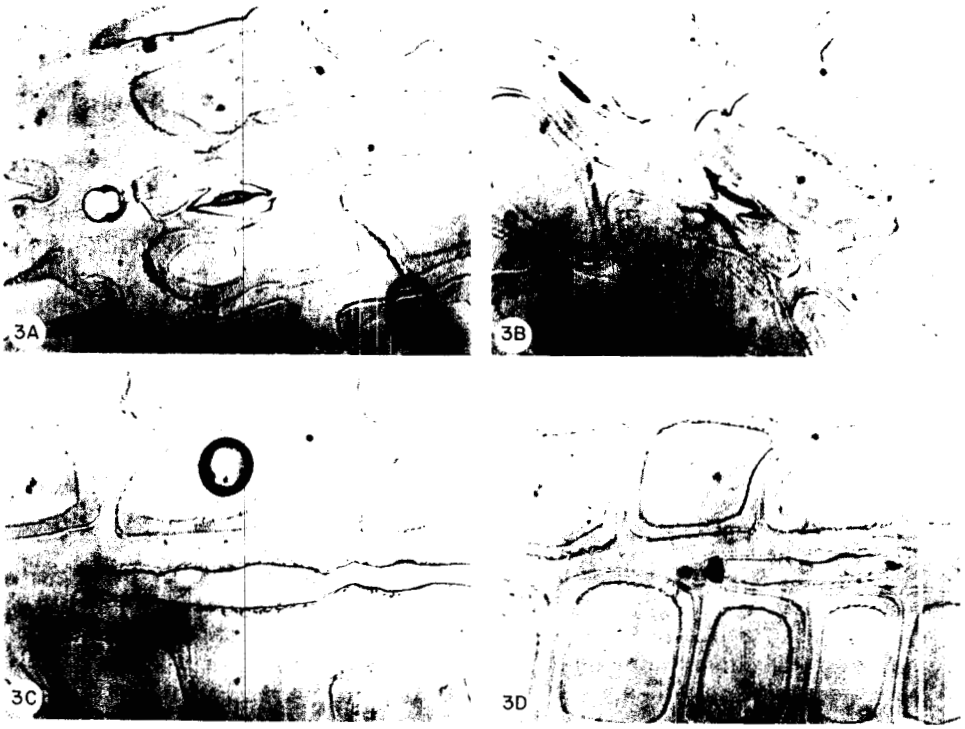


FIG. 3. A. Cross section, sulfite-cooked sapwood chip. Torus (arrow). Epon embedded. UV micrograph. wm = 85 μm. B. Cross section, sulfite-cooked heartwood chip. Tori (arrows). Epon embedded. UV micrograph. wm = 85 μm. C. Cross section, sulfite-cooked sapwood chip. Note UV absorbing material lining the ray cell (arrow). Epon embedded. UV micrograph. wm = 85 μm. D. Cross section, sulfite-cooked heartwood chip. UV absorbing material lining ray cell and half-bordered pit membrane (arrows). Epon embedded. UV micrograph. wm = 85 μm.

condensed and are thus blocked for further sulfonation and subsequent solution. This reaction may be similar to the well-known behavior of pine wood in acid sulfite pulping (Erdtman 1949; Rickey and Hergert 1974), and to the inhibition of sulfite pulping of tannin-soaked sapwood of spruce when unbarked logs are stored in ponds (Erdtman 1949). These condensed polymers would also absorb ultraviolet light at the same wave length and intensity of the uncondensed polymers, resulting in data that represent an absorption composite of compounds present.

The relative absorbances in Table 4 show that the secondary wall near the torus has delignified at about the same rate as the secondary wall remote from the torus. The data also show that the ray cell lignin is somewhat more difficult to dissolve then the cell-wall lignin in the case of heartwood. This effect is not seen for the sapwood.

The data for the Epon-embedded specimens support, in general, the results from freeze-sectioning (Tables 3 and 4). In the Epon-embedded sections, the higher resistance of the ray cell lignin to dissolution is about the same for sapwood and heartwood. This also may suggest that the ray cells also contain certain phenolic polymers that condense under acidic conditions thus blocking sulfonation and subsequent solution.

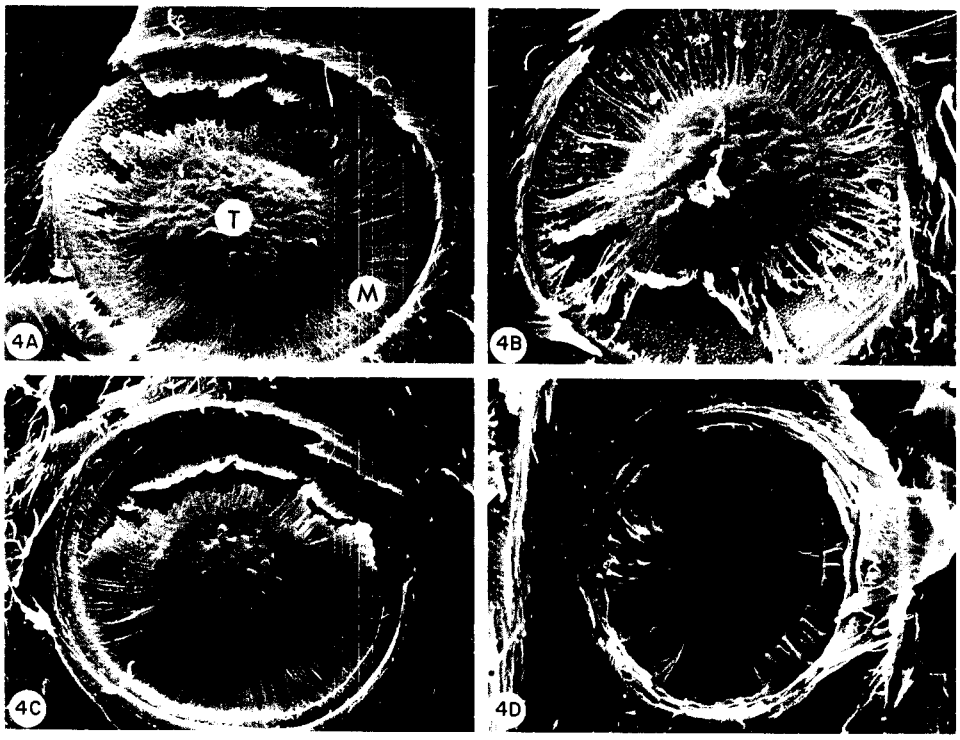


FIG. 4. A. Bordered pit torus (T) and margo region (M). Unextracted sapwood. Critical-point dried (CPD). Scanning electron micrograph (SEM). wm = 25 μm. B. Bordered pit torus and margo region. Extracted sapwood. CPD. SEM. wm = 25 μm. C. Bordered pit torus and margo region. Unextracted heartwood. CPD. SEM. wm = 25 μm. D. Bordered pit torus and margo region. Extracted heartwood. CPD. SEM. wm = 25 μm.

Photomicrographs of thin cross sections from representative sulfite-cooked chips (Epon-embedded) confirm the absorbance data in that residual concentrations of UV-absorbing material are seen at the bordered-pit tori in both sapwood (Fig. 3A) and heartwood (Fig. 3B). Note also an apparent residual concentration in a ray cell wall shown Fig. 3C, and in a half-bordered-pit membrane between a ray cell and the delignified secondary wall of a longitudinal tracheid (Fig. 3D).

SEM microscopy

Observations of samples representative of each treatment condition by SEM also provided useful information for this study. For example, the effect of acetone extraction on bordered-pit tori of green wood is illustrated in Fig. 4. Note the apparent loss of "incrusting" type material from the pit torus (T) and margo region (M) in the sapwood (Fig. 4A and 4B) while the heavy incrustant in the heartwood tori appears to be unaltered (Fig. 4C and 4D).

The sulfite cooking process did remove some material from the sapwood tori, leaving a somewhat porous structure (Fig. 5A and 5C), while the heartwood tori still appear impermeable (Fig. 5B and 5D). This suggests that the heartwood tori UV-absorbing material may be chemically different from that found in sapwood

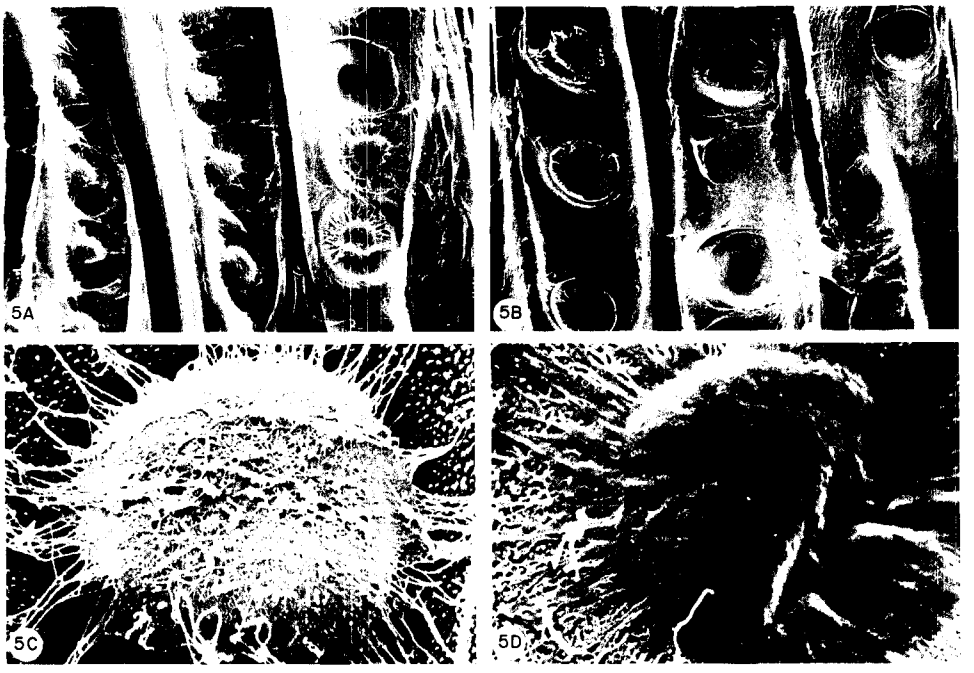


FIG. 5. A. Bordered pits. Sulfite-cooked sapwood. CPD. SEM. wm = 110 μm. B. Bordered pits. Sulfite-cooked heartwood. CPD. SEM. wm = 110 μm. C. Bordered pit torus and margo region. Sulfite-cooked sapwood. CPD. SEM. wm = 10 μm. D. Bordered pit torus and margo region. Sulfite-cooked heartwood. CPD. SEM. wm = 10 μm.

tori. Note also that most heartwood pits have remained aspirated during the cooking process.

CONCLUSIONS

Several conclusions pertaining to western hemlock can be made as a result of this study:

1. The lignin concentrations in the ray cell wall and in the tracheid secondary wall near the torus are the same in the sapwood and heartwood and are unchanged by solvent extraction.
2. Approximately one-half of the UV-absorbing material in the torus of the sapwood is removed by solvent extraction.
3. There is an increase of about 20% in the concentration of UV-absorbing material in the torus on heartwood formation. Little if any, of this material is removed by solvent extraction.
4. The concentration of UV-absorbing material in most of the tori in both sapwood and heartwood appears to be unchanged by a sulfite cook in spite of the fact that the concentration of lignin in the secondary wall is decreased more than tenfold during the cook.
5. The secondary wall near the torus is delignified to about the same extent as the secondary wall remote from the torus during a sulfite cook.

6. There is some evidence that for both sapwood and heartwood the delignification of the ray cells is not as extensive as that of the secondary wall during sulfite cooking.
7. Pit membranes are aspirated in western hemlock heartwood and remain in that condition during sulfite cooking.

The above conclusions are based on the following assumptions:

1. The lignin concentration is proportional to the UV absorbance at a wavelength of 280 nm.
2. The lignin concentration in the secondary walls of the tracheids remains the same in sapwood and in heartwood and is not affected by solvent extraction.

The data support assumption (2) and although they do not refute assumption (1), it clearly reveals that other materials absorb UV at a wavelength of 280 nm. These materials, found in sapwood and heartwood tori, are most likely low molecular weight procyanidins that polymerize into unextractable polymers during heartwood formation. The sulfite-cooking phase of this study reinforces this theory in that little, if any, of these polymers are removed during cooking in either the sapwood or heartwood tori.

If, (a) neutral solvent-insoluble procyanidin (tannin) and other polymers are formed during heartwood formation in western hemlock, (b) condensation of these polymers occurs under the strongly acidic conditions of acid bisulfite pulping, and (c) the site of this reaction is the bordered pit torus, we have adequate explanation (accompanied by heartwood pit aspiration) for the inhibition of sulfite pulping of hemlock heartwood. Blockage of pulping liquid flow through the torus will result in uncooked chips and increased screenings. Since the condensation of tannin and other polymers does not take place under neutral or alkaline conditions, we would expect that a two-stage cook (neutral sulfite followed by acid sulfite) or a kraft cook would be more effective in pulping heartwood. In either of these processes, removal of UV-absorbing materials from the tori would occur prior to condensation and liquid-flow blocking reactions.

Although this study did not specifically set out to prove the presence or absence of lignin in the heartwood tori of western hemlock, the data clearly indicate that the UV-absorbing material in the tori is not lignin.

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