BROWN STAIN FORMATION AND THE PHENOLIC EXTRACTIVES OF WESTERN HEMLOCK (*Tsuga heterophylla* (Raf.) Sarg.)

by

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FOREWORD

Hemlock brown stain, which occurs only on the surface of hemlock sapwood, is an innocuous brown pigment chemically indistinguishable from tannin. Good evidence that this pigment is formed from catechin, a normal phenolic constituent of sound hemlock sapwood, was obtained by simulating brown stain formation in the laboratory. It is postulated that catechin is transported with moisture to the surface of the lumber during drying and, accumulating there with evaporation of the water, reacts with air in the presence of an enzyme to form a brown polymerized pigment. The cross-sectional and seasonal variation of catechin and other naturally-occurring phenolic constituents of hemlock sapwood and heartwood, such as matairesinol, hydroxymatairesinol, phenolic glucosides, monomeric and polymeric leucoanthocyanidins, is also presented.

Although many chemicals were effective in inhibiting brown colorations in laboratory screening tests, none showed more than a short initial improvement in field tests, emphasizing the great difficulty in maintaining an effectively high concentration of control chemical on the surface of green hemlock lumber during yard seasoning.

AVANT-PROPOS

La coloration brune dc la pruche, qui ne s'observe qu'à la surface de l'aubier de cette essence, est une anodine pigmentation brune qu'on ne saurait distinguer du tanin, chimiquement parlant. Grâce à une coloration brune obtenue artificiellement en laboratoire, on a pu établir que cette pigmentation provient tout probablement de la catéchine, résine phénolique normale de l'aubier sain de la pruche. Ceci permet de postuler que la catéchine est amenée par l'humidité à la surface du bois pendant le séchage, s'y accumule à mesure que l'eau s'évapore, puis réagit au contact de l'air sous l'influence d'un enzyme et forme un pigment polymérisé de couleur brune. Suit un exposé de la variation transversale autant que saisonnière de la concentration de catéchine et d'autres constituants phénoliques qui se trouvent naturellement dans l'aubier et le bois de coeur de la pruche, tels le matairésinol, l'hydroxymatairésinol, les glucosides phénoliques, les leucoanthocyanilines monomères et polymères.

Bien que, lors d'épreuves d'efficacité effectuées en laboratoire, plusieurs produits chimiques se soient avérés efficaces à empêcher la formation de colorations brunes, nul n'a accusé, lors des tests exécutés sur le terrain, guère plus qu'une brève amélioration initiale, ce qui démontre combien il est difficile de maintenir l'efficacité d'une forte concentration de tout agent chimique répressif à la surface du bois vert de la pruche lors du séchage à l'air dans les cours à bois.

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ACKNOWLEDGEMENTS

The authors wish to thank Mr. John Pickford and Mr. Jack Stephens of the Eburne Sawmills Division, Canadian Forest Products Ltd., for their co-operation in obtaining western hemlock lumber samples and for the use of yard facilities during chemical control treatments.

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The experimental work was undertaken by Mr. John Manville whose technical assistance is hereby acknowledged.

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INTRODUCTION

During the summer and fall of 1960 many overseas buyers complained about the appearance of hemlock lumber (*Tsuga heterophylla* (Raf.) Sarg.) from the west coast of Canada. Stains, particularly on the ends of the lumber, ranging in colour from orange to almost black, were observed on both air- and kiln-dried hemlock. Although opinions from the lumber industry differed widely on the cause, it was generally agreed that the incidence of the stain had risen to undesirable levels. Unlike fungal stain, the objectionable colour referred to in the trade as hemlock brown stain was always confined to the surface of the cross-section or the side of the lumber, and could be removed permanently by planing provided the lumber remained dry. Although, in many instances, the stain was confined entirely to that part of the cross-section surface corresponding to the sapwood, it was concentrated in two main zones, the heartwood-sapwood boundary and the sapwood-cambium boundary.

Preliminary investigation of the stain showed the absence of fungal decay organisms and indicated that a chemical investigation was necesssary. Scrapings from heavily brown-stained lumber ends were removed and subjected to analyses. The brown material dissolved with difficulty in common solvents and gave colour reactions characteristic of tannins. Infra-red and ultra-violet analyses supported the indication of a phenolic tannin-like structure (Figure 1). In order to find out which component, or components, in western hemlock was responsible for this tannin-like stain, a study of the phenolic extractives of this species was undertaken. This publication outlines the results of this study and makes certain recommendations to the industry.

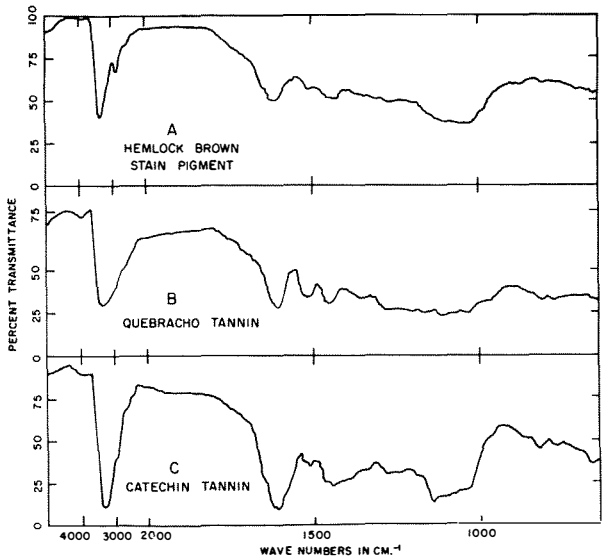

Figure 1. Infra-red spectra of hemlock brown stain and tannins.

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PHENOLIC EXTRACTIVES IN HEMLOCK WOOD AND THEIR CROSS-SECTIONAL VARIATION

A concurrent study on the chemical composition of tannins and polyphenols from conifer wood by Hergert (1960), as well as examination of western hemlock for lignin precursors by Goldschmid and Hergert (1961) demonstrates the great variety of phenolics to be found in this species. Of these, only water soluble phenolics occurring in reasonable concentration such as leucoanthocyanins, catechins, lignans, and the unknown phenolic glucosides encountered by Hergert (1960) would be expected to contribute significantly to brown stain formation.

Because of the observation that brown stain was more prevalent on surfaces at the heartwood-sapwood boundary it was considered necessary to investigate the distribution of the phenolic extractives in this region. Although it was known from previous work that sapwood and heartwood extractives differed qualitatively, it was important to know the change in concentration of the major phenolic components from heartwood to outer sapwood.

A cross-section from the butt log of a sound, 150-year-old hemlock grown in the University of British Columbia Haney Forest, which showed signs of brown stain was selected (Figure 2) and samples for analysis were obtained within one week after felling. Each segment was macerated in the Wiley Mill and extracted quantitatively with methanol. The methanol extracts were adjusted to the same concentration and separated into their individual components by means of two-dimensional paper chromatography (Hergert, 1960; Goldschmid and Hergert, 1961). Rectangular strips, pointed at one end, were excised from the two-dimensional papergram at seven independent locations corresponding to those phenolics A to G in Figures 3 and 4. Quantitative elution of these strips with water (saturated with carbon dioxide) in a carbon dioxide atmosphere followed by ultra-violet absorption measurements of the aqueous eluant at 280 milli-microns gave a comparison of the relative amounts of the major water soluble phenolic constituents present in the original extract. These results are presented in graphical form (Figures 3 and 4). Optical density figures are adjusted to correspond to 1 gram of extractive-free, moisture-free wood.

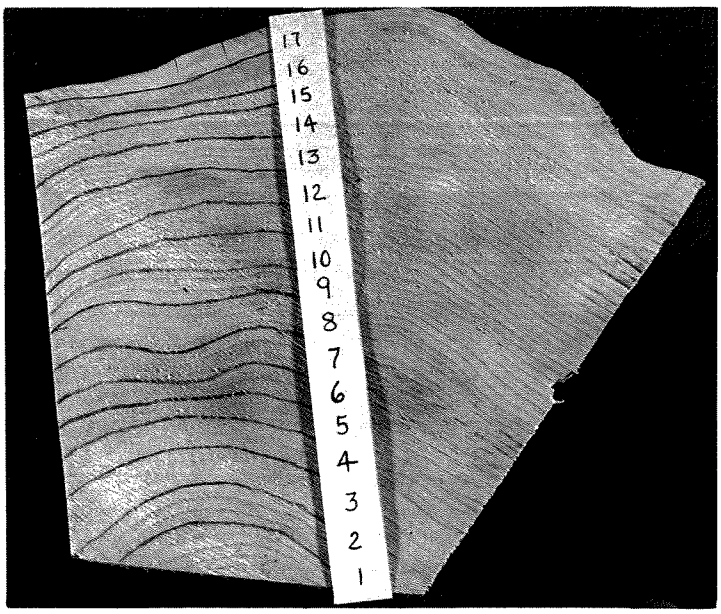

Figure 2. Cross-sectional segment pattern of a 150-year-old hemlock tree.

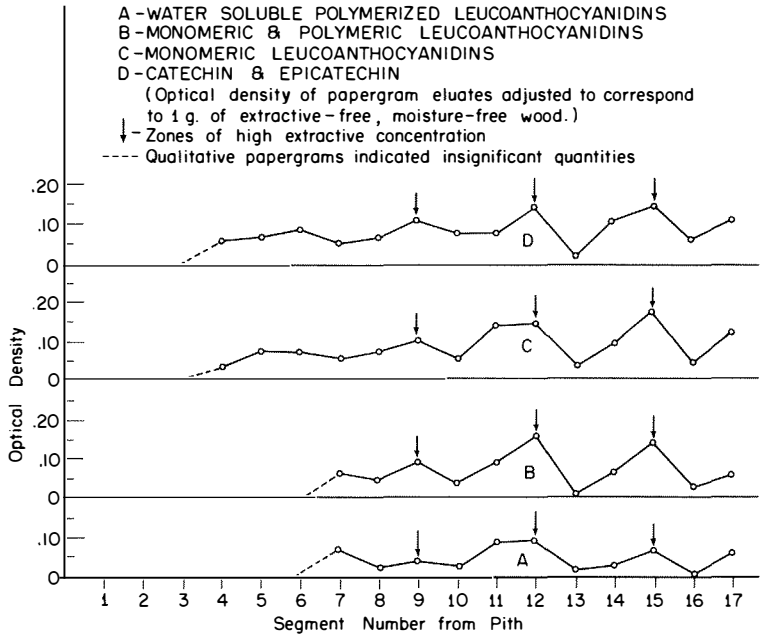

Figure 3. Variation of phenolic components from inner heartwood to outer sapwood in a 150-year-old hemlock tree.

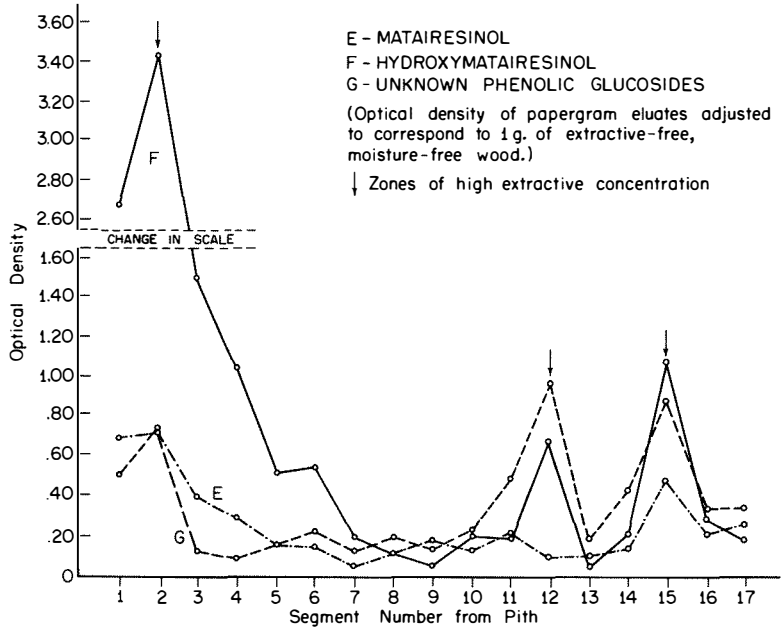

Figure 4. Variation of phenolic components from inner heartwood to outer sapwood in a 150-year-old hemlock tree.

Inner heartwood was characterized by a high concentration of stable propylphenol dimers, called lignans, such as matairesinol and particularly hydroxymatairesinol, and an absence of other phenolics such as catechin, epicatechin, monomeric and polymeric leucoanthocyanidins. Outer sapwood, on the other hand, had generally a much lower concentration of lignans and a relatively higher concentration of the other phenolics. Two unknown phenolics which were believed to be glucosides by Goldschmid and Hergert (1961) also showed a higher concentration in the outer sapwood, although they were present to a considerable extent in the inner heartwood. An unexpected feature of the cross-sectional study was the extremely wide sapwood-heartwood transition zone ranging from Segment Number 3 to Segment Number 11 (Figures 3 and 4). This zone contained extractives common to both heartwood and sapwood with no one extractive predominating. Also of interest were the areas of high extractive concentration such as found in Segments 9, 12, and 15 (Figure 3). Based on the general observation that heartwood-sapwood boundaries exhibit higher extractive concentration this particular cross-section would therefore contain three such boundaries. Confirmation of a diffuse heartwood-sapwood boundary was obtained by treatment of the original cross-section with colorimetric differentiation indicators such as glycerol-hydrochloric acid (Barton and Gardner, 1963) or perchloric acid (Eades, 1958). Both reagents showed weak colour development typical of a transition zone in Segments 3 to 11 (Figure 3) but with increased intensity on Segments 12 to 17.

Subsequently it was observed that the sapwood section of the butt from which the original sample was taken developed a brown stain after standing several days in water. The segments which turned brown correspond to Number 6, 7, 8, and 9 (Figure 3) which contained a reasonable level of catechin, monomeric and polymeric leucoanthocyanidins and a low lignan level.

Because of the wide transition zone encountered in this sample another cross-section for analysis was taken from a 60-year-old hemlock tree growing on the same site. Yields of individual phenolic extractives were obtained by a quantitative paper chromatographic-densitometric method developed in this laboratory. Some of the results of this study are presented graphically in Figures 5, 6, and 7. Although sapwood and heartwood zones are more distinct in this younger tree the previous pattern of distribution of extractives was maintained, namely lignans in the heartwood, other phenolics in the sapwood, and extractives common to both in the transition wood.

Hydroxymatairesinol (Figure 7), the lignan in highest concentration in hemlock wood, showed the greatest variation in yield ranging from values of 2.9 per cent near the heartwood-sapwood boundary to 0.004 per cent in the sapwood. Matairesinol (Figure 7) varied in a parallel way from a high of 0.5 per cent to a low of 0.005 per cent. The unknown phenolic glucosides (Figure 6) showed the same distribution preference for sapwood experienced in the previous sample and varied between 0.06 and 0.009 per cent. Monomeric leucoanthocyanidins (Figure 6) and the catechins (Figure 5) also predominated in the sapwood and varied from 0.05 per cent and 0.04 per cent respectively in the sapwood to none in the heartwood.

SEASONAL VARIATION OF THE PHENOLIC SAPWOOD EXTRACTIVES

In order to investigate the possibility that the time of year in which hemlock trees were felled influenced the development of brown stain in the resultant lumber, a study of seasonal changes in the components of sapwood extractives was necessary. A vigorous second-growth 60-year-old hemlock tree growing on the University Campus site was selected for the study. Each month from November 1st 1961, to October 1st 1962, a sample of sapwood was removed from this living tree. The sample was immediately immersed in methanol to prevent enzymatic change, and quantitatively Soxhlet-extracted with additional methanol. After adjusting each extract to the same concentration of 25 milligrams per millilitre, its phenolic

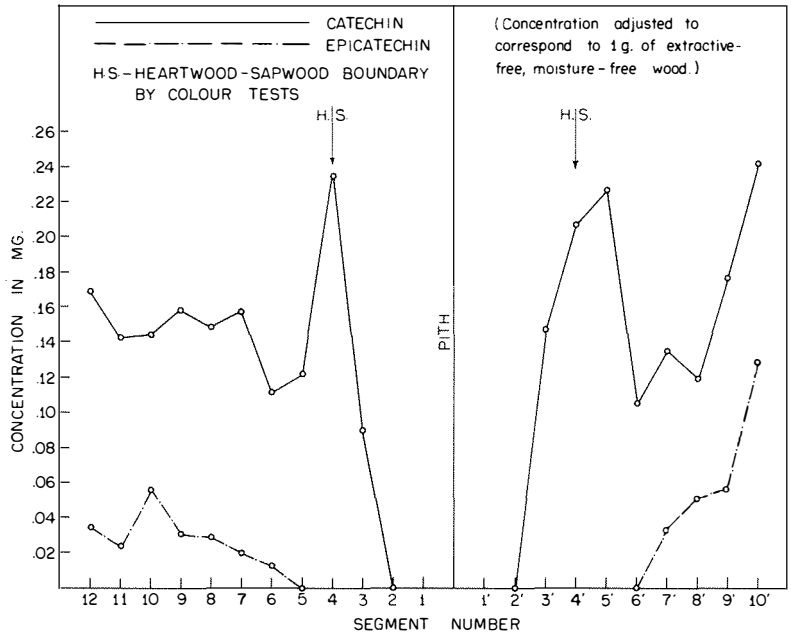

Figure 5. Variation of catechin and epicatechin from the pith to outer sapwood in a 60-year-old hemlock tree.

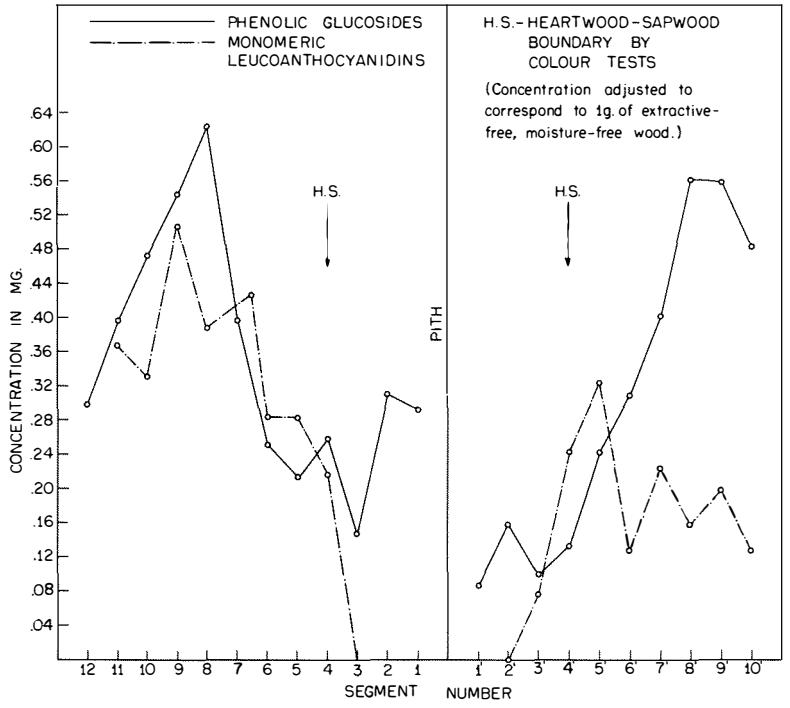

Figure 6. Variation of monomeric leucoanthocyanidins and phenolic glucosides from the pith to outer sapwood in a 60-year-old hemlock tree.

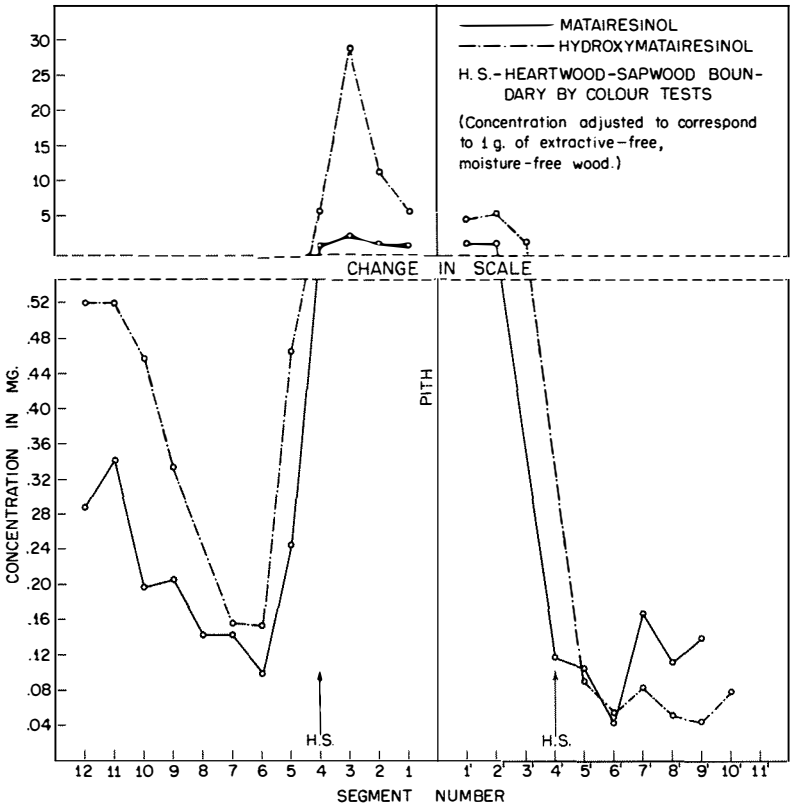

Figure 7. Variation of matairesinol and hydroxymatairesinol from the pith to outer sapwood in a 60-year-old hemlock tree.

components were separated by two-dimensional paper chromatography. As in the case of the first cross-section, the appropriate areas were quantitatively eluted and the resultant solutions analysed by ultra-violet absorption in the Beckman DK2 Spectrophotometer. Results of this study are presented graphically in Figures 8 and 9, optical density figures being adjusted to correspond to 1 gram of extractive-free, moisture-free wood.

A similar pattern of variation for each of the phenolic extractives is evident. As would be expected there was relatively little change in the concentration of the extractives during the winter months of November, December, January, and February. Beginning, however, in March, a rise in concentration occurred that continued to high values during April, May, June and July, followed by a decline to lower but appreciable levels during August, September and October. Since the interval between felling a tree and producing the lumber may be three to four months, the prevalence of brown stain in later summer might be explained on the higher extractive content prevalent during felling.

Some anomalies in the pattern, such as the high maximum for the phenolic glucosides in September and the increase in many of the extractives in October, could be explained in part by variation in the seasons from 1961 to 1962. For example, October 1962 had a higher-than-average overnight temperature with no frost during the month. These milder conditions could have resulted in a delay of dormancy in the tree and hence higher-than-normal phenolic extractive content. Also, since samples were taken at different positions around the circumference of the living tree, some variations in extractive content were to be expected.

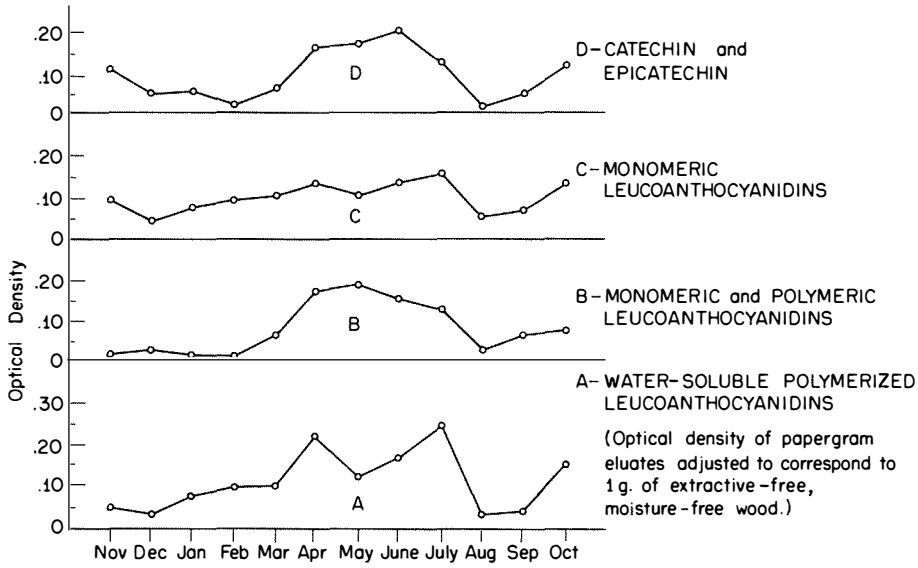

Figure 8. Seasonal variation of phenolic sapwood components in a 60-year-old hemlock tree.

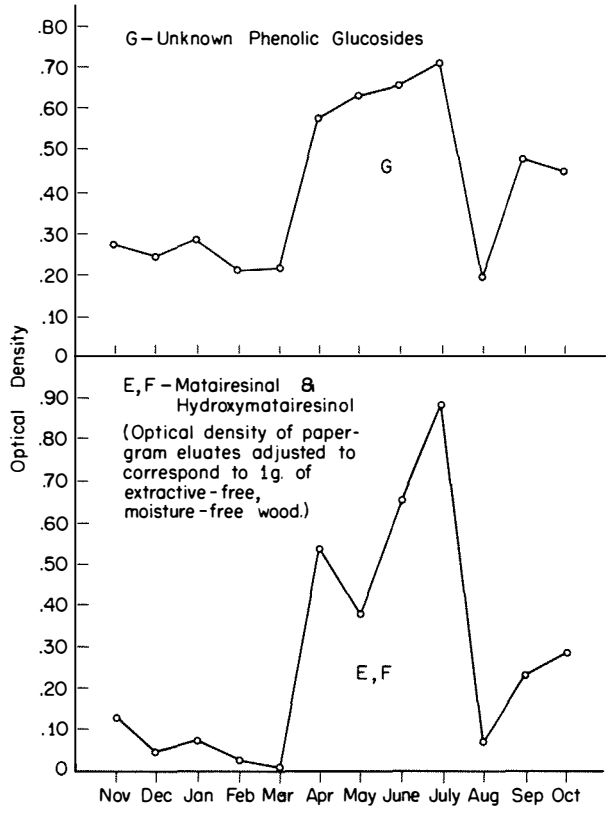

Figure 9. Seasonal variation of phenolic sapwood components in a 60-year-old hemlock tree.

PHENOLIC COMPONENTS OF THE EXTRACTIVE WHICH CAUSE BROWN STAIN

The above-mentioned cross-sectional and seasonal variation studies on hemlock sapwood extractives gave an over-all knowledge of the distribution and changes in concentration of the normal phenolic extractives. It was necessary to determine which of these components was responsible for the brown stain on hemlock lumber. Although concurrent work by Evans and Halvorson (1962) had stressed the importance of monomeric leucoanthocyanidins in this role, no definite proof had been presented.

An effective solution to this problem was devised by simulating the humidity and biochemical requirements of brown stain formation on a papergram containing the separated hemlock sapwood components. In this way, only those components susceptible to browning would react and thus identify the brown-stain precursor.

Enzyme preparations of peroxidase and polyphenol oxidase, frequently used on phenolic substrates to promote browning, were only partially successful in developing a brown colour. However, by applying a higher concentration of sapwood extractive on Whatman No. 17 paper and using juice expressed from hemlock sapwood by pressure as a detecting reagent, a well-defined brown coloration in the area corresponding to catechin was easily observed after several hours storage of the sprayed chromatogram in the humidity chamber. It was significant that, except for a slight discoloration at the monomeric leucoanthocyanidin site, the remainder of the papergram remained colourless. This work was repeated several times with synthetic catechin, synthetic leucocyanidin, and with mixtures of the two compounds, and each time the catechin zone developed the brown colour with only a slight colour in the leucocyanidin zone. Although little is known about the biochemical constituents of hemlock sapwood juice that caused catechin to turn brown, an enzyme system was suspected. Some evidence of this was obtained by reacting catechin with a filtered starch-dextrose nutrient in which bacteria isolated from a heavily brown-stained stump had been successfully cultured. This cell-free solution gave brown colorations similar to those encountered with catechin and expressed sapwood juice. The possibility of a cysteinyl-catechin complex participation (Roberts, 1959) in an oxidative browning reaction was precluded by an investigation of the amino acids present in hemlock sapwood. Cysteine was undetectable, only aspartic acid and glycine were confirmed by paper chromatographic examination of a methanolic extract of the sapwood. An additional amino acid, either leucine or isoleucine, was also present.

MECHANISM OF THE BROWN STAIN REACTION

A reasonable explanation for hemlock brown stain is that catechin, normally present in the sapwood along with a water soluble enzyme, is transported with moisture to the surface of the lumber during drying and, accumulating there with evaporation of the water, reacts with air to form a brown polymerized tannin. This theory was further supported by the higher-than-average extractive content found immediately beneath the brown-stained surface of the hemlock sapwood. A similar concentration of extractives on the surface of lumber was observed by Anderson and co-workers in the case of redwood seasoning (Anderson, *et al.*, 1960). It is also significant that those areas of hemlock most susceptible to brown stain formation, namely the surface of the heartwood-sapwood and the sapwood-cambium zones, contain higher concentrations of catechin and epicatechin (Figures 3 and 5) than other segments.

The chemical mechanism for brown stain formation is uncertain. It may involve condensation of the catechin monomers by quinone formation as outlined

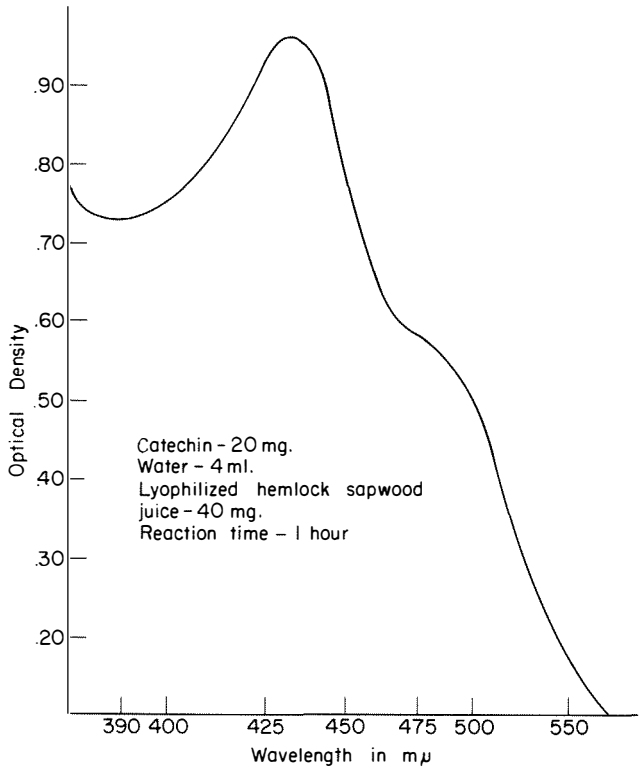

Figure 10. Catechin — brown pigment absorption spectrum.

for catechin polymers by Hathway (1962). Some evidence in support of this possibility is provided by the brown stain visible region absorption spectrum (Figure 10) showing a maximum in the 430 millimicron region with a shoulder near 500 millimicrons suggested as being indicative (Hathway, 1962) of the head-to-tail condensation of catechin polymers (Figure 11). Polymerization by extended quinone formation (Bocks, *et al.,* 1962) must also be considered a possibility (Figure 11). The oxidative degradation of o-quinones known to occur under mild conditions would further contribute to these discolorations.

While it is believed that this catechin enzyme reaction is chiefly responsible for hemlock brown stain pigment, other extractives such as epicatechin and the leucoanthocyanidins could contribute to the final colour by dehydration, polymerization, etcetera. For example, the stereo-chemical configuration of (−)epicatechin (2R,3R) permits the easy dehydration of the reactive flavene nucleus. Also, the presence of 3,4-*cis*-diols in the leucocyanidin isomers could result in dehydration to coloured cyanidin-type products (Hergert, 1960).

CHEMICALS WHICH INHIBIT BROWN COLOUR FORMATION IN CATECHIN SUBSTRATES

Laboratory Screening Tests

Since the ultimate purpose of this investigation was to find an economical remedy for the brown stain problem it was considered essential to devise a simple laboratory screening test for the large number of potentially-useful chemicals suggested by the chemical work. A test which fulfilled these requirements consisted of comparing the change in colour absorption of a standard solution of expressed hemlock sapwood juice prepared from a stable lyophilized solid with a duplicate

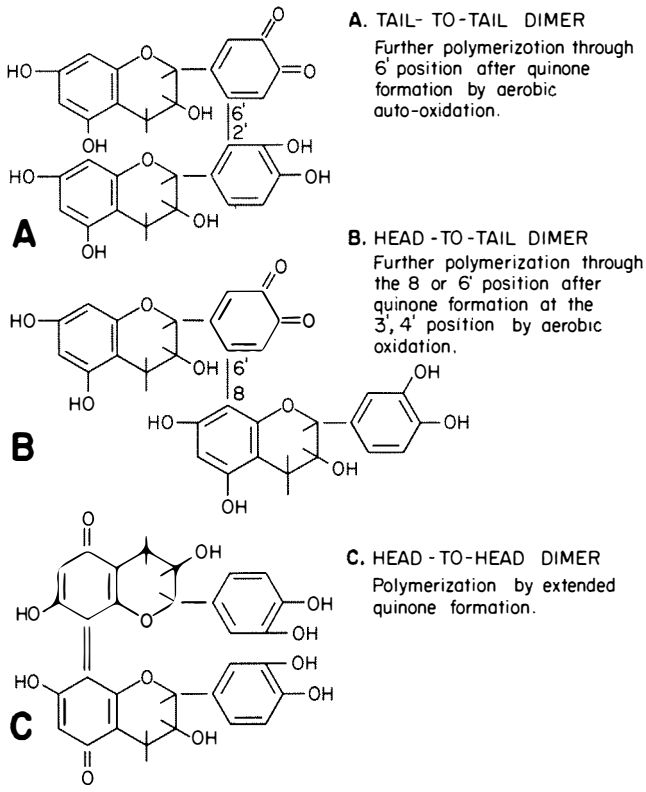

Figure 11. Possible structures for hemlock brown stain.

containing the proposed chemical. This change in colour with time — from an original pale yellow to a dark brown — was measured quantitatively in a Beckman DK2 Spectrophotometer in the range 900 to 330 millimicrons. Comparisons of the brown colour formation with and without the addition of the proposed control substance established whether inhibition was significant or not. Later, when the importance of catechin in the brown stain reaction had been established, a small amount of catechin was added together with the standard lyophilized sapwood juice and control chemical to accentuate the formation of the browning reaction. By means of this technique, a number of potential control chemicals were screened, and those showing brown colour control are listed in Table I.

Since the browning reaction of a phenolic compound occurs in an oxidizing environment and is frequently catalysed by a high pH in the presence of trace elements, chemicals were selected for their effect upon reduction, pH, and chelation ability with trace metals. Chemicals were rated from 1 to 4. A rating of 1, as shown in Table I, was given to chemicals which inhibited brown colour formation in the test for 24 hours as well as an initial lightening of the original pale yellow colour of the test solution. Both sulphurous acid and sodium bisulphite, which were pH-lowering agents as well as reducing agents, merited this high rating of 1, as did cysteine, which functioned by chemical combination (Roberts, 1959). Most of the effective chemicals were given a 2-rating, which meant inhibition for 24 hours but without the original colour being lightened. A rating of 3 or 4 meant moderate and slight inhibition of the brown colour respectively. Certain chemicals with more than one function such as salicylic acid, which is both an acid and a chelating agent, were classified under their separate functions.

It is evident from the results of this screening technique (Table I) that chemicals which lowered the pH of the resultant solution, such as acids or acid

TABLE I — Evaluation of Chemicals in Laboratory Screening Tests

Inhibited Brown Colour Formation

(a) Control by pH

sulphurous acid (1)*
sulphamic acid (2) F.T.
ascorbic acid (2)
sulphanilic acid (2)
benzoic acid (2)
monochloroacetic acid (2)
phthalic acid (2)
salicyclic acid (2)* F.T.
citric acid (2) F.T.
oxalic acid (2)* F.T.
ammonium bifluoride (2)
sodium fluoborate (2)
potassium acid phthalate (2)
ammonium sulphate (2)
aluminum potassium sulphate (2)
aluminum ammonium sulphate (2)
copper sulphate (2) F.T.

(b) Control by chelation

ethylenediaminetetraacetic acid (EDTA) (2)
γ-thujaplicin (2) F.T.
salicylic acid (2)* F.T.
salicylaldehyde (3)

(c) Control by reduction

sulphurous acid (1)*
sodium bisulphite (1)
waste sulphite liquor (2) F.T.
sodium sulphite (2)
zinc hydrosulphite (2) F.T.
sodium hydrosulphite (2) F.T.
hydroquinone (2) F.T.
formaldehyde (2) F.T.
sodium formaldehyde sulphonylate (3)
benzaldehyde (3)
paraldehyde (3)
paraformaldehyde (3)
oxalic acid (2)* F.T.
sodium oxalate (2) F.T.

(d) Control by chemical combination

cysteine (1)
sodium thioglycollate (2)

(e) Miscellaneous

dioxane (2) F.T.
thioacetamide (2)
thiourea (4) F.T.
dihydroquercetin (4)
potassium ferricyanide (3)

No Significant Inhibition

ammonium thiocyanate F.T.
copper acetate
dilauryl thiodipropionate (Dillydap)
2,6-ditertiarybutyl-p-cresol (Oxygard) F.T.
6-ethoxy-1,2-dihydro-2,2,4-trimethyl-quinoline (Oxyquin) F.T.
sodium fluoride
hypochlorous acid
sodium arsenate
hexamethylenetetramine
ammonium carbonate
ammonium hydroxide
diethylaminobenzaldehyde
ethylene glycol
sodium azide
α-conidendrin F.T.
potassium cyanide
acetanilide
acetamide
sodium acetate
dimethylsulphoxide F.T.
Versene — sodium salt of EDTA
papain
Santobrite — technical sodium pentachlorophenate 85%
hydrogen peroxide

NOTES:

* Appeared under more than one heading because of the dual function of the chemical.
F.T. also used in pilot scale field tests.
(1) inhibited brown coloration for more than 24 hours and also lightened colour already formed.
(2) inhibited brown coloration for more than 24 hours.
(3) moderate inhibition of brown coloration.
(4) slight inhibition of brown coloration.

salts, inhibited brown colour formation. On the other hand, chemicals which raised the pH generally accelerated brown colour formation. This pH dependence seemed reasonable in view of the behaviour of (+)catechin under various reaction conditions. Hathway and Seakins (1955) showed there were three types of reactions: an acid-catalysed polymerization; a reaction under alkaline conditions which involved ring fission; and an auto-oxidation at pH 6 to pH 9 to form a polymeric tannin.

The above reasoning was found to be true in that, if an enzyme system were involved, chemicals which deprived this biochemical system of trace elements (such as iron, etcetera) would reduce brown colour formation. Good chelating agents such as γ-thujaplicin and ethylenediaminetetraacetic acid (EDTA) did inhibit the formation of brown colours. Unfortunately, EDTA has poor solvent solubility and its sodium salt (Versene) is ineffective due to the higher pH of its aqueous solution.

As would be expected, reducing agents generally were found to inhibit brown colour formation. Some of these which also lowered the pH, such as sodium bisulphite, oxalic acid, and sulphurous acid were particularly effective.

The fourth group of chemicals which inhibited brown colour formations were collected under a general category of chemical combination. Cysteine, and probably sodium thioglycollate, react with pyrocatechol groups (Roberts, 1959) to form colourless compounds which cannot be converted to brown orthoquinones.

The miscellaneous group contains chemicals which inhibit brown colour for reasons other than those already discussed or for reasons unknown. Thiourea, although highly rated by Evans and Halvorson (1962) showed only slight inhibition under the described test conditions. This finding is in harmony with industrial results, since thiourea is no longer used for brown stain control. Its role in brown stain inhibition is probably that of an antioxidant.

The colour-inhibiting property of dihydroquercetin, a normal component of Douglas-fir wood (Pew, 1948) has interesting implications in that, although Douglas-fir sapwood contains catechin (Hergert, 1960), this species exhibits a low incidence of brown stain. It could be reasoned that in spite of its low rating of 4, dihydroquercetin occurs in concentrations of up to 0.56 per cent in fir sapwood and thus could be significant in preventing brown stain. Other factors, such as large differences in moisture content between unseasoned fir and hemlock, must also be considered. The reason for its inhibition of brown colour is not certain, but may be due simply to the inhibition of quinone formation described for other phenols by James, *et al.*(1938) and Rich *et al.*(1954).

The reason for the effectiveness of dioxane and potassium ferricyanide in the screening test for brown colour control chemicals is unknown.

Chemicals which did not prevent hemlock sapwood stain — and in some cases accentuated it — such as ammonium hydroxide, ammonium carbonate, and hexamethylenetetramine are also included in Table I.

Field Tests on Lumber

A number of chemicals were applied to green lumber in an attempt to inhibit hemlock sapwood brown stain under actual field conditions. These compounds are identified in Table I by the letters F.T. Variations of testing with proposed chemicals were tried. The following small-scale testing technique was found to be satisfactory. Freshly-cut lengths of hemlock lumber, 2 by 4 inches by 8 feet long, which had not been dipped or sprayed with sapstain or mould preventive chemicals, were cut into two pairs of matching pieces, approximately 2 feet in length. In all, 20 pieces

for the proposed test, together with the same number of matching pieces for controls, were used in each experiment. Application of the control chemical in concentrations of from 2.5 to 10 per cent solution by weight was made by either dipping for 30 seconds or by spraying with an atomizer. Periodic inspection was made to determine the effectiveness of the treatment.

Results of the field tests can be summarized as follows. None of the control chemicals used in the field tests showed more than a short initial improvement over the controls. These results emphasize the great difficulty in maintaining an effectively high concentration of control chemical on the surface of green hemlock lumber which, during yard seasoning, is being supplied with fresh amounts of catechin and enzyme because of continuing moisture movement to the surface. Undoubtedly, the very high initial moisture content of green hemlock compared with other species is important, accounting for the prevalence of the problem with hemlock.

CONCLUSIONS AND RECOMMENDATIONS

(1) Hemlock sapwood brown stain, unlike fungal stain, is entirely confined to the surface of the wood and can be removed permanently by planing, provided the lumber remains dry. The objectionable colour is due to an innocuous brown pigment, chemically indistinguishable from tannin.

(2) Inner heartwood of western hemlock is characterized by lignans such as matairesinol, hydroxymatairesinol, and conidendrin, whereas the outer sapwood contained monomeric phenols such as catechin, epicatechin, and leucoanthocyanidins, as well as polymeric leucoanthocyanidins. An unexpectedly wide sapwood-heartwood transition zone in one tree contained phenolic extractives common to both heartwood and sapwood.

(3) An examination of the seasonal variation of the sapwood showed that during the period of dormancy from November to February, there was relatively little change in the concentration of phenolic extractives from a living tree. Beginning, however, in March a rise in concentrations was noted which continued to maximum values for all seven major phenolic constituents during April, May and June. Concentrations then declined to lower but still appreciable levels for the remaining months of July, August, September and October. Assuming a time lag of three to four months in log processing, these higher extractive concentrations found early in the year may contribute to the increased incidence of brown stain noticed during the late summer.

(4) Of the major phenolic extractives found in sound hemlock wood, only catechin and, to a far lesser extent, leucocyanidin, reacted with expressed hemlock juice to form brown pigments. It is suggested, therefore, that hemlock brown stain is due to the interaction of an enzyme system with catechin both of which are normal constituents of sound hemlock sapwood. The possibility of some contribution by epicatechin and 3,4-*cis*-diol isomers of leucocyanidin to the final coloured brown stain pigment by other mechanisms is not excluded (Hergert, 1960).

(5) Chemicals were found to inhibit brown colour formation in a laboratory screening test according to their effect on pH, chelation, reduction, and chemical combination. Best results were obtained from reducing agents and acidic chemicals which maintained the pH between 4 and 6.

(6) Large-scale tests with chemicals found to be effective in the laboratory screening tests were not successful in the field. This may be explained in part by the fact that the moisture content of western hemlock, compared with other species, is very high and during normal air-seasoning there is a long period of moisture movement to the surface. Thus, it is very difficult to

maintain concentrations of the control chemical sufficiently high enough to inhibit brown stain during this long period. In addition, the incompatibility of most brown stain control chemicals which are acids, with the alkaline pentachlorophenol solutions widely used for sapstain and mould prevention aggravates this problem.

It should be emphasized that hemlock sapwood brown stain is an innocuous tannin-like surface stain and is in no way connected with decay, sapstain, or mould. Also, since the stain can be permanently removed by planing, provided the lumber is dry, it is not detrimental to the end utilization of the species except where light colour on rough lumber is a necessity.

Since it has been shown that high pH conditions favour the formation of hemlock sapwood brown stain, it is recommended that strict controls on the preparation and application of alkaline pentachlorophenol sapstain and mould solutions be maintained.

Until an acidic sapstain and mould preventive solution is developed, the incorporation of a control chemical in a dip or spray treatment of the type currently in use would not appear promising. In the meantime, while the practice of end-painting to provide uniform colour and to decrease end-checking does not solve the problem of brown stain on the sides of the lumber, it is used widely by the lumber industry.

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