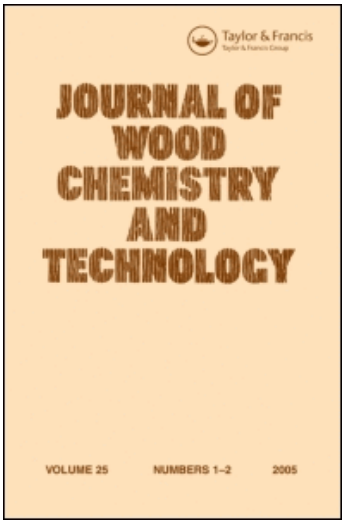

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COLOR FORMATION IN WESTERN HEMLOCK

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ABSTRACT

Loss of brightness in mechanical pulp as a result of storage time of Western Hemlock chips has been correlated with a decline in d-catechin in the chips. Oxidative polymerization of the d-catechin to an insoluble polymer containing catechol groups is suggested as the cause of the brightness loss.

INTRODUCTION

Western Hemlock has a long history of observation of color development in solid wood products[1] and in groundwood[2]. It is generally concluded that at least part of this coloration is due to the presence of certain flavonoids among the extractives present in the wood and bark of this species. Evans, investigating the cause of brown stain formation in Western Hemlock lumber, implicated bacterial infection of the wood followed by oxidation of sap-soluble components as the mechanism responsible and also showed antioxidants to be effective in controlling the stain formation[2]. Barton, studying the same problems, has specifically identified d-catechin as a brown stain precursor using a crude Hemlock enzyme preparation to develop the color. The color formation required relatively high concentrations of d-catechin and was best inhibited or controlled by low pH and antioxidants.

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Polcin and Rapson[3] have shown that the acetone-water extracts from Western Hemlock groundwood are responsible for loss of brightness of the pulp on aging. The extracted pulp has better brightness and the extracts were very sensitive to oxidation, discoloring rapidly on exposure to air. The discoloration was accelerated by the presence of peroxide-forming compounds such as unsaturated fatty acids[4]. Among the flavonoids in Western Hemlock, the order of importance in discoloration was shown to be o-diphenols (d-catechin)>3-hydroxy flavanones>flavones.

Barton has studied the influence of a variety of chemical additives in controlling loss of brightness during refining of mechanical pulp from Hemlock, obtaining best results with antioxidants such as sulfur dioxide and thioglycolic acid, followed by metal chelating agents[5]. Recently, Springer has shown bisulfite treatment of hemlock chips to be effective in controlling brightness loss during outside chip storage[6].

Our interest in Western Hemlock is mainly concerned with the changes in the initial brightness of refiner mechanical pulp, as a function of the storage time of the chips, and in how the polyphenolic extractive d-catechin may be involved in this loss of brightness. Thus, fresh Hemlock chips have been placed in a chip pile and monitored for RMP brightness and for d-catechin content as a function of chip age.

RESULTS AND DISCUSSION

HPLC Analysis of d-Catechin

After a chip sample is exhaustively extracted with ethanol, quantification of d-catechin in the complex extract solution can now be done using HPLC. The HPLC technique developed involves only direct injection of the diluted extract solution. As a result, errors involving steps for further purification are

eliminated. The separation of d-catechin from the other ethanol extractives is complete. Therefore, the concentration of d-catechin can be accurately measured as a function of its peak area by relating it to a calibration curve made from a d-catechin standard.

Pulp Brightness vs. Chip Storage Time

Brightness determinations were made on refiner mechanical pulp made from stored Hemlock chips sampled at time intervals during a summer and a winter chip storage period. Since we were particularly interested in initial brightness loss following chipping, every effort was made to process standing trees to chips and to prepare the first samples for analysis as rapidly as possible. This was done in about four hours from felling time.

Brightness values were found to decline from about 59 to 53 in a period of two weeks of storage, and remained stable in the 53 to 52 range for the duration of the storage periods which were about six weeks. The data from the two storage periods are tabulated in Table 1 and plotted in Figure 1.

The brightness data has been evaluated by standard curve fitting techniques and found to be best correlated by the logarithmic equation $y = a + b\ (\ln x)$. Using the constants $a = 57.1$ and $b = -1.4$, the curve fit gives an r value of 0.79. The principal feature of these data is the extremely rapid initial loss of brightness, i.e., in three days the brightness has decreased 5 to 6 points.

Effect of Hemlock Chip age on d-Catechin Concentration

d-Catechin concentration was also determined on the above chip samples using the HPLC method, and is tabulated in Table 1 and plotted in Figure 1. Following chipping, the d-catechin concentration decreases rapidly from the 0.3% range down to 0.1%

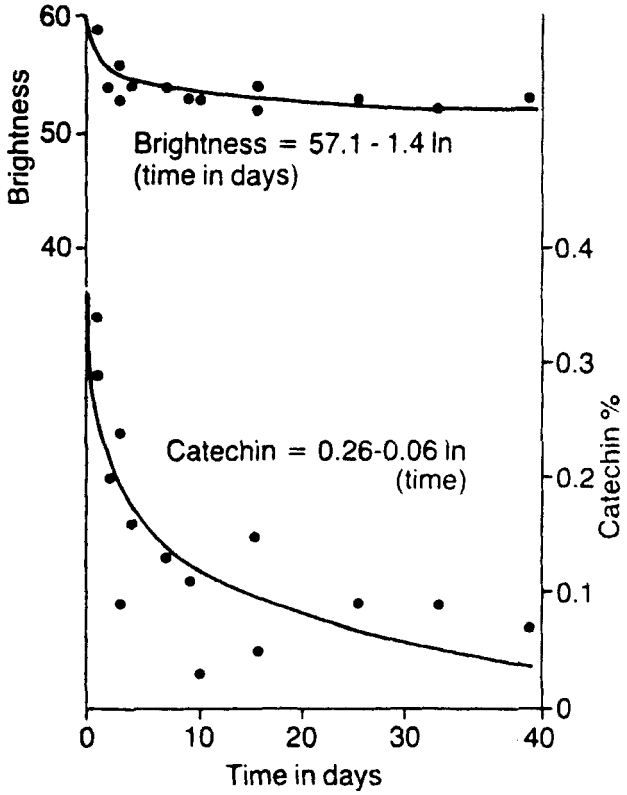

Figure 1. RMP Brightness and d-catechin concentration of Hemlock's Chips and Pulp.

where it is fairly stable. The data have been curve fitted giving a logarithmic curve (d-catechin) = 0.26 - 0.06 ln(time) with an r value of 0.81.

Brightness Loss and d-Catechin

Oxidation of d-catechin to brown colored material may in part be responsible for the loss of brightness. An indication of the extent of involvement of d-catechin in RMP brightness is how well the formation of colored material, as measured by loss of the d-catechin monomer, correlates with the decline in brightness.

Table 1

Effect of Chip Age on d-Catechin and RMP Brightness

Sample Day	% d-Catechin Summer	% d-Catechin Winter	Brightness Summer	Brightness Winter
1	0.29	0.34	59	59
2	--	0.20	--	54
3	0.09	0.24	53	56
4	--	0.16	--	54
7	--	0.13	--	54
9	0.11	--	53	--
10	--	0.03	--	53
15	0.05	0.15	52	54
24	0.09	--	53	--
31	0.09	--	52	--
39	0.07	--	53	--

Brightness is plotted vs. d-catechin concentration in Figure 2, and the correlation was tested by linear regression analysis, giving an r value of 0.93 indicating satisfactory correlation.

Oxidation of d-Catechin

The darkening of freshly cut Hemlock observed in this study fits the pattern of a classical enzymatic browning reaction in which d-catechin is oxidatively polymerized to brown colored polymers. We have examined Hemlock cambial area sap using the syringaldazine reagent[7]. This reagent with added hydrogen peroxide gives a strong response, indicating the presence of a

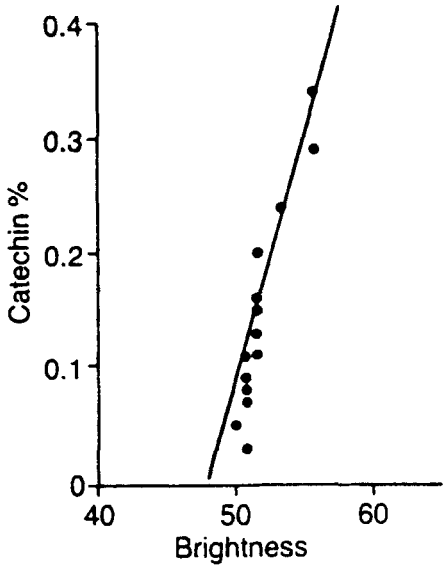

Figure 2. Correlation of brightness and d-catechin concentration.

peroxidase enzyme. Treatment of the cambial area of freshly debarked Hemlock wood with mushroom peroxidase and hydrogen peroxide causes brown coloration.

It is not clear whether the color forming reaction is catalyzed by enzymes or is direct air oxidation. Both pathways have been shown to give the same product, i.e. d-catechin undergoes oxidation of the catechol ring followed by dimerization.[8]

Several reports on the chemistry of d-catechin oxidation have appeared since Hathway's initial observations which describe the reaction sequence in detail and substantiate his proposals; these are summarized in Figure 3.

d-Catechin is oxidized only in the B-ring as shown by epr spectra[9] to an ortho quinone which has been trapped by reaction with benzene sulfinic acid[10]. The quinone condenses, probably by

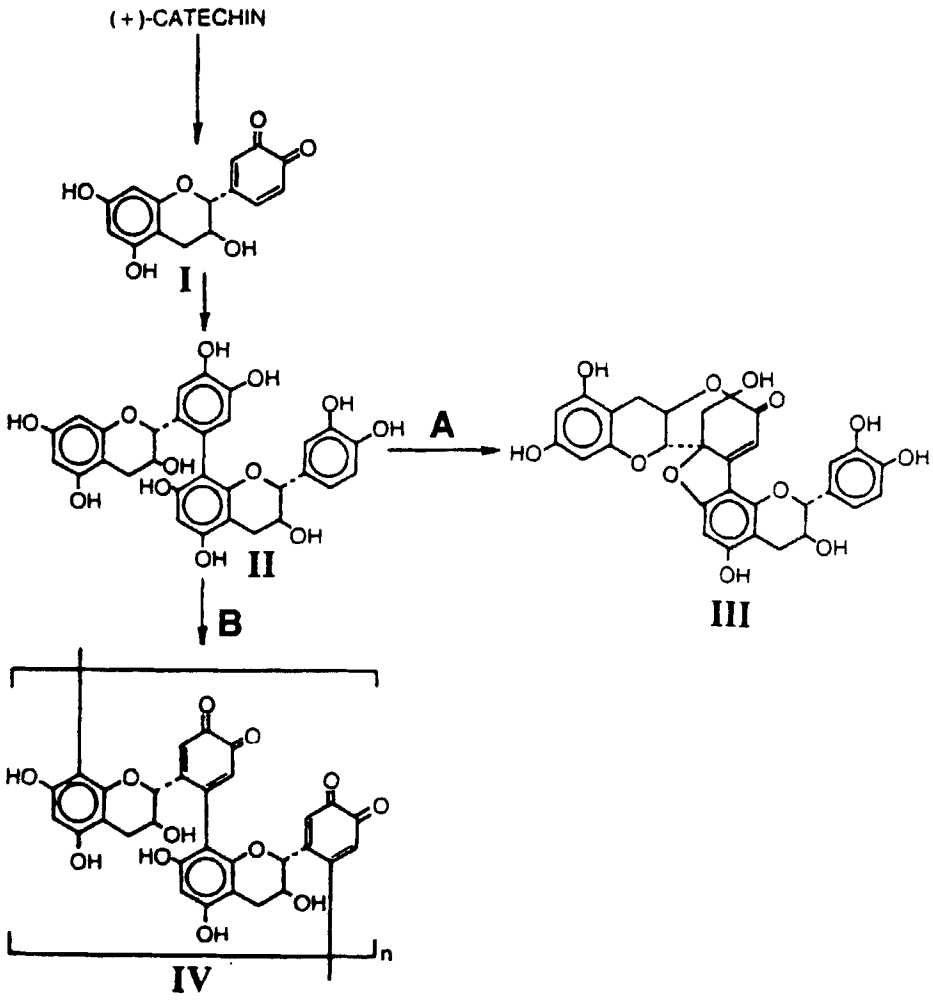

Figure 3. d-Catechin oxidation to colored polymers.

an ionic mechanism, with the A-ring of another d-catechin forming only 6' to 8 linked dimers II[11]. Further oxidation of II to an ortho quinone, pathway A, is verified by the formation of dimer III in 10 percent yield from d-catechin oxidation[12]. Structure

IV, formed by pathway B, is a good model for the structure of the brown polymer formed in Western Hemlock[13].

CONCLUSIONS

The use of HPLC analysis provides an easy means to determine the amount of d-catechin present in Hemlock wood. This has been applied to Hemlock chips during storage and the decline in d-catechin concentration has been found to correlate closely to the initial loss of brightness of mechanical pulps produced from the chips. This correlation is interpreted as providing support to the idea that in fresh chips d-catechin is oxidized, giving brown colored polymers which in turn are retained in the wood fibers and cause brightness loss.

EXPERIMENTAL

Materials

Freshly felled Western Hemlock Trees were immediately debarked by hand, washed and chipped in a Black Clawson unit. The fresh chips were placed outdoors in a cone-shaped pile. In the present work, 6 log bolts from three trees were used to prepare a pile of four foot height and a seven foot base.

Equipment

The chips were converted to refiner groundwood pulp using a Sprout-Waldron 12" Laboratory Refiner fitted with number 18034NH plates.

Liquid chromatography (HPLC) was done with a Waters 262 instrument, equipped with an ISCO 1840 detector and a Hewlett-Packard 3390A integrator. The column used was a 30 cm uBondapak C-18 with 10 u particle size packing.

Brightness measurements were made on an Alinco brightness meter.

Procedures

Chip samples (600 gms) were brought to the laboratory and divided as follows: a) 100 gms were weighed out for moisture determination; b) 120 gms were placed in a Kontes Soxhlet extractor and extracted 7 hours with 95% ethanol for catechin determination; c) 100 gms were soaked for one hour in a 0.1% EDTA solution at pH 6.5, then were passed through the refiner at settings of 0.060", 0.030" and 0.010". A brightness loss of about 2 units occurs across the refining step without the EDTA treatment. Shives were removed with a flat screen and five handsheets were made from the pulp. These were air dried overnight and the brightness determined.

For d-catechin analysis, the alcohol extract was made up to one liter in a volumetric flask and a 50 cc aliquot was removed and evaporated to dryness on a rotavap. The solids were dissolved in 2 cc of methanol, and 15 ul was injected into the HPLC. Elution begins with 1:9 methanol:2% HOAc held constant five minutes, then changed by a gradient to 9:1 methanol: 2% HOAc over 25 minutes to elute the sample. The detector was set at 280 nm. The d-catechin quantity was estimated from the peak area on the chromatogram using a grams d-catechin vs. peak area curve and correcting for moisture content of the original sample.

The procedures using syringaldazine to test for peroxidase activity were similar to those found in reference 7.

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