Sapwood and heartwood groundwood samples were prepared separately from a second growth, coastal range, young Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco). The bleaching responses of these two groundwoods to zinc hydrosulfite were examined, and the roles of both dihydroquercetin and quercetin in this bleaching reaction were investigated.

Heartwood groundwood was identified to be the major culprit in the bleaching of Douglas-fir groundwood. For this particular sample, the bleachability of its heartwood groundwood was inversely linearly proportional to the pulp freeness at the lower freeness levels.

The addition of pure dihydroquercetin to sapwood groundwood had a minor effect on both brightness and bleachability of this groundwood, but the addition of quercetin resulted not only in decreased
unbleached brightness but also in insignificant brightness gain during groundwood bleaching with zinc hydrosulfite.

Paper and gas chromatographies were employed for the quantitative determinations of dihydroquercetin present in heartwood groundwoods treated in various ways, such as bleaching and/or aging. The brightnesses and bleachabilities of these heartwood groundwoods showed poor correlation with their dihydroquercetin contents.

The effect of aging and the bleached brightness reversion were similar for both sapwood and heartwood groundwoods. Solvent extractions did not improve either the unbleached or bleached brightness of heartwood groundwood.

No commercially feasible method of improving the brightness of Douglas-fir heartwood groundwood to a commercially acceptable level has been developed in this research.
An Investigation of the Effect of Dihydroquercetin and Quercetin on Bleaching of Douglas-Fir Groundwood

by

Tommy Yi Meng

A THESIS submitted to Oregon State University

in partial fulfillment of the requirements for the degree of

Master of Science

June 1972
APPROVED:

Signature redacted for privacy.

Associate Professor of Pulp and Paper in charge of major

Signature redacted for privacy.

Head of Department of Forestry

Signature redacted for privacy.

Dean of Graduate School

Date thesis is presented February 29, 1972

Typed by Muriel Davis for Tommy Yi Meng
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>LITERATURE REVIEW</strong></td>
<td>3</td>
</tr>
<tr>
<td>Effects of Polyphenolic Extractives on Processing of</td>
<td>3</td>
</tr>
<tr>
<td>Coniferous Wood for Pulp and Paper Manufacturing</td>
<td></td>
</tr>
<tr>
<td>Distribution of Dihydroquercetin in Douglas-fir</td>
<td>4</td>
</tr>
<tr>
<td>Bleaching of Douglas-fir Groundwood</td>
<td>5</td>
</tr>
<tr>
<td>Bleaching of Coniferous Groundwood Other Than</td>
<td>7</td>
</tr>
<tr>
<td>Douglas-Fir</td>
<td></td>
</tr>
<tr>
<td>Reductive Bleaching with Zinc Hydrosulfite</td>
<td>10</td>
</tr>
<tr>
<td>Historical Review</td>
<td>10</td>
</tr>
<tr>
<td>Hydrosulfite Groundwood Bleaching Variables</td>
<td>11</td>
</tr>
<tr>
<td>Reaction Mechanism</td>
<td>13</td>
</tr>
<tr>
<td><strong>EXPERIMENTAL PROCEDURE</strong></td>
<td>16</td>
</tr>
<tr>
<td>Sample Selection</td>
<td>16</td>
</tr>
<tr>
<td>Sample Preparation</td>
<td>16</td>
</tr>
<tr>
<td>Beater Processing of Pulp</td>
<td>17</td>
</tr>
<tr>
<td>Testing for Iron Contamination</td>
<td>19</td>
</tr>
<tr>
<td>Reflectance Testing of Brightness Handsheets</td>
<td>20</td>
</tr>
<tr>
<td>Purification of Dihydroquercetin</td>
<td>20</td>
</tr>
<tr>
<td>Aging of Groundwood</td>
<td>21</td>
</tr>
<tr>
<td>Bleaching of Groundwood</td>
<td>21</td>
</tr>
<tr>
<td>Extractives Preparation</td>
<td>23</td>
</tr>
<tr>
<td>Chromatography</td>
<td>24</td>
</tr>
<tr>
<td>Paper Chromatography</td>
<td>24</td>
</tr>
<tr>
<td>Gas-Liquid Chromatography</td>
<td>25</td>
</tr>
<tr>
<td><strong>RESULTS AND DISCUSSION</strong></td>
<td>28</td>
</tr>
<tr>
<td>The Bleaching Response of Sapwood Pulp</td>
<td>28</td>
</tr>
<tr>
<td>The Bleaching Response of Heartwood Pulp</td>
<td>28</td>
</tr>
<tr>
<td>A Comparison Between the Two Douglas-Fir Groundwoods</td>
<td>31</td>
</tr>
<tr>
<td>Bleaching of Sapwood and Heartwood Mixture</td>
<td>34</td>
</tr>
<tr>
<td>Reaction of Dihydroquercetin and Quercetin with Zinc Hydrosulfite</td>
<td>36</td>
</tr>
<tr>
<td>Effect of Dihydroquercetin on Bleaching Response of Sapwood Groundwood</td>
<td>38</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION (continued)

- Effect of Quercetin on Brightness and Bleachability of Sapwood Groundwood 41
- Correlation of Dihydroquercetin Content with Brightness and Bleachability 44
- Effect of Solvent Extractions on Bleachability 46
- Effect of Aging on Bleachability 47
- Bleached Brightness Reversion 49

SUMMARY AND CONCLUSION 52

BIBLIOGRAPHY 55
<table>
<thead>
<tr>
<th>Table</th>
<th>Physical tests on Douglas-fir groundwood.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Bleaching of western hemlock groundwood.</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Groundwood refining conditions.</td>
<td>9</td>
</tr>
<tr>
<td>3.</td>
<td>Bleaching of Douglas-fir sapwood groundwood pulp.</td>
<td>17</td>
</tr>
<tr>
<td>4.</td>
<td>Bleaching of Douglas-fir heartwood groundwood pulp.</td>
<td>29</td>
</tr>
<tr>
<td>5.</td>
<td>The influence of heartwood groundwood on the bleachability of sapwood groundwood.</td>
<td>30</td>
</tr>
<tr>
<td>6.</td>
<td>Effect of dihydroquercetin on brightness and bleachability of sapwood groundwood.</td>
<td>35</td>
</tr>
<tr>
<td>7.</td>
<td>Effect of quercetin on brightness and bleachability of sapwood groundwood.</td>
<td>39</td>
</tr>
<tr>
<td>8.</td>
<td>Effect of acetone extraction on brightness of unbleached groundwood.</td>
<td>42</td>
</tr>
<tr>
<td>9.</td>
<td>Dihydroquercetin content in heartwood groundwood.</td>
<td>44</td>
</tr>
<tr>
<td>10.</td>
<td>Effect of solvent extraction on bleachability of heartwood groundwood.</td>
<td>46</td>
</tr>
<tr>
<td>11.</td>
<td>Effect of aging on brightness and bleachability.</td>
<td>47</td>
</tr>
<tr>
<td>12.</td>
<td>Effect of acetone extraction on brightness and bleachability of aged heartwood groundwood.</td>
<td>48</td>
</tr>
<tr>
<td>13.</td>
<td>Bleached brightness reversion.</td>
<td>50</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Peroxide brightening</td>
<td>8</td>
</tr>
<tr>
<td>2.</td>
<td>Flow sheet for production and treatment of Douglas-fir refiner groundwood</td>
<td>18</td>
</tr>
<tr>
<td>3.</td>
<td>Dihydroquercetin purification scheme</td>
<td>22</td>
</tr>
<tr>
<td>4.</td>
<td>Calibration curve for a quantitative analysis of dihydroquercetin</td>
<td>27</td>
</tr>
<tr>
<td>5.</td>
<td>Bleachability of sapwood and heartwood groundwoods vs. freeness.</td>
<td>32</td>
</tr>
<tr>
<td>6.</td>
<td>The influence of dihydroquercetin on brightness and bleachability of sapwood groundwood</td>
<td>40</td>
</tr>
<tr>
<td>7.</td>
<td>Oxidation of dihydroquercetin to quercetin</td>
<td>41</td>
</tr>
<tr>
<td>8.</td>
<td>The influence of quercetin on brightness and bleachability of sapwood groundwood</td>
<td>43</td>
</tr>
</tbody>
</table>
AN INVESTIGATION OF THE EFFECT OF Dihydroquercetin AND Quercetin ON BLEACHING OF DOUGLAS-FIR GROUNDWOOD

INTRODUCTION

Extensive stands of Douglas-fir are found throughout the Pacific Northwest, which because of its prevalence and excellent structural qualities, makes it the major lumber species in this region. It is the principal species used in the plywood industry, accounting for over 95% of this country's past softwood plywood production. Although its use as a pulpwood is confined almost entirely to the kraft process, Douglas-fir residues (chips and sawdust) are cheaper and more readily available than those of any other softwood. However, Douglas-fir is known to make dark colored groundwood that is difficult to bleach by conventional processes.

Because of the development of high yield pulping processes and increasing competition in some of the lumber's traditional markets, pulp bleaching difficulties due to the presence of pigments or their precursors in wood are often accentuated by the new high yield processes because more of the minor components are retained by the pulp. Little is known about the pigments and pigment precursors in many important woods, the need for knowledge of these minor components is of growing practical significance.
The objective of this study was to verify whether dihydroquercetin, one of the major flavonoids, and its oxidized form i.e. quercetin, have any effect on bleaching of Douglas-fir groundwood.

Two basic goals were set:

1. To establish the bleaching responses of groundwoods from Douglas-fir heartwood and sapwood respectively.

2. To determine the role of dihydroquercetin and quercetin in interfering with bleaching of Douglas-fir groundwood by establishing the correlation between the amount of a flavonoid and its bleaching response.
Effects of Polyphenolic Extractives on Processing of Coniferous Wood for Pulp and Paper Manufacturing

Wood extraneous components are formed as a by-product of the elementary physiological processes of tree growth, but they do not form a structural part of the macromolecular or highly polymeric cell wall constituents. They occur in part as extractives, meaning fractions that may be removed by various solvents without seriously affecting the basic cell wall structure.

Owing to solubility criteria or location, not all extraneous components are obtained as extractives. Various coniferous wood extractives have been recovered and studied, usually as components in mixtures. They are known to vary in amount, diversity, and complexity, and, in some few cases, as regards location and associations.

Although coniferous wood extractives occur in small amounts, they can influence almost every stage of pulp, paper and cellulose derivative processing. Effects ranging from processing restrictions to instability of products have been extensively reviewed (Hillis, 1962). Examples include selection of pulping process, chemical consumption and yield from cooking, resistance to bleaching and color permanence, resin coagulation and self-sizing, and foaming in pulp and liquor recovery streams.
In particular, Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco) flavonoids affect pulp processing in several serious ways. Metallic contamination of wood and pulp can occur during mechanical comminution stages, and oxidation during this stage can create less soluble, colored compounds. The yellow color of Douglas-fir acid sulphite pulps has been related to conversion of dihydroquercetin to quercetin during cooking (Geissman, 1962; Hodge, 1954; Kurth, 1953).

**Distribution of Dihydroquercetin in Douglas-Fir**

Douglas-fir flavonoids contain dihydroquercetin, dihydrokaempferol, pinobanksin and quercetin (Geissman, 1962; Hemingway, 1970; Squire, 1967). Dihydroquercetin (taxifolin) has been documented frequently as the major flavonoid of Douglas-fir heartwood in quantities as high as 2%, and up to 12% in the bark (Rydholm, 1965). The minor flavonoids, dihydrokaempferol (aromadendrin) and pinobanksin have been less studied in this regard, and the maximum quantitative value for these two flavonoids are 0.3% and 0.1% respectively (Kurth, 1953; Pew, 1948; Squire, 1967). Squire, Swan, and Wilson (1967) observed significant amounts of quercetin (0.1%) existing in Douglas-fir heartwood. In a recent study of heartwood formation by Hemingway and Hillis (1970), they claimed that there was no quercetin observed in their samples of Douglas-fir heartwood.
Gardner, Barton (1960) and Hancock (1957) found that the dihydroquercetin content of Douglas-fir varies considerably within trees and between trees, increasing from the pith toward the periphery in a somewhat stepwise irregular manner to a maximum at the heartwood-sapwood boundary, and falling off sharply in the sapwood.

**Bleaching of Douglas-Fir Groundwood**

The physical properties of Douglas-fir groundwood pulps are listed in Table 1 (Textor, 1957).

Douglas-fir refiner groundwood was low in brightness, both unbleached and bleached, while the brightness gain by bleaching was also lower than anticipated from hemlock groundwood bleaching experience.

It has been generally known that Douglas-fir heartwood is darker and frequently more resistant to penetration than sapwood. Bublitz (1967) found that sapwood groundwood was easy to bleach, but heartwood groundwood was difficult. Brightness were 52 and 60 for unbleached and bleached sapwood vs. 34 and 39 for unbleached and bleached heartwood respectively.

Styan (1970) hypothesized that the low brightness of Douglas-fir groundwood is due to the oxidation products of the flavanones of Douglas-fir. He also pointed out that metal-flavonoid complexes also contribute, but to a considerably lower extent. He concluded from his
Table 1. Physical tests on Douglas-fir groundwood.

<table>
<thead>
<tr>
<th>Freeness (cc CSF)</th>
<th>TAPPI factors</th>
<th>Strength (% basis)</th>
<th>Unbleached brightness</th>
<th>Bleached brightness</th>
<th>Opacity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Burst m²/cm²</td>
<td>Tear 100dm²</td>
<td>Burst m</td>
<td>Tear</td>
<td>Tensile m</td>
</tr>
<tr>
<td>242</td>
<td>8</td>
<td>66</td>
<td>17</td>
<td>108</td>
<td>14</td>
</tr>
<tr>
<td>180</td>
<td>9</td>
<td>49</td>
<td>21</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>90</td>
<td>12</td>
<td>66</td>
<td>28</td>
<td>108</td>
<td>26</td>
</tr>
</tbody>
</table>

* Pulp bleached with 1% ZnS₂O₄.
model studies, by adding various amount of quercetin to western hemlock groundwood, resulting in a bleaching response similar to that of Douglas-fir groundwood, that 100 to 200 year old Douglas-fir contains 4 to 5% flavonoid material as shown in Figure 1. This large flavonoid content results in very poor response to oxidizing agents such as hydrogen peroxide. He also proposed that the majority of chromophores in Douglas-fir groundwood are condensed products from polyphenol autoxidations. Model compound studies show that these condensed chromophores are not very responsive to hydrosulfite bleaching either.

Styan (1971) also proved that young Douglas-fir is more easily bleached than old growth wood, implying a relationship between flavonoid content and bleaching inhibition.

Since dihydroquercetin, as the major flavonoid of Douglas-fir, is readily converted in high yield to quercetin and is well recognized as the major hindrance in bisulfite pulping reactions (Gregory, et al., 1957; Kurth, 1951, 1953), it could be one of the major causes of the inhibited bleaching of Douglas-fir groundwood.

**Bleaching of Coniferous Groundwood Other Than Douglas-Fir**

More recently, Rapson et al. (1965, 1968, 1969, 1971) published a series of articles in which they extensively studied the bleaching
Figure 1. Peroxide brightening. (Condensed from Styan's unpublished paper, "Brightening of Douglas-fir groundwood," 1971).
characteristics of western hemlock groundwood prepared from heartwood and sapwood respectively. The groundwoods were bleached with zinc hydrosulfite, peroxide, peracetic acid and two-stage bleaches, peroxide-hydrosulfite and peracetic acid-hydrosulfite.

They found that western hemlock heartwood and sapwood groundwoods displayed only very small differences in brightness and responded quite similarly to the hydrosulfite and the oxidizing bleaches (Table 2).

Table 2. Bleaching of western hemlock groundwood

<table>
<thead>
<tr>
<th>Bleaching agent</th>
<th>Brightness</th>
<th>Sapwood</th>
<th></th>
<th>Heartwood</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before aging</td>
<td>After aging</td>
<td>Before aging</td>
<td>After aging</td>
<td></td>
</tr>
<tr>
<td>(blank)</td>
<td>53.0</td>
<td>49.0</td>
<td>52.2</td>
<td>48.1</td>
<td></td>
</tr>
<tr>
<td>1% ZnS$_2$O$_4$</td>
<td>61.4</td>
<td>54.0</td>
<td>60.6</td>
<td>53.1</td>
<td></td>
</tr>
<tr>
<td>1% H$_2$O$_2$</td>
<td>61.5</td>
<td>57.8</td>
<td>57.4</td>
<td>54.4</td>
<td></td>
</tr>
<tr>
<td>1% H$_2$O$_2$ + 1% ZnS$_2$O$_4$</td>
<td>61.3</td>
<td>57.7</td>
<td>57.3</td>
<td>53.9</td>
<td></td>
</tr>
</tbody>
</table>

Note: Aged for 18 hours in an air-circulating oven at 105°C (Wayman, et al., 1968).

The polyphenolic extractives in western hemlock heartwood have been identified as conidendrin and matairesinol. They were suspected of consuming bleaching agents and sequestering metals from grinding, which form colored compounds very difficult to bleach, or catalyze decomposition of bleaching agents.
The application of ethylene diamine tetraacetic acid (EDTA) removed most of the manganese present in western hemlock groundwood pulps and improved the brightness. Organic solvent extraction following EDTA extraction resulted in no further response to bleaching agents, suggesting that these chromophores either grafted onto lignin or in a homopolymeric form which could not be removed efficiently by solvent extractions (Polcin et al., 1969, 1971).

**Reductive Bleaching with Zinc Hydrosulfite**

**Historical Review**

The reducing agents used in commercial bleaching of groundwood pulps include sulfurous acid, its salts (sodium and calcium sulfite and bisulfite), and the products of its reduction with zinc and sodium to form dithionites, which are more commonly called "hypo-sulfites" and "hydrosulfites."

The hydrosulfites can be considered to be the most important of the reducing agents used in pulp bleaching. Practically all the newsprint manufactured on the west coast of North America is made with groundwood bleached with zinc hydrosulfite, because it offers the advantage of greater stability than the sodium salt, particularly at low pH and at high bleaching temperature. Also, it can be formed readily by reduction of sulfurous acid or sulfur dioxide with zinc dust:
Zn + 2 H₂SO₃ = ZnSO₄₂ + 2 H₂O

Zn + 2 SO₂ = ZnSO₄

The first known application of hydrosulfites to pulp bleaching was described in 1928 by Hirschkind, who claimed that with 0.5 and 1.5% hydrosulfite (air-dry pulp basis), 5 and 15 units of brightness increase could be obtained on western hemlock, spruce, and balsam fir. He stated that the reaction of hydrosulfites in groundwood was completed in 5 to 10 minutes at ordinary temperatures (50°F), and that the same results were obtained with temperatures to 120°F.

**Hydrosulfite Groundwood Bleaching Variables**

In a large number of studies, the optimum conditions of temperature, pH, retention time, and consistency have been determined, as well as the effect of metallic contaminants. Sodium tripolyphosphate has been found to reduce the effect of metallic ions significantly. The effectiveness of the sequestering agent is limited by the fact that it may be competing with color-producing sequestering agents present in the wood (tannins, etc.). Also the reducing conditions in the hydrosulfite treatment change the iron to the ferrous state in which it is less easily complexed. The suggested bleaching conditions can be found in Virginia Chemicals Bulletin 407C and 407N. The amount of bleaching is proportional to the amount of zinc hydrosulfite up to about
1% chemical based on wood, but little brightness increase results from adding more bleaching agent.

Gavelin (1966) proposed that hydrosulfite may hydrolyze in five different ways as shown in the formulae below:

1. \[ \text{S}_2\text{O}_4^{-2} + 2\text{H}_2\text{O} = 2\text{HSO}_3^{-1} + 2\text{H}^+ + 2\text{e} \]
2. \[ \text{S}_2\text{O}_4^{-2} + 2\text{H}_2\text{O} = \text{S}_2\text{O}_6^{-2} + 4\text{H}^+ + 4\text{e} \]
3. \[ \text{S}_2\text{O}_4^{-2} + 3\text{H}_2\text{O} = \text{HSO}_3^{-1} + \text{HSO}_4^{-1} + 4\text{H}^+ + 4\text{e} \]
4. \[ \text{S}_2\text{O}_4^{-2} + 4\text{H}_2\text{O} = 2\text{HSO}_4^{-1} + 6\text{H}^+ + 6\text{e} \]
5. \[ 2\text{S}_2\text{O}_4^{-2} + \text{H}_2\text{O} = \text{S}_2\text{O}_3^{-2} + 2\text{HSO}_3^{-1} \]

The electrons released in formulae 1 through 4 react with the pulp, thereby reducing colored constituents of pulp into substances of lower color intensity.

During the action of hydrosulfites, the pH of the stock will drop 0.3 to 1.0 pH units, depending on the level of treatment and on the temperature. In general, the greater the degree of stock aeration during processing, the lower the pH tends to become. This effect results not only from the formation of sulfuric acid, but also from decomposition of the hydrosulfite to hydrogen sulfide, thiosulfuric acid, and sulfurous acid as illustrated by the following equation (Rapson, 1963):

\[ \text{S}_2\text{O}_4^{-2} + \text{H}_2\text{O} + \text{O}_2 = \text{HSO}_3^{-1} + \text{HSO}_4^{-1} \]

For this reason, air entrainment in the pulp to be bleached must be avoided. As far as formula 5 is concerned, it shows an
auto-oxidation/reduction process which also means a loss of bleaching chemical which should be avoided. This reaction is catalyzed by acidity, being rapid below pH 5 and practically instantaneous below pH 4.2.

The reducing potentials of the hydrosulfite in acid and basic solutions are given by Latimer (1959) and Cotton and Wilkinson (1966):

In acid solution:

\[2H_2O + HS_2O_4^- = 2H_2SO_3^- + H^+ + 2e\]

\[E^0 = -0.08v\]

In basic solution:

\[4OH^- + S_2O_4^{2-} = 2SO_3^{2-} + 2H_2O + 2e\]

\[E_B = -1.18v\]

These values indicate that the hydrosulfites are far more powerful reducing agents in alkaline than in acid solution. A high pH is always desirable for the stability of the salt in solution, but a lower pH may be required in order to attain sufficient brightening effect. Curran, Schafer, and Pew (1935) have attributed part of the detrimental effect of high pH on the brightness of western wood pulps to the presence in the ray cells of phlobatannins, which dissolve in alkaline media. Other pH-sensitive colored compounds are present in wood pulp, and, as a result, acidification of the pulp may produce a gain of one to two brightness units.

**Reaction Mechanism**

For groundwood and other types of very high yield pulps,
removal of the main light-absorbing substances such as lignin and resin would involve a substantial loss in yield. Therefore, such pulps are usually bleached without destroying the lignin. This can be done with hydrosulfites and other reducing or oxidizing agents. The mechanism by which the solid lignin and resin are made whiter by bleaching reagent is not completely known, despite efforts by Curran, Schafer, and Pew (1935), Buchanan (1951), and recently by Polcin and Rapson (1969, 1970, 1971).

According to the present concepts, the lignin macromolecule is composed of guaiacylpropane units, which are essentially colorless. However, some guaiacyl building units contain functional groups with chromogene properties in the side chain which, if conjugated with the benzene ring, increase light absorption in the ultra violet region. Auxochrome groups in a suitable position relative to a chromogene can further increase the absorption and shift it to the visible region.

Polcin and Rapson (1970) investigated the chromophores which are responsible for the typical yellow-brown color of unbleached groundwood pulps. They indicated that carbonyl groups and double bonds are the main chromogene groups in lignin. They can form "chromophoric systems" with the benzene ring and with auxochromes, thus causing the yellowish-brown color of wood. They also found that spruce has more carbonyls of \( \alpha,\beta \)-unsaturated aldehyde and simple quinoid structures, while western hemlock has mainly ring-conjugated
carbonyls and condensed quinoid structures.

Theoretically, removal of color or "bleaching" of colored substances can be done by interruption of conjugation between individual chromogenes, by changing the chemical structure of chromogenes, by elimination of auxochromes, or by interruption of their connection with chromogenes. Oxidation and reduction are the simplest reactions causing these changes, so all present bleaching technology of groundwood pulps is based on these principles.

The individual reducing agents possess different reactivity towards different types of carbonyls, but dithionite predominantly attacks simple quinoid, \( \alpha, \beta \)-unsaturated aldehyde and anthocyanidine structures. However, dithionite also reacts with double bonds of flavone type compounds, leaving the carbonyl group untouched, and produces the corresponding flavanone as a main product (Polcin, 1971).

\[
\begin{align*}
\text{Flavone} & \quad \xrightarrow{2H} \quad \text{Flavanone} \\
\text{Flavanone} & \quad \xrightarrow{2H} \quad \text{Flavanol}
\end{align*}
\]

It seems that zinc hydrosulfite can react relatively specifically with quercetin, dihydroquercetin, or many other flavonoids present in groundwood and convert them to the corresponding colorless flavanols.
EXPERIMENTAL PROCEDURE

Sample Selection

The raw material for this experiment was selected at the Hobin-Lumber Company in Philomath, Oregon. The heartwood and sapwood samples were collected in the form of freshly cut, green, dimension lumbers from a single 72 year old coastal range Douglas-fir, 19 inches dbh. This type of Douglas-fir was selected as being representative of the type of tree which is becoming more widely utilized. Mature, virgin growth Douglas-fir is becoming scarcer, whereas the young growth trees represent an increasingly larger segment of the total Douglas-fir harvest. Hence future Douglas-fir pulpwood will be predominantly young growth material, and was the logical choice for this study. However, Douglas-fir wood is known to be quite variable in its physical, chemical, and morphological characteristics, and the results of this study are strictly applicable only to young growth type wood of the coastal variety.

Sample Preparation

The heartwood boards were cut to eliminate sapwood and knots, the sapwood boards were cut to eliminate heartwood, bark, and knots, and each was chipped separately in a twin knife laboratory chipper. Fines and excessively large chips were screened from the samples.
The acceptable chips, 15 to 25 mm in length and 2 to 4 mm in thickness, were reduced into groundwood in two passes through a Bauer double disc refiner powered by two 50-horsepower electric motors. A variable speed auger fed the chips to the center of the rotating discs and a continuous flow of hot water helped move the material through the mill. The conditions for groundwood refining are outlined in Table 3.

### Table 3. Groundwood refining conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clearance (inch)</th>
<th>Water charged at 140°F (gal/min)</th>
<th>Freeness (cc CSF)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First pass</td>
<td>Second pass</td>
<td>First pass</td>
</tr>
<tr>
<td>Sapwood</td>
<td>0.018</td>
<td>0.015</td>
<td>0.8</td>
</tr>
<tr>
<td>Heartwood</td>
<td>0.018</td>
<td>0.015</td>
<td>0.8</td>
</tr>
</tbody>
</table>

*Canadian Standard Freeness.

The refiner groundwood pulp was collected, sealed in polyethylene bags containing a few drops of formaldehyde, and stored in a cold room maintained at 36°F. The schematic processing procedures of sample preparations and further treatments are outlined in Figure 2.

**Beater Processing of Pulp**

Multiple pass refining through disk mills is the industrial
DOUGLAS-FIR

Heartwood chips
1st pass through Bauer refiner
380 CSF pulp
2nd pass through Bauer refiner
200 CSF pulp
Further refining in Valley beater
Pulp at 160, 135, and 110 CSF

Sapwood chips
Pulp at 360 CSF pulp
170 CSF pulp
Pulp at 170, 140, and 110 CSF

Aging (50°C)
Various Heartwood-
solvent Sapwood
extraction mixture
Various %DHQ or QU added (50°C)

Unbleached pulp measure brightness

Acetone extraction

Bleach with one percent zinc hydrosulfite

Bleached pulp measure brightness

Figure 2. Flow sheet for production and treatment of Douglas-fir refiner groundwood.
method of producing refiner groundwood to the desired freeness, usually 100 CSF or less for newsprint. However, it is difficult to reach this degree of refining in the laboratory without metallic contamination of the pulp due to plate-to-plate contact. Thus the chips were disintegrated and refined to only 170-200 CSF in two passes through the mill, followed by further refining in a Valley Beater in accordance with TAPPI Standard T 200 ts-66. The beater refining operation was performed in distilled water to eliminate the effect of tap water which was contaminated with iron.

Samples at 160, 135 and 110 CSF were collected from heartwood groundwood, and samples of 170, 140 and 110 CSF were obtained from sapwood groundwood. The Canadian Standard Freeness (CSF) evaluations were made in accordance with TAPPI standard T 227 m-58. After refining, the water was squeezed out by hand, and the pulp chunks were broken and mixed thoroughly by hand in a five gallon bucket. The dewatered pulp was stored in polyethylene bags and allowed to come to moisture equilibrium. Two solids content determinations were made from each sample and averaged to give the value used for calculating the oven-dry weight of the pulp used in further bleaching experiments.

Testing for Iron Contamination

Ortho-phenanthroline hydrochloride solution (C₁₂H₈N₂·HCl·H₂O)
(10%) was applied to pulp samples in accordance with TAPPI Standard T 242 su-69. No red color spots appeared, indicating that both sap-wood and heartwood pulps were not contaminated with iron.

Reflectance Testing of Brightness Handsheets

Handsheets were formed in accordance with TAPPI Standard T 218 os-69. The 1000 cc stock samples were formed into pads on a Buchner funnel, and conditioned for 48 hours in a controlled environment room at 73°F and a relative humidity of 50% as set by TAPPI Standard T 402 m-49. The brightness was determined with an Elrepho Colorimeter at filter position number eight, which measures the percent reflectance at 457 nm. wavelength relative to an absolute standard of MgO at 100%.

Purification of Dihydroquercetin

An effort was made to convert quercetin to dihydroquercetin with sodium carbonate and sodium hydrosulfite (Geissman, 1952, 1962; Kurth, 1953; Pew, 1948; Shimizu and Yoshikawa, 1952). This method was too inefficient for producing dihydroquercetin in the quantity and quality desired. Production of 10 gm of dihydroquercetin would have required over a month's effort, and the purity of the dihydroquercetin thus produced was poor (m. p. 234-235°C vs 238-242°C for the pure material).
Crude reddish-brown dihydroquercetin obtained from the Weyerhaeuser Company was subjected to acetone-carbon tetrachloride extraction (Figure 3). The extracts were dissolved in hot water, decolorized with activated charcoal, and dihydroquercetin was obtained in the form of white needles, m.p. 240 to 242°C, by recrystallization from a water solution (Graham and Kurth, 1949; Gregory, Brink, Dowd and Ryan, 1957; Kurth, 1950, 1953). A mixed melting point determination with chemically pure dihydroquercetin (m.p. 240°C) gave no decrease in the melting point.

Aging of Groundwood

Refiner groundwood at 14% solids was placed in capped glass jars and stored in an oven at 50°C for six days. These aging conditions were arbitrarily chosen because the temperature is not severe enough to cause significant thermal deterioration of pulp but sufficiently high to accelerate the aging process.

Bleaching of Groundwood

The bleaching procedures followed the suggestions of Rapson, Wayman and Anderson (1965, 1968) and TAPPI Monograph 27 (Rapson, 1963). Duplicate 10 gm samples of each pulp were placed in 12 oz. glass jars and each jar was filled with distilled water to a final consistency of 3%. The pulp slurry was heated to a reaction
Crude dihydroquercetin
(Extracted with acetone)
Soluble
(Add CCl₄, heat)
Soluble
(Add charcoal, heat, filter)
Filtrate
(Concentrate by boiling, filter)
Solution
Precipitate
(Add boiling water, charcoal, filter)
(2 to 3 times)
Filtrate
(Add boiling water)
Crystal
(Dry)
Dihydroquercetin
m.p. 239-241°C

Figure 3. Dihydroquercetin purification scheme.
temperature of 50°C, buffered with either sulphuric acid or sodium carbonate, and 1% bleaching chemical added together with 0.3% sodium tripolyphosphate (STPP) to complex heavy metal impurities which might be present. All chemicals were calculated on an oven-dry pulp basis. Zinc hydrosulfite was used as the bleaching chemical. After one hour reaction time, the pulp was dewatered and then washed repeatedly with distilled water. Brightness pads were made, air dried, and the percent reflectance measured. The strength of zinc hydrosulfite was determined by the azo rubine method (Virginia Bulletin 401A) with the following calculation:

\[
\text{Assay (} \% \text{ZnS}_2\text{O}_4 \text{)} = \frac{(0.288) (100)}{(\text{Weight of ZnS}_2\text{O}_4 \text{ for titration})}
\]

When dihydroquercetin or quercetin were added to the pulp, the chemical was first dissolved in acetone and added to the pulp prior to the dilution to 3% consistency.

**Extractives Preparation**

Pulp Samples were air dried in the dark at 23°C and 50% R. H. Six each bleached, unbleached-aged, and unbleached-unaged Douglas-fir heartwood groundwood samples were exhaustively extracted with acetone (Graham and Kurth, 1949). Standard techniques and Soxhlet extraction apparatus were used. Extraction was performed for 30 hours with an average solvent exchange rate of two to three per hour,
yielding an average of 75 solvent exchanges.

After completion of the extraction, the samples were removed and formed into brightness pads. The extracts were taken to constant weight by evaporation at room temperature under vacuum.

**Chromatography**

**Paper Chromatography**

One dimensional paper chromatography was employed in the qualitative analysis of the acetone extracts. Whatman no. 1 filter paper was used in conjunction with the following solvents (volume-volume mixtures) (Manners, 1965; Harborne, 1962, 1967):

1. Chloroform, acetic acid, water (8:12:5) (CAW) lower layer.
2. Upper layer (CAW), 1-butanol (3:1) (ULCB).
3. 1-Butanol, acetic acid, water (4:1:5) (BAW) upper layer.

Portions of the extracts were dissolved in pyridine and spotted on the chromatographic paper (7" x 18"), which was hung in a glass cylinder. The chromatographic solvent was added and the chromatogram developed twice. In the first stage of development, which lasted about three hours, the solvent front advanced about one quarter of the length of the strip. At that point, the paper strip was removed and air dried. Then, the same strip was put back to the cylinder and developed again to its full length. After the second development, the
strip was air dried and examined under ultraviolet light. The ULCB solvent system gave the best separation for quercetin and dihydroquercetin. Diazotized p-nitroaniline was employed as the chromogenic spray reagent (Block, 1952; Bray, 1950).

In terms of a readable signal for absolute quantities of both quercetin and dihydroquercetin, this method requires about $3 \times 10^{-6}$ gm for minimum detection.

Gas-liquid Chromatography

1. **Trimethylsilylation** -- The acetone extracts were first evaporated to get rid of the solvent, then the thoroughly dried samples were dissolved in 2 ml of anhydrous pyridine, from which an aliquot of 0.5 ml was transferred to a 2 ml vial with a syringe, to which 0.1 ml hexamethyldisilazane and 0.05 ml trimethyl-chlorosilane were added. The mixture was shaken vigorously for about 30 seconds and allowed to stand for 10 minutes in a hot water bath at 50°C to ensure complete reaction (Furuya, 1965).

2. **Gas chromatography** -- The instrument used for this work was a Hewlett Packard model 5750 research gas chromatography with a hydrogen flame ionization detector.

Dihydroquercetin was measured as its trimethylsilyl ether derivative (TMS-DHQ) (Furuya, 1965; Hemingway and Hillis, 1969; Keith and Powers, 1966). TMS-DHQ was separated on the column,
and peak areas compared to the internal standard TMS-phloretin. The chromatograph oven temperature was set at 187°C for 20 minutes, and then programmed to 250°C at 1°C/min. The injection port and detector temperatures were 250°C and 260°C respectively. Columns were 5 feet long, 1/8 inch ), D. stainless steel tubes, packed with 4.79% of silicone rubber SE-30 on acid washed, DMCS treated chromosorb Q (100 to 120 mesh). The helium carrier gas flow rate was 48 ml/min. while hydrogen and oxygen flows were 34 and 200 ml per minute respectively.

The calibration curve was prepared by plotting the ratio of peak areas (TMS-DHQ/TMS-phloretin) against the ratio of weights (TMS-DHQ/TMS-phloretin) as shown in Figure 4. Peak areas were measured with a planimeter several times and averaging the values.

The SE-30 gas chromatographic column has been reported in the literature to be the most efficient tool for the separation of the trimethylsilyl ethers of flavonoids and related compounds, yet the first attempt to separate mixtures of pure dihydroquercetin and quercetin with this method was unsuccessful, completely failing to separate these two compounds.

Therefore, it was necessary to test for the presence of quercetin in various extracts that were tested in this work before gas chromatography analysis could be attempted. The extracts were
tested by paper chromatography, which effectively separates dihydro-
quercetin and quercetin. If no quercetin was thus detected, then the
GLC peak for dihydroquercetin-quercetin was assumed to be 100%
dihydroquercetin.

Figure 4. Calibration curve for a quantitative analysis
of dihydroquercetin.
RESULT AND DISCUSSION

The Bleaching Response of Sapwood Pulp

The initial brightnesses and the bleachabilities at three different freeness levels of the off-white Douglas-fir sapwood groundwood are tabulated in Table 4. The initial brightness of Douglas-fir sapwood groundwood is about 7 points brighter than that of hemlock sapwood groundwood, which is very desirable (Tables 2 and 4). The bleachability of Douglas-fir sapwood to 1% ZnS₂O₄ is about 10 to 12 points gain compared to the 8 point gain by western hemlock sapwood groundwood (Tables 2 and 4).

This suggests that Douglas-fir sapwood groundwood does not create problems in bleaching, and coincides with Bublitz’s finding concerning groundwood brightness improvement of the Douglas-fir sapwood in his report to the Publisher's Paper Company in 1967.

The Bleaching Response of Heartwood Pulp

The initial brightness of Douglas-fir heartwood groundwood is much lower than that of western hemlock heartwood groundwood as shown in Tables 2 and 5. Furthermore the brightness of bleached Douglas-fir heartwood groundwood does not equal the initial brightness of western hemlock heartwood groundwood. This suggests that the
<table>
<thead>
<tr>
<th>Freeness (cc CSF)</th>
<th>Before bleaching</th>
<th>Brightness</th>
<th>After bleaching</th>
<th>Gain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trial 1</td>
<td>Trial 2</td>
<td>Trial 3</td>
<td>Average</td>
</tr>
<tr>
<td>170</td>
<td>60.6</td>
<td>60.6</td>
<td>60.6</td>
<td>60.6</td>
</tr>
<tr>
<td>140</td>
<td>61.0</td>
<td>60.9</td>
<td>60.5</td>
<td>60.8</td>
</tr>
<tr>
<td>110</td>
<td>60.6</td>
<td>60.6</td>
<td>60.7</td>
<td>60.6</td>
</tr>
</tbody>
</table>
Table 5. Bleaching of Douglas-fir heartwood groundwood pulp.

<table>
<thead>
<tr>
<th>Freeness (cc CSF)</th>
<th>Before bleaching</th>
<th>Brightness</th>
<th>After bleaching</th>
<th>Gain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trial 1</td>
<td>Trial 2</td>
<td>Trial 3</td>
<td>Average</td>
</tr>
<tr>
<td>160</td>
<td>37.2</td>
<td>37.3</td>
<td></td>
<td>37.3</td>
</tr>
<tr>
<td>135</td>
<td>37.4</td>
<td>37.4</td>
<td></td>
<td>37.4</td>
</tr>
<tr>
<td>110</td>
<td>37.5</td>
<td>37.8</td>
<td>37.4</td>
<td>37.6</td>
</tr>
</tbody>
</table>
problem of bleaching Douglas-fir groundwood resides in the heartwood fraction.

A Comparison Between the Two Douglas-fir Groundwoods

The bleachabilities for sapwood and heartwood groundwoods at different freenesses are shown in Figure 5. For heartwood, the bleachability is inversely related to freeness, but the sapwood pulp bleachability is relatively constant and not affected by the freeness of the pulp.

In order to explain this phenomenon, we must know the function of the beating process and the effects which are produced on pulp fibers during beating.

Beating is primarily a mechanical process resulting in physical changes in the fibrous structure and colloidal nature of the pulp. No major chemical changes normally take place during beating. The main effects of beating on pulp are as follows:

1. Shortening of the fibers by cutting, and formation of fines.
2. Fracture and removal of the fiber wall.
3. Increase in the specific surface area.
4. Swelling of the fibers.
5. Increase in the flexibility of the fiber due to breaking of internal bonds in the fiber.
6. Formation of fibrils extending from the fiber wall.
Figure 5. Bleachability of sapwood and heartwood groundwoods vs. freeness.
Groundwood fibers retain their stiffness longer on beating than chemical pulps because of their greater lignin content and consequently cannot take much beating without excessive fracturing of the fibers. Therefore, the negative relationship between the bleachability of Douglas-fir heartwood groundwood and its freeness can be explained as follows:

1. The extraneous components which are confined in substantial amounts to Douglas-fir heartwood ray cells rather than to sapwood would be broken up, rubbed off or dissolved in water, if they were water soluble, while the fibers are being opened up by beating.

2. As the fibers swell, the specific surface increases, more surface area is available and susceptible to bleaching chemicals.

From Figure 5, it is obvious that the bleachabilities of both the sapwood and heartwood groundwoods are very close to each other at the 110 CSF level. However, since the unbleached heartwood groundwood is 23 points darker than the unbleached sapwood groundwood, the former material bleached is still about 23 points darker than the latter material bleached. In other words, sapwood and heartwood groundwoods retain about the same brightness difference, whether bleached or unbleached at 110 CSF. However, the samples used here were taken from a second growth, young Douglas-fir; this finding may not be the same for old, aged Douglas-fir groundwood.
Bleaching of Sapwood and Heartwood Mixture

The bleachabilities of heartwood and sapwood groundwood are essentially equal at 100-110 CSF, so mixtures of these two would be expected to be equally bleachable. However, for the mixture of sapwood groundwood at 170 CSF and heartwood groundwood at 160 CSF, the bleachability is quite different from that of either 100% sapwood groundwood or 100% heartwood groundwood as shown in Table 6.

The brightness of the mixture of the two groundwoods should be close to that predicted by using the Kubelka-Munk theory. The Kubelka-Munk equation of interest is the following:

\[
R_\infty = 1 + \frac{K}{S} - \left[ \left( \frac{K}{S} \right)^2 + 2 \left( \frac{K}{S} \right) \right]^{0.5}
\]

\( R_\infty \) = the reflectance of a pad of paper thick enough to be opaque.
\( K \) = absorption coefficient of the material.
\( S \) = scattering coefficient of the same material.

The \( (K/S) \) value for the mixture is additive:

\[
(K/S) \text{ mixture} = C_1 (K/S)_1 + C_2 (K/S)_2
\]

\( C \) = the fraction of each component present in the mixture and the subscripts refer to the first and second component.

The predicted brightnesses for the mixture of Douglas-fir sapwood and heartwood groundwoods, before and after bleaching, are shown in parentheses in Table 6. The experimental measurements
Table 6. The influence of heartwood groundwood on the bleachability of sapwood groundwood.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness</th>
<th>Brightness gain</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before bleaching</td>
<td>After bleaching</td>
</tr>
<tr>
<td>Sapwood (A) (140 CSF)</td>
<td>61.0</td>
<td>72.6</td>
</tr>
<tr>
<td>Heartwood (B) (110 CSF)</td>
<td>37.5</td>
<td>48.7</td>
</tr>
<tr>
<td>Mixture of (A) and (B) *</td>
<td>45.3 (45.6)**</td>
<td>55.9 (57.1)</td>
</tr>
<tr>
<td>Sapwood (C) (170 CSF)</td>
<td>60.6</td>
<td>72.2</td>
</tr>
<tr>
<td>Heartwood (D) (160 CSF)</td>
<td>37.3</td>
<td>42.0</td>
</tr>
<tr>
<td>Mixture of (C) and (D) *</td>
<td>45.0 (45.5)</td>
<td>51.7 (51.6)</td>
</tr>
</tbody>
</table>

* 50/50 mixture by weight.

** The figure shown in parentheses is the predicted brightness according to Kubelka-Munk equation.
are very close to the predicted brightness, indicating that there was no significant interaction between the two types of groundwood during bleaching. However, the effects of the heartwood fraction on the brightnesses and bleachabilities of Douglas-fir groundwoods are apparent. It not only lowers the unbleached brightnesses about 15 to 16 points but also decreases the bleached brightnesses about 16 to 20 points, depending on the freeness levels. This data presents strong evidence that the Douglas-fir heartwood is the culprit in bleaching Douglas-fir groundwood, but that the sapwood can make acceptable groundwood pulp, with regard to brightness.

Since previous work (Styan, 1971) has suggested that flavonoids in heartwood are responsible for inhibition of groundwood bleaching, and since dihydroquercetin is one of the major flavonoids in Douglas-fir heartwood, it was decided to investigate the role of dihydroquercetin in the bleaching reaction with zinc hydrosulfite. Similarly, since dihydroquercetin can be converted to quercetin with bisulfite (which is a potential product of zinc hydrosulfite bleaching), it was reasonable to study the affect of quercetin on bleaching with zinc hydrosulfite.

**Reaction of Dihydroquercetin and Quercetin with Zinc Hydrosulfite**

In order to examine the possibility of the following reactions occurring either during groundwood bleaching with zinc hydrosulfite
or during groundwood aging by heat:

\[
\begin{align*}
\text{A.} & \quad 2\text{S}_2\text{O}_3^- + \text{H}_2\text{O} = \text{S}_2\text{O}_3^- + 2\text{HSO}_3^- \\
& \quad \text{DHQ} + \text{HSO}_3^- \longrightarrow \text{QU} \\
& \quad \text{(white)} \quad \text{yellow)
\end{align*}
\]

\[
\begin{align*}
\text{B.} & \quad \text{DHQ} \xrightarrow{\text{aging}} \text{QU} \xrightarrow{\text{grinding}} 
\end{align*}
\]

0.1 gm of dihydroquercetin and quercetin were each reacted separately with 0.1 gm zinc hydrosulfite in a test tube containing 10 cc of water under groundwood bleaching conditions. The colorless solution of dihydroquercetin-zinc hydrosulfite persisted throughout the reaction. Both solutions were then concentrated, spotted along with standard dihydroquercetin and quercetin on Whatman no. 1 filter paper, and processed as previously described. The chromatogram of the dihydroquercetin-zinc hydrosulfite reaction mixture showed no spot for quercetin, nor was there any detectable spot of dihydroquercetin in the reaction mixture of quercetin with zinc hydrosulfite.

In addition, another 0.1 gm of pure dihydroquercetin was dissolved in 5 cc of water and oven-aged at 50°C for six days. The aged dihydroquercetin solution changed from a colorless to a light yellow solution. This aged dihydroquercetin solution was also separated and identified by the paper chromatographic technique (3 x 10^-6 gm sensitivity), but no significant spot for quercetin was observed, despite the considerable overloading of the dihydroquercetin spot.
From this data, the maximum efficiency of conversion of dihydroquercetin to quercetin can be calculated. The 20 µl sample contained about $4 \times 10^{-4}$ gm of dihydroquercetin from the original 0.1 gm of dihydroquercetin. Since less than $3 \times 10^{-6}$ gm of quercetin were present in the 20 µl sample used for paper chromatography, then the efficiency of conversion of dihydroquercetin to quercetin could not have been greater than:

$$\frac{3 \times 10^{-6}}{4 \times 10^{-4}} = 0.0075 \text{ or } 0.75\%$$

This is a very minor degree of chemical conversion, and suggests that the conversion of dihydroquercetin to quercetin during the bleaching reaction with zinc hydrosulfite is negligible.

**Effect of Dihydroquercetin on Bleaching Response of Sapwood Groundwood**

Purified dihydroquercetin obtained from Douglas-fir bark was added to Douglas-fir sapwood groundwood stepwise to a maximum of 4% (based on oven-dry pulp). The brightnesses of the samples before and after bleaching with 1% zinc hydrosulfite, are given in Table 7. Since dihydroquercetin is a colorless compound, the brightnesses of the unbleached sapwood groundwood did not change significantly with increasing amounts of dihydroquercetin. Even after bleaching, however, the bleached brightnesses and the bleachabilities did not show
Table 7. Effect of dihydroquercetin (DHQ) on brightness and bleachability of sapwood groundwood.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness</th>
<th>Brightness</th>
<th>Brightness</th>
<th>Brightness</th>
<th>Brightness</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before bleaching</td>
<td>After bleaching</td>
<td></td>
<td>Gain</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trial 1</td>
<td>Trial 2</td>
<td>Average</td>
<td>Trial 1</td>
<td>Trial 2</td>
<td>Average</td>
</tr>
<tr>
<td>Sapwood</td>
<td>61.0</td>
<td>60.5</td>
<td>60.7</td>
<td>72.7</td>
<td>72.5</td>
<td>72.6</td>
</tr>
<tr>
<td>Sapwood + 0.5% DHQ</td>
<td>-</td>
<td>59.6</td>
<td>59.6</td>
<td>72.6</td>
<td>-</td>
<td>72.6</td>
</tr>
<tr>
<td>Sapwood + 1.0% DHQ</td>
<td>-</td>
<td>59.3</td>
<td>59.3</td>
<td>71.7</td>
<td>71.3</td>
<td>71.5</td>
</tr>
<tr>
<td>Sapwood + 1.5% DHQ</td>
<td>-</td>
<td>59.4</td>
<td>59.4</td>
<td>72.1</td>
<td>-</td>
<td>72.1</td>
</tr>
<tr>
<td>Sapwood + 2.0% DHQ</td>
<td>60.0</td>
<td>59.4</td>
<td>59.7</td>
<td>71.2</td>
<td>70.1</td>
<td>70.6</td>
</tr>
<tr>
<td>Sapwood + 3.0% DHQ</td>
<td>-</td>
<td>59.2</td>
<td>59.2</td>
<td>71.1</td>
<td>70.2</td>
<td>70.6</td>
</tr>
<tr>
<td>Sapwood + 4.0% DHQ</td>
<td>59.4</td>
<td>59.2</td>
<td>59.3</td>
<td>69.4</td>
<td>69.3</td>
<td>69.4</td>
</tr>
</tbody>
</table>
Figure 6. The influence of dihydroquercetin on brightness and bleachability of sapwood groundwood.
any significant depression with increasing amounts of dihydroquercetin added (Figure 6). Therefore, the hindrance observed in the bleaching of Douglas-fir heartwood groundwood is probably not due to dihydroquercetin. In addition, the maximum amount of dihydroquercetin added here was much more than that actually present in the Douglas-fir heartwood (4% vs. 2%).

**Effect of Quercetin on Brightness and Bleachability of Sapwood Groundwood**

Quercetin, the oxidation product of dihydroquercetin (Figure 7), was suspected to be the real culprit of the low brightness and poor bleaching response of Douglas-fir groundwood. Adding increasing amounts of quercetin to Douglas-fir sapwood groundwood decreased not only the unbleached brightness, but also the bleaching response as illustrated in Table 8 and Figure 8. However, the yellow color of the
Table 8. Effect of quercetin (QU) on brightness and bleachability of sapwood groundwood.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness Before bleaching</th>
<th>Brightness After bleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapwood</td>
<td>60.0</td>
<td>70.5</td>
</tr>
<tr>
<td>Sapwood + 0.05% QU</td>
<td>53.8</td>
<td>60.0</td>
</tr>
<tr>
<td>Sapwood + 0.25% QU</td>
<td>50.3</td>
<td>55.8</td>
</tr>
<tr>
<td>Sapwood + 0.50% QU</td>
<td>46.7</td>
<td>49.2</td>
</tr>
<tr>
<td>Sapwood + 0.75% QU</td>
<td>47.1</td>
<td>47.9</td>
</tr>
<tr>
<td>Sapwood + 1.00% QU</td>
<td>46.7</td>
<td>46.9</td>
</tr>
<tr>
<td>Sapwood + 2.00% QU</td>
<td>42.7</td>
<td>42.2</td>
</tr>
<tr>
<td>Sapwood + 3.00% QU</td>
<td>41.0</td>
<td>41.4</td>
</tr>
<tr>
<td>Sapwood + 4.00% QU</td>
<td>40.5</td>
<td>39.5</td>
</tr>
</tbody>
</table>
Figure 8. The influence of quercetin on brightness and bleachability of sapwood groundwood.
quercetin is substantially different from the pink color of the heartwood, suggesting two different chromophores. In addition, this added yellow colored pigment could be removed by acetone extraction which did not remove the pink colored materials that seem to exist firmly in Douglas-fir heartwood (Table 9).

Table 9. Effect of acetone extraction on brightness of unbleached groundwood.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness Before extraction</th>
<th>Brightness After extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapwood</td>
<td>60.6</td>
<td>61.0</td>
</tr>
<tr>
<td>Sapwood + 3% QU (bleached)</td>
<td>41.4</td>
<td>62.9</td>
</tr>
<tr>
<td>Heartwood</td>
<td>37.3</td>
<td>37.7</td>
</tr>
</tbody>
</table>

Table 9. Effect of acetone extraction on brightness of unbleached groundwood.

Correlation of Dihydroquercetin Content with Brightness and Bleachability

Six each bleached, unbleached-aged, and unbleached-unaged Douglas-fir heartwood groundwood samples were air dried and subsequently exhaustively extracted with acetone in Soxhlet extractors. After completion of the extraction, the extracts were concentrated in a rotatory evaporator at room temperature and dried to constant weight in a desiccator under vacuum.

Paper chromatography of all extracts showed positive results for dihydroquercetin but negative results for quercetin. This was
followed by quantitative determination of dihydroquercetin in a Hewlett Packard model 5750 gas chromatograph. As outlined in the experimental section, the conditions of GLC used did not resolve quercetin and dihydroquercetin. However, since the paper chromatography method was sensitive (3 x 10^-6 gm) and showed no quercetin in all extracts than it was possible to contribute the peak on the GLC as due only to dihydroquercetin. The average values of replicate tests for dihydroquercetin present in Douglas-fir heartwood groundwood fractions, together with the brightnesses of those pulps are listed in Table 10.

The brightnesses and bleachabilities of Douglas-fir heartwood groundwoods showed poor correlation with the amount of dihydroquercetin present in the groundwood pulps. These differences in dihydroquercetin content may be related to other factors. For example, the lower dihydroquercetin content of the low freeness pulp was probably due to water extraction of dihydroquercetin during the extra refining necessary to achieve the lower freeness. Furthermore, the dihydroquercetin lost during bleaching was probably the consequence of the hot water (50°C) extraction during the bleaching stage, followed by a 1000 cc distilled water washing while the brightness pad was formed. The lower amount of dihydroquercetin in the aged pulp was also probably due to the water extraction during aging, and leaching while the pulp was dewatered from the original moisture content of 86% to
a lower value of 77%. In addition, heat might cause dihydroquercetin to undergo self-condensation or grafting onto lignin, and these forms might not be extractable. The unusually low dihydroquercetin content in aged pulp at 160 CSF cannot be explained.

Table 10. Dihydroquercetin content in heartwood groundwood.

<table>
<thead>
<tr>
<th>Freeness (cc CSF)</th>
<th>% DHQ (O.D. pulp basis)</th>
<th>Initial</th>
<th>After bleaching</th>
<th>After aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td></td>
<td>0.56</td>
<td>0.25</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(37.5)*</td>
<td>(42.0)</td>
<td>(30.8)</td>
</tr>
<tr>
<td>110</td>
<td></td>
<td>0.29</td>
<td>0.13</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(37.5)</td>
<td>(48.7)</td>
<td>(34.3)</td>
</tr>
</tbody>
</table>

*The figure shown in parentheses is the brightness of the corresponding pulp.

Effect of Solvent Extractions on Bleachability

Attempts to improve the unbleached brightness as well as the bleaching response of Douglas-fir heartwood groundwood at 160 CSF level by various solvent extractions were largely unsuccessful. Water and acetone extractions were supposed to remove dihydroquercetin, tannins, and phlobaphenes effectively, which should increase the initial brightness and also bleachability. As Table 11 shows this was not the case. Though both the warm water and the acetone extractions did not increase the bleached brightness significantly, they did increase the bleached brightness by two points which is a questionable
In order to remove as much tannins and phlobatannins as possible, the groundwood was extracted with ethyl acetate. The brightness after extraction dropped unexpectedly by 3 points, and this brightness difference remained throughout the bleaching process. Therefore, it was thought that some of the coloring material has been relocated onto the fiber surface during ethyl acetate extraction, which could neither be removed by ethyl acetate extraction nor by bleaching.

**Effect of Aging on Bleachability**

Both sapwood (170 CSF) and heartwood (160 CSF) groundwood samples were stored in the mild wet room (32°C, 90% R.H.) for six
Table 12. Effect of aging on brightness and bleachability.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Brightness</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td></td>
<td>aging</td>
<td>aging</td>
</tr>
<tr>
<td>Sapwood (110 CSF)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>60.6</td>
<td>57.1</td>
</tr>
<tr>
<td>Bleaching</td>
<td>(-3.5)</td>
<td>(-3.1)</td>
</tr>
<tr>
<td>After</td>
<td>70.5</td>
<td>64.0</td>
</tr>
<tr>
<td>Bleaching</td>
<td>(+9.9)</td>
<td>(+6.9)</td>
</tr>
<tr>
<td>Heartwood (110 CSF)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleaching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After</td>
<td>72.2</td>
<td>62.8</td>
</tr>
<tr>
<td>Bleaching</td>
<td>(+11.6)</td>
<td>(+7.9)</td>
</tr>
</tbody>
</table>

Note: All pulps aged at 50°C for 6 days.

Table 13. Effect of acetone extraction on brightness and bleachability of aged heartwood groundwood.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Brightness</th>
<th>Brightness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before bleaching</td>
<td>After bleaching</td>
</tr>
<tr>
<td>Aged pulp at 110 CSF</td>
<td>Reference 34.3</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>Extracted 33.4</td>
<td>38.4</td>
</tr>
<tr>
<td>Aged pulp at 160 CSF</td>
<td>Reference 30.8</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>Extracted 30.7</td>
<td>35.1</td>
</tr>
</tbody>
</table>
days. Under this mild condition, the brightness and bleachability losses of both samples were only about one point. However, the loss of brightness and bleachability during storage of Douglas-fir groundwoods at 50°C for a period of six days is considerable, as shown in Table 12.

There is the same loss of brightness on aging on unbleached Douglas-fir sapwood groundwood at different freeness levels as for Douglas-fir heartwood groundwood. The heartwood groundwood, which contains more extractives than the sapwood groundwood would be expected to show a greater brightness loss from the aging process, but there does not seem to be a significant difference between the two.

Furthermore, acetone extraction, which was intended to remove most or all of the quercetin and dihydroquercetin in the pulp, did not affect either the brightnesses or bleachabilities of the aged heartwood groundwoods (Table 13). The materials which could not be removed by this extraction might be polymerized tannins or phlobaphenes which are distributed throughout the tracheids during heartwood formation. Heat or radiated energy might cause increased condensation or polymerization, thus explaining the aging effect.

**Bleached Brightness Reversion**

The problem of bleached brightness reversion has been studied for a long time, and the basic reactions are still not entirely known yet.
Table 14. Bleached brightness reversion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical application</th>
<th>Bleached</th>
<th>Aged</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heartwood (110 CSF)</td>
<td></td>
<td>47.3</td>
<td>41.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Heartwood (160 CSF)</td>
<td></td>
<td>42.2</td>
<td>35.9</td>
<td>6.3</td>
</tr>
<tr>
<td>Sapwood (170 CSF)</td>
<td></td>
<td>69.9</td>
<td>63.0</td>
<td>6.9</td>
</tr>
<tr>
<td>50% Ht. (110 CSF) &amp; 50% Sap (140 CSF)</td>
<td></td>
<td>54.3</td>
<td>48.3</td>
<td>6.0</td>
</tr>
<tr>
<td>50% Ht. (160 CSF) &amp; 50% Sap (170 CSF)</td>
<td></td>
<td>51.6</td>
<td>45.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Sapwood (140 CSF)</td>
<td>3% DHQ</td>
<td>67.7</td>
<td>61.9</td>
<td>5.8</td>
</tr>
<tr>
<td>Sapwood (140 CSF)</td>
<td>4% DHQ</td>
<td>66.6</td>
<td>60.6</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Note: Brightness measured from handsheets, not from brightness pads. Handsheets aged for 3 hours at 104°C.
In the present experiments, bleached sapwood groundwood with and without added dihydroquercetin, heartwood groundwood handsheets, and the handsheets of their mixtures were aged in an oven at 104°C for three hours. There seems to be no significant differences in the brightness reversions of any of the samples studied (Table 14).

Thus it seems that dihydroquercetin played no part in the brightness reversion under this set of conditions. The main cause of brightness reversion is probably the reactions of the lignin or tannins present in the sheets.
SUMMARY AND CONCLUSION

1. Douglas-fir heartwood is the major culprit in the bleaching of Douglas-fir groundwood. For heartwood, the bleachability is inversely related to freeness but sapwood pulp bleachability is independent of the freeness of the pulp.

2. The bleachabilities of both the sapwood and heartwood groundwoods are very close to each other at the lower freeness level (110 CSF). However, since this relationship was observed for a second growth, young Douglas-fir tree, the same statement may not apply to groundwoods from older trees.

3. Dihydroquercetin and quercetin are not interconvertible under the specific bleaching conditions utilized herein. The brightnesses and bleachabilities of heartwood groundwoods showed poor correlation with dihydroquercetin content of groundwood pulps. Model compound studies also indicated that dihydroquercetin does not hinder the groundwood bleaching reaction, and has little effect on either bleached or unbleached brightnesses of sapwood groundwood.

4. Quercetin decreases not only the unbleached brightness, but also the bleachability of Douglas-fir groundwood. Fortunately, at most only minor amounts of quercetin have been found in Douglas-fir heartwood, and in this sample, quercetin was not detected at all. Therefore, even though quercetin is extremely detrimental to
groundwood bleaching when present in large amounts, it must be discounted as a major hindrance in actual Douglas-fir groundwood bleaching.

5. The effect of aging on the brightness of heartwood groundwoods is the same as on that of sapwood groundwoods. It showed no correlation between the extractive content and brightness loss on aging. The removal of dihydroquercetin and some other flavonoids by solvent extraction did not affect either the brightness or bleachability of these aged heartwood groundwoods.

6. The bleached brightness reversions were similar for handsheets made from sapwood groundwood with or without added dihydroquercetin, from heartwood groundwood, and from the mixtures of sapwood and heartwood groundwoods. This suggested that dihydroquercetin played no part in the brightness reversion reaction under these specific conditions.

7. Solvent extractions did not result in any improvement in either the unbleached brightness or the bleachability of heartwood groundwood. The pink color of Douglas-fir heartwood, which is probably responsible for the lower unbleached brightness of Douglas-fir groundwood, is not affected by various solvent extractions.

8. No feasible method of improving the brightness of Douglas-fir heartwood groundwood to a commercially acceptable level has been found in this research. Therefore, if Douglas-fir is to be
utilized for newsprint groundwood, only sapwood should be considered for its production.

9. In order to understand the fundamentals of this bleaching difficulty, the chemical constitution and the mode of physiological formation of the pink colored material should be more intensively investigated. This information should lead to better bleaching techniques and more efficient use of this material.
BIBLIOGRAPHY


