Isolation and Characterization of Hemicellulose from a Ginkgo Nut Shell*

Eiichi MAEKAWA** and Koichiro KITAO**

**Abstract**—A preliminary investigation was attempted for characterization of hemicelluloses occurring in a ginkgo nut shell. The hemicellulose was isolated by successive extraction of a preparative meal treated with sodium chlorite with 24% aqueous KOH and with 17.5% aqueous NaOH containing 5% boric acid. The hemicellulose was subjected to fractional precipitation repeatedly with barium hydroxide. A galacto-glucomannan which was obtained by further fractionation on QAE-Sephadex A-50 (acetate form) of the glucomannan fraction was electrophoretically and ultracentrifugally homogeneous. The polysaccharide which contained the residues of D-galactose, D-glucose and D-mannose in the molar ratio of 0.3:1.0:1.7, respectively, gave a specific rotation of \([\alpha]_D^{20} -19.3^\circ\) (c=1.80, H2O). The hemicellulose of a ginkgo nut shell gave an arabino-(4-O-methyl-D-glucurono) xylan, a galacto-glucomannan and other polysaccharides in the respective yields of 9.8%, 2.6% and 0.8% on the basis of a preparative defatted meal. These results showed that the hemicellulose of ginkgo nut shell contained much higher amounts of the xylan fraction rather than the glucomannan fraction.

1. INTRODUCTION

It has been established that hemicelluloses of the softwoods are characterized by the presence of three types of polysaccharides, namely galacto-glucomannan, arabino-(4-O-methyl-D-glucurono) xylan and arabinogalactan\(^\text{19}\). Among them, the glucomannan (15–20% of the wood) and the xylan (10–15% of the wood) constitute the predominant hemicelluloses of the softwoods, although there is the only exception that a larchwood contains 10–20% of arabinogalactan.

A hemicellulose from the wood of *Ginkgo biloba*\(^\text{2,3}\), which is classified as a gymnosperm, was studied with a view to a biogenetic comparison with hemicelluloses of other softwoods. The result showed that hemicellulose of the ginkgo had a structural feature similar to those of the softwoods. However, the wood of *Ginkgo biloba* is different from other softwood in that it contains only trace amounts of arabinogalactan\(^\text{15}\).

A seed of the ginkgo, commonly called a ginkgo nut, is usually covered and protected with a hard shell. The lignified shell corresponds to the outer coating husk or hull of the cereal grains. Therefore, hemicelluloses of such a shell are expected

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** Division of Wood Chemistry.
to be different structurally from those in the wood and bark, in view of difference of its biological function in the particular part. From such a point of view, this preliminary investigation was undertaken for isolation and characterization of hemicelluloses from a preparative meal of ginkgo nut shell.

2. EXPERIMENTAL

2.1 Analytical methods

Paper chromatography was carried out with the descending method by using the following solvent systems; a) n-butanol/pyridine/water (6:4:3, v/v), b) ethyl acetate/pyridine/water (8:2:1, v/v). Spray reagents used for detecting the locating sugars were aniline hydrogen phthalate and p-anisidine hydrochloride.

Acid hydrolysis of water-soluble fractions was made under reflux with 1.25 N H₂SO₄ for 4~5 hr. On the other hand, acid hydrolysis of water-insoluble hemicellulose and the residue was made according to the method⁴ of Saeman et al. The complete hydrolyzate was neutralized with barium hydroxide or barium carbonate and barium sulfate produced was removed by filtration through a Celite layer. The filtrate and washings were desalted with Amberlite IR 120 B (H) exchange resin, filtered and evaporated to give a sirup. Quantitative analysis of the sugars was carried out according to a colorimetric method⁵ described by Wilson. A part of the sugars after acid hydrolysis was reduced with sodium borohydride to the corresponding alditols, followed by acetylation with acetic anhydride and conc. H₂SO₄ (25:2, v/v). Gas chromatograph of JGC 1100 type of JEOL Co., Ltd. was used for analysis of the alditol acetates with a column (0.3×200 cm) containing 3 % (w/w) ECNSS-M on Gas Chrom Q (100~120 mesh). Conditions of measurement; column temp. 195°C, detect temp. 280°C, inject temp. 300°C, carrier gas He, rate of flow of carrier gas 30 ml/min, detector FID. The determination of uronic acid was made according to the decarboxylation method in acid solution. Non-carbohydrate content was determined as Klason lignin insoluble in 72 % H₂SO₄. Other analytical methods were carried out according to those described in a previous paper.

All evaporations were carried out under reduced pressure below 40°C.

2.2 Preparation of the material

A ginkgo nut shell was ground in a Wiley mill, and the meal was defatted with a mixed solvent of methanol and benzene (1:2, v/v). The defatted meal (170 g, oven-dried weight 153.2 g) was delignified according to the acid-chlorite method. The air-dried residue was obtained in a yield of 158 g. While the product obtained by one treatment with sodium chlorite still contained 28.9 % of non-carbohydrate, it was submitted tentatively for extraction of the hemicellulose. The analytical values of the meal prepared from a ginkgo nut shell were as follows; (%) holocellulose 64.0,
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α-cellulose 36.5, Klasson lignin 38.4, hemicellulose (as 17.5% NaOH soluble fraction) 21.4, methanol and benzene (1:2, v/v) extract 1.5

2.3 Isolation and fractionation of hemicellulose from a ginkgo nut shell

The meal prepared as described above was extracted overnight with 24% aqueous potassium hydroxide (1.2 liter) under nitrogen atmosphere at room temperature. The extract was filtered through a cloth on a Büchner funnel, and then the filtrate was acidified with acetic acid and dialyzed with a seamless cellulose tubing against running water for 2 days. After the dialyzed solution was evaporated to ca. 200 ml, three or four volumes of ethanol was added into the concentrated solution to give a

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Fig. 1. Isolation and fractionation of hemicellulose of ginkgo nut shells

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precipitate. The precipitate was collected by centrifugation, and dissolved in water and further treated with barium hydroxide. A small amount of precipitate (P-2) was filtered off and the filtrate was further separated into fractions of P-3 and P-4, as shown in Fig. 1.

The residue after extraction with 24% aqueous potassium hydroxide was extracted successively with 17.5% aqueous sodium hydroxide (800 ml) containing 5% boric acid under the same conditions as described above. The extract was treated in the same manner and precipitated by the addition of ethanol. The precipitate was dissolved in water (300 ml) and a gel-complex produced by the addition of saturated barium hydroxide solution (150 ml)\(^7\) into the solution was collected by centrifugation, and it was dissolved in 2 N acetic acid (300 ml). After evaporation to a half volume of the solution, the addition of ethanol (3~4 volumes) gave a precipitate. The precipitate was collected and obtained as an amorphous powder by drying over phosphorus pentoxide \textit{in vacuo} (yield 3.96 g). Further purification was repeated with barium hydroxide in the same manner as described above (yield 2.56 g) but this fraction P-5 still contained 11.7% of non-carbohydrate. All fractions were dissolved in water and reprecipitated with ethanol. The outline of isolation and fractionation of hemicellulose from a preparative meal of ginkgo nut shell is shown in Fig. 1.

The final residue after extraction was suspended in a large amount of water. The suspension of cellulosic material containing a small quantity of Klason lignin which was separated by mechanical stirring and repeated decantation. The suspension collected by above procedure was filtered to give a residue, R-I. On the other hand, the residue containing much larger quantity of Klason lignin remained in the bottom, which was named R-II.

2.4 Further isolation and fractionation of hemicellulose from the residues of R-I and R-II

Each residue of R-I and R-II was further delignified with the acid-chlorite method, and then was extracted with 24% aqueous potassium hydroxide, followed with 17.5% aqueous sodium hydroxide containing 5% boric acid under the similar conditions as described at the previous part. Further isolation and fractionation of hemicelluloses from the residues of R-I and R-II were carried out as shown in Fig. 2. The hemicelluloses isolated were separated to a glucomannan fraction and a xylan fraction by fractional precipitation with a saturated solution of barium hydroxide as described previously. As a result, a xylan-rich fraction was obtained from the filtrate as the fractions of R-IA, R-IIA and R-IB\(_a\), whereas the fractions of R-IB\(_1\) and R-IIB from the precipitates gave a glucomannan fraction.

2.5 Attempted gel-filtration on Sephadex G-75

Gel-filtration was carried out with a column packed with Sephadex G-75 to a gel
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Fig. 2. Isolation and fractionation of hemicellulose from the residues of R-I and R-II

\[ \text{Residue (R-I, R-II)} \]

\[ \text{NaClO}_2 + \text{AcOH} \]

\[ \text{Product} \]

\[ 24\% \text{ KOH} \]

\[ \text{Ext.} \]

\[ \text{acidiﬁed with AcOH} \]

\[ \text{desalted by dialysis} \]

\[ \text{concent. (ca. 50ml)} \]

\[ \text{EtOH (3-4 vol.)} \]

\[ \text{Ppt} \]

\[ \text{Filt.} \]

\[ \text{dissolved in water (100ml)} \]

\[ \text{discard} \]

\[ \text{Ba(OH)}_2 \]

\[ \text{centri.} \]

\[ \text{Ppt} \]

\[ \text{Sol.} \]

\[ \text{AcOH} \]

\[ \text{desalted by dialysis} \]

\[ \text{concent. (ca. 100ml)} \]

\[ \text{EtOH (3-4 vol.)} \]

\[ \text{R-1A} \]

\[ \text{R-1B} \]

\[ \text{Res.} \]

\[ 17.5\% \text{ NaOH + 5\% boric acid} \]

\[ \text{Ext.} \]

\[ \text{acidiﬁed with AcOH} \]

\[ \text{desalted by dialysis} \]

\[ \text{concent. (ca. 50ml)} \]

\[ \text{EtOH (3-4 vol.)} \]

\[ \text{Ppt} \]

\[ \text{Filt.} \]

\[ \text{dissolved in water (100ml)} \]

\[ \text{discard} \]

\[ \text{Ba(OH)}_2 \]

\[ \text{centri.} \]

\[ \text{Ppt} \]

\[ \text{Sol.} \]

\[ \text{dissolved in 2N AcOH} \]

\[ \text{EtOH (3-4 vol.)} \]

\[ \text{R-1B} \]

\[ \text{R-2B} \]

Fig. 3. Gel-ﬁltration on Sephadex G-75 of P-3-I and P-3-II Gel layer 3.8 x 45 cm

- P-3-I, • P-3-II
Fig. 4. Gel-filtration on Sephadex G-75 of P-5 Gel layer 3.8 x 45 cm

bed volume of 3.6 x 45 cm. The individual hemicellulose fractions of P-3-I, P-3-II and P-5 (ca. 130 mg) were dissolved in water (10 ml) and applied onto the upper of the column of gel bed layer. The column was eluted continuously with distilled water, and each of the eluates collected (10 ml) was analyzed for carbohydrate content with the phenol-sulfuric acid method. The elution diagrams are shown in Fig. 3 and 4. Fraction P-5 was separated into two fractions of P-5-I (28%) and P-5-II (72%) having different molecular weight distribution.

2.6 Further fractionation of P-5-II on QAE-Sephadex A-50 (acetate form)

P-5-II (212 mg) obtained as a main fraction by gel-filtration on Sephadex G-75 of fraction P-5 was dissolved in water (10 ml) and applied further for purification onto a column (3.6 x 46 cm) of QAE-Sephadex A-50 prepared in the acetate form. The column was eluted with distilled water, and then with ammonium acetate solution consecutively by raising the concentration from 0.05 M to 0.5 M, stepwisely. Finally, complete elution was made with the eluents of 0.25 N sodium hydroxide and 0.5 M potassium chloride. The eluate was collected by a portion of constant volume (10 ml) and the carbohydrate content in each tube was determined with the phenol-sulfuric acid method.

2.7 Ultracentrifugal analysis

The sedimentation pattern of P-5-II was observed at 59,780 rpm in 0.15 M KCl using a Spinco model E analytical ultracentrifuge equipped with a schlieren optical system. The result gave a single pattern as shown in Fig. 5.

2.8 Electrophoresis

Electrophoresis was carried out with a Hitachi's Tiselius electrophoresis apparatus (HTB-2B type).

Polysaccharide sample, which was dissolved in 0.05 M borate buffer solution (pH 9.3, ionic strength (μ) 0.14) to a concentration of 1% and dialyzed against the same buffer for 24 hr at 5°C, was submitted for observation of electrophoretic pattern. The
Fig. 5. Sedimentation pattern of P-5-II in 0.15 M KCl
The photographs of sedimentation pattern were taken at indicated times after reaching full speed at 59,780 rpm.

Fig. 6. Electrophoretic pattern of P-5-II
P-5-II is a galacto-glucomannan obtained by gel-filtration on QAE-Sephadex A-50 (acetate from). The pattern shows that of ascending after movement for 1 hr in 0.05 M borate buffer solution.

result is shown in Fig. 6.

2.9 Determination of polysaccharides
A constant volume (0.1~0.2 ml) of the solution containing polysaccharides was pipetted out and diluted to a constant volume (1 ml) with distilled water. To the solution one ml of 5% aqueous phenol solution was added and mixed, and then 5 ml of conc. H$_2$SO$_4$ (super special grade of Wako Pure Chemical Ind.) was added and mixed vigorously. After the mixture was allowed to stand at room temperature (20~25°C) for 20 min, the optical density of yellow-orange color was read at 490 mp$\mu$ for hexosans and at 480 mp$\mu$ for pentosans against a blank solution with a spectrophotometer.
3. RESULTS

A preparative meal of ginkgo nut shell which was defatted previously with a mixed solvent of methanol and benzene (1:2, v/v) was delignified according to the usual acid-chlorite method. However, the product obtained by one treatment with sodium chlorite still contained 28.9% of non-carbohydrate substances as Klason lignin. Therefore, the preparative meal still contained considerable amounts of substances which were more difficult to remove on delignification than wood meal, but the meal was used for extraction of the hemicellulose without further delignification.

The hemicellulose was isolated by extraction with 24% aqueous potassium hydroxide, followed successively with 17.5% aqueous sodium hydroxide containing 5% boric acid from the above meal. Each of the extracts was acidified with acetic acid, dialyzed for desalting and evaporated, and then hemicellulose was precipitated by the addition of a large amount of ethanol. Hemicellulose fraction containing a glucomannan was fractionally precipitated repeatedly with barium hydroxide. The yields and properties of the fractions of hemicellulose as shown in Fig. 1 are summarized in Table 1.

Table 1. Yields and properties of polysaccharides obtained by fractionation of hemicellulose of a ginkgo nut shell

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield (g)</th>
<th>( \left[ \alpha \right]_{D}^{25} (\text{H}_2\text{O}) ) degrees</th>
<th>OMe (%)</th>
<th>Sugar composition (%)</th>
<th>Uronic anhydride (%)</th>
<th>Non-carbohydrate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gal</td>
<td>Glu</td>
<td>Man</td>
<td>Ara</td>
</tr>
<tr>
<td>P-1</td>
<td>0.43</td>
<td>-8.4</td>
<td>10.7</td>
<td>+</td>
<td>15.5</td>
<td>73.8</td>
</tr>
<tr>
<td>P-2</td>
<td>0.23</td>
<td>-32.5</td>
<td>+</td>
<td>7.4</td>
<td>6.5</td>
<td>4.6</td>
</tr>
<tr>
<td>P-3-I</td>
<td>9.61</td>
<td>4.61</td>
<td>+</td>
<td>+</td>
<td>8.8</td>
<td>91.2</td>
</tr>
<tr>
<td>P-3-II</td>
<td>7.01</td>
<td>-28.7</td>
<td>+</td>
<td>+</td>
<td>9.1</td>
<td>90.2</td>
</tr>
<tr>
<td>P-4</td>
<td>0.67</td>
<td>4.51</td>
<td>7.5</td>
<td>+</td>
<td>+</td>
<td>7.0</td>
</tr>
<tr>
<td>P-5</td>
<td>2.56</td>
<td>-20.8</td>
<td>7.2</td>
<td>21.8</td>
<td>48.2</td>
<td>+</td>
</tr>
<tr>
<td>Res.</td>
<td>82.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

P-3-I: Fraction precipitated with 50% ethanol, P-3-II: Fraction recovered from the remaining solution of P-3-I.

Gal, galactose; Glu, glucose; Man, mannose; Ara, arabinose; Xyl, xylose.

+: present on paper chromatogram.

Table 1. The predominating fraction, which corresponds to an arabino-(4-O-methyl-D-glucurono) xylan, was separated into the fraction (P-3-I) precipitated by the addition of ethanol to a concentration of 50% and the fraction (P-3-II) recovered from the filtrate of P-3-I. These fractions contained significant amounts of non-carbohydrates, as shown in the respective values of 27.9% for P-3-I and 18.4% for P-3-II as Klason lignin, giving somewhat high methoxyl content. From sugar composition analysis, significant amounts of galactose residues were found in the fractions of P-1 and P-4, but further examination was not carried out.
The final residue gave R-I (49.6 g) containing 5.8% of Klason lignin and R-II (33.1 g) containing 43.5% of it, respectively. The yields and properties of R-I and R-II are shown in Table 2. These residues were found to contain substantial amounts of xylan and mannan, in addition to non-carbohydrate. Therefore, after further mild treatment with the acid-chlorite method, hemicellulose was isolated by additional extraction with aqueous alkali and separated through a fractional precipitation with barium hydroxide. The yields and properties of the hemicellulose thus isolated and fractionated from R-I and R-II are summarized in Table 3. Fraction extracted with 24% aqueous potassium hydroxide mainly gave a xylan containing a small amount of a galacto-glucan. On the other hand, from fraction extracted with 17.5% aqueous sodium hydroxide containing 5% boric acid, a galacto-glucan composed of the residues of D-galactose, D-glucose and D-mannose in a molar ratio of 0.1:1.0:3.7, respectively, was obtained as the predominating product. The yields and properties of R-I and R-II after additional extraction with aqueous alkali are shown in Table 4.

Table 2. Yield and properties of the residues of R-I and R-II

<table>
<thead>
<tr>
<th></th>
<th>Yield (g)</th>
<th>Klason lignin (%)</th>
<th>Sugar composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gal</td>
</tr>
<tr>
<td>R-I</td>
<td>49.6</td>
<td>5.8</td>
<td>0.6</td>
</tr>
<tr>
<td>R-II</td>
<td>33.1</td>
<td>43.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 3. Yields and properties of hemicellulose isolated from the residues of R-I and R-II after additional extraction with aqueous alkali

<table>
<thead>
<tr>
<th>Fraction extracted with 24% KOH</th>
<th>Yield (g)</th>
<th>[α]D° H2O</th>
<th>Sugar composition (%)</th>
<th>Uronic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-IA</td>
<td>0.76</td>
<td>-32.5</td>
<td>3.7 4.0 10.8 7.4</td>
<td>74.4</td>
</tr>
<tr>
<td>R-HA</td>
<td>1.89</td>
<td>-34.0</td>
<td>2.3 2.8 9.5 7.3</td>
<td>78.1</td>
</tr>
<tr>
<td>R-IB1</td>
<td>0.94</td>
<td>-20.1</td>
<td>2.3 20.9 76.8 ±</td>
<td>+</td>
</tr>
<tr>
<td>R-IB2</td>
<td>0.04</td>
<td></td>
<td>1.5 5.8 15.8 7.2</td>
<td>69.7</td>
</tr>
<tr>
<td>R-IB3</td>
<td>0.53</td>
<td>-20.9</td>
<td>2.0 19.6 72.8</td>
<td>5.6</td>
</tr>
<tr>
<td>Fraction extracted with 17.5% NaOH containing 5% boric acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Yields and properties of the residues of R-I and R-II after additional extraction with aqueous alkali

<table>
<thead>
<tr>
<th></th>
<th>Yield (g)</th>
<th>Klason lignin (%)</th>
<th>Sugar composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-I</td>
<td>37.9</td>
<td>-</td>
<td>+ 96.2 3.8 --</td>
</tr>
<tr>
<td>R-II</td>
<td>15.3</td>
<td>4.7</td>
<td>+ 88.5 8.8 +</td>
</tr>
</tbody>
</table>

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in Table 4. The residues of R-I and R-II still contained minute quantities of mannan resistant to remove, but, in view of the yields and sugar composition, a greater part of hemicellulose may be considered to have been isolated from the final residue of ginkgo nut shell.

Fraction P-5, which corresponds to a water-soluble galacto-glucomannan, was purified by repeated fractional precipitation with barium hydroxide and gel-filtration on Sephadex G-75. The yields and properties of two fractions (P-5-I and P-5-II) separated by gel-filtration on Sephadex G-75 are shown in Table 5. However, since the main

<table>
<thead>
<tr>
<th>Yield (%)</th>
<th>$[\alpha_{D}]_{20}^{20}$ (H$_2$O) degrees</th>
<th>Sugar composition (%)</th>
<th>Mole ratio of sugars</th>
<th>Uronic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Xyl</td>
<td>Man</td>
<td>Glu</td>
</tr>
<tr>
<td>P-5-I</td>
<td>28.2</td>
<td>13.8</td>
<td>41.4</td>
<td>37.1</td>
</tr>
<tr>
<td>P-5-II</td>
<td>71.8</td>
<td>5.2</td>
<td>57.2</td>
<td>33.1</td>
</tr>
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</table>

Table 6. Fractionation by gel-filtration on QAE-Sephadex (A-50, acetate form) of watersoluble galacto-glucomannan (P-5-II)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Eluent</th>
<th>Fraction number</th>
<th>Yield (mg)</th>
<th>$[\alpha_{D}]_{20}^{20}$ (H$_2$O) degrees</th>
<th>Mole ratio of sugars</th>
<th>Uronic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Xyl</td>
<td>Man</td>
</tr>
<tr>
<td>F-1</td>
<td>0.05 M</td>
<td>AcONH$_4$</td>
<td>30-80</td>
<td>90.2</td>
<td>-19.3</td>
<td>1.7</td>
</tr>
<tr>
<td>F-2</td>
<td>0.1 M</td>
<td>AcONH$_4$</td>
<td>83-120</td>
<td>10.9</td>
<td>-25.8</td>
<td>1.6</td>
</tr>
<tr>
<td>F-3</td>
<td>0.5 M</td>
<td>AcONH$_4$</td>
<td>125-200</td>
<td>24.7</td>
<td>-26.8</td>
<td>+</td>
</tr>
<tr>
<td>F-4</td>
<td>0.25 N</td>
<td>NaOH</td>
<td>201-220</td>
<td>9.9</td>
<td>+</td>
<td>1.0</td>
</tr>
<tr>
<td>F-5</td>
<td>0.5 M</td>
<td>KCl</td>
<td>221-270</td>
<td>38.6</td>
<td>-23.6</td>
<td>1.4</td>
</tr>
<tr>
<td>F-6</td>
<td>0.5 N</td>
<td>HCl</td>
<td>285-305</td>
<td>5.9</td>
<td>+</td>
<td>1.0</td>
</tr>
</tbody>
</table>

fraction of P-5-II still contained a small amount of xylose residues, an attempt was further made for fractionation through gel-filtration on QAE-Sephadex A-50 prepared in the acetate form. Consequently, the water-soluble galacto-glucomannan was fractionated into six fractions as shown in Table 6. The main fraction eluted with 0.05 M ammonium acetate solution gave a pure galacto-glucomannan having no residues of xylose and uronic acid. This polysaccharide which was homogeneous electrophoretically and in ultracentrifugal analysis showed a specific rotation of $[\alpha_{D}]_{20}^{20} -19.3^\circ$ ($c=1.80$, H$_2$O), and it contained the sugar residues of d-galactose, d-glucose and d-mannose in a molar ratio of 0.3 : 1.0 : 1.7, respectively.

Thus, from the result of composition analysis of the polysaccharides obtained by fractionation, a preparative defatted meal of ginkgo nut shell was found to contain a
galacto-glucomannan (2.6 %), an arabino-(4-O-methyl-D-glucurono) xylan (9.8 %) and other polysaccharides (0.8 %). Therefore, hemicellulose occurring in a ginkgo nut shell is mainly composed of the similar glucomannan and xylan as that of the wood, except that hemicellulose of the nut shell contains much higher amounts of the xylan fraction rather than the glucomannan fraction.

4. DISCUSSION

Various properties of hemicelluloses of a ginkgo nut shell were compared with those of the wood. Table 7 and 8 show their general characteristics of hemicelluloses of the wood and the nut shell. Hemicellulose of the nut shell gives an arabino-(4-O-methyl-D-glucurono) xylan in higher yield than a glucomannan.

Table 7. A comparison of general characteristics of arabino-(4-O-methyl-D-glucurono) xylans isolated from wood and nut shells of ginkgo.

<table>
<thead>
<tr>
<th></th>
<th>Yield (%)</th>
<th>Xylose, per acid res.</th>
<th>Xyl/Ara</th>
<th>([\alpha]_{D, \text{g}}) degrees</th>
<th>Rotation solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>6</td>
<td>9.0</td>
<td>4.0</td>
<td>-35</td>
<td>Alkali</td>
<td>(1)</td>
</tr>
<tr>
<td>(Ginkgo biloba)</td>
<td>9.8</td>
<td>11~12</td>
<td>10~11</td>
<td>-26.8</td>
<td>Water</td>
<td>present</td>
</tr>
</tbody>
</table>

Table 8. A comparison of general characteristics of galacto-glucomannans isolated from wood and nut shells of ginkgo.

<table>
<thead>
<tr>
<th></th>
<th>Yield (%)</th>
<th>Molar ratio of sugars</th>
<th>([\alpha]_{D, \text{g}}) degrees</th>
<th>Rotation solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>0.8</td>
<td>1.0</td>
<td>1.0</td>
<td>-7</td>
<td>Water</td>
</tr>
<tr>
<td>(Ginkgo biloba)</td>
<td>5.0</td>
<td>0.2</td>
<td>1.0</td>
<td>-36</td>
<td>Alkali</td>
</tr>
<tr>
<td>Ginkgo nut shell</td>
<td>1.5</td>
<td>0.3</td>
<td>1.0</td>
<td>-19.3</td>
<td>Water</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>0.1</td>
<td>1.0</td>
<td>-20.5</td>
<td>Water</td>
</tr>
</tbody>
</table>

The occurrence of two types of glucomannans in the softwoods has been pointed out and verified by Timell\textsuperscript{1). In general, one type of a water-soluble galacto-glucomannan contains the sugar residues of D-galactose, D-glucose and D-mannose in a common ratio of 1.0:1.0:3.0, respectively, and its specific rotation most frequently shows the values of \(-7^\circ\) to \(-8^\circ\). Other widespread type is an alkali-soluble glucomannan, having a higher molecular weight, a negative specific rotation of \(-30^\circ\) to \(-40^\circ\) and the respective residues of D-galactose, D-glucose and D-mannose in a ratio of 0.1:1.0:3.0. In the ginkgo nut shell, a water-soluble galacto-glucomannan containing a different sugar composition was isolated in a yield of 1.5 % based on a preparative defatted meal, and a so-called alkali-soluble galacto-glucomannan was 1.1 %. On the contrary, a xylan fraction amounted to 9.8 %. It seems to be noteworthy that a xylan fraction
constitutes the predominating hemicellulose in the ginkgo nut shell, because the finding differs from the pattern of usual hemicelluloses in the heartwood of the softwoods.

REFERENCES