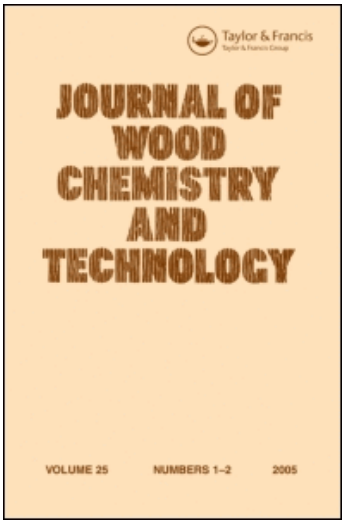

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RESIDUAL LIGNIN IN UNBLEACHED KRAFT PULP. Part 2

-Analysis of Unbleached Kraft Pulp by New Permethylation Method-

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ABSTRACT

Unbleached kraft pulp (UKP), its residue after extraction with concentrated alkali (α-UKP), bleached kraft pulp prepared from UKP (BKP) and its residue after extraction with concentrated alkali (α-BKP) were permethylated with powdered NaOH and CH_3I in their SO_2-diethylamine (DEA)-dimethylsufoxide (DMSO) solutions.

The permethylated samples were separated into three fractions by gel filtration chromatography, according to molecular weights. Lignin contents and sugar compositions in the three fractions inidcated that: 1) the residual lignin in UKP had some alkali-stable chemical linkages with both hemicelluloses and cellulose, and certainly those linkages with cellulose cause the resistance of the residual lignin to further delignification reactions, and 2) the residual hemicellulose, at least in the fraction having the highest molecular weight, is most likely linked chemically to cellulose with direct and/or indirect linkages.

INTRODUCTION

It is very important to elucidate the characteristics and the structures of the residual lignin in UKP for modifications of pulping and bleaching processes.

In the preceding paper[1], we reported a study of the extractability of the residual lignin with various solvents from

homogeneous UKP/SO_2-DEA-DMSO solutions. By using aqueous NaOH, 10-50% of the residual lignin was extracted together with alkali-extractable polysaccharides such as xylan, glucomannan and low molecular weight cellulose, whereas by using solvents for kraft lignin, only several percent of the residual lignin was extracted.

These results suggested that the residual lignin extracted by the alkali treatments had some chemical linkages to the extracted polysaccharides. It also suggested that the resistance of the residual lignin to further delignification reactions is caused not only by chemical linkages between the residual lignin and polysaccharides, but also by trapping the extractable lignin-polysaccharide complexes in cell wall matrices.

On the other hand, approximately one-half of the residual lignin still remained in the alkali-insoluble parts of UKP solutions, together with large amounts of glucose mainly originating from cellulose and with small amounts of sugars originating from hemicellulose. The reason why some residual lignin and hemicellulose still remain in the alkali-insoluble part of UKP is not known.

We now report a new, facile permethylation method for cellulosic samples, in which the SO_2-DEA-DMSO, powdered NaOH, and CH_3I are used as the solvent, base, and methylation reagent, respectively. This method is superior to other methods proposed previously for cellulosic samples from the viewpoints of yield, complete methylation, little depolymerization, stability of reagents, simple handling, etc.[2]

Various UKP samples were permethylated by the new method, and the permethylated samples were fractionated into three parts by gel filtration chromatography. Each fraction was analysed by UV and GLC to characterize the residual lignin and hemicellulose.

EXPERIMENTAL

General analyses: Infrared (IR) spectra were measured with a Shimazu IR-400 spectrometer on films deposited from chloroform

solutions. Gel permeation chromatograms were obtained using a Waters ALC/GPC 244 system with Styragel columns 10^5, 10^4, 10^3, 500 and 100 A in series and chloroform as an eluent.

Samples and reagents: A commercial kraft pulp produced from mixed soft woods by Tokai Pulp Co. Ltd. was used as a UKP sample after defibration by a mixer. Bleached kraft pulp (BKP) was prepared from UKP by single stage treatment with $NaClO_2$-CH_3COOH in water at 75°C for 1 h.[3]. α-UKP and α-BKP were prepared from UKP and BKP, respectively, by the usual procedure for complete extraction of hemicellulose. Namely, the sample was stirred in 24% NaOH solution containing 3% Na_2BO_3 and 1% $NaBH_4$ at room temperature for 12 h under N_2 atmosphere. Then, the alkali-soluble portion was removed by filtration with a glass filter (1G2), and the residue was washed successively with dilute NaOH, a large volume of water, dilute CH_3COOH, a large volume of water, and acetone, and dried at 60°C in vacuo.

Pure grade DMSO was dried over molecular sieve 3A. CH_3I was used after distillation. The SO_2/DMSO solution and powdered NaOH were prepared as described in the previous paper.[2] Other reagents and solvents were used without further purifications.

Dissolution of samples in the SO_2-DEA-DMSO system: Dry sample (1 g) was dispersed in 87.7 ml DMSO, and the suspension was heated at 60°C for 0.5 h. After cooling to room temperature, an accurate amount of the SO_2/DMSO solution containing 1.19 g SO_2, and then 1.91 ml DEA was added to the mixture. A clear solution was obtained within 3 h.

Permethylation of samples: UKP samples and fractions were permethylated products of UKP as described in the previous paper.[2] The extent of methylation was checked by hydroxyl absorption in their IR spectra.

Fractionation of permethylated samples: A Sepharose CL-4B column (37 X 2.5 cm) was prepared with $CHCl_3$-MeOH (9:1, vol) as an eluent in a SR 25/45 column (Pharmacia Fine Chemicals). Permethylated sample (ca. 12 mg) was dissolved in a few ml of the solvent, and injected into the column at room temperature with a

flow rate 1.2 ml/min. Eluates were checked by UV absorbance at 280 nm. Fractions of 5.6 ml were collected.

Analysis of sugar composition: Pulp samples were hydrolyzed by the method of Saeman et al.[4] The monosaccharides were analysed as alditol acetates by GLC, using a column (2 m X 3 mm) of Gas Chrom P coated with a mixture of 0.2% PEGA, 0.2% PEGS and 0.4% silicone XF-1150.

Analysis of methylated sugars: The permethylated samples were successively hydrolyzed with 90% HCOOH and with 0.25M H_2SO_4. The hydrolyzates were neutralized with $BaCO_3$, and the precipitated $BaSO_4$ and excess $BaCO_3$ were removed by centrifugation and filtration. Liberated partially methylated sugars were reduced with $NaBH_4$ and converted into the corresponding methylated alditol acetates. They were separated by GLC using a capillary column (50 m X 0.27 mm) coated with silicone OV-101 from 150°C to 220°C at 2°C/min with a helium flow rate 1 ml/min. For separation of 2,3,6-Man, 2,3,6-Gal and the unknown peak F in Fig. 4, another capillary column (40 m X 0.28 mm) coated with SP-1000 was used. Peak areas were measured with a Hewlett-Packard 3380 A integrator. GLC-MS was performed with a Hitachi M-80 mass spectrometer (20 eV) using a column of OV-101. Each peak was identified by fragmentation and retention time.

Lignin contents: Lignin contents of the pulp samples were measured by the Klason method. Lignin contents in permethylated samples were determined from UV absorbance of their $CHCl_3$ solutions at 280 nm. The gram absorption coefficient of the lignin at 280 nm (E_{280}) was calculated as described in a later section.

RESULTS

Permethylation of UKP, α-UKP, BKP, and α-BKP

α-UKP, BKP and α-BKP samples were prepared from UKP as shown in Experimental. Sugar compositions and Klason lignin contents in these samples are shown in Table 1.

TABLE 1

Sugar compositions and lignin contents in samples

Sample	Sugar composition (%)*						Klason lignin
	Rha	Ara	Xyl	Man	Gal	Glc	content (%)
UKP	0.3	0.6	6.9	6.8	+	85.4	4.7
α-UKP	0.5	0.9	2.5	4.1	+	91.9	3.3
BKP	0.4	0.5	5.0	5.8	+	88.3	trace
α-BKP	0.5	0.7	2.1	3.1	+	93.6	trace

* Total adjusted to 100%.

The amount of hemicellulosic sugars in UKP decreased substantially with alkaline extraction, and approximately 30% of the the residual lignin was removed. Klason lignin contents in BKP and α-BKP were negligible as a result of the $NaClO_2$-CH_3COOH treatment. As these four samples were completely soluble in the SO_2-DEA-DMSO system, they were methylated easily and completely.[2]

IR spectra of the four methylated samples (Me-UKP, Me-α-UKP, Me-BKP, and Me-α-BKP) showed no absorption around 3400 cm^{-1} due to hydroxyl groups (Figure 1).

These permethylated samples were separated into three fractions by gel filtration chromatography. Fig. 2 shows the gel filtration chromatograms of the four methylated samples (detection by UV absorbence at 280 nm). Dividing lines for the fractionations are also shown in the figure. The fractionation should depend only on the molecular weight of the component to be separated, since association between the polysaccharides and the residual lignin solutions should be essentially eliminated by the etherification of the hydroxl groups.

Each fraction was analysed by UV and GLC in order to elucidate the characteristics of the residual lignin and the residual hemicellulose in the samples.

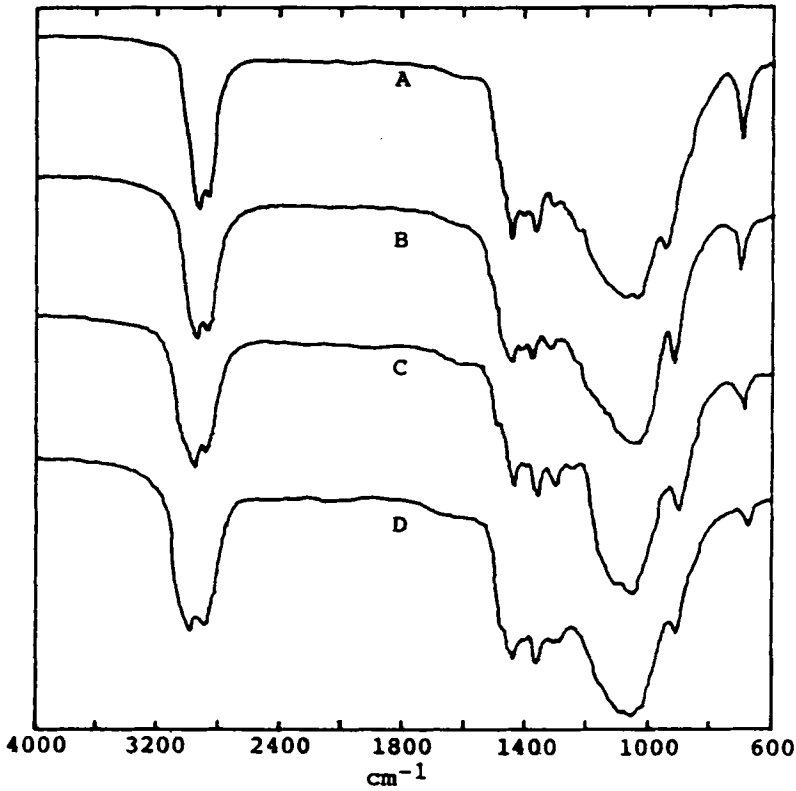

Figure 1 IR spectra of methylated samples. A:Me-UKP, B:Me-α-UKP, C:Me-BKP, D:Me-α-BKP.

Analysis of Me-UKP

Fig. 3 shows the UV spectra of Me-UKP, its three fractions, permethylated cellulose powder and permethylated starch. The gram absorption coefficient of lignin at 280 nm (E_{280}) was calculated by the use of the following equations.

$$E_{280} = (1\ cm/g)(A_{280})/(C'1) \quad (1)$$

$$L = M/(M + N) \quad (2)$$

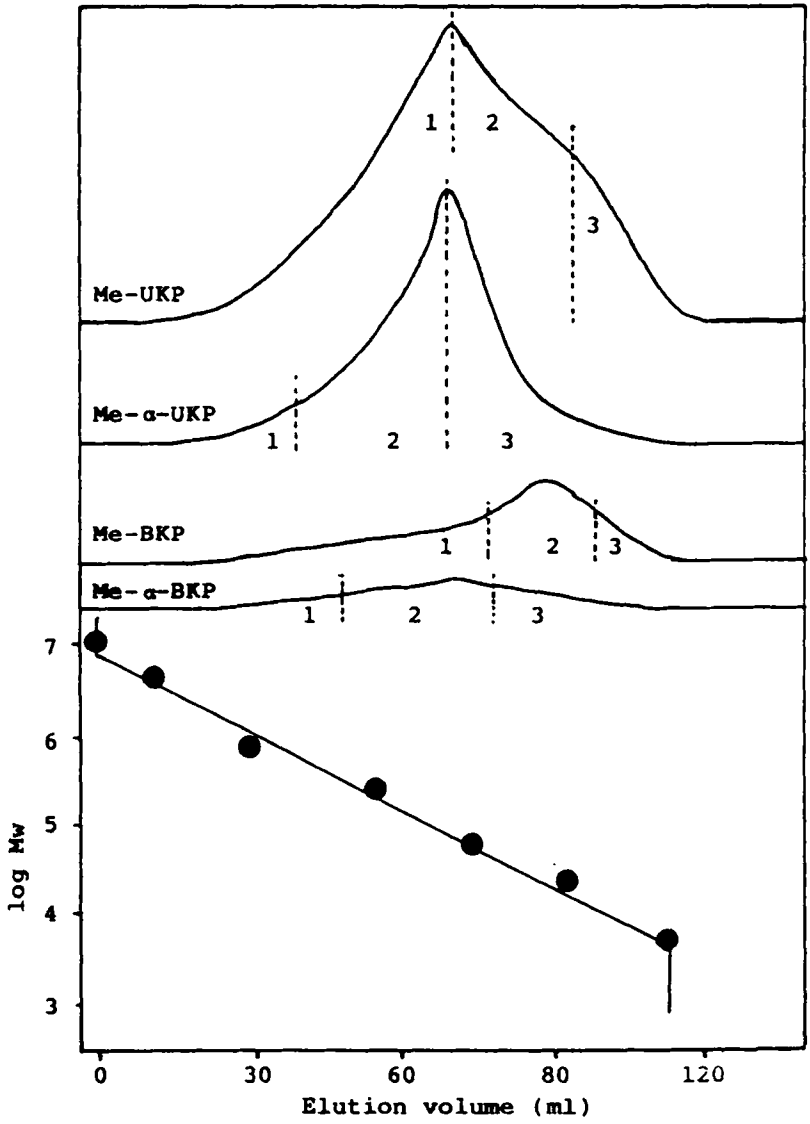

Figure 2 Gel filtration curves of permethylated samples and a calibration curve determined by using polystyrene standards. Dotted lines indicate the fractionations.

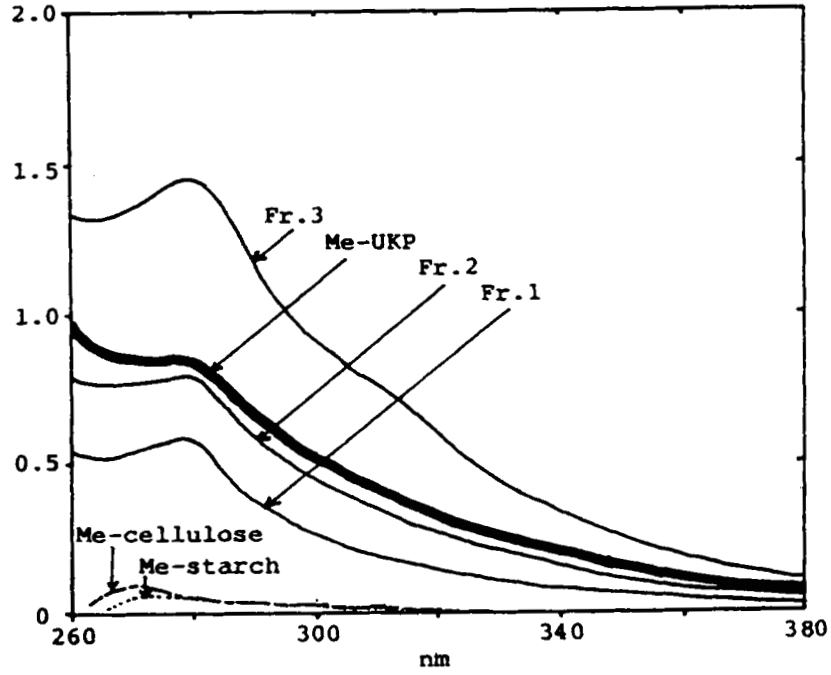

Figure 3 UV spectra of Me-UKP, its three fractions, permethylated cellulose powder and permethylated starch.

where $M = Y(180 + 14*1.4)/180$

and $N = X(162 + 14*3)/162$

$$C' = C*L \qquad (3)$$

where C' = lignin content in the solution, A_{280} = absorbence at 280 nm, l = cell thickness, C = concentration (g/l) of the methylated sample in the solution, L = lignin % in the methylated sample, X = carbohydrate % in the sample (See Table 1), Y = lignin % in the sample (Table 1), 162 = molecular weight of an anhydroglucose unit, 180 = molecular weight of a phenylpropane unit in lignin, 14 = weight increase of a hydroxyl group by methylation, and 1.4 = total OH/phenylpropane unit[5].

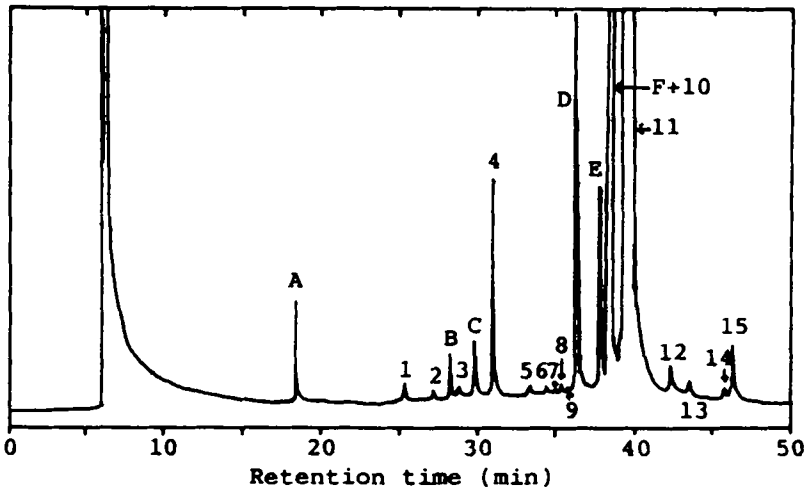

Figure 4 Gas chromatogram of partially methylated alditol acetates obtained from Me-UKP, run on a column of OV-101. 1:2,3,5-Ara, 2:2,3,4-Xyl, 3:2,5-Ara and 3,5-Ara, 4:2,3-Xyl and 3,4-Xyl, 5:2,3,4,6-Glc, 6:2,3,4,6-Gal, 7:2-Ara, 8:3-Xyl, 9:3-Rha, 10:2,3,6-Man, 2,3,6-Gal and unknown F, 11:2,3,6-Glc, 12:2,6-Glc, 13.3,6-Glc, 14:2,3-Man, 15:2,3-Glc, A-F:unknown.

All of the carbohydrates in the methylated samples were calculated as cellulose. E_{280} of Me-UKP was calculated as 20.0 (1 cm/g).

Fig. 4 shows a gas chromatogram from methylated sugar analysis. Since peak F overlapped 2,3,6-Man and 2,3,6-Gal, this separation was performed using a capillary column (SP-1000) as described in the Experimental section.

Table 2 shows the compositions of methylated sugars obtained from Me-UKP and its three fractions. Noticeably, the amount of 2,3-Glc is more than twice as much as that of 2,6-Glc and 3,6-Glc in all of the fractions.

Sugar compositions calculated from the data in Table 2, and lignin contents calculated from UV absorbencies and the value of

TABLE 2

Composition of methylated sugars of Me-UKP and its three fractions

	Retention coefficient[a]	Me-UKP	Fr.1	Fr.2	Fr.3
3-Rha[b]	1.05	0	0	0	0.8
2,3,5-Ara	0.74	0.5	0.2	0.3	0.4
2,5 | 3,5 -Ara	0.86	0.	0.1	0	0.1
2-Ara	1.02	0.3	0	0	0.1
2,3,4-Xyl	0.79	0	0.1	0.2	0.2
2,3 | 3,4 -Xyl	0.92	4.3	2.9	5.0	6.3
3-Xyl	1.04	1.3	0.4	0.6	0.9
2,3,6-Man	1.11	5.9	5.1	5.7	5.7
2,3-Man	1.31	0.7	0.3	0.3	0.4
2,3,4,6-Gal	1.00	0.3	0.1	0	0.2
2,3,4-Gal	1.21	0	0	0	0.1
2,3,4,6-Glc	0.97	0.3	0.4	0.6	0.3
2,3,6-Glc	1.13	82.7	86.5	83.6	80.0
2,6-Glc	1.23	1.1	0.6	0.7	0.6
3,6-Glc	1.26	0.4	1.0	0.4	0.9
2,3-Glc	1.33	2.2	2.3	2.6	3.0

a - Relative to 2,3,4,6-Gal.
b - 3-Rha = 1,2,4,5-tetra-O-acetyl-3-O-methyl-rhamanitol, etc.

E_{280} are summarized in Table 3. The highest percentage of residual lignin and hemicellulose occur in Fr. 3, the lowest molecular weight fraction. However, residual lignin and hemicellulose also occur in Fr. 1, the highest molecular weight fraction.

Analysis of Me-α-UKP

Fig. 5 and Table 4 show the UV spectra and compositions of methylated sugars, respectively, of fractions separated from Me-α-UKP.

The absorption coefficient (E_{280}) of the residual lignin in Me-α-UKP was 20.4 (1 cm/g), very similar to that of Me-UKP (20.0).

TABLE 3

Sugar compostions and lignin contents of Me-UKP and its three fractions

Sample	Yield (%)	Lignin content(%)	Sugar composition (%)[a]					
			Rha	Ara	Xyl	Man	Gal	Glc
Me-UKP		4.2[b]	+	0.8	5.6	6.6	0.3	86.7
Fr.1	54.0	3.5[c]	+	0.3	3.4	5.4	0.1	90.8
Fr.2	23.9	4.2[c]	+	0.3	5.8	6.0	0	87.9
Fr.3	22.1	7.3[c]	0.8	0.6	7.4	6.1	0.3	84.9
Fr.1-3	100.0	4.5	0.2	0.4	4.9	5.7	0.1	88.7

a - Total adjusted to 100%.
b - Calculated according to the formula (2).
c - Calculated by using E_{280} and A_{280}.

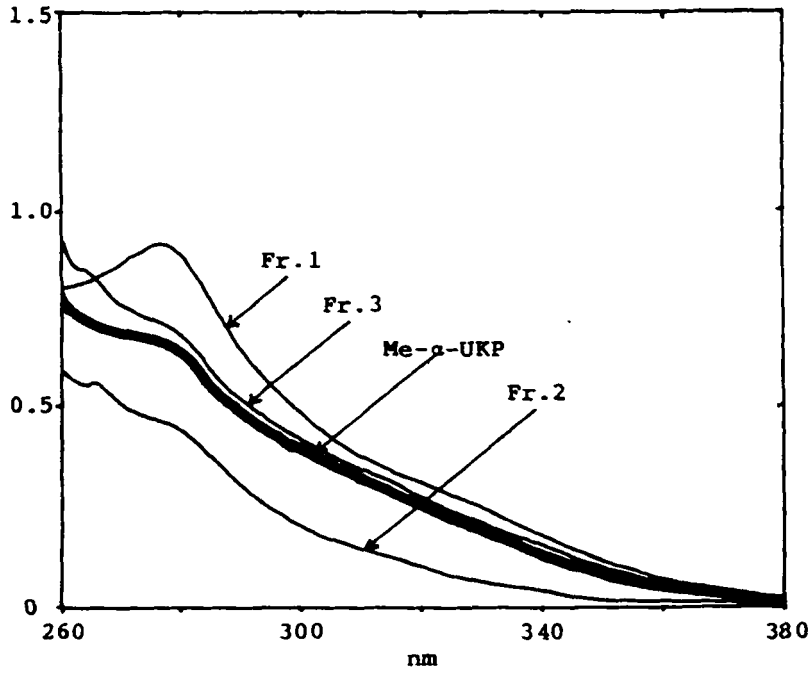

Figure 5 UV spectra of Me-α-UKP and its three fractions.

TABLE 4

Composition of methylated sugars of three fractions separated from Me-α-UKP

	Fr.1	Fr.2	Fr.3
3,4-Rha	0	0.8	0.6
3-Rha	0	0.5	0
2,3,5-Ara	0	0	1.2
2,5-Ara	0	0.4	0.4
3,5-2,3-Ara	0	0.1	0.4
2,3,4-Xyl	0.5	0.2	0.8
2,3-3,4-Xyl	2.1	0.6	1.6
3-Xyl	0.8	0.4	0.6
2,3,6-Man	2.2	1.5	4.0
4,6-Man	0	0.1	0.4
2,3-Man	0.4	0.8	1.1
2,3,4,6-Gal	0.3	0.4	0.9
2,3,4-Gal	0	0.6	0
2,3,6-Glc	90.3	89.0	84.4
2,6-Glc	0.7	1.1	0.9
3,6-Glc	0.7	1.3	1.2
2,3-Glc	2.0	2.2	1.7

The lignin contents and sugar compositions of the Me-α-UKP fractions are summarized in Table 5. Compared with the values shown in Table 3, the lignin contents in Fr.2 and Fr.3 are significantly decreased. However, Fr.1, the highest molecular weight fraction, still has a high lignin content. In addition, xylose and mannose still remain in Fr.1. The percentages of 2,3-Glc in all fractions are higher than those of 2,6-Glc and 3,6-Glc, which is similar to the case of Me-UKP.

Analysis of Me-BKP

Fig. 6 and Table 6 show the UV spectra and compositions of methylated sugars, respectively, of each fraction separated from Me-BKP.

TABLE 5

Sugar compositions and lignin contents of fractions separated from Me-α-UKP*

Sample	Yield (%)	Lignin content(%)	Sugar composition (%)					
			Rha	Ara	Xyl	Man	Gal	Glc
Me-α-UKP		2.9						
Fr.1	5.6	4.5	0	0	3.4	2.6	0.3	93.7
Fr.2	55.0	2.2	1.3	0.5	1.2	2.4	1.0	93.6
Fr.3	39.4	3.4	1.6	2.0	2.8	5.5	0.9	88.2
Fr.1-3	100.0	2.8	0.9	1.1	2.0	3.6	0.9	91.5

* See the footnote in Table 3.

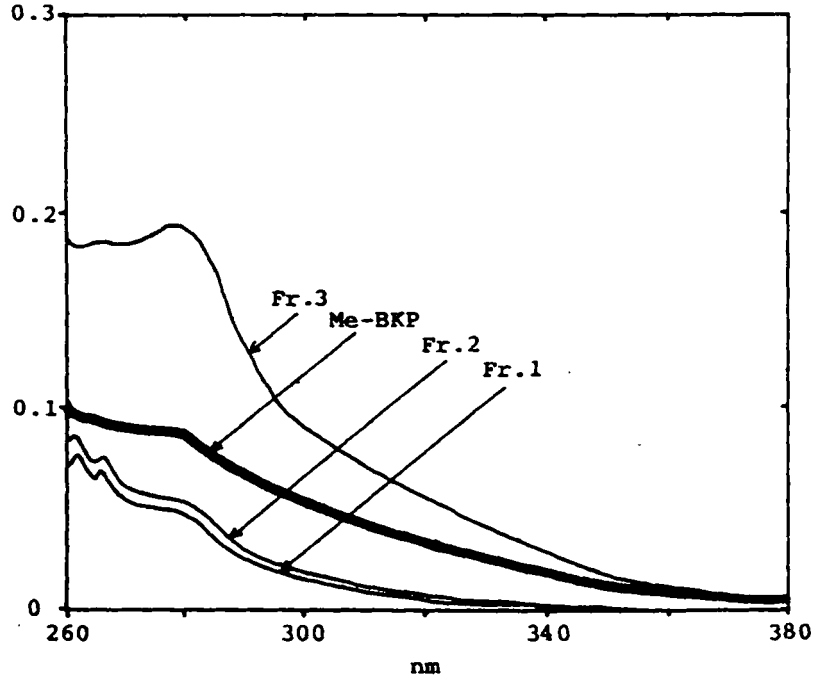

Figure 6 UV spectra of Me-BKP and its three fractions.

TABLE 6

Compositions of methylated sugars of fractions separated from Me-BKP

	Fr.1	Fr.2	Fr.3
2,3,5-Ara	0.1	0.2	0.3
2,5-Ara	0	0.1	0.1
3,5			
2,3,4-Xyl	0.1	0.1	0.2
2,3-Xyl	1.5	3.5	6.1
3,4			
3-Xyl	0.2	0.3	0.4
2,3,6-Man	2.2	2.5	1.9
2,3-Man	0.1	0.1	0
2,3,4,6-Glc	0.1	0.3	0.4
2,3,6-Glc	93.4	90.8	88.4
2,6-Glc	0.5	0.5	0.5
3,6-Glc	0.6	0.5	0.5
2,3-Glc	1.2	1.1	1.2

As the result of the single stage treatment of UKP with $NaClO_2$-CH_3COOH, the UV absorbance of Me-BKP at 280 nm due to the residual lignin decreased remarkably, when compared with that of Me-UKP and that of Me-α-UKP. Fr.3 still had a relatively high absorbance at 280 nm. Since this BKP sample had little Klason lignin, E_{280} could not be calculated using equations (1)-(3). Furthermore, since the chemical structure of the residual lignin in BKP should be different from that in UKP due to the oxidation with $NaClO_2$-CH_3COOH, the lignin contents in the fractions cannot be calculated from UV absorbences by using the value of E_{280} obtained from Me-UKP and Me-α-UKP. Hardell and Sousa[6] reported that E_{280} of lignin in BKP bleached with Cl_2 is 3-14. Thus, lignin contents in fractions separated from Me-BKP are roughly calculated by using 14 for E_{280}, and are summarized in Table 7 together with sugar compositions. Compared with the sugar composition of BKP (Table 1), clearly some sugars originating

TABLE 7

Sugar compositions and lignin contents of fractions separated from Me-BKP

Sample	Yield (%)	Lignin content(%)*	Sugar composition (%)					
			Rha	Ara	Xyl	Man	Gal	Glc
Me-BKP		0.5						
Fr.1	62.5	0.3	0	0.1	1.8	2.3	0	95.8
Fr.2	24.2	0.4	0	0.3	3.9	2.6	0	93.2
Fr.3	13.3	1.1	0	0.4	6.7	1.9	0	91.0
Fr.1-3	100.0	0.4	0	0.2	3.0	2.3	0	94.5

* - Calculated from A_{280} assuming that E_{280} = 14.

from hemicellulose in BKP are removed during the methylation and/or isolation procedure.

Analysis of Me-a-BKP

Fig. 7 and Table 8 show the UV spectra and composition of methylated sugars, respectively for Me-a-BKP fractions. These results are summarized in Table 9. When compared with the lignin contents of the corresponding fractions of Me-BKP, that of Fr. 3 of Me-a-BKP was much lower, but those of Fr.1 and Fr.2 were similar. The glucose contents increased a little in all fractions as the result of alkali-extraction. Fr.1 accounting for 10.7% of Me-a-BKP still contained xylose and mannose residues.

DISCUSSION

As discussed in the introduction, the permethylation method was applied to the four samples related to UKP in order to elucidate the characteristics of the residual lignin and the residual hemicellulose in UKP. Fig. 3 indicates that very little absorption in the UV is caused by the permethylated polysaccharides, as shown for cellulose powder and starch. Thus, the residual lignin in the four methylated samples was determined

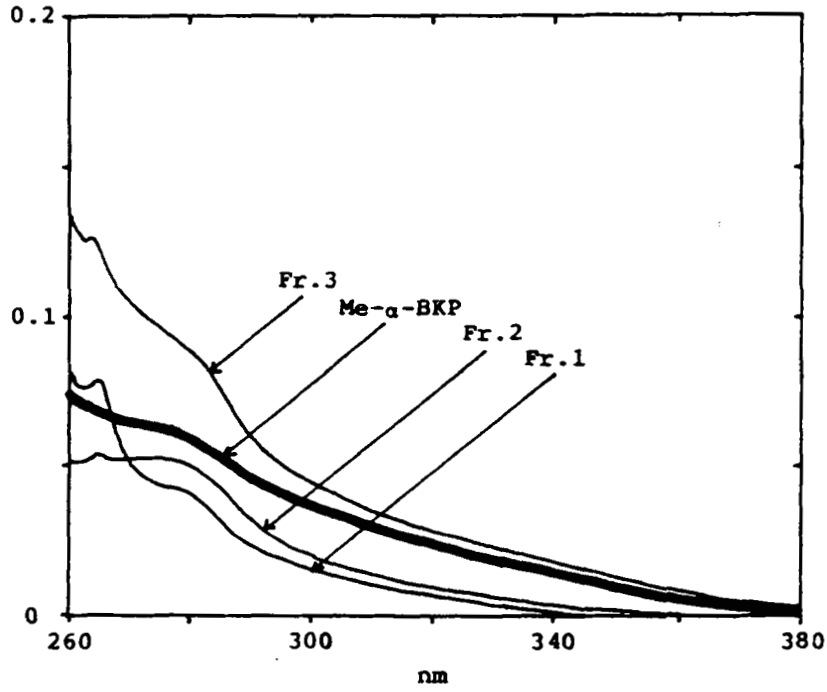

Figure 7 UV spectra of Me-α-BKP and its thre fractions

by UV spectroscopy. A small loss of hemicelluloses was detected by comparing the sugar compositions of the methylated samples (Fr. 1-3 in Table 3,5,7 and 9) with the corresponding data in Table 1.

The methylated samples were subjected to gel filtration chromatography and separated into three fractions. As described in the previous section, a relatively high proportion of the residual lignin and the residual hemicellulose in UKP were contained in Fr.3. On the other hand, as shown in Table 3, approximately 40% of the residual hemicellulose existed in Fr. 1, which contained the higher molecular weight molecules in Me-UKP and constituted 54% of Me-UKP. These results can be explained by

TABLE 8

Compositions of methylated sugars of fractions separated from Me-α-BKP

	Fr.1	Fr.2	Fr.3
3-Rha	0	0.1	0.2
2,5-Ara	0	0.2	0.5
3,5-Ara	0	0	0.2
2,3-Ara	0	0.1	0.2
2,3,4-Xyl	0	0.1	0.3
2,3-Xyl	1.2	0.5	1.5
3,4-Xyl	0.6	0.3	0.6
2,3,6-Man	1.4	1.4	3.6
2,3-Man	0.3	0.4	0.6
2,3,4,6-Gal	0	0.2	0.5
2,3,6-Glc	92.8	93.2	88.6
2,6-Glc	0.6	0.8	0.7
3,6-Glc	1.1	1.0	0.9
2,3-Glc	2.0	1.7	1.8

TABLE 9

Sugar compositions and lignin contents of fractions separated from Me-α-BKP

Sample	Yield (%)	Lignin content(%)*	Sugar composition (%)					
			Rha	Ara	Xyl	Man	Gal	Glc
Me-α-BKP		0.4						
Fr.1	10.7	0.4	0	0	1.8	1.7	0	96.5
Fr.2	58.5	0.3	0	0.3	0.9	1.8	0.2	96.7
Fr.3	30.8	0.6	0	0.9	2.7	4.2	0.5	92.0
Fr.1-3	100.0	0.4	0	0.5	1.4	2.5	0.3	95.3

*:Calculated from A_{280} under an assumption of E_{280}=14.

the following two hypotheses: 1) a part of the residual lignin and the residual hemicellulose in UKP are present as high polymers comparable to cellulose, or 2) the residual lignin and the residual hemicellulose are linked chemically to high molecular weight cellulose. In the latter case, three models of chemical linkages among the residual lignin may be assumed. First, the residual hemicellulose is directly linked to cellulose, and the residual lignin is linked to the hemicellulose. In this case, no direct chemical linkages would exist between cellulose and the residual lignin (Fig. 8, A). Second, the residual lignin is directly linked to cellulose, and the hemicellulose is linked to the lignin (Fig. 8, B). Third, chemical linkages exist between cellulose, the residual lignin and the residual hemicellulose (Fig. 8, C). These possibilities will be discussed again later.

As α-UKP was the residue from extraction of UKP with 24% NaOH containing Na_3BO_3 and $NaBH_4$, its lignin and hemicellulose contents were lower than those of UKP. Nevertheless, Fr.1 of Me-α-UKP still contained 4.5% lignin and more than 6.3% sugars originating from hemicellulose. Yamazaki et al.[5] reported that the residual lignin isolated enzymatically from UKP is soluble in both 0.1N NaOH solution and 0.1N Na_2CO_3 solution, and that after alkali-cooking a mixture of the above lignin and the holocellulose, the holocellulose was easily obtained by washing without any adsorption of the lignin. Thus, if the residual lignin in Fr.1 of Me-α-UKP had no chemical linkages with the polysaccharides, it should have been easily separated from the hemicelluloses by alkali-extraction. However, since Fr.1 still had 4.5% lignin, the existence of chemical linkages between the residual lignin and polysaccharides seems to be probable.

Most of the residual lignin was removed by bleaching UKP with $NaClO$-CH_3COOH, as shown in Table 7. Fr.3 still contained, however, 1.1% lignin, which is more than twice that of Fr.1 or Fr.2. This result indicates that the residual lignin, which cannot be easily bleached is present mainly in the low molecular part, Fr.3.

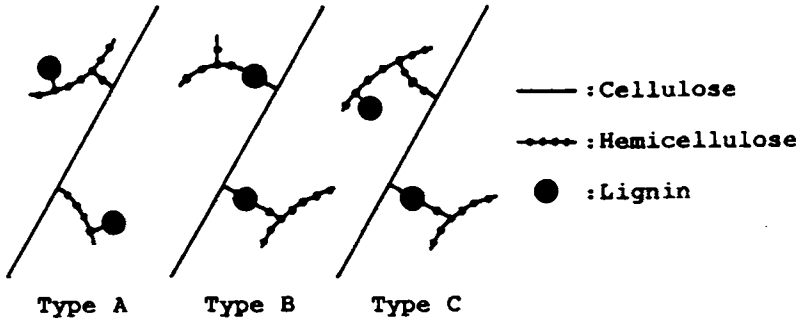

Figure 8 Possible models of chemical linkages between cellulose, the residual hemicellulose, and the residual lignin.

Approximately 4% of sugars other than glucose still remained in Fr.1 of Me-BKP, whereas only 0.3% lignin existed in the same fraction. This result suggests the existence of direct linkages between cellulose and hemicellulose, and/or the existence of high molecular weight hemicellulose mixed with cellulose in Fr.1 of Me-BKP.

The lignin content of Fr.3 was decreased remarkably by alkali-extraction of BKP. The lignin content of Fr.1 of Me-α-BKP, which contains higher molecular weight molecules and is 10.7% of Me-α-BKP, was also small (0.4%). However, the content of sugars other than glucose was still 3.5%. Present knowledge indicates that the molecular weights of hemicelluloses are much lower than those of cellulose. Moreover, during kraft cooking the hemicelluloses are more accessible to deploymerization reactions such as alkaline hydrolysis and oxidation followed by β-elimination reactions. Therefore, it seems more probable that the residual hemicelluloses have lower molecular weights than cellulose and remain in Fr.1 by direct and/or indirect chemical linkages with cellulose. Here, indirect chemical linkages mean that the hemicellulose is chemically linked to the lignin which in turn is linked to cellulose.

Furthermore, in all fractions, 2,3-Glc was detected in relatively higher percentages than those of 2,6-Glc and 3,6-Glc.

This result suggests the existence of a small amount of 6-O-linked glucose residues in samples.

In summary, the residual lignin in UKP is most likely linked chemically not only to hemicellulose but also to cellulose. These chemical linkages cause the resistance of the residual lignin to further delignification reactions, because the linkages are stable under alkaline conditions. The frequency of chemical linkages between the residual lignin and polysaccharides also has an effect on the difficulty in bleaching of the residual lignin. On the other hand, by alkali-extraction, some of the residual hemicellulose in UKP can be removed together with some of the residual lignin to which it is linked chemically. However, the residual hemicellulose remaining after alkali-extraction has probably direct and/or indirect chemical linkages to cellulose. Thus, Type A-C in Fig. 8 seems to be probable as the model showing the relation among the three main components of wood.

CONCLUSIONS

Unbleached kraft pulp (UKP) and its related three samples (α-UKP, BKP and α-BKP) were completely soluble in the SO_2-DEA-DMSO system, and were permethylated with powdered NaOH and CH_3I in their solutions.

The residual lignin and the residual hemicellulose in UKP were characterized by analyses of lignin contents and sugar compositions in fractions separated from permethylated samples by gel filtrations.

Chemical linkages between the residual lignin and polysaccharides (hemicellulose and cellulose) exist in UKP, and some of these linkages seem to cause the resistance of the lignin to further delignification reactions.

Some of the residual hemicellulose in UKP also has chemical linkages directly and/or indirectly to cellulose.

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