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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION (UNIDO)

VIENNA INTERNATIONAL CENTRE

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EXAMINATION OF THE CHEMICAL COMPOSITION  
OF LOCAL LIGNIN COMPOUNDS

UNIDO Project DP/BUR/85/015/11-01/32.1.E

by

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#### STATEMENT

Chemical and physico-chemical analyses of kraft lignins recovered from the bamboo kraft liquor provided by the Sittang Pulp and Paper Mill, Burma, show a good potential for the development of commercially viable products.

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## 1. OBJECTIVES

The research on lignins from a bamboo kraft black liquor provided by the Sittang pulp mill in Burma conducted in two phases is aimed at the following objectives:

### Phase I

To examine chemically the composition of bamboo kraft lignin isolated by ultrafiltration and precipitation techniques, and in

### Phase II

To critically examine the chemical data of bamboo kraft lignins with commercial soft- and hardwood kraft lignin samples manufactured in the United States and to examine whether there is a potential of modifying the bamboo lignin into lignin products which have a market potential in Burma.

## 2. APPROACH

- a) Isolation and purification of a kraft lignin sample representative for the bulk of the lignin in bamboo black liquor.
- b) Characterization of the purified bulk sample by chemical and physico-chemical means comprising of classical wet-chemical analysis (elemental analysis and methoxyl group content) and functional group analysis employing spectrophotometric methods based on infrared (IR) and ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra.
- c) Establishment of the molecular weight distribution pattern by gel permeation chromatography.
- d) Comparison of bamboo kraft lignin data with those obtained from a "native bamboo lignin sample".

- e) Comparison of bamboo kraft lignin data with those obtained from technical soft- and hardwood kraft lignin preparations.

### 3. BACKGROUND

Burma imports two high-priced lignin preparations, Indulin-AF and Indulin-C from the USA, which are used as battery additives and drilling muds, respectively. Production of technical lignins suitable for above and other uses (e.g. extenders in phenol-formaldehyde (PF) resins, concrete additives (super plastisizers) from locally available black liquors and thus having not to rely on imports is indeed economically attractive. Further, utilization of products from such liquors would also improve the economics of small pulp mills which cannot afford chemical recovery and would otherwise have to dispose of it and thus contribute in a major way to pollution.

### 4. INTRODUCTION

Lignins are major constituents in woody plants, where their prime functions are to impart strength to the cell wall to resist compressive forces and to act as a binder to hold the individual fibers together.

The molecular architecture of lignins is extremely complex and quite different from polysaccharides and other natural polymers. Phenylpropane units are linked by a variety of carbon to carbon- and carbon to oxygen bonds in a random fashion to form a highly branched, moderately crosslinked, polydisperse polymer system. Lignins are heteropolymers composed of three building units which are present in a wide range of proportions. As a consequence, the structural variations in lignins are enormous. There are great differences not only between species, but also between different

locations in the plant or even between different morphological regions, for example between early and late wood or between middle lamella and cell wall.

This, of course, poses tremendous analytical problems in structural work. Even with the most sophisticated analytical instrumentation and methods, we are only able to generate overall rather than detailed data.

Since single methods are furnishing only limited information, we have to rely on data gathered from a host of methods ranging from classical wet chemical methods to most advanced spectrophotometric techniques in order to achieve satisfactory results. Very helpful in many instances were comparative studies on similar lignins and lignin preparations.

The major thrust of fundamental and applied lignin research had been and is still being directed towards lignins of gymnosperms (softwoods), because softwoods constitute the major resource for fiber production. Further, structures of gymnosperm lignins are far less complex than those of hardwoods and, in particular, of grasses. Consequently, our present knowledge about softwood lignins is rather satisfactory. However, less is known about hardwood lignins and only very little about lignins from grasses.

Although bamboo is a major source of raw material for pulp and paper production, particularly in South and Southeast Asia, very little research was done on the structures of bamboo lignins and practically nothing on their behaviour in pulping.

Native bamboo lignin is composed mainly of guaiacyl- and syringyl units with a relatively high content of p-hydrophenyl propane structures. Most of the latter are linked to the lignin core in the form of p-hydroxycinnamic esters. A part of p-coumaric acid structures may also be linked by ether bonds. From nitrobenzene oxidation studies, a molecular ratio of vanillin

(4), syringaldehyde (5) and para-hydroxybenzaldehyde (6) of 1:1-2:0.5 was determined (Figure 5b; Table 6).

The chemical make-up of technical grass lignins, particularly of bamboo kraft lignin has not been investigated so far. Consequently, in our effort to build up a data base required for the development of economically viable processes for technical bamboo lignin preparations, we felt it necessary to conduct a comparative study on the nature of both the native lignin (i.e. milled bamboo lignin) and bamboo kraft lignins. We, therefore, will investigate first the chemical make-up of both milled bamboo lignin (MBL) and bamboo kraft lignin (BKL), then the changes in the chemical structure of bamboo lignin during the kraft pulping and finally the pertinent features of bamboo kraft lignin in comparison to those of hardwood kraft lignins and commercial softwood (pine) kraft lignins (Indulin series).

## 5. MATERIALS AND METHODS

### 5.1 Bamboo Kraft Black Liquor

Concentrated black liquor from the Sittang pulp mill was provided by the Paper and Chemical Industries Corporation, Rangoon, Burma. Unfortunately, some of the material was spilled during shipment. Therefore, we had only about 4 kg of liquor (total solids 19.9%, pH 12.7) at our disposal.

To remove suspended matter, the liquor was filtered through a bed of purified sea sand.

#### 5.1.1 Analytical methods

Total solids, total alkali, sulfate ash and organic matter were determined according to TAPPI Standard T625ts-64.

The pH-measurements were made using a pH-meter (Fisher Accumet Model 320, expanded scale research instrument). The viscosity was determined at 20°C

using a Brookfield Synchroelectric Viscometer. The lignin content was determined by UV absorption at 280 nm of a diluted alkaline solution (1:2500, 0.05 N NaOH) using an absorption coefficient of 25.4 g/(l·cm). The silicium content was determined by plasma emission spectroscopy and corresponds to 2.72 g/l silica (SiO<sub>2</sub>). The analytical data of the bamboo black liquor are given in Table 1.

## 5.2 Properties of Bamboo Kraft Lignin Samples

Lignins are polydisperse polymers which require careful isolation and purification for chemical characterisation. The following methods were used.

### 5.2.1 Isolation (precipitation)

The kraft lignin was precipitated from vigorously stirred black liquor at room temperature by acidification to pH 2 by dropwise addition of 2M H<sub>2</sub>SO<sub>4</sub>. The mixture was then heated in a water bath (80°C) for 1 hour to improve coagulation of the precipitate (PPT). After cooling, the PPT was isolated by centrifugation and washed three times by suspending it in dilute aqueous acid (pH 3) and decanting the supernatant after centrifugation. The last wash was carried out with deionized water and kraft lignin was recovered by centrifugation. Nearly 90% of the total lignin in the black liquor could be thus recovered. The so obtained crude product was purified employing the following methods.

### 5.2.2 Purification

Method A. The crude kraft lignin (vacuum dried) was treated with 96% dioxane at room temperature. About 86% of the material dissolved. Inorganics and some organics (lignins and carbohydrate degradation products) remained insoluble. The dioxane solution was added dropwise to ten times the volume of ether under stirring. The precipitate was washed with dionized water and

freeze dried (yield 69%). About 17% of the material, apparently a very low molecular weight portion of the lignin, remained in solution.

Method B. The crude kraft lignin was treated with acetone. After removing the insoluble portion by sedimentation in the centrifuge, the solvent was removed by evaporation. The residue was dried under vacuum at 50°C.

### 5.3 Milled Bamboo Lignin (MBL)

The lignin was isolated from extractive-free, healthy bamboo meal (60-80 mesh) prepared by ball milling following a procedure given for preparation of "milled wood lignin". Such products prepared under extremely mild conditions are considered to represent lignins in their unchanged native state ("native lignins"). The MBL preparation was used for reference purposes. Comparison of "native lignins" with lignins isolated from black liquor provide valuable information on lignin degradation patterns during kraft cooking.

### 5.4 Technical Soft- and Hardwood Kraft Lignins

The samples were provided by Westvaco Corporation, Charleston, SC 29406, USA, producers of Indulin AT and Indulin C, the two technical lignin products imported to Burma.

Indulin AT and Indulin C are kraft lignins isolated from southern pine kraft black liquor by precipitation with carbon dioxide at pH 9-9.5. Indulin C is the crude sodium salt of kraft lignin (sodium lignate) with considerable amounts of  $\text{Na}_2\text{CO}_3$  (total ash content about 15%). The product is soluble in water. Indulin AT is formed by washing the crude product (Indulin C) with dilute acid and water (final washing pH 3). The so obtained "free kraft lignin" contains very little ash ( $\text{Na}_2\text{SO}_4$ ) and is insoluble in water.

With regard to chemical structure and polydispersity (molecular weight distribution) both products are practically identical.

The hardwood lignin was recovered from a black liquor obtained from a kraft cook of a southern hardwood mixture containing mainly oaks and some gums employing the same method as described above for the softwood samples. Technical hardwood kraft lignins are not produced anymore. Their major application was as extenders in phenolic formaldehyde resins. Up to 20% of the unmodified product could be used without impairing the performance of the resin.

### 5.5 Acetylation of Lignin Preparations

By acetylating the hydroxyl functions, lignins become soluble in a wide variety of organic solvents including chloroform (deutero-chloroform) and thus are amenable to analyses by nuclear magnetic resonance (NMR) spectroscopic methods.

Acetylated samples are prepared by dissolving about 1 g of lignin in about 20 ml pyridine. After addition of about 10 ml acetic anhydride, the solution is allowed to stand about 48 hours at room temperature to ensure complete reaction. Then the solution was poured on crushed ice. The precipitate was filtered and washed with cold dilute HCl followed by ice water and finally dried over  $P_2O_5$  in vacuum.

### 5.6 Elemental and Functional Group Analyses

Elemental analysis, acetyl, carboxyl and ash determinations of lignin samples were performed by the E&R Microanalytical Laboratory, Inc., New York. The determination of methoxyl groups was carried out in our laboratory using a modified Zeisel method.

### 5.7 Molecular Weight Distribution (MWD)

The bamboo lignin preparations (about 0.3 mg) were subjected to gel permeation chromatography on a Sephadex G-75 column (120 x 1.0 cm) using a 0.1 NaOH containing 0.1M LiCl as eluent. A flow rate of about 17 ml/hr was

maintained (peristaltic pump). The effluent was monitored by UV-absorption at 280 nm.

## 5.8 Spectroscopic Analyses

### 5.8.1 UV spectra

UV spectra were obtained using a Pye-Unicam Sp8-100 Ultraviolet Spectrophotometer. Extinction coefficients of lignin preparations were determined from three-point Beer-Lambert plots.

### 5.8.2 IR Spectra

IR spectra were recorded using a Beckman Model Acculab 8 Spectrophotometer. The samples were analyzed as 0.5% (w/w) KBr pellets.

### 5.8.3 Proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra

The  $^1\text{H-NMR}$  spectra were recorded using an IBM NMR-100F spectrometer. The concentration of acetylated lignins were 7% in  $\text{CDCl}_3$ , (w/v). The samples were placed in 0.5 mm tubes and the PMR spectra were obtained employing the FT mode, pulse width 8  $\mu\text{sec}$  (flip angle  $60^\circ$ ), repetition time of 1 sec. and number of scans 8. TMS was used as internal standard for  $\delta$  value.

### 5.8.4 Carbon-13 nuclear magnetic resonance ( $^{13}\text{C-NMR}$ ) spectra

The  $^{13}\text{C-NMR}$  spectra were obtained at 15 MHz for  $^{13}\text{C}$  nuclei, using a JEOL FX 60 Fourier transform spectrometer. The spectra were recorded at  $50^\circ\text{C}$  employing a pulse width 20  $\mu\text{sec}$  (flip angle  $60^\circ$ ) and a repetition time of 2.0 seconds with approximately 10,000 accumulations. The concentration of samples in  $\text{DMSO-}d_6$  was 20% (w/v). The samples were placed in a 10 mm (I.D.) sample tube.

## 6. RESULTS AND DISCUSSION

For the sake of clarity only the principal findings of our study are presented in this section of the report, while the details as well as additional Tables and Figures are compiled in the Appendix.

### 6.1 Gel Permeation Chromatography

Both, milled bamboo lignin (MBL) or "native bamboo lignin" and the purified kraft lignin samples exhibit extensive polydispersity with materials ranging from the range of monomers/dimers up to polymers with molecular weights around 20,000. The gel permeation chromatogram for MBL suggests a binodal distribution of the polymers with maxima at the MW 8,000 and MW 800 regions. The distribution pattern of the kraft lignin samples suggest that a substantial amount of the lower molecular weight components were degraded to very low molecular weight products which remained in solution on acidification of the black liquor to precipitate lignin. The increase in excluded materials (about MW > 25,000) suggests occurrence of condensation reactions during pulping. The bulk of the material centered around MWs ranging from about 1,500-9,000 (Figure 1).

It is interesting to note the rather minor changes in the overall MW-distribution of kraft lignins from bamboo and Southern hardwoods caused by purification with acetone where the bulk of the low molecular weight materials is retained (Figure 2).

Table 2 and Figures 3 and 4 show the MW-distribution of purified samples of technical kraft lignins from Southern Pine (Indulin AT), Southern hardwood mixture, both provided by Westvaco Corporation, Charleston, SC, USA, and from bamboo isolated from black liquor provided by the Sittang mill in Burma. As expected Indulin AT, a pine kraft lignin preparation, exhibits the highest

average MW. However, it was not expected that the average MW for bamboo kraft lignins will be higher than for the hardwood sample.

## 6.2 Chemical and Functional Group Analysis

The overall chemical properties of the lignins were determined on purified representative samples. Purification resulted in an increase in methoxyl content indicating the removal of non-lignin, apparently carbohydrate degradation products (Table 3). The analyses performed include elemental analysis, methoxyl-carboxyl and quantitative H-NMR analysis of acetylated samples. The  $^1\text{H-NMR}$  spectra (Figures A-3 and A-4) were integrated for their aromatic and aliphatic acetoxy-, aromatic- and methoxyl protons. The so obtained data were used to calculate the average  $\text{C}_9$ -molecular formulae of lignin preparations.

The computation of  $\text{C}_9$ -units (phenyl propane units) is a common practice in lignin chemistry despite the fact that not all units have a complete propane side-chain. This is particularly true for alkali lignins (soda- and kraft lignins) due to extensive splitting along side-chains and elimination of side-chain during pulping. Nevertheless, the molecular formulae of the average  $\text{C}_9$ -unit represent the overall chemical properties of each lignin. These formulae are therefore quite helpful in evaluating the chemical properties of a lignin and in the comparison of properties between different lignins. The analytical data are compiled in Tables 4 and 5.

## 6.3 Structural Changes of Bamboo Lignins in Kraft Cooking

Bamboo lignins are random polymers composed of guaiacyl propane (1), syringylpropane (2) and p-hydroxyphenyl propane (3) units (Figure 5a) as indicated by the UV-, IR-,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra (Figures A-1 to A-5). Additional information on the above mentioned three basic constituents were obtained by determining the yields of hydroxybenzaldehydes, namely vanillin

(4), syringaldehyde (5) and p-hydroxybenzaldehyde (6) in the reaction mixture of nitrobenzene oxidation of lignins in aqueous alkali (Figure 5b). During kraft cooking, the p-hydroxypropane structures in bamboo lignin are extensively removed apparently by alkaline hydrolysis suggesting that the bulk of such structures are originally linked by ester-, respectively ether- bonds, to the polymer core composed of guaiacyl- and syringyl-propane units (Table 6).

Extensive splitting of ether unit linkages is evidenced by the increase in phenolic hydroxyl content as shown in the  $^1\text{H-NMR}$  spectra of acetylated MBL and bamboo kraft lignin (Figure A-3).

The rather drastic structural changes during pulping of bamboo can be seen in the  $^{13}\text{C-NMR}$  spectra presented in Figure A-5. Interpretation and detailed discussion is given in the appropriate sections in the Appendix.

#### 6.4 Kraft Lignin Structures (Comparative Analyses)

So far, the emphasize of our discussion was directed towards structural changes in bamboo lignin during the cooking processes. In the following, the focus is on the structures of kraft lignins from pine (Indulin AT), bamboo and southern hardwoods.

In Table 7, the contents of principal functional groups are expressed in group per 100 phenylpropane or  $\text{C}_9$ -units. In contrast to Indulin AT, the bamboo kraft lignin contains much more phenolic hydroxyls and less than half of alcoholic hydroxyl groups. The latter finding and the  $^{13}\text{C-NMR}$  spectra suggest extensive changes in the side chains including condensation and fragmentations (Figure A-6). Results from quantitative  $^1\text{H-NMR}$  spectral analysis (Tables 8 and 9) support this interpretation. Of interest for lignin modifications is the content of aromatic hydrogens which lies with  $2.26/\text{C}_9$ -units between the values found for the soft- and hardwood preparation.

## 7. CONCLUSIONS

The properties and chemical reactivity of technical lignin products are primarily governed by three factors:

- a) The average molecular weight ( $\overline{MW}$ ) and molecular weight distribution (MWD),
- b) the functional groups such as phenolic hydroxyls and carboxylic (sulfonic) acid groups, and
- c) the content of unsubstituted sites in aromatic rings of phenolic structures, preferentially in ortho- position to the phenolic hydroxyls.

Ad a) Our gel permeation chromatography studies revealed that MWD-patterns of bamboo kraft lignins are quite similar to those exhibited by Indulin AT (pine kraft lignin) and the technical hardwood sample. The average MW lies in-between the two commercial products. Further, it seems very likely that the average MW could be increased substantially by chemical means, if so desired.

Ad b) The content of phenolic structures and particular of carboxylic acid groups are rather high, which should affect positively certain properties (e.g. solubility in basic media, gel formation) and the potential for product development (chemical modification of the kraft lignin).

Ad c) The kraft lignins from hardwood and bamboo are composed of guaiacyl- and syringylpropane units. The guaiacylpropane units in the phenolic structures amount to 60% in both lignins. However, in comparison to the hardwood sample, the bamboo kraft lignin shows a substantially higher aromatic proton content, which suggest that the latter should exhibit an enhanced potential for chemical modification involving reactive sites in the aromatic rings of

phenolic structures. The reactivities towards methylation, sulfomethylation and oxidative sulfonation are expected to be definitely better than those of hardwood, but somewhat inferior to those of Indulin AT. Figure 6 shows the reactive sites in phenolic structures and some of the major modification reactions.

In summary, the results of our studies on molecular weight distribution, chemical and functional group analysis of lignins recovered from bamboo kraft black liquor clearly show a good potential for the development of commercially viable products, such as extenders in phenolic formaldehyde resins and industrial surfactants for a host of applications.

#### 8. RECOMMENDATIONS

Further studies should concentrate on modification processes to explore their viability in developing commercial products. The reaction between formaldehyde and bamboo kraft lignin in aqueous alkali leading to the introduction of hydroxymethyl groups in phenolic structures plays a key-role in modification processes and, therefore, should be given top priority in future studies.

Hydroxymethylated products occupy a central position in the family of modified kraft lignin. For instance in the preparation of precursors for crosslinking components in phenol-formaldehyde (PF) resins, or in preparation of sulfonate and amine derivatives.

The modified products should be prepared in kg-quantities required for extensive testing program.

Table 1. Analytical Data of Bamboo Black Liquor (prefiltered)

Total Solids	19.5%
Total Alkali (as Na <sub>2</sub> O)	52.1 g/l
Sulfate Ash (as NaOH)	42.5% (including sodium silicate) **
Organic Matter	57.3% **
Si *	1.27 g/l
Lignin	54.40 g/l
Viscosity (20°C)	20.00 cps

\* The rather low content suggests that some silica (polymeric form) is retained in the filter (sea sand).

\*\* Based on total solid content.

Table 2. Molecular Weight Distribution of Kraft Lignins

Molecular Weight Ranges	Area %		
	Softwood Kraft Lignin	Bamboo Kraft Lignin	Hardwood Kraft Lignin
> 20,000	13	8	5
10,000 - 20,000	13	11	4
5,000 - 10,000	22	20	9
2,000 - 5,000	24	30	23
1,000 - 2,000	12	18	25
500 - 1,000	9	8	18
< 500	7	6	17

Table 3. Methoxyl Group Content of Crude and Purified Bamboo and Hardwood Kraft Lignins

<u>Bamboo Kraft Lignin</u>		<u>Hardwood Kraft Lignin</u>	
<u>Crude</u>	<u>Purified</u>	<u>Crude</u>	<u>Purified</u>
15.28%	15.95%	17.05%	17.41%

Table 4. Elemental Composition of Lignin Preparations\*

Lignin Preparations	(%)							
	C	H	O	N	S	OCH <sub>3</sub>	COOH	OAC
Softwood Kraft	65.73	5.61	27.12		1.34	13.38	2.44	
Bamboo Kraft	61.81	5.25	31.26	--	1.69	15.99	8.04	
Hardwood Kraft	61.94	5.27	31.25		1.54	17.05	3.53	
Acetylated Bambo Kraft	62.32	5.04	31.29	--	1.35	13.17	6.32	18.60
Acetylated Hardwood Kraft	62.16	5.21	31.44		1.19	12.63	2.75	22.46
-----								
Milled Bambo	60.45	5.58	32.36	1.11	--	17.06	4.73	
Acetylated Milled Bambo	59.88	5.38	34.51	0.23	--	13.86	25.14	

\* Milled bamboo lignins contain significant amounts of carbohydrates.

Table 5. C<sub>9</sub>-unit Formulae of Bamboo, Hardwood and Pine Kraft Lignins

	C <sub>9</sub> -unit Formulae	C <sub>9</sub> -unit Weight
Softwood Kraft Lignin	C <sub>9</sub> H <sub>7.66</sub> O <sub>2.10</sub> S <sub>0.08</sub> (OCH <sub>3</sub> ) <sub>0.75</sub> (COOH) <sub>0.10</sub>	180
Bamboo Kraft Lignin	C <sub>9</sub> H <sub>7.04</sub> O <sub>2.19</sub> S <sub>0.11</sub> (OCH <sub>3</sub> ) <sub>1.04</sub> (COOH) <sub>0.36</sub>	194
Hardwood Kraft Lignin	C <sub>9</sub> H <sub>7.03</sub> O <sub>2.50</sub> S <sub>0.10</sub> (OCH <sub>3</sub> ) <sub>1.05</sub> (COOH) <sub>0.16</sub>	195
Acetylated Bamboo Lignin	C <sub>9</sub> H <sub>5.49</sub> O <sub>1.93</sub> S <sub>0.10</sub> (OCH <sub>3</sub> ) <sub>1.01</sub> (OAC) <sub>1.03</sub> (COOH) <sub>0.35</sub>	240
Acetylated Hardwood Lignin	C <sub>9</sub> H <sub>5.66</sub> O <sub>2.23</sub> S <sub>0.09</sub> (OCH <sub>3</sub> ) <sub>1.02</sub> (OAC) <sub>1.28</sub> (COOH) <sub>0.15</sub>	247

Table 6. Yields of Aromatic Aldehydes from Bamboo and Hardwood Kraft Lignins

<u>Lignin Preparations</u>	<u>Yield, Mole % per C<sub>9</sub>-unit*</u>				<u>Molar Ratio (V:S:H)</u>
	<u>Vanillin</u>	<u>Syring-aldehyde</u>	<u>p-hydroxy-benzaldehyde</u>	<u>Total aldehyde</u>	
Bamboo Milled Wood Lignin	16.4	22.5	7.0	45.9	1 : 1.4 : 0.4
Bamboo Kraft Lignin	7.2	4.5	+	11.7	1 : 0.6
Hardwood Kraft Lignin	6.1	4.2	-	10.3	1 : 0.7

\* "+" = trace amount; "-" = not detected.

Table 7. Functional Groups of Bamboo, Hardwood and Pine Kraft Lignins (Indulin AT)

<u>Lignin Preparations</u>	<u>100 C<sub>9</sub>-units</u>				
	<u>OCH<sub>3</sub></u>	<u>COOH</u>	<u>ph-OH</u>	<u>Aliphatic-OH</u>	<u>Total-OH</u>
Pine Kraft	77	~10-15	55	84	139
Bamboo Kraft	104	36	73	40	113
Hardwood Kraft	105	16	79	59	138

Table 8. Chemical Shift of  $^1\text{H}$  Nuclei in Substructure of Acetylated Lignins

<u>Region</u>	<u>Chemical Shift</u> ( $\delta$ in ppm)	<u>Types of <math>^1\text{H}</math> Nucleus</u>
1	6.25 - 8.00	aromatic region, ortho to $\alpha$ -carboxyl, $\alpha$ -vinyl
2	5.75 - 6.25	non-cyclic benzylic region (H on C- $\beta$ of arylvinylene group, $\beta$ -vinyl, H on C- $\alpha$ of $\beta$ - <u>0-4</u> , $\beta$ -1 and aryl, glycerol stochem.)
3	5.20 - 5.75	cyclic benzylic region (H on C- $\alpha$ of $\beta$ -5 and $\alpha$ - <u>0-4</u> ).
4	2.50 - 5.20	Methoxyl and major aliphatic region
5	2.20 - 2.50	aromatic acetoxy region
6	1.60 - 2.20	aliphatic acetoxy region
7	0.75 - 1.60	non-oxygenated aliphatic region

Table 9. Protons per  $\text{C}_9$ -unit in Acetylated Kraft Lignins According to Quantitative NMR Spectra

<u>Region</u>	<u>Softwood Kraft Lignin*</u>		<u>Bamboo Kraft Lignin</u>		<u>Hardwood Kraft Lignin</u>	
	<u>H%</u>	<u>H/C<sub>9</sub></u>	<u>H%</u>	<u>H/C<sub>9</sub></u>	<u>H%</u>	<u>H/C<sub>9</sub></u>
1	20.10	2.95	19.48	2.26	15.78	1.98
2	2.11	0.31	3.28	0.38	2.55	0.32
3	3.17	0.47	1.64	0.19	1.67	0.21
4	38.09	5.59	39.74	4.61	41.99	5.27
5	16.14	2.37	18.79	2.18	18.96	2.38
6	13.49	1.98	10.26	1.19	14.18	1.78
7	<u>6.88</u>	<u>1.01</u>	<u>6.81</u>	<u>0.79</u>	<u>4.86</u>	<u>0.61</u>
	99.98	14.68	100.00	11.60	100.09	12.55

\* Fraction Mw  $\sim$  1000.

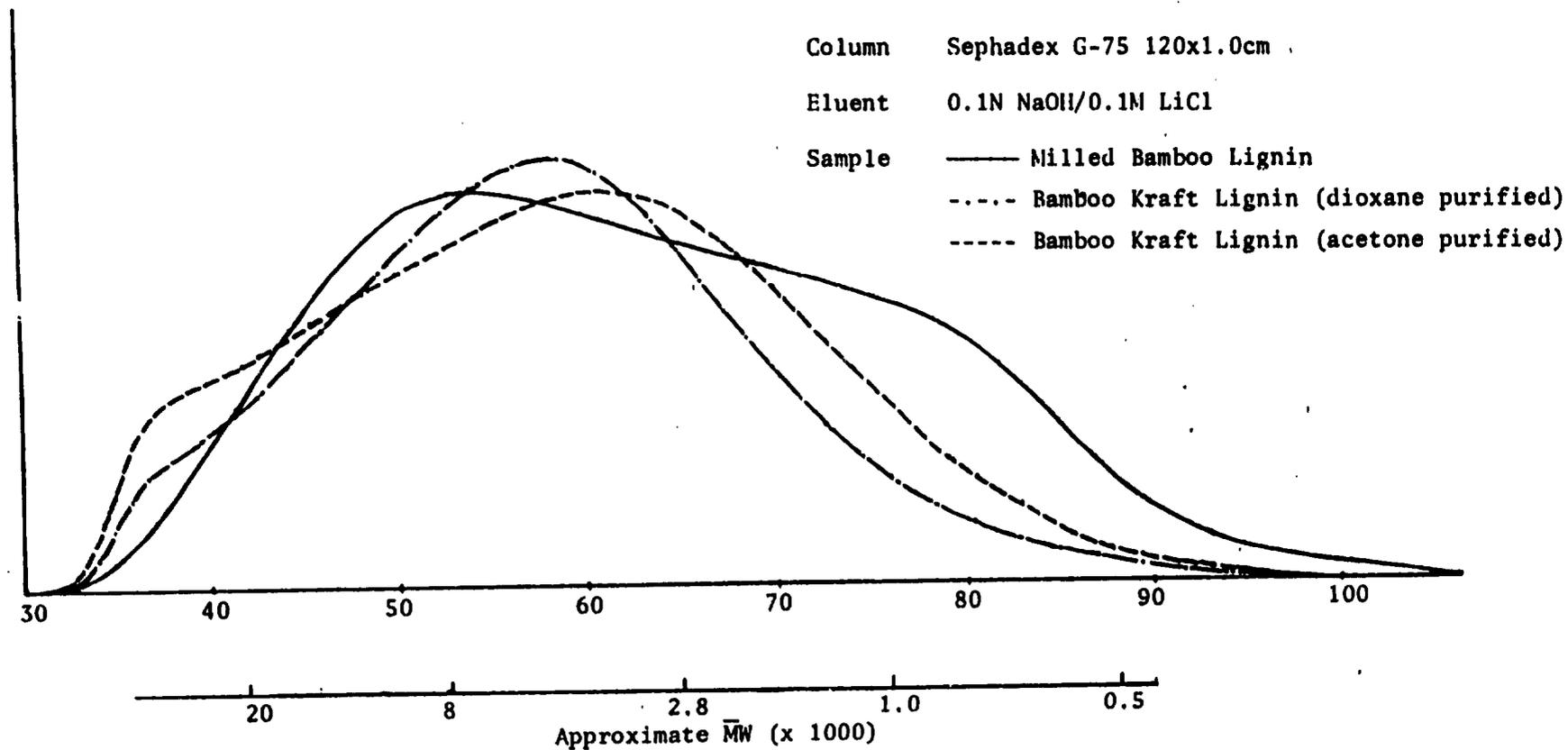


Figure 1. Molecular Weight Distribution of Bamboo Lignin Preparations

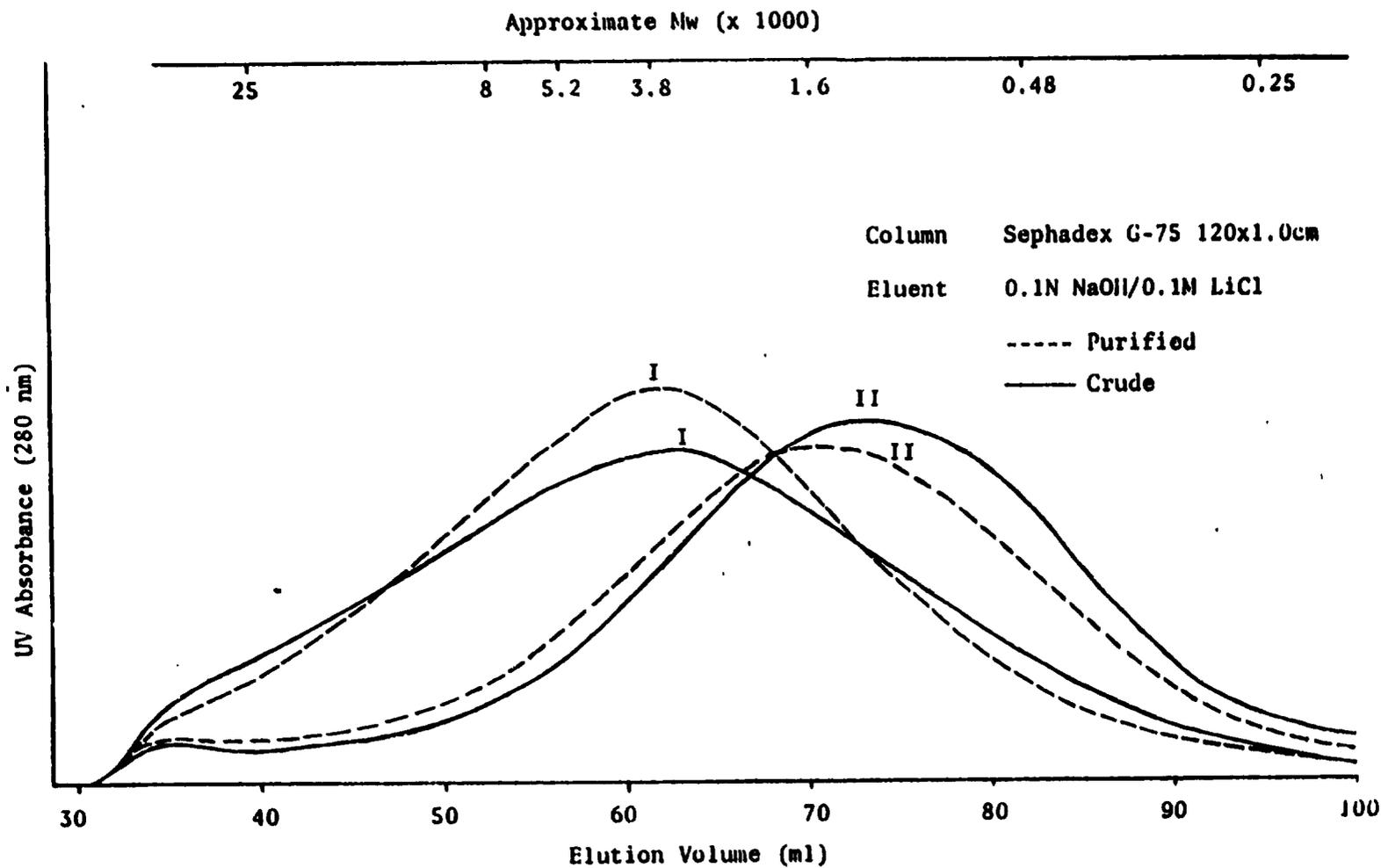


Figure 2. Molecular Weight Distribution of Crude and Purified Kraft Lignin from Bamboo (I) and Hardwoods (II)

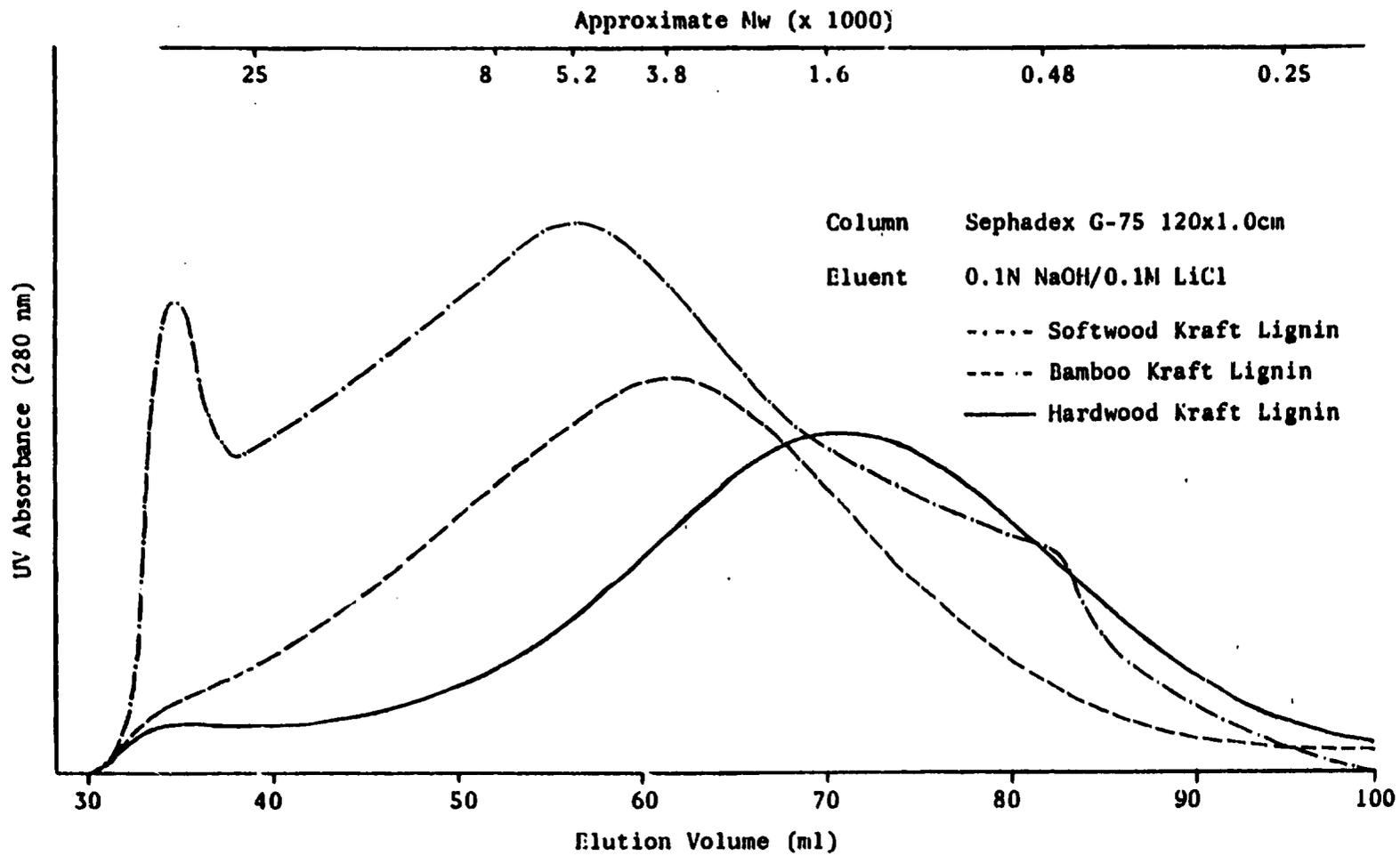


Figure 3. Molecular Weight Distribution of Kraft Lignin Preparations (Gel Permeation Chromatogram)

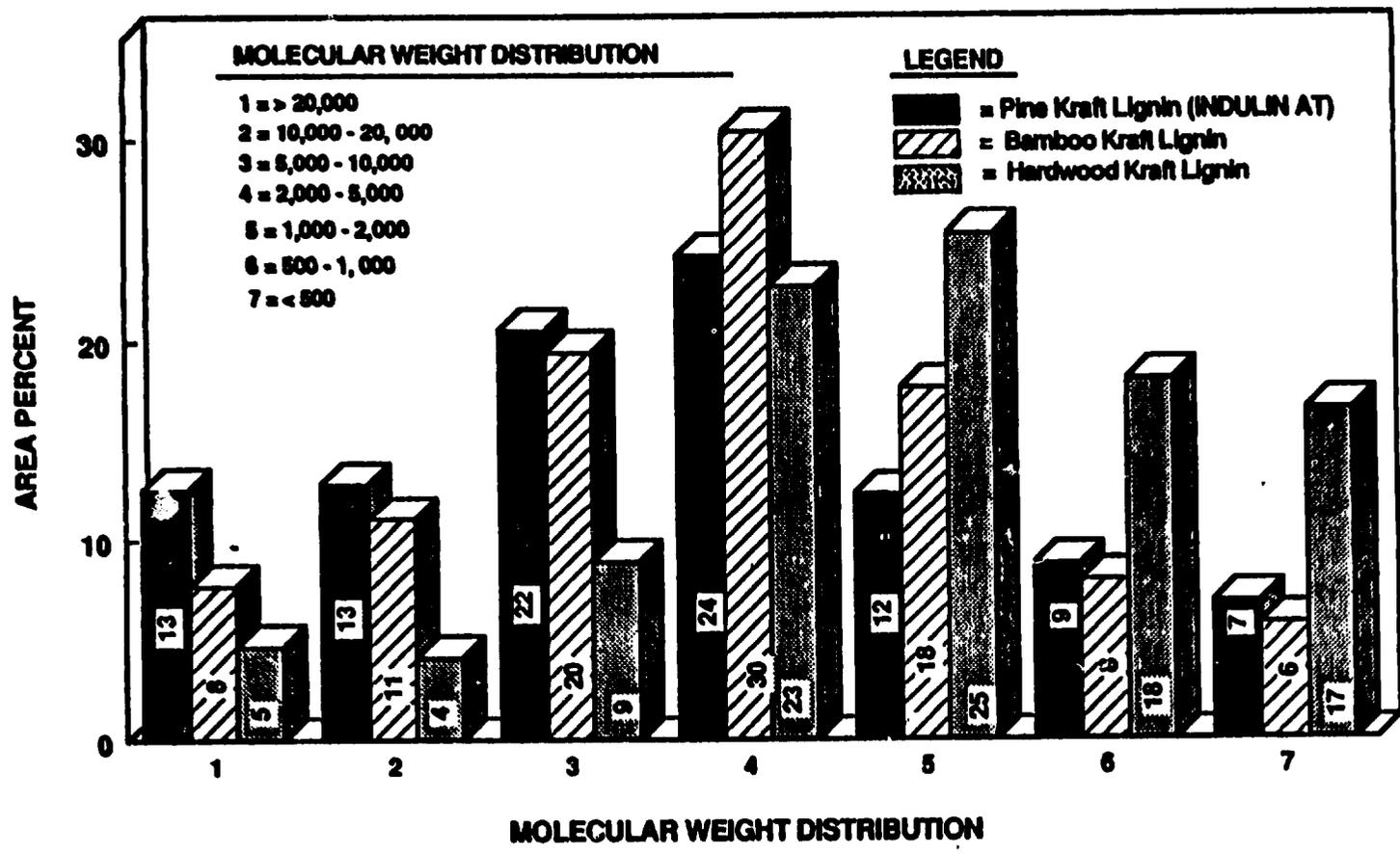


Figure 4. Molecular Weight Distribution of Kraft Lignin Preparations (Block Diagram)

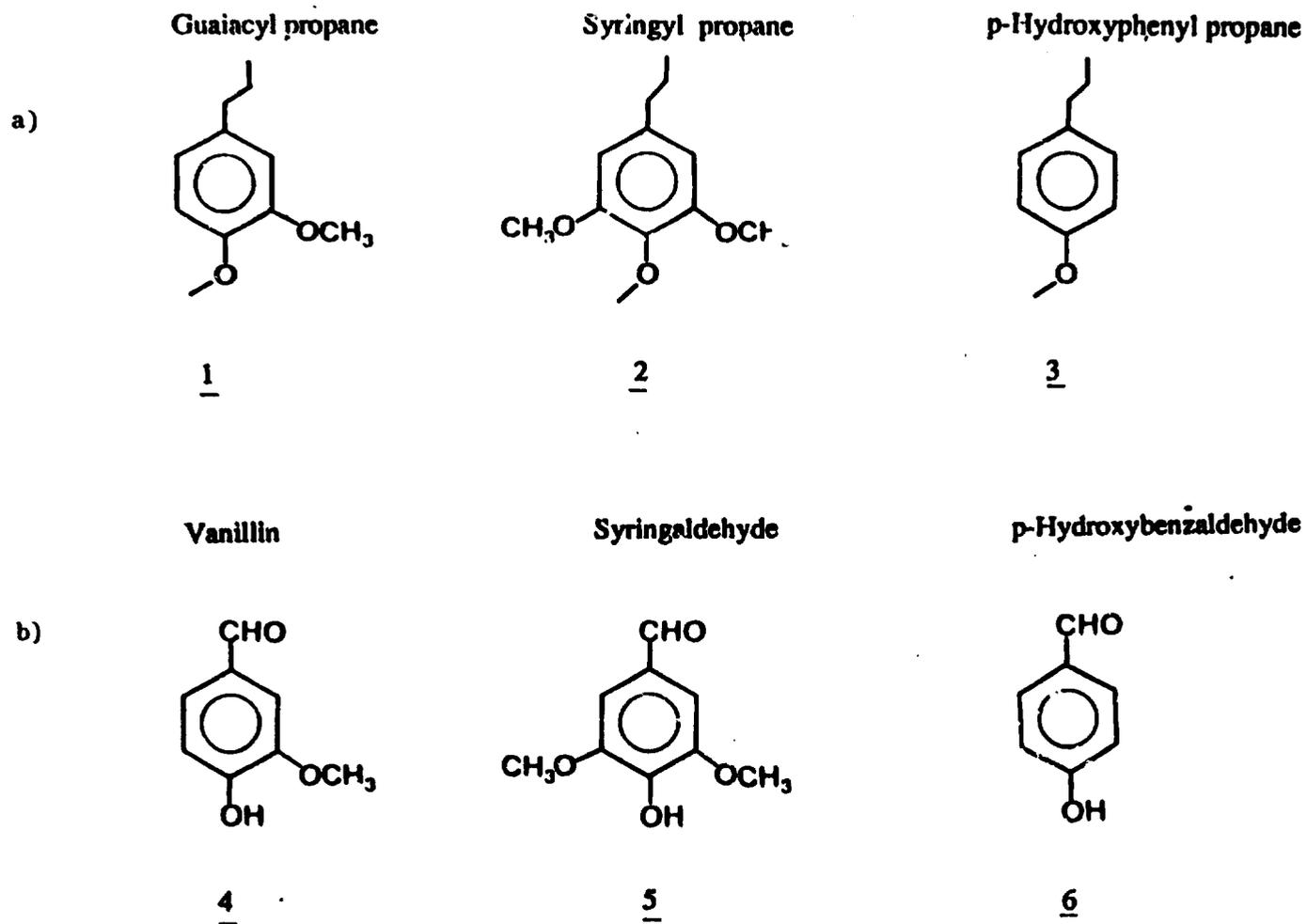
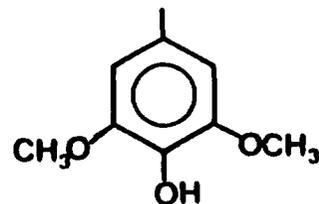
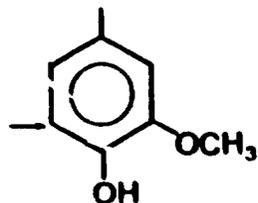
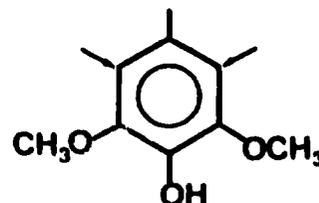
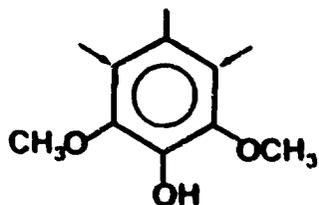


Figure 5. a) Structures of Phenylpropane Units and b) Major Hydroxybenzaldehydes Formed in Nitrobenzene Oxidation of Lignins

Alkali



Acid



Reactant

Product

CH<sub>2</sub>O

-CH<sub>2</sub>OH

Hydroxymethylation

CH<sub>2</sub>O, SO<sub>3</sub>H

-CH<sub>2</sub>SO<sub>3</sub>H

Sulfomethylation

CH<sub>2</sub>O, R-NH<sub>2</sub>

-CH<sub>2</sub>=N-R

Amination

Figure 6. Condensation of Reactive Sites of Aromatic (Phenolic) Structures

**APPENDIX**

## 9. APPENDIX

### 9.1 Interpretation of Bamboo Lignin Spectra

The spectra from the various methods applied exhibit all the features characteristic of Gramineae lignins. Further, the spectra allowed to study structural differences between milled bamboo lignin and bamboo kraft lignin as well as between kraft lignin preparations from different species.

#### 9.1.1 UV spectra

As seen in Figure A-1, the UV spectra of milled bamboo lignin have two maxima at 281 nm and 315 nm, respectively, originating from *p*-coumaric and ferulic acid moieties linked by ester bonds. The absence of the maxima at 315 nm in the spectra of the kraft lignin preparation suggests the cleavage (hydrolysis) of the ester linkages. The shift of the maximum from 315 nm to 274 nm and the changes in the extinction coefficient from 21.5 l/(g·cm) to 23.0 l/(g·cm) is due to structural changes in kraft pulping.

#### 9.1.2 IR spectra

The spectra of milled bamboo lignin and bamboo kraft lignin are shown in Figure A-2. The absorption bands in the 1400 - 1000  $\text{cm}^{-1}$  region are reasonably well resolved. It is believed that bands at 1270, 1230 and 1130  $\text{cm}^{-1}$  in guaiacyl structures and at 1335 and 1234  $\text{cm}^{-1}$  in syringyl compounds are assignable to ring breaking with C-O stretching in methoxyl groups. Guaiacylic bands at 1160 and 1040  $\text{cm}^{-1}$  and syringyl bands at 1130 are assigned to aromatic C-H in plane deformation. The relative weak intensity of the bands assigned to guaiacyl structures to those originating from syringyl structures suggest the abundance of the latter in the bamboo lignins. The spectra of the kraft lignin preparation show a lower intensity of the 1335  $\text{cm}^{-1}$  band. Absorption at 1715 and 1170  $\text{cm}^{-1}$  assigned to conjugated .

$\alpha,\beta$  unsaturated ester linkages are weaker in the kraft lignin than in the milled bamboo lignin preparation representing lignin in its native state.

### 9.1.3 $^1\text{H-NMR}$ spectra

In the  $^1\text{H-NMR}$  spectra of milled bamboo lignin (Figure 3-4), three signals center at  $\delta$  7.51 ppm, 6.98 ppm and 6.61 ppm) appear in the range of  $\delta$  6.24 - 7.83 ppm, corresponding to aromatic hydrogens in the *p*-hydroxyphenyl, guaiacyl and syringyl moieties and to hydrogens in conjugated double bonds in cinnamic acid structures. In contrast to the milled bamboo lignin spectra, the spectra of kraft lignin exhibit rather weak signals centered at  $\delta$  6.61 and 7.51 ppm corresponding to H- $\beta$  and H- $\alpha$  of cinnamic acid moieties, such as *p*-coumaric acid and ferulic acid moieties. This indicates that the presence of cinnamic acid structures in native lignin mostly in the form of cinnamic acid esters, which undergo base-catalyzed hydrolysis to corresponding acids such as *p*-coumaric acid and ferulic acid under the condition of the kraft pulping. In addition, the spectra of kraft lignin does not contain a distinct signal centered at  $\delta$  6.07 ppm in contrast to the spectra of the "native lignin". The signal corresponds to H- $\alpha$  in acetylated  $\beta$ -O-aryl glycerol moieties in the lignin. This further suggests that modification of lignin side chains involving C- $\alpha$  has occurred during pulping.

### 9.1.4 $^{13}\text{C-NMR}$ spectra

The  $^{13}\text{C-NMR}$  spectra of milled bamboo lignin (Figure 4a) clearly show that bamboo lignins are of the guaiacyl-syringyl type. They are rich in syringyl units, with a high proportion of *p*-hydroxyl phenyl propane units linked to the lignin core. The intensive signals 6 and 23/24 correspond to C-3/C-5 and C-2/C-6 in syringyl units. The moderately intense signals 7, 8, 19, 21 and 22 correspond to C-3, C-4, C-6, C-5 and C-2 in guaiacyl units. The presence of *p*-coumaric units are indicated by the signals 4, 5, 11, 16, 18 and 20,

corresponding to -COO- of C- $\gamma$ , C-4, C- $\alpha$ , C-2/C-6, C-1 and C-3/C-5 of p-coumaric ester structures. Signals 25, 27 and 29 correspond to C- $\beta$ , C- $\alpha$  and C- $\gamma$  of  $\beta$ -aryl ether structures in guaiacyl and syringyl units. The assignment of signals are given in Table A-1. In the bamboo kraft lignin spectra (Figure A-4), and in the spectra of kraft lignins (Figure A-5) the intensity of the signals corresponding to C- $\alpha$ , C- $\beta$  and C- $\gamma$  of  $\beta$ -aryl ethers are decreased, indicating extensive modification in lignin side chains under kraft pulping. The decrease in the intensities of the signals (Figure A-4) corresponding to p-coumaric units suggests that hydrolysis of the ester bonds has occurred. The cleavage of the  $\alpha$ -aryl ether bonds in phenolic, cyclic  $\alpha$ -aryl ether under kraft pulping conditions results in the formation of p,o'-stilbenes. Signals 16a ( $\delta$  128.3 ppm) and 19 ( $\delta$  121.5 ppm) include contributions from the olefinic carbons (C- $\alpha$  and C- $\beta$  respectively) of this type of stilbene. Conjugated double bonds may also be introduced into the side chains as a result of formation of coniferyl alcohol structures as a result of  $\beta$ -aryl ether cleavage. The olefinic carbons may contribute to the signals located at about 120-135 ppm. Carboxyl groups are apparently introduced into the lignin molecule by autooxidation of double bonds in side chain particularly stilbenes type structures. The overlap signals at  $\delta$  167.0 - 175.2 ppm suggest that the carboxyl groups are of aromatic and aliphatic type as well.

In Figure A-6, the relative intensities of the signals corresponding to C- $\alpha$ , C- $\beta$  and C- $\gamma$  (signals 25, 27 and 29) indicate that bamboo kraft lignin underwent the most extensive cleavages of  $\beta$ -aryl ether bonds and sidechain modification among the three kraft lignins. Bamboo kraft lignin contains the highest amount of the carboxyl groups, as indicated by the relative intensities of the signals at  $\delta$  167.0 - 175.2 ppm. These findings agree with the results obtained from  $^1\text{H-NMR}$  spectra and functional group analyses.

Table A-1. Chemical Shifts and Signal Assignments in the  $^{13}\text{C}$  NMR Spectra of Milled Bamboo Lignin (MBL)

Signal No.	Chemical Shift	Assignments
1	172.0	-COOH aliphatic
2	170.2	
3	169.6	-COO- acetyl in xylan
4	166.3	-COO- in Cr of PC ester
5	159.8	C-4, PC ester
6	152.2	C-3/C-5 S; C-3/C-3' in G etherified <u>5-5</u>
7	149.5	C-3, G etherified
8	147.5	C-4, G etherified, C-3/C-5 S non-etherified
9	147.0	C-3, G non-etherified
10	145.5	C-4, G non-etherified
11	144.6	C- $\alpha$ , PC ester
12	138.0	C-4, S etherified
13	136.1	C-4, S non-etherified
14	135.0	C-1, S and G etherified
15	132.2	C-1, S and G non-etherified
16	130.2	C- $\beta$ , C-2/C-6 PC ester
17	128.0	C-2/C-6, H
18	125.1	C-1, PC ester
19	119.6-119.2	C-6, G
20	115.9	C-3/C-5, PC ester
21	114.6	C-5 G
22	112.3	C-2 G
23	105.8-106.5	C-2/C-6 S with $\alpha$ -CO
24	104.5	C-2/C-6 S
25	86.2	C- $\beta$ , $\beta$ -aryl ether
26	75.5	C-4, xylan interunit
27	72.4	C- $\alpha$ , $\beta$ -aryl ether
28	62.6	C- $\gamma$ in $\beta$ - <u>O</u> -4 with $\alpha$ -C=O; in $\beta$ -5 and $\beta$ -1
29	60.3	C- $\gamma$ in $\beta$ - <u>O</u> -4 G and S
30	56.0	Ar-OCH <sub>3</sub> in G and S
31	54.5	C- $\beta$ in $\beta$ - $\beta$
32	53.5	C- $\beta$ in $\beta$ -5
33	20.9	CH <sub>3</sub> , acetyl in xylans

\* G = Guaiacyl; S = Syringyl; H = p-hydroxyphenyl; PC = p-coumaric acid.

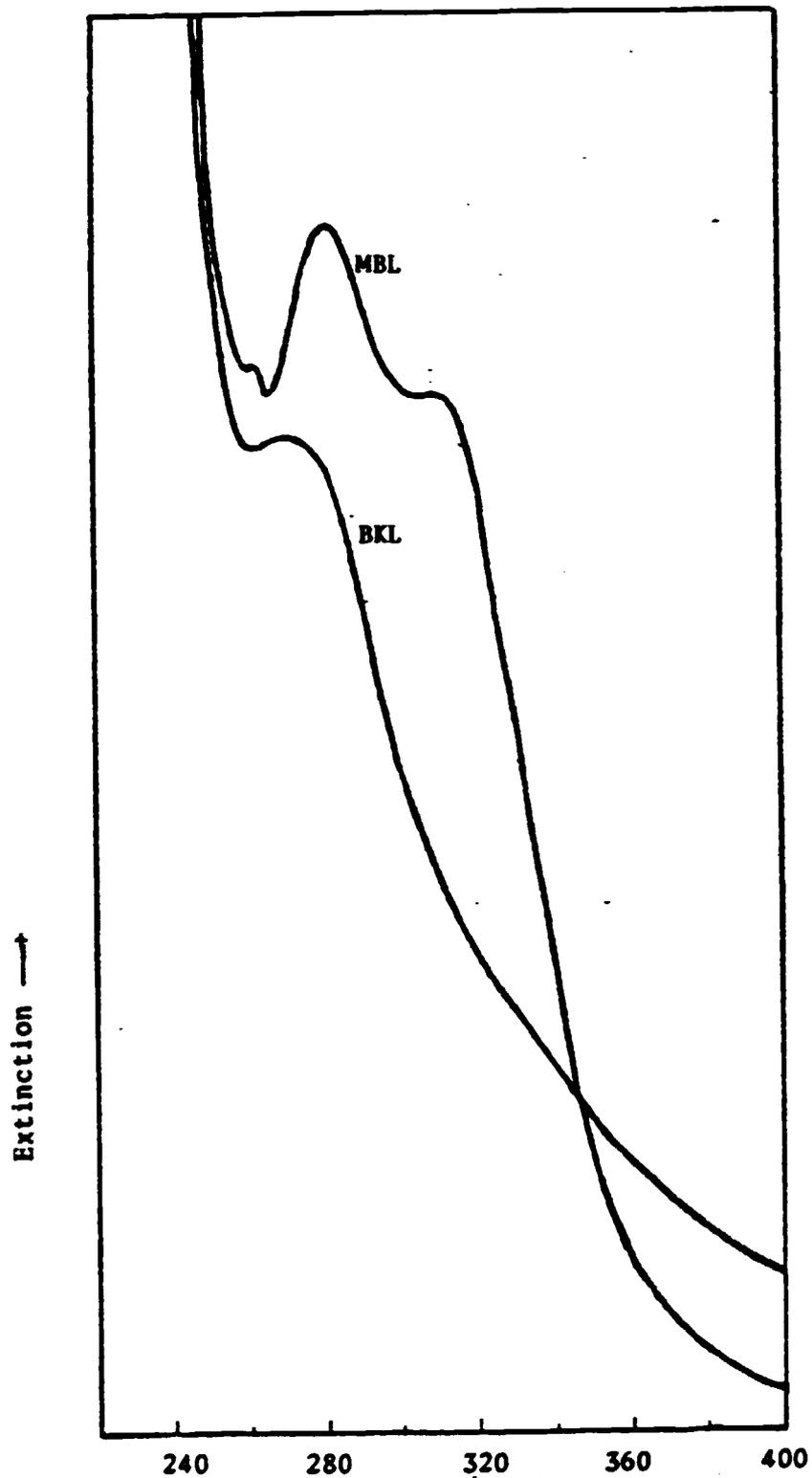


Figure A-1. UV Spectra of Milled Bamboo Lignin (MBL) and Bamboo Kraft Lignin (BKL) (Solvent: dioxane/water 1:1)

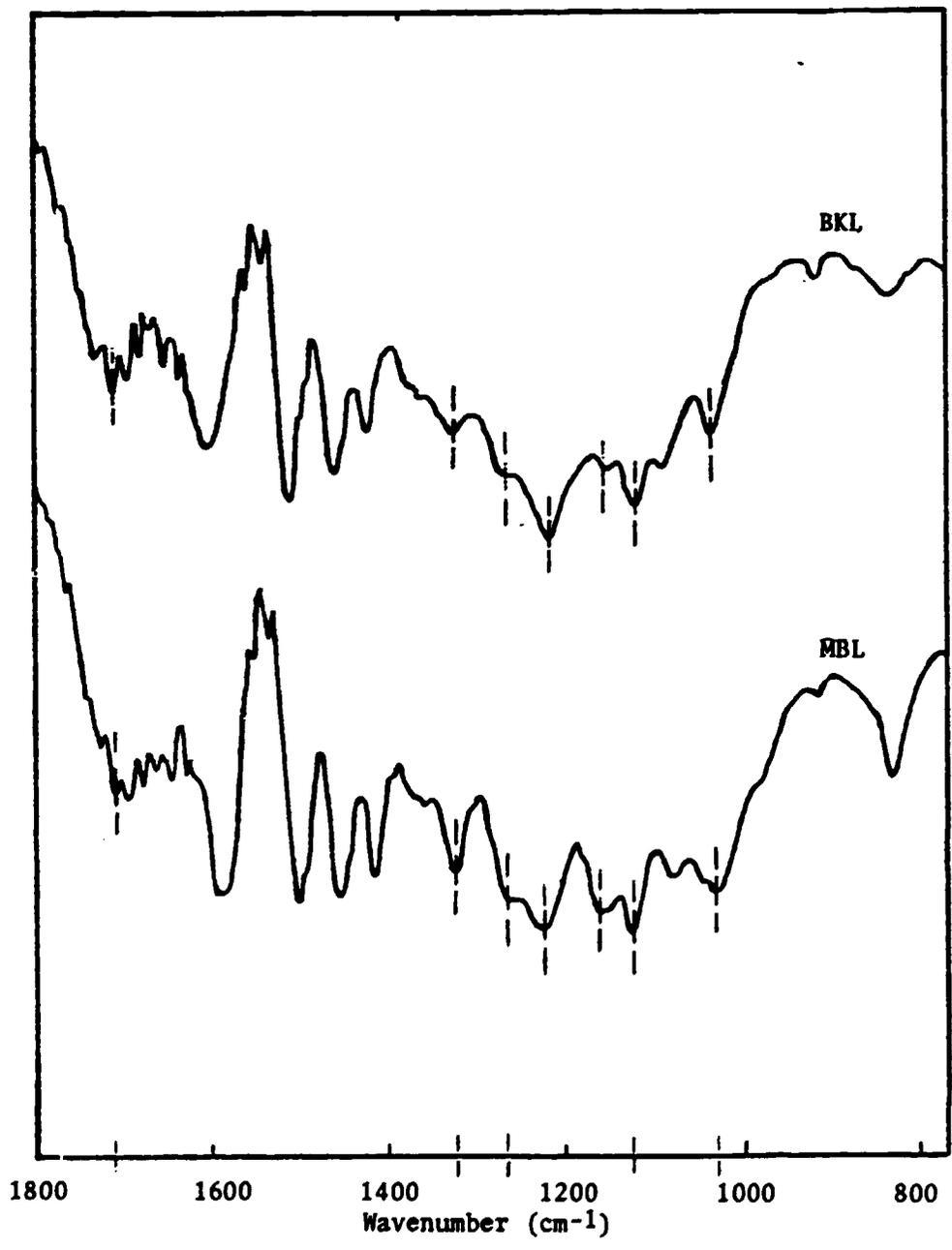


Figure A-2. IR Spectra of Milled Bamboo Lignin (MBL) and Bamboo Kraft Lignin (BKL)

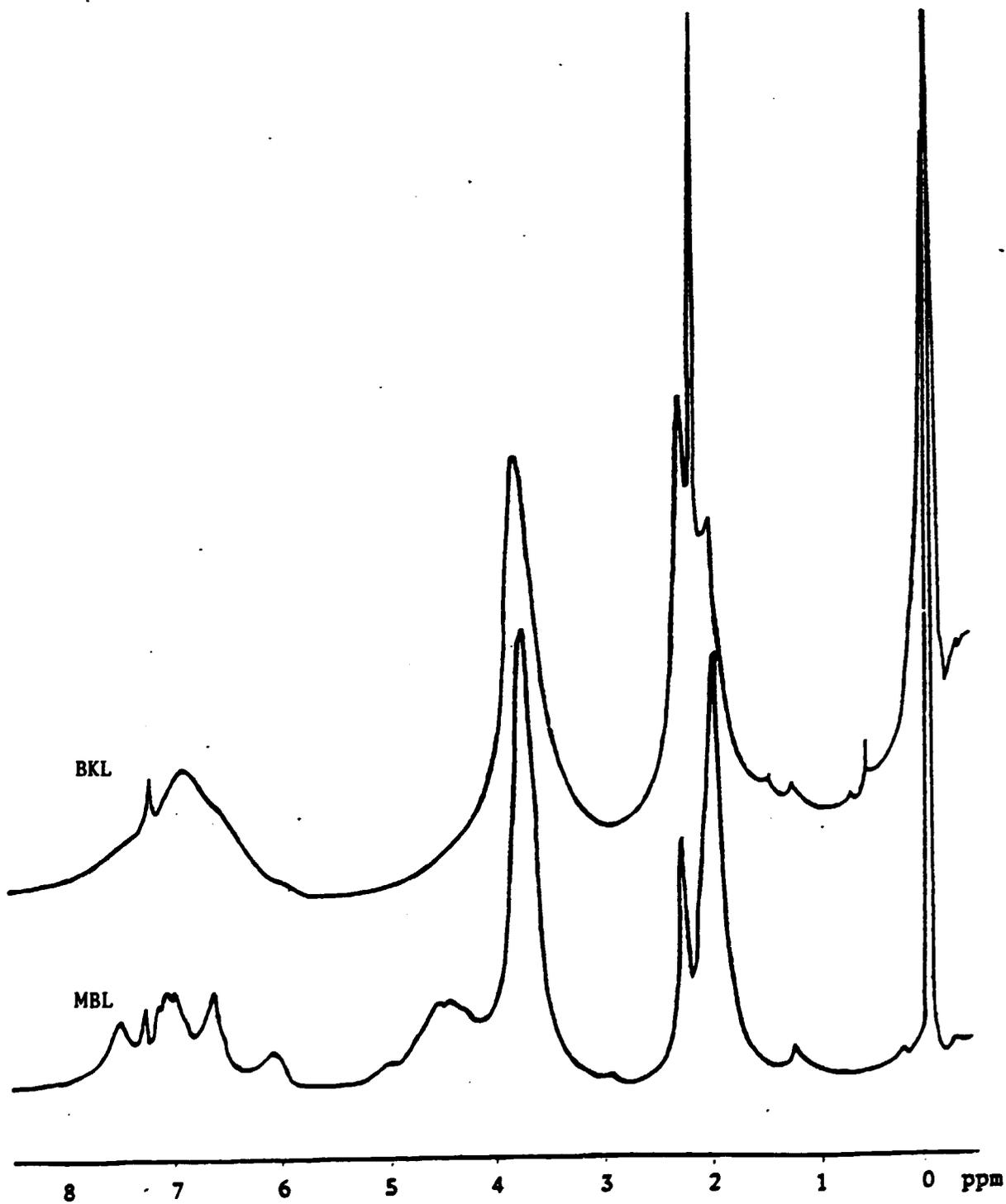


Figure A-3.  $^1\text{H-NMR}$  Spectra of Milled Bamboo Lignin (MBL) and Bamboo Kraft Lignin (BKL)

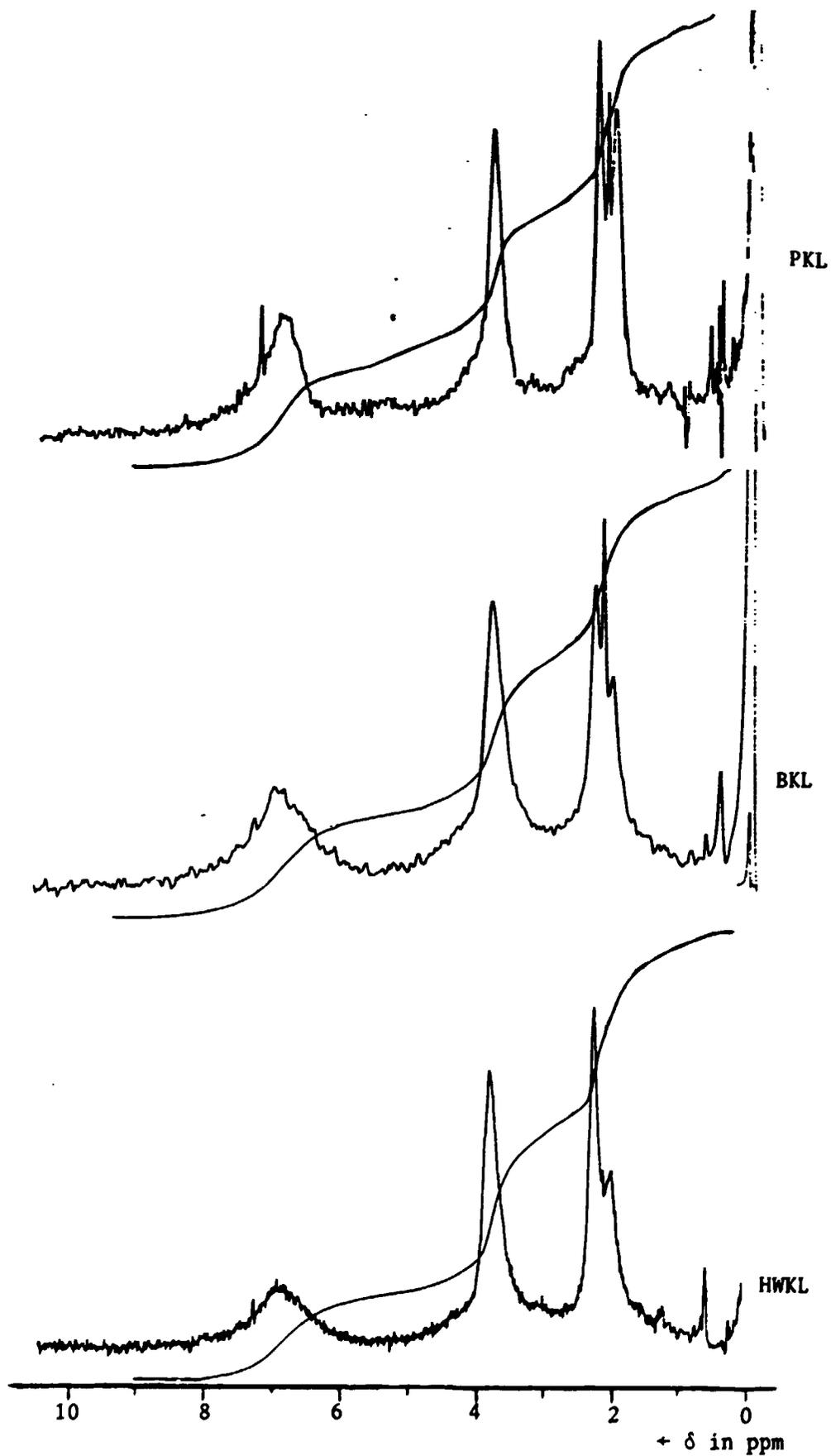


Figure A-4.  $^1\text{H-NMR}$  Spectra of Acetylated Kraft Lignins from Pine (PKL), Bamboo (BKL) and Hardwood (HWKL)

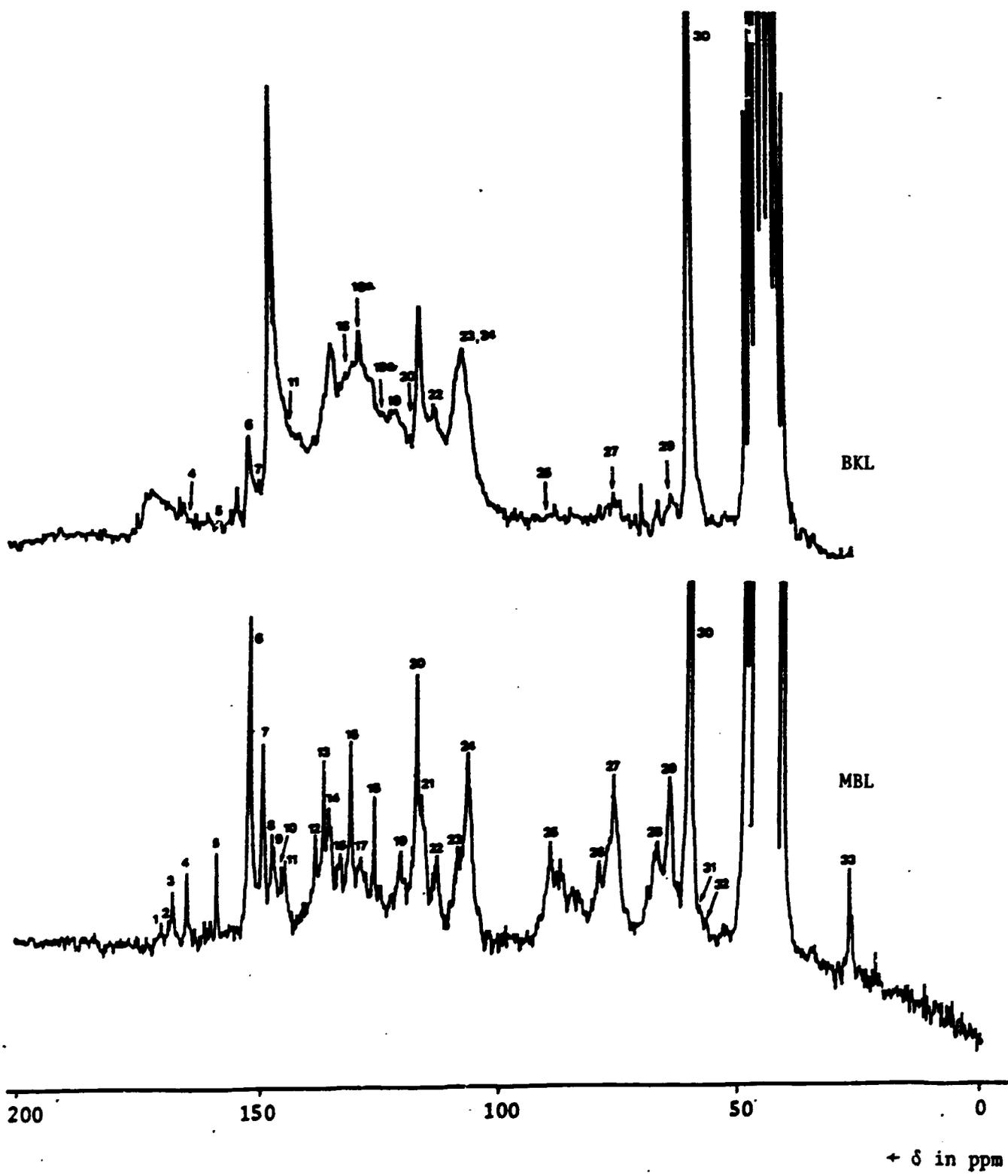


Figure A-5.  $^{13}\text{C}$ -NMR Spectra of Milled Bamboo Lignin (MBL) and Bamboo Kraft Lignin (BKL)

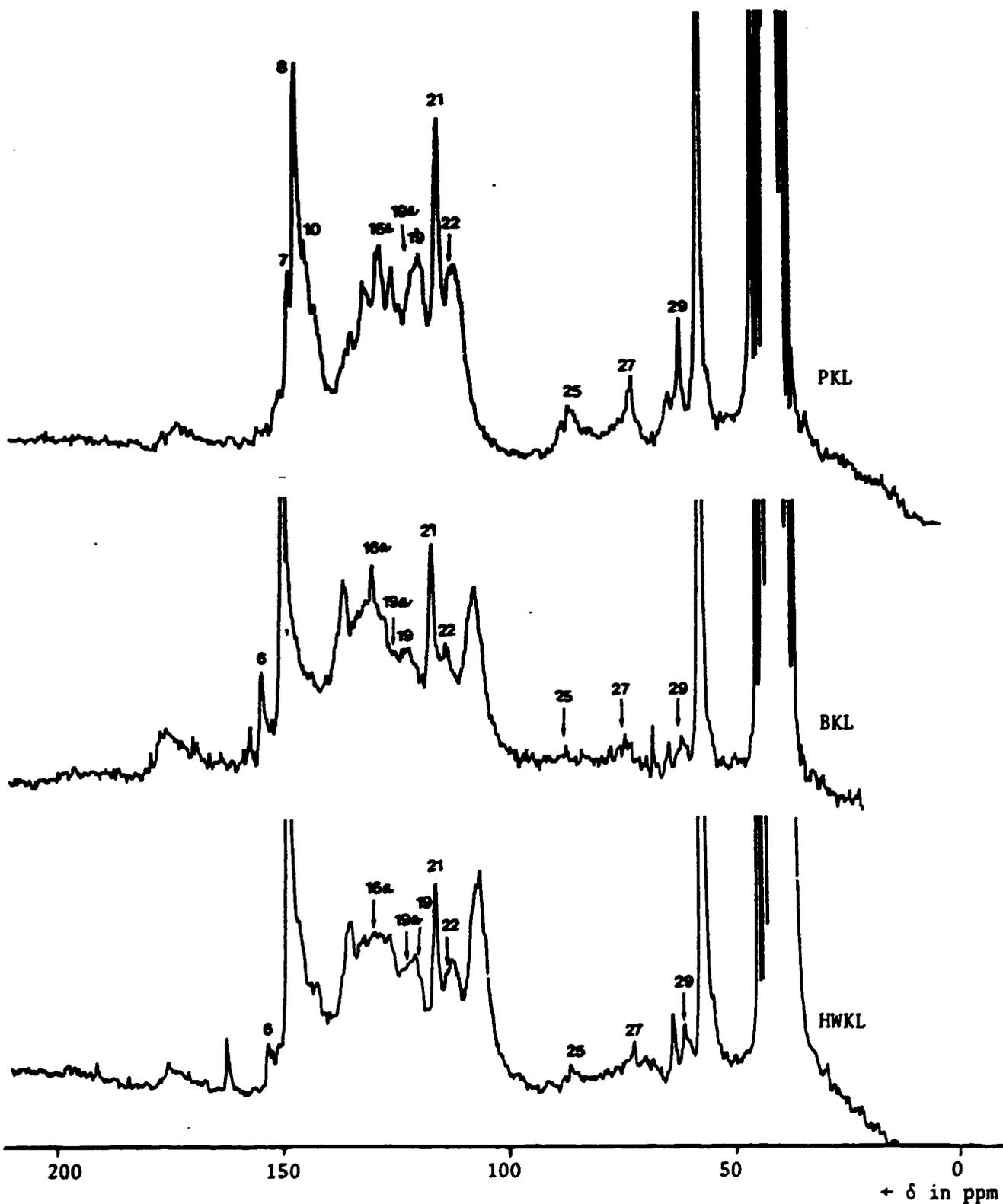


Figure A-6.  $^{13}\text{C}$ -NMR Spectra of Kraft Lignin From Pine (PKL), Bamboo (BKL) and Hardwood (HWKL)