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CONTENTS OF α -O-4 AND β -O-4 BONDS IN NATIVE LIGNIN AND ISOLATED LIGNIN PREPARATIONS

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An analytical calculation method for the estimation of the contents of alkyl aryl ether bonds (α -O-4 and β -O-4) in lignin was developed. In the framework of the method, Alkyl–O–Aryl type bonds are described as coupled phenolic hydroxyls (OH_{phen}). The method is based on the balance equation including the free and coupled OH_{phen} contents in dissolved and residual lignins, on the one hand, and their respective contents in native lignin, on the other. The free OH_{phen} content is calculated on the basis of the OH_{phen} contents of dissolved and residual lignin, determined by the aminolysis method in the course of kraft cooking of softwood. The calculation results for soluble lignin preparations are in good agreement with the ¹³C NMR (nuclear magnetic resonance) spectral data for the solutions. The content of Alkyl–O–Aryl bonds in native softwood (pine, spruce) lignin was estimated at 79/100 PPU (phenylpropane unit). In isolated lignin preparations, the contents of these bonds decrease in the sequence: Freudenberg lignin (71/100 PPU) > Bjorkman lignin (61/100 PPU) > Pepper lignin (44/100 PPU). Dissolved alkaline lignin still contains small amounts of Alkyl–O–Aryl bonds (36/100 PPU in soda lignin and an average of 23/100 PPU in soda-AQ lignin, kraft lignin, and kraft-AQ lignin). Residual lignin which represents the fraction of native lignin with inter-unit bonds resistant to kraft pulping contains 66/100 PPU of such bonds. A relatively high content of Alkyl–O–Aryl bonds (61/100 PPU) is preserved in technical hydrolysis lignins.

KEYWORDS. Lignin, Alkyl–O–Aryl bonds, phenolic hydroxyls, ¹³C NMR spectroscopy

INTRODUCTION

Lignin is the second most abundant biopolymer on earth, and, therefore, it has constantly been the focus of basic and applied research. Being a polyfunctional, polydisperse, and irregular heteropolymer, lignin represents a relatively complicated object in terms of the assessment of its structure and properties. The wide use of physical methods, such as NMR spectroscopy^[1] and mass spectrometry,^[2] in lignin chemistry opened up new possibilities for

studying the structure of this biopolymer. These methods provided convincing evidence showing that lignin or, at least, lignin preparations isolated from wood, are linear oligomers.^[3–7]

¹³C NMR spectroscopy in solution has improved our knowledge of lignin structure and, in particular, of the contents of inter-unit bonds and functional groups of different types in it.^[8–11] Notable achievements relate to lignin preparations soluble in some organic solvents and aqueous alkalis. However, there is a group

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of lignin preparations, specifically Freudenberg lignin,^[12] residual lignin,^[13] technical hydrolysis lignin^[14] and some others, which are insoluble in these solvents. At the same time, to know the structure of such lignin preparations is essential for understanding the structure of native lignin and its chemical transformations in technological processes. Attempted structural assessment of insoluble lignin preparations by means of solid-state NMR has been reported.^[15–17] However, no quantitative estimates proved possible at the available level of development of this promising technique.

Functionalization of lignin plays a fundamental role in its dissolution, in wood delignification processes inclusive.^[18,19] In an alkaline medium, functionalization involves cleavage of alkyl aryl ether bonds and formation of phenolic hydroxyl groups (OH_{phen}) at the site of bond cleavage. We previously found a linear correlation between the number of the cleaved bonds and the number of the OH_{phen} groups formed.^[20]

Based on these results, in the present work we developed a new method for the determination of the total content of alkyl aryl ether bonds (α -O-4 and β -O-4) in native wood lignin, as well as in soluble and insoluble lignin preparations. ^{13}C NMR spectroscopy in solution was used as a comparison method.

EXPERIMENTAL

Methods of isolation of lignin preparations are described in the following works: Freudenberg lignin,^[12] Bjorkman lignin,^[21] Pepper lignin,^[22] hydrolysis lignin,^[14] and alkaline lignins.^[19] Methoxyl groups were determined by the reaction of lignins with hydroiodic acid.^[23] Phenolic hydroxyl groups were determined by aminolysis using the Mansson method.^[24] Carbohydrates were determined by photolorimetry using the phenol–sulfuric acid method.^[25] The resulting analytical data are listed in Table 1.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer equipped with a 5-mm broadband-observed probe head, at 400.13 MHz (^1H) and

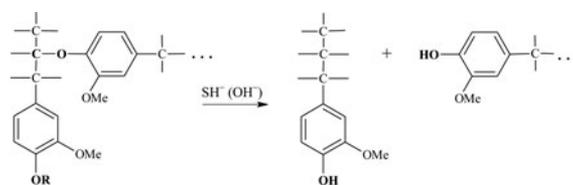
TABLE 1. Content of functional groups and carbohydrates in preparations of spruce lignin, %

Preparation	OMe	OH_{phen}	Carbohydrates
Freudenberg lignin	15.11	2.00	6.5
Bjorkman lignin	15.78	2.97	5.3
Pepper lignin	15.08	4.52	3.7
Soda lignin	13.24	5.32	7.3
Soda-AQ lignin	12.90	6.43	7.2
Kraft lignin	13.27	6.48	7.1
Kraft-AQ lignin	12.96	6.63	7.0
Hydrolysis lignin	11.96	3.00	6.4

100.61 MHz (^{13}C) at 296 K. The spectra were referenced through the solvent lock (^2H) signal according to IUPAC-recommended secondary referencing method. The samples were prepared by dissolving lignin (80 mg) in DMSO (dimethyl sulfoxide)- d_6 (0.7 ml). The spectra were recorded over a 24-kHz spectral width in 64 K data points (acquisition time 1.36 s), with power-gated decoupling using a 30-degree flip angle pulse and a 2.0-s relaxation delay. The free induction decay (FIDs) were zero-filled to 128 K data points and multiplied by an exponential window function with line broadening of 30 Hz before Fourier transformation.

METHOD

The cleavage of alkyl aryl ether bonds in lignin in the course of alkaline wood pulping can be considered as a transition of phenolic hydroxyl groups from the bound to free state^[20]:



Then, at any moment of the pulping process, Equation (1) is valid.

$$Q_{\text{OH,d}} + Q_{\text{OH,r}} + Q_{\text{OR,d}} + Q_{\text{OR,r}} = \sum Q, \quad (1)$$

where

$Q_{\text{OH,d}}$ is the amount of free phenolic hydroxyl groups in dissolved lignin;

$Q_{OH,r}$ is the amount of free phenolic hydroxyl groups in residual lignin;

$Q_{OR,d}$ is the amount of bound phenolic hydroxyl groups in dissolved lignin;

$Q_{OR,r}$ is the amount of bound phenolic hydroxyl groups in residual lignin; and ΣQ is a constant value.

$$\Sigma Q = Q_{OH,n} + Q_{OR,n}, \quad (2)$$

$Q_{OH,n}$ is the amount of free phenol hydroxyls in native lignin and $Q_{OR,n}$ is amount of bound phenolic hydroxyls in native lignin.

It should be noted that in Equation (1) all values represent the amounts of alkyl aryl ether bonds and functional groups in lignin (mmol) but not their contents. The $Q_{OH,n}$, $Q_{OH,d}$, and $Q_{OH,r}$ were calculated from the analytical data on the amounts of native wood lignin and dissolved and residual lignins (g) and the phenolic hydroxyl contents of these lignins (mmol/g). All the obtained data were reduced to 100 g of the starting absolutely dry spruce wood containing 27.2 g of lignin.

The degree of delignification (A , %) was calculated by the formulas:

$$A = 100\% - L$$

$$L = \frac{L_p Y}{L_w} \cdot 100,$$

where L is the content of residual lignin, related to the content of Klason lignin in wood, %; L_p is the content of residual lignin in pulp, %; L_w is the content of Klason lignin in wood, %; and Y is yield of pulp, %.

The ΣQ constant can be determined by knowing the amount of phenolic hydroxyl groups in dissolved lignin at a 100% degree of delignification, when lignin has completely dissolved and all inter-unit bonds have cleaved to form exclusively free phenolic hydroxyl groups:

$$\Sigma Q = Q_{OH,d} \quad (3)$$

However, alkaline pulping of wood never results in 100% delignification. Therefore, the target value was determined from the $Q_{OH,d}-A$

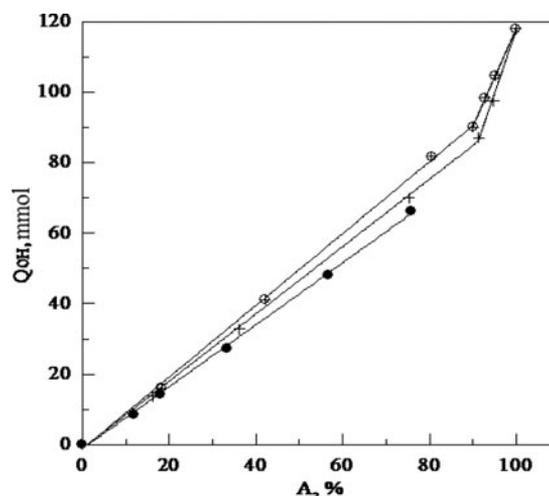


FIGURE 1. Dependence of the quantity of free phenolic hydroxyls on the degree of delignification in dissolved lignin under soda (●), soda-AQ (+), and kraft-AQ (⊕) cooking of spruce wood.

dependence for soda-AQ and kraft-AQ pulping by extrapolating the curve segment corresponding to the final stage of the process to $A = 100\%$ (Figure 1). The extrapolation gave an estimate of 118 mmol for the ΣQ constant.

It should be noted here that there is another route for the production of phenolic hydroxyl groups in the course of alkaline pulping, specifically lignin demethylation. However, had this reaction contributed much to the total yield of phenolic hydroxyl groups, we would have observed in the $Q_{OCH_3}-A$ dependence a change in the slope, equal in magnitude but opposite in sign to that in the $Q_{OH}-A$ dependence (at the same stage of pulping). As seen from Fig. 2, the quantity of methoxy groups in dissolved lignin is linearly related to the delignification degree at all stages of the cooking procedures studied on.

Thus, the major source of phenolic hydroxyl groups in the pulping process is the cleavage of inter-unit alkyl aryl ether bonds of lignin. This conclusion is consistent with the results of Gellerstedt and Lindfors^[26] who found that the content of the pyrocatechol units formed by lignin demethylation during kraft pulping changed but did not exceed 3/100 PPU.

The $Q_{OH,d}-A$ dependence for kraft pulping of pine (Figure 3, curve 1) is similar to those in Figure 1. Note that to calculate the position

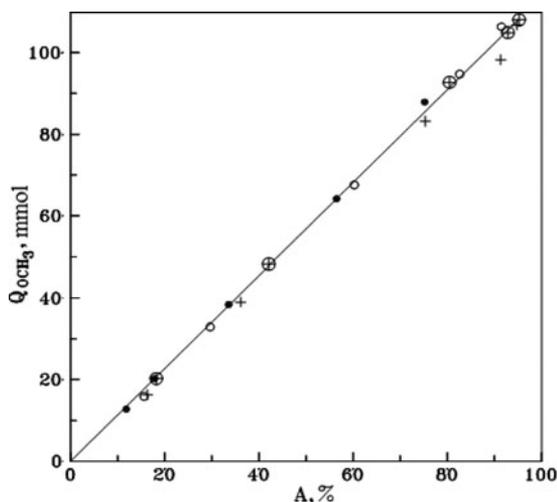


FIGURE 2. Dependence of the quantity of methoxyl groups on delignification degree for dissolved lignin obtained by soda (●), soda-AQ (+), kraft (○) and kraft-AQ (⊕) cooking of spruce wood.

of points in Figures 3 and 4, we made use of the experimental data of Gellerstedt and co-authors.^[26–28]

The OH_{phen} amount of residual lignin (Figure 3, curve 2) changes in a different way. At the initial stage of pulping ($A < 30\%$) it remains almost constant and equal to $Q_{OH,n}$, after which it sharply decreases. In other words, at the initial stage of pulping lignin dissolves due to phenolic hydroxyl groups formed by

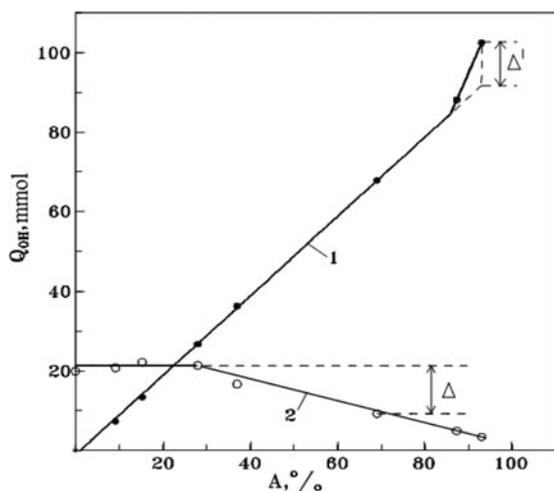


FIGURE 3. Dependence of the quantity of free phenolic hydroxyls on the degree of delignification in dissolved (1) and residual (2) lignins under kraft cooking of pine wood.

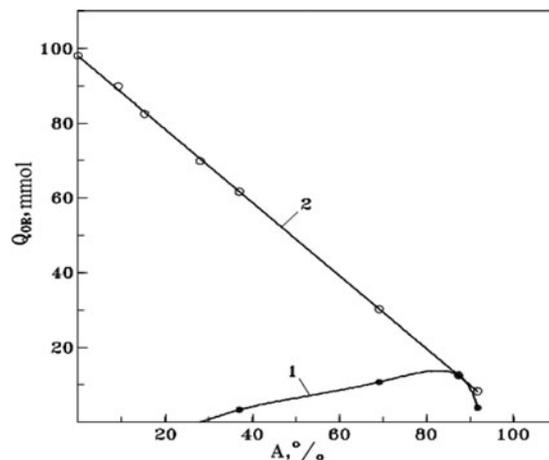


FIGURE 4. Dependence of the quantity of bound phenolic hydroxyls on the degree of delignification in dissolved (1) and residual (2) lignins under kraft cooking of pine wood.

cleavage of alkyl aryl ether bonds, but at subsequent stages, phenolic hydroxyl groups present in native lignin are also involved. Since the sharp decrease in $Q_{OH,r}$ at $A > 30\%$ is not accompanied by a change in the slope of the $Q_{OH,d}-A$ straight line (Figure 3, curve 1), we can suggest that the amount of uncleaved bonds in dissolved lignin ($Q_{OR,d}$) is equal to the amount of phenolic hydroxyl groups passed from residual to dissolved lignin (labeled Δ in Figure 3). Thus, at the bulk pulping stage Equation (4) is valid.

$$Q_{OR,d} = Q_{OH,n} - Q_{OH,r} \quad (4)$$

At the bulk stage of pulping, when the process of bond cleavage in dissolved lignin becomes noticeable (Figure 3, curve 1), an additional term relating to this process appears in Equation (4):

$$Q_{OR,d} = Q_{OH,n} - Q_{OH,r} - \Delta' \quad (5)$$

$$\Delta' = Q_{OH,d} - mA, \quad (6)$$

where m is the slope of curve 1 (Figure 3) for the bulk pulping stage ($m = 0.98$). The amount of bound phenolic hydroxyl groups in residual lignin ($Q_{OR,r}$) was calculated by Equation (1). The calculated $Q_{OR,d}$ and $Q_{OR,r}$ values are presented in Figure 4.

Comparison of Figures 3 and 4 shows that in the course of kraft pulping of wood the amount of phenolic hydroxyl bonds in dissolved lignin (Figure 3, curve 1) changes in inverse proportion to the amount of alkyl aryl ether bonds in residual lignin (Figure 4, curve 2). This finding provides further evidence for the important conclusion that the cleavage of Alkyl–O–Aryl bonds in lignin is the main source of OH_{phen} groups in the kraft pulping process.

Then, the content of Alkyl–O–Aryl bonds in the isolated lignin preparations can be determined by subtracting their OH_{phen} content (mmol/g) from the ΣQ constant (mmol/g). Note that the n/100 PPU units are more illustrative but less accurate, since the molecular mass of the PPU for different lignin preparations may differ from the used value of 183. One should preliminarily compare the calculated values with the experimental data for the best known Bjorkman lignin. Using the ΣQ constant of 118 mmol calculated per 27.2 g of lignin, we obtain 4.34 mmol/g (79/100 PPU). The OH_{phen} content of Bjorkman lignin is 32/100 PPU (Table 2). Then the content of the Alkyl–O–Aryl bonds in Bjorkman lignin can be estimated at 79–32 = 47/100 PPU.

The following data for spruce Bjorkman lignin are available in the literature. According to the results of the study on the degradation products of spruce Bjorkman lignin, summarized in the review,^[29] the contents of α-O-4 and β-O-4 bonds in it are 6–13/100 PPU and 49–51/100 PPU, respectively. According to Freudenberg,^[30] the corresponding values are 17 and 44/100 PPU, respectively. Almost

coincident estimates, 16 and 45/100 Ar, were obtained from ¹³C NMR data.^[10] Thus, the most realistic estimate for the total content of α-O-4 and β-O-4 bonds in spruce Bjorkman lignin is 61/100 PPU. The difference between this and calculated values is 14/100 PPU.

It should be borne in mind that the ΣQ constant was obtained by the extrapolation of the section corresponding to the final pulping stage to A = 100% in the Q_{OH,d}–A dependence (Figure 1). In other words, the 14/100 PPU difference testifies that wood lignin contains Alkyl–O–Aryl bonds resistant under alkaline pulping conditions. As shown by ¹³C NMR, kraft pine lignin contains ~5/100 PPU ether bonds in enol ether type structures.^[8] In this type of structures (**1**) formed by the reaction of native lignin with pulping reagents during alkaline treatment of wood, β-O-4 bonds are resistant to cleavage.^[31] In addition, type (**2**) structures in native lignin are assumed to contain ~7/100 PPU of β-O-4 bonds.^[32] The β-O-4 bond in similar structural fragments of lignin does not cleave under the action of pulping reagents, since a necessary condition for this bond to cleave is the presence of either the α- or γ-side chain capable of being ionized in an alkaline medium.^[33]

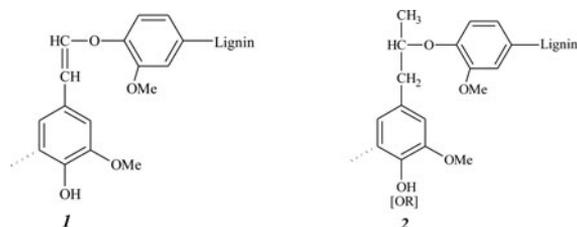


TABLE 2. Content of phenolic hydroxyls and Alkyl–O–Aryl bonds in preparations of spruce lignin

Preparation	OH _{phen}		Alkyl–O–Aryl bonds		
	mmol/g	n/100 PPU	mmol/g	n/100 PPU	n/100 Ar (NMR)
Native lignin	0.73*	13*	4.34	79	—
Freudenberg lignin	1.18	22 ± 4	3.89	71	—
Bjorkman lignin	1.75	32 ± 3	3.32	61	64
Pepper lignin	2.66	49 ± 3	2.41	44	41
Soda lignin	3.13	57 ± 4	1.94	36	42
Soda-AQ lignin	3.78	69 ± 2	1.29	24	26
Kraft lignin	3.81	70 ± 4	1.26	23	34
Kraft-AQ lignin	3.90	71 ± 3	1.17	22	34
Hydrolysis lignin	1.76	32 ± 4	3.31	61	—

* Data from Ref.^[28]

In view of what has been said, the ΣQ constant should be increased by 14/100 PPU or 20 mmol in counting of wood lignin, i.e. $\Sigma Q = 138$ mmol. Counting the content, we obtain 5.07 mmol/g (93/100 PPU) per 27.2 g of lignin. Using this value of the constant, we have calculated the contents of Alkyl–O–Aryl bonds in both native lignin and isolated lignin preparations. The results are presented in Table 2.

RESULTS AND DISCUSSION

To obtain independent experimental evidence for the calculated data, the soluble lignin preparations were studied by ^{13}C NMR spectroscopy (Figures 5–10). Quantification of Alkyl–O–Aryl bonds was carried out by the method of Capanema et al.^[10] According to this method, the integral of the 162–102 ppm

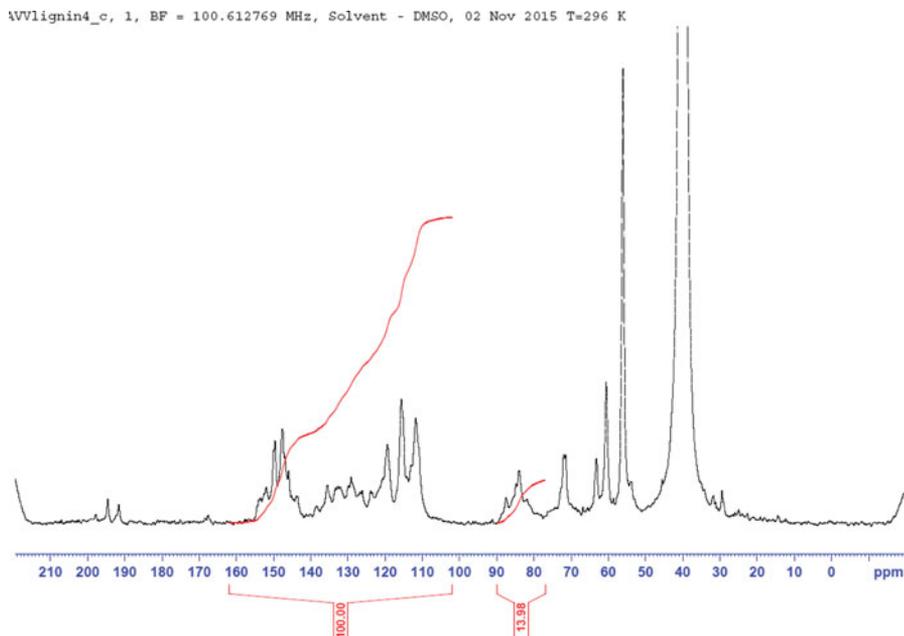


FIGURE 5. ^{13}C NMR spectrum of spruce Bjorkman lignin in DMSO-d₆.

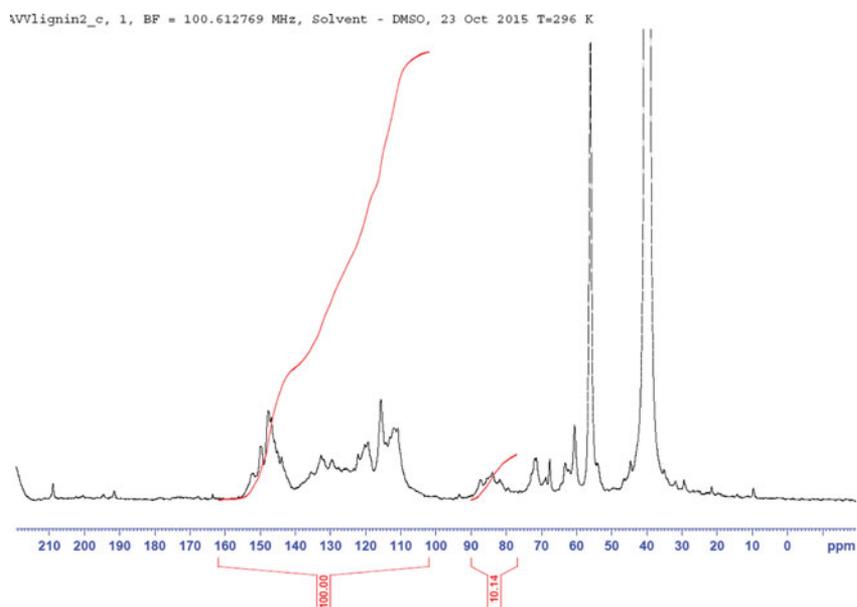


FIGURE 6. ^{13}C NMR spectrum of spruce Pepper lignin in DMSO-d₆.

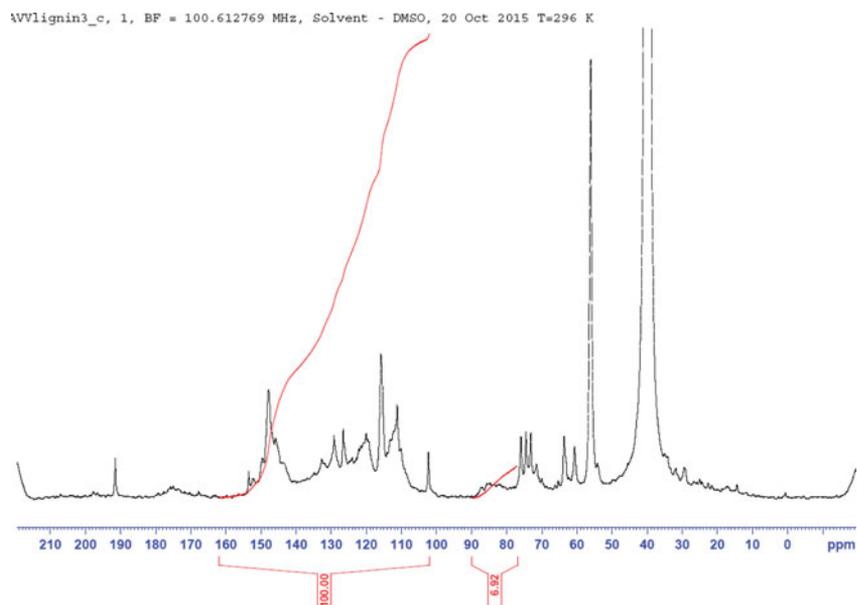


FIGURE 7. ^{13}C NMR spectrum of spruce soda lignin in DMSO- d_6 .

region was set as reference, assuming that it includes six aromatic carbons and 0.12 vinyl carbons. It follows that the integral value divided by 6.12 is equivalent to one aromatic ring (Ar). To determine the total content of α -O-4 and β -O-4 bonds, the cluster of signals at 90–77 ppm was used. The cluster relates to different Alkyl–O–Aryl (α - and β -) and α -O-Alk

moieties. In spruce Bjorkman lignin, the content of α -O-Alk moieties reaches 0.21/Ar.^[10] Therefore, the corresponding correction was included when determining the total content of α -O-4 and β -O-4 bonds for this lignin.

The contents of α -O-Alk moieties in the other soluble lignin preparations studied (Table 2) were unknown. For them no

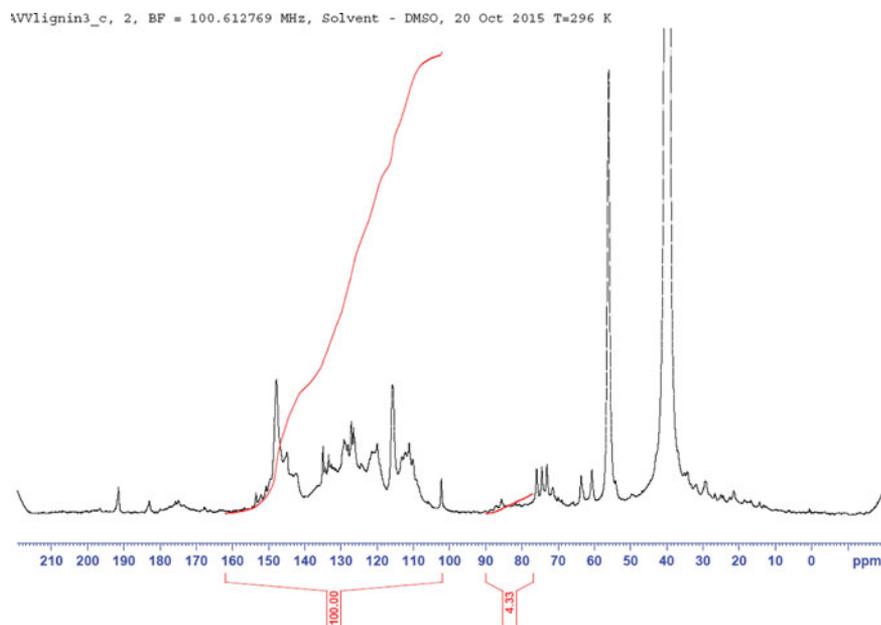


FIGURE 8. ^{13}C NMR spectrum of spruce soda-AQ lignin in DMSO- d_6 .

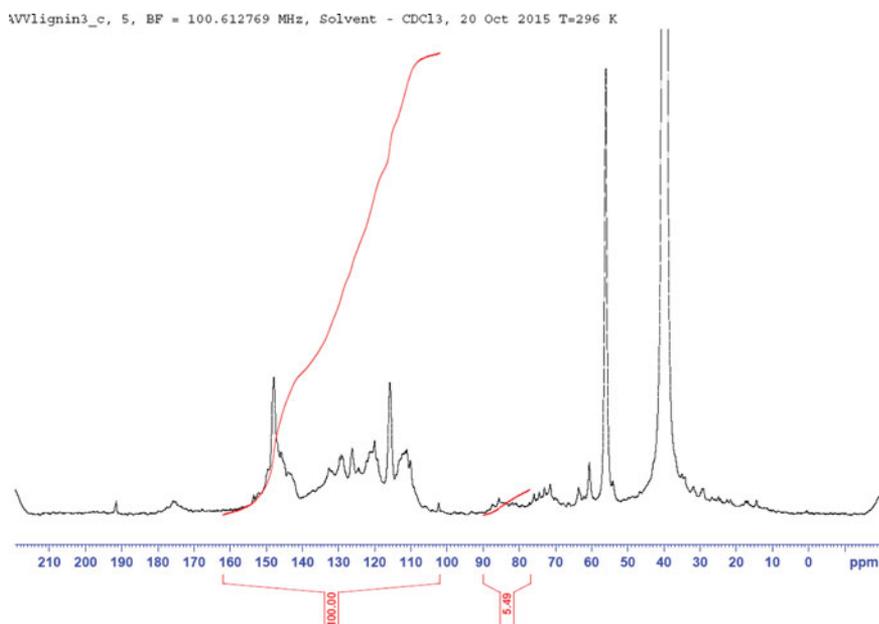


FIGURE 9. ^{13}C NMR spectrum of spruce kraft lignin in DMSO-d₆.

corrections were applied, except for Pepper lignin. Therewith, we relied on the following reasoning. As indicated in,^[10] the exact structure of all α -O-Alk moieties is not yet established, but the most representative among them are pinoresinol structures. The Pepper lignin preparation is isolated

from wood by acidolysis.^[22] Pinoresinol structures are fairly stable under these conditions, as judged from the fact that they were found among the other lignin acidolysis products.^[34]

Alkaline lignins (Table 2) apparently contain very little pinoresinol structures, since the α -

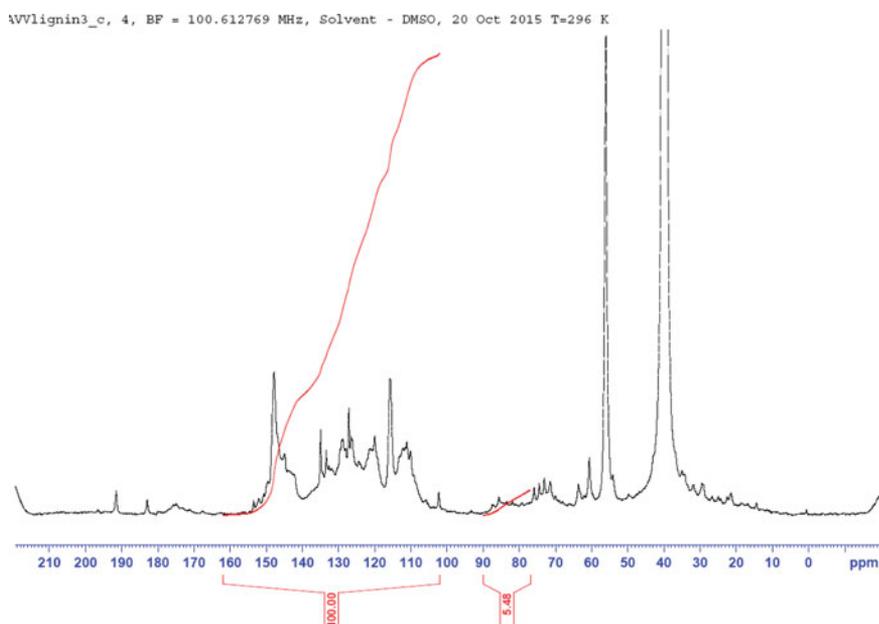


FIGURE 10. ^{13}C NMR spectrum of spruce kraft-AQ lignin in DMSO-d₆.

O-Alk bonds in pinoresinol are cleaved under soda and kraft pulping conditions.^[35]

The results of the ¹³C NMR quantification of the α -O-4 and β -O-4 bonds are listed in Table 2.

As seen from Table 2, for Bjorkman and Pepper lignins the calculated and experimental values of bond content are very close to each other within the errors of determining bonds (Table 2). Table 2 shows the standard deviations for the OH_{phen} contents, since we calculated the bond contents based on these values.

It should be noted that because of the low contents of α -O-4 and β -O-4 bonds in alkaline lignins, the signal-to-noise ratios in their ¹³C NMR spectra are very low (Figures 7–10). This explains why the gap between the experimental and calculated values for these preparations is larger than the standard deviation.

Further evidence for the correctness of the developed analytical calculation method for the quantification of Alkyl–O–Aryl bonds was obtained by summing the contents of these bonds in dissolved and residual lignins during kraft pulping of pine wood, calculated by the formula $93/100 \text{ PPU} - \text{OH}_{\text{phen}}/100 \text{ PPU}$ at a given degree of delignification. The OH_{phen} contents of dissolved and residual lignins are taken from.^[27,28] It is obvious that at any moment of pulping, the total content of Alkyl–O–Aryl bonds should be close to $\Sigma Q = 93/100 \text{ PPU}$. The results are presented in Table 3.

The significant deviation of the total content of Alkyl–O–Aryl bonds from 93/100 PPU at the initial stage of pulping ($A = 9.2\%$) deserves special attention. In the course of cooking,

this deviation gradually decreases to reach as little as 4.3% of the ΣQ constant at the final stage ($A = 91.6\%$). In our opinion, the most likely reason for such differences is the formation of enol type structures (**1**) in lignin (*vide supra*). This reaction was investigated in detail by Gellerstedt and Lindfors,^[36] who found that the content of enol ether structures in dissolved and residual lignins during kraft pulping of pine wood reaches a maximum when the temperature has been increased to 170°C and then sharply decreases.

Since the content of Alkyl–O–Aryl bonds was determined as the difference between the ΣQ constant and the OH_{phen} content, the presence in lignin of enol ether structures which are incapable of degrading under kraft pulping conditions, leads to an underestimation of the OH_{phen} content and, consequently, to an overestimation of the Alkyl–O–Aryl bond content. In view of the above-mentioned relative error of the determination, it turns out that at the end of kraft pulping dissolved lignin (in black liquor) contains $23 \pm 1/100 \text{ PPU}$ of Alkyl–O–Aryl bonds and residual lignin (in kraft pulp) contains $66 \pm 3/100 \text{ PPU}$ of these bonds. Note that dissolved kraft spruce lignin also contains $23/100 \text{ PPU}$ of Alkyl–O–Aryl bonds (Table 2).

Our estimates for the contents of Alkyl–O–Aryl bonds in dissolved pine and spruce lignin are consistent with the respective values for technical softwood kraft lignins. Thus, the total contents of Alkyl–O–Aryl (α - and β -) and α -O-Alk moieties in commercially available Indulin and Curan (technical softwood kraft lignin) preparations are $29 \pm 1.5/100 \text{ Ar}$ and $20/100 \text{ Ar}$, respectively.^[37] The OH_{phen} contents of these preparations are $66 \pm 1.0/100 \text{ Ar}$ and $69/100 \text{ Ar}$, respectively. Then, the total OH_{phen} and bond contents of each of Indulin and Curan will be $95/100 \text{ Ar}$ and $89/100 \text{ Ar}$, respectively, which is sufficiently close to ΣQ (93/100 PPU).

Comparison of calculation results with experimental data for residual lignin is difficult, since currently there is no reliable method for its isolation. The most common methods are acidolysis,^[38] enzymatic hydrolysis^[39], or their combination.^[40] The yield of residual lignin

TABLE 3. Dependence of the content of Alkyl–O–Aryl bonds (n/100 PPU) on the degree of delignification in dissolved and residual lignins at kraft cooking of pine wood

A (%)	9.2	15.6	28.0	37.0	69.0	87.3	91.6
Dissolved lignin	38	37	32	30	31	30	23
Residual lignin	78	75	73	75	73	67	66
Sum of bonds	116	112	105	105	104	97	89
Relative error (%)	24.7	20.4	12.9	12.9	11.8	4.3	–4.3

isolated by acidolysis (RLA) from black spruce kraft pulp was 40%, and its OH_{phen} content was estimated at 2.2 mmol/g or 40/100 PPU.^[40] The respective values for residual lignin isolated by enzymatic hydrolysis (RLE) from kraft pulp loblolly pine were 41.3–45.7% and 36–38/100 PPU.^[39] Thus, both methods allow one to isolate less than half of residual lignin. The question thus arises to what extent these preparations represent the whole residual lignin?

The OH_{phen} content directly in residual pine kraft pulp lignin, i.e. before it has been isolated, is 27/100 PPU,^[28] i.e. 1.3–1.5 less than in the above two preparations. This fact suggests that Alkyl–O–Aryl bond cleavage occurs on isolation by both the RLA and RLE methods. Assuming that the contents of these bonds in the native lignin of black spruce and loblolly pine is the same as in pine wood, specifically 79/100 PPU (Table 2), the isolation of residual lignin by the described methods leads to the cleavage of half of the Alkyl–O–Aryl bonds. Here it is appropriate to quote the speculations of Gellerstedt and Lindfors^[36] on the content of Alkyl–O–Aryl bonds in residual lignin: «... the total quantity of β -aryl ether structure, non-condensed and condensed, in the residual lignin must be assumed to be substantial».

Analyzing the data in Table 2, we can see how the isolation conditions affect bond cleavage in native lignin. In terms of the content of Alkyl–O–Aryl bonds, the closest to native lignin is Freudenberg lignin. Apparently, as a consequence, this lignin is similar to native lignin in other properties. It is insoluble in usual lignin solvents, including aqueous alkali at room temperature, and its solution curve for kraft pulping is similar to the delignification curve of wood.^[41] Furthermore, the yield of Freudenberg lignin from spruce wood is 80% of Klason lignin.^[42]

Although Bjorkman lignin is isolated under very soft conditions, the mechanochemical reactions that occur in the course of fine grinding of spruce wood, 79–61 = 18/100 PPU of Alkyl–O–Aryl bonds (Table 2) are cleaved, and the yield is about 25% of Klason lignin.^[43]

Since Pepper lignin is the product of acidolysis of native lignin, and this reaction

destroys α -O-4 and β -O-4 bonds,^[34] it is not surprising that 79–44 = 35/100 PPU of Alkyl–O–Aryl bonds in Pepper lignin are cleaved (Table 2), and its yield from spruce wood is 37.8% of Klason lignin.^[22]

Under the harsh conditions of soda and kraft pulping of native lignin, most parts of α -O-4 and β -O-4 bonds are cleaved to form phenolic hydroxyls, which ensures dissolution of lignin fragments under these conditions. Nevertheless, at the end of pulping, dissolved lignin still preserves a small amount of Alkyl–O–Aryl bonds: 36/100 PPU in soda lignin and, on average, 23/100 PPU in soda-AQ lignin, kraft lignin, and kraft-AQ lignin (Table 2).

As for residual lignin, the calculation shows that it contains 66/100 PPU of Alkyl–O–Aryl bonds at the end of pulping (Table 3). As already noted, these results are presently impossible to verify experimentally. However, some experimental evidence for the validity of this estimate still can be provided. This residual lignin contains 27/100 PPU of OH_{phen} .^[28] We earlier established that lignin dissolved in an alkaline medium should contain no less than 31/100 PPU of phenolic hydroxyls.^[18] Thus, residual lignin whose content in kraft pulp is as little as 4.7%, represents a fraction of native lignin with inter-unit bonds resistant to kraft pulping. It was shown by Fourier transform infrared (FTIR) spectroscopy that these are β -O-4 bonds in type 2 structures (*vide supra*).^[32]

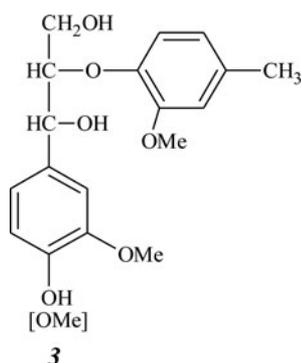
Hydrolysis lignin contains 61/100 PPU of Alkyl–O–Aryl bonds (Table 2). In our opinion, the high stability of these bonds under the harsh conditions of acid hydrolysis of wood can be explained in terms of a combination of reactions involved in this process.

As known, there are main competing reactions that occur in lignin in an acidic medium: destruction and condensation, and they both have the same benzyl carbocation intermediate.^[44] In a weakly acidic medium under mild conditions, the prevailing reaction route involves nucleophilic substitution in the α -position to form a β -aryl enol ether structure followed by solvolysis of the β -O-4 bond to give Hibbert ketone type products.

Under the action of concentrated mineral acids or dilute acids but at high temperature,

lignin prefers to undergo condensation involving "internal" nucleophiles (electron-rich positions in the phenylpropane units). As a result, new C–C bonds form. In phenolic guaiacyl propanoic units, the α -5 bond is predominantly formed. The formation of these C–C bonds is likely to "stabilize" the adjacent β -O-4 bonds, since the formation of the benzyl carbocation and β -aryl enol ether structure becomes impossible. Industrial hydrolysis of wood to form hydrolysis lignin proceeds in 0.7–0.85% H_2SO_4 at the temperature 187°C.^[45]

As an example illustrating the behavior of lignin in an acid medium we can mention the study of Yasuda and Ota,^[46] on the transformations of dimer **3** in 72% sulfuric acid. It was found that under these conditions dimer **3** or its methylated analog form a polymer with its units linked by α -6 bonds, while the neighboring β -O-4 bonds are preserved.



CONCLUSION

The developed analytical calculation method allows a relatively simple and sufficiently precise quantification of inter-unit Alkyl–O–Aryl bonds in native lignin and isolated lignin preparations, both soluble and insoluble. Native softwood (pine, spruce) lignin contains 79/100 PPU of such bonds.

On the isolation of lignin preparations from wood by known methods, more or less of its Alkyl–O–Aryl bond are cleaved. Freudenberg lignin is the most similar to native lignin.

Kraft wood pulping and other alkaline pulping processes destroy most parts of Alkyl–O–Aryl bonds in native lignin, leading to the

formation of phenolic hydroxyl groups and thereby imparting solubility to the destruction products. Dissolved lignin still contains a little of Alkyl–O–Aryl bonds, 36/100 PPU in soda lignin and an average of 23/100 PPU in soda-AQ lignin, kraft lignin, and kraft-AQ lignin. Residual lignin which represents the fraction of native lignin with inter-unit bonds resistant to kraft pulping contains 66/100 PPU of such bonds.

The condensation reactions forming α -5 and α -6 carbon-carbon bonds that to a certain degree "stabilize" the adjacent β -O-4 bonds prevail among the reactions of native lignin under the harsh conditions of acid wood hydrolysis. Therefore, the hydrolysis lignin formed under these conditions has a relatively high content of Alkyl–O–Aryl bonds (61/100 PPU).

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