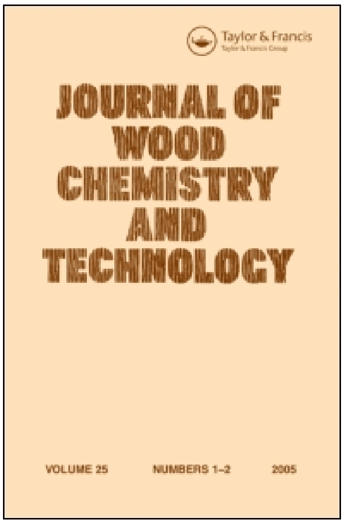

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THE DISTRIBUTION OF PHENOLIC HYDROXYL GROUPS IN HARDWOOD LIGNINS

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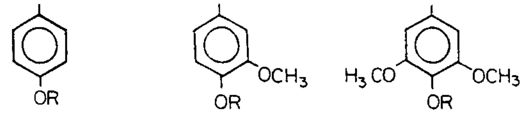
Dedicated to the momory of Kyösti V. Sarkanen

ABSTRACT

Periodate oxidation, because of its high selectivity in the degradation of free-phenolic units, has been used along with the combined phenyl nucleus exchange and nitrobenzene oxidation techniques to estimate the distribution of phenolic hydroxyl groups in hardwood lignins. Analyses of the aspen and white birch wood lignin in situ indicate that the percentage of uncondensed structures having a phenolic hydroxyl group was considerably higher for guaiacyl (~20%) than for syringyl (~5%) units. Thus, the total phenolic hydroxyl groups of hardwood lignins are largely associated with the guaiacyl propane units.

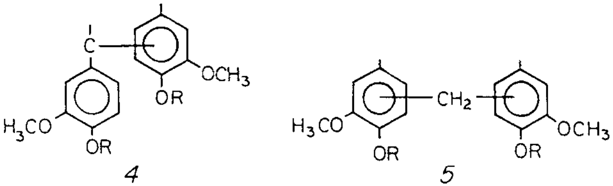
INTRODUCTION

The major types of lignin structures[2,3] based on the nature of substitution on phenyl nuclei, are generally divided into uncondensed and condensed units (Figure 1). Uncondensed units refer to those basic p-hydroxyphenyl (1), guaiacyl (2), and syringyl (3) nuclei which contain no substituents at 2,3,5, or 6-carbons other than methoxyl groups. Otherwise, the units are termed condensed units, which consist of mainly the β-5 (6), 4-O-5 (7), and 5-5 (8)-linked structures. In addition, the diphenylmethane (DPM)-type condensed structures (4 and 5), which are not present in wood lignins, may be formed under acidic or alkaline pulping conditions[3-7].



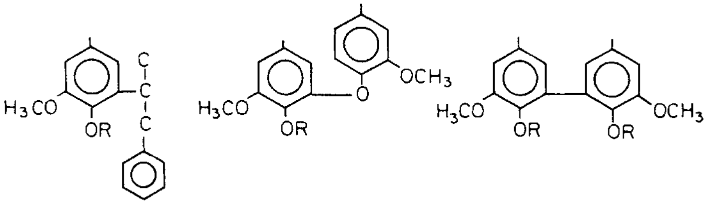
1 2 3

Uncondensed



4 5

Diphenylmethane type



6 7 8

Condensed unit other than DPM type

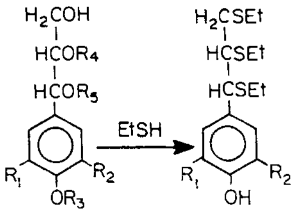
Figure 1. Major Types of Lignin Phenyl Nuclei.

It is well known that the phenolic hydroxyl group plays a dominant role in nearly all the chemical reactions of lignin polymers[3-7], which range from the discoloration of wood to the delignification process. Although a variety of physical and chemical methods[8-10] can be used to provide quantitative measurements on the total content of this functional group, they generally do not reveal the structural environment in which they occur. There is a special need to develop facile procedures for measuring the phenolic hydroxyl groups in condensed structures, especially those present in kraft pulps. This quantitative information is pertinent to understanding the mechanism of condensation reactions and the reactivity of residual lignin toward bleaching agents.

Survey of Analytical Approaches

Chemical methods[7] that can provide quantitative information on the nature of lignin phenolic hydroxyl groups are briefly outlined below.

Thioacidolysis[11-13], a solvolysis of lignin in ethanethiol with boron trifluoride etherate, selectively degrades the uncondensed β-O-4 aryl ether structures to yield the corresponding 1-phenyl 1,2,3-trithioethylpropane derivatives (9). The uncondensed β-O-4 units of the free-phenolic type can be determined by the yield of the methyl derivative 10 produced from thioacidolysis of the premethylated samples. The proportion of phenolic units in uncondensed β-O-4 structures, estimated from the relative yield of compounds 9 and 10, has been examined for wood and grass lignin[11,12].



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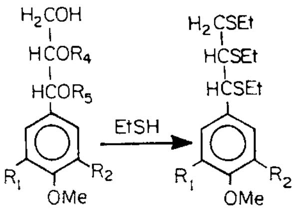

10

where R_1, R_2 = H or oMe

R_3, R_4, R_5 = H or lignin side chain

Both thioacidolysis and acidolysis[14,15] are effective in the cleavages of the β-aryl ether linkages. The thioacidolysis method, however, has the advantages of providing simpler products in higher yields. In addition to monomeric products, several dimeric products represented by the β-5, 5-5, and β-1 linkages have also been identified by a combined thioacidolysis and desulfurization technique[13].

Permanganate oxidation[14-19], a method specific for the analysis of the phenolic units of lignin, involves an initial ethylation of these functional groups followed by sequential oxidation with permanganate and with hydrogen peroxide. From the substitution pattern of the resulting benzoic acid derivatives produced, the nature of the parent lignin structures may be revealed. However, one of the major drawbacks of this technique is that the product yield from individual structural units was not quantitative. Also, this method cannot analyze specifically for the DPM-type structures.

The phenyl nucleus exchange (NE) technique, originally developed by Funaoka and Abe[20,21], is based on the degradation of lignin by boron trifluoride in the presence of excess phenol (Figure 2). This method appears to be the most direct procedure for determining the content of uncondensed units in the wood lignins, which are converted initially to guaiacol (3) and pyrogallol-1,3-dimethyl ether (6) from the guaiacyl (1) and syringyl (5) units, respectively. Under typical NE conditions conducted at 180°C, guaiacol and pyrogallol-1,3-dimethyl ether are partially demethylated to give catechol (4) and pyrogallol-1-methyl ether (7), plus pyrogallol (8), respectively. The yield of these NE products (NEP) has been shown to be nearly quantitative[20,21].

Recently, we have shown[22-24] that the total phenolic hydroxyl groups of lignin in wood or pulp samples can be conveniently

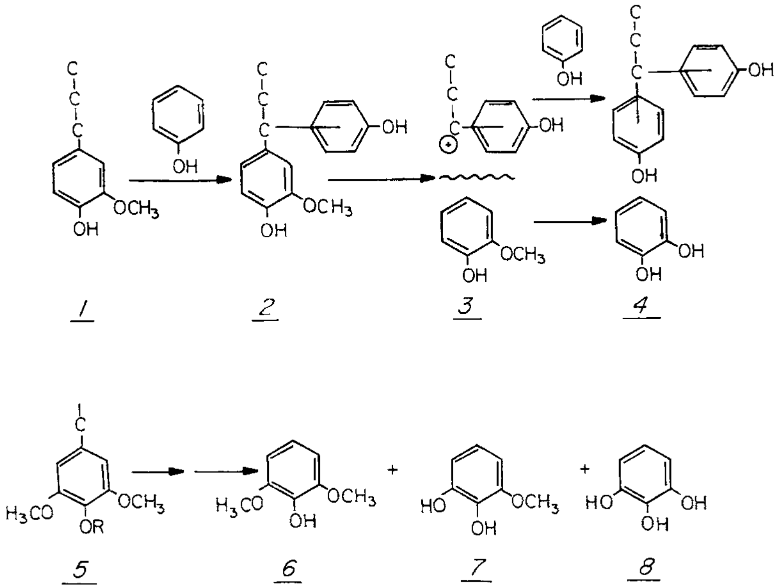

Figure 2. Major monomeric products from phenyl nuclei exchange reactions of uncondensed lignin units.

measured in situ by a periodate oxidation (PO) method, which appears to be relatively specific toward the degradation of phenolic units. Conceptually, PO when combined with the NE reaction may be used to estimate the proportion of phenolic units in the uncondensed lignin structures.

In addition, the DPM-type structures, as demonstrated by Funaoka and Abe[20,21,25], can be quantitatively estimated by the combined NE and alkaline nitrobenzene oxidation (NO) analyses. The underlying principle of this technique is that the DPM structures, like uncondensed units, undergo typical NE reactions. It follows that the yield of NEP from modified lignin samples would be equivalent to the sum of the uncondensed plus DPM units.

On the other hand, the NO reaction selectively degrades the uncondensed structures to yield vanillin plus vanillic acid from the guaiacyl units and syringaldehyde plus syringic acid from the syringyl units. The yield of these NO products (NOP) from uncondensed units, however, varies with the side-chain structures. Although the apparent yield of the NOP is not quantitative, it can be adjusted with a conversion factor obtained by comparing the NEP and NOP yields of wood lignins, which contain no DPM units. Since the NEP yield from the uncondensed units is nearly quantitative, the maximum formation of the NOP from these units can then be determined. With the assumption that the ratio of the NOP and NEP yields for the uncondensed units does not change significantly with chemical treatments, the content of the uncondensed and of the DPM units in treated samples can be separately determined. Thus, the proportion of phenolic units in the DPM structures, conceptually, can also be estimated by a combined NE and NO analyses of samples both before and after periodate treatments.

This report estimates the distribution of the phenolic hydroxyl groups among the uncondensed guaiacyl and syringyl units for the aspen and white birch wood lignins *in situ* by a combination of the NE, NO, and PO techniques.

EXPERIMENTAL

Preparation of Wood Samples

Samples of the extractive-free wood meal (passed through 80 mesh) from aspen (*Populus tremuloides*) and white birch (*Betula papyrifera*) were prepared by the extraction with ethanol-benzene (1:2 by volume) in a Soxhlet extractor for 48 h. Prior to the NE and NO analyses, the air dried samples were thoroughly dried over P_2O_5 under reduced pressure for at least one week.

Periodate Oxidation

A saturated sodium periodate solution was prepared by stirring the chemical (20 g) in distilled water (90 mL) at 4°C overnight. The saturated solution, after filtering off the excess chemical, was kept at 4°C.

For PO experiments, the wood sample (3 g o.d.) was treated with the saturated sodium periodate solution (45 mL) at 4°C in Erlenmeyer flasks. The suspension was homogenized and placed in a refrigerator at 4°C with occasional stirring for 48 h. After treatment, the sample was filtered, washed with cold distilled water, and then air-dried.

Alkaline Nitrobenzene Oxidation

The wood samples (40 mg), 2 M sodium hydroxide (3.2 mL), nitrobenzene (0.2 mL), and two stainless steel balls were placed in small stainless steel autoclaves (5 mL) and heated in an oil bath at 170°C for 3 h.

The reaction mixture after cooling was transferred quantitatively into a separatory funnel and extracted thrice with ethyl ether. The aqueous phase, after addition of the internal standard (2,6-dimethoxyphenol in dioxane), was acidified to pH 2 with 18% hydrochloric acid.

The acidified solution, after being saturated with sodium chloride, was extracted thrice with ethyl ether. The combined ether extracts were dried over Na_2SO_4 and concentrated to dryness. The products were dissolved in pyridine (1 mL). An aliquot of the pyridine solution (0.05 mL) was derivatized with N,O-bis(trimethylsilyl)acetamide (0.1 mL) and few drops of pyridine in a small glass vial at ambient temperature for 1 h. The trimethylsilyl derivatives were then analyzed by gas chromatography (GC).

Nucleus Exchange Reaction

A procedure similar to that previously described by Funaoka and Abe[20,21] was used. The NE reagents were a mixture of phenol, boron trifluoride-phenol complex, and xylene in a volume ratio of 19:4:10, respectively.

In general, wood samples (56 mg) and two small stainless steel balls placed in small autoclaves were treated with the NE reagent (2 mL). The autoclaves, after sealing, were shaken manually for about 5 min followed by heating at 180°C in an oil bath for 4 h, with shaking every 30 min. The content after cooling was carefully transferred into a beaker (100 mL).

The reaction mixture, after adding a known amount of the internal standard (bibenzyl in benzene), was filtered on a glass-fiber filter paper (Whatman GF/A), and washed with ethyl ether. The combined filtrates in a separatory funnel were shaken vigorously with a NaCl-saturated solution to deactivate the residual boron trifluoride. The separated ether layer was then concentrated to about 20 mL and dried over Na_2SO_4. The subsequent preparation of reaction products for the GC analyses was similar to that described earlier for the NO products.

Analytical Methods

Lignin (Klason plus acid-soluble lignin) contents were determined by Tappi Standard Methods. A Hewlett Packard 5890A gas chromatograph equipped with flame ionization detectors, a computerized integrator, and a Quadrex fused silica capillary column (50 m x 0.25 mm x 0.25 μm) packed with an 007 series methyl silicone was used for analyses of the NOP and NEP yields. Nitrogen was used as the carrier gas.

For the NOP analyses, the column temperature was initially held at 160°C for 15 min and then raised at the rate of 5°C/min to 270°. The final temperature was maintained for 30 min. The molar yield of vanillin plus vanillic acid was determined for the guaiacyl unit while the yield of syringaldehyde plus syringic acids was measured for syringyl units.

For the NEP analyses, the column temperature was initially held at 150°C for 15 min and then raised to 180°C at the rate of 5°C/min. After maintaining at 180°C for 5 min, the temperature was further raised to 270° at 30°C/min where it was kept for 30 min to bleed the high molecular weight products. The molar yield of guaiacol plus catechol was determined for the guaiacyl unit.

RESULTS AND DISCUSSION

Influence of Periodate Treatments

Table 1 summarizes the yields of NOP from the original and periodate-treated wood samples. The PO treatment, which was conducted at 4°C for 48 h, should have completely degraded the free phenolic units according to the behavior of the Norway spruce wood lignin. Although PO is known to degrade the phenolic nuclei with a simultaneous release of methanol, we have observed that the amount of lignin dissolved during the treatment (at 4°C) was quite small, being less than 2% even after a four-day treatment. Thus, the periodate-treated sample should have contained nearly all the etherified structures of lignin in the wood.

For both aspen and birch wood lignins, the NOP-yield reduction resulting from the PO treatment was substantially higher for the guaiacyl units (26%) than for the syringyl moieties (10-12%) indicating a considerable difference between these two structural units in the phenolic hydroxyl group content.

As shown in Table 2, the PO treatment of the aspen and white birch wood lignins resulted in a 20-22% reduction in the NEP

TABLE 1

Influence of Periodate Oxidation on the Yield of Nitrobenzene Oxidation Products from the Aspen and White Birch Wood Lignins

Wood species	Periodate treatment	NOP, mole % of Lignin			
		Guaiacyl Unit		Syringyl Unit	
		Vanillin	Vanillic acid	Syring-aldehyde	Syringic acid
Aspen	No	15.3	1.6	33.1	4.3
	Yes	11.2	1.3	30.1	3.4
Birch	No	11.8	1.1	34.9	4.6
	YES	8.6	0.9	31.1	3.5

yield for the guaiacyl units. It is noticeable that the ratio of the NOP and NEP yield for the guaiacyl units was slightly lower for the birch than for the aspen wood lignin. For both species, this ratio was decreased slightly after the PO treatments, which may be caused by a slight modification of the side-chain structures.

Syringyl Units

The content of the total syringyl units in hardwood lignins was estimated from the NOP (syringaldehyde plus syringic acid) yield (Table 1), which was divided by the conversion factor (the NOP- and NEP-yield ratio) shown in Table 2. The assumption that the conversion factor is the same for both the uncondensed guaiacyl and syringyl units is probably valid because of their similarity in the response to the NE reaction[20,21]. Such analyses indicate that the birch wood lignin contains a higher content of the syringyl propane units (55%) than the aspen wood lignin (45%). Interestingly, Musha and Goring[26] reported essentially

TABLE 2

Influence of Periodate Treatments on the Yield of Nucleus Exchange Products and the Ratio of the NOP and NEP Yield for the Guaiacyl Units in the Aspen and White Birch Wood Lignins

Wood species	Periodate treatment	NEP Yield, mole % of Lignin			$(NOP/NEP)_G$
		Guaiacol	Catechol	Total	
Aspen	No	5.5	14.6	20.1	0.84
	Yes	4.0	11.8	15.8	0.79
Birch	No	4.8	13.2	18.0	0.72
	Yes	4.2	10.3	14.5	0.66

identical values from infrared analyses of the thioglycolic lignin samples.

Similarly, the proportion of syringyl units of the etherified type was estimated from analyses of the periodate-treated samples (Tables 1 and 2). The content of the phenolic syringyl units was then estimated.

As indicated in Table 3, only about 5% of the syringyl units in the aspen and birch wood lignins possesses a phenolic hydroxyl group. Lapierre <u>et</u> <u>al</u>.[11,12] obtained a similar finding based on the thioacidolysis technique. They estimated that about 3-4% of the syringyl β-O-4 aryl ether structures in the poplar wood lignin was the free-phenolic type.

Guaiacyl Units

The content of the total guaiacyl propane units in hardwood lignins, estimated from the difference between 100 and the syringyl unit content, was higher for the aspen (55%) than for the birch (45%) wood lignin. The percentage of the uncondensed

TABLE 3

Composition of Structural Units in the Aspen and White Birch Wood Lignins

Unit Type	% of C_9 Units	
	Aspen	Birch
Syringyl	45	55
phenolic	2	3
etherified	43	52
Guaiacyl		
uncondensed	20	18
phenolic	4	3
etherified	16	15
condensed	35	27
Total phenolic[23]	10	8

guaiacyl units, obtained directly from the NEP (vanillin plus catechol) yield (Table 2), was approximately the same for both the aspen (20%) and birch (18%) wood lignins. Similarly, the content of uncondensed guaiacyl structures of the etherified type, obtained from the NEP yield of periodate-treated samples, showed little difference between the two species. It follows that the proportion of the uncondensed guaiacyl units containing a phenolic hydroxyl group was about 20%. A slightly higher value (29%) was reported[11,12] for the percentage of uncondensed guaiacyl β-O-4 structures in the poplar wood lignin, which carry a free-phenolic unit.

Distribution of Structural Units

Table 3 summarizes the structural information for the aspen and birch wood lignins obtained by the combined NO, NE, and PO techniques. It is clear that the proportion of phenolic units in the syringyl structures (5%) is considerably lower than that of the uncondensed guaiacyl units (20%). As noted earlier, Lapierre et al.[11,12] reported a similar finding that the percentage of phenolic units in the uncondensed β-O-4 structures of the poplar wood lignin was about 3 and 29% for the syringyl and guaiacyl units, respectively. These data quantify the general contention that the syringyl units present in hardwood lignins are primarily of the etherified type.

Also, it appears that approximately 30% of the phenolic units in hardwood lignins were associated with the condensed guaiacyl structures. This estimate was based on the total phenolic hydroxyl group content[23] of the aspen and birch wood lignins determined by a periodate oxidation method (Table 3).

CONCLUSIONS

This study shows that periodate oxidation is a convenient method for measuring the total phenolic structures of lignin, and it can be used along with the NE and NO techniques to further estimate the proportion of these phenolic units of the uncondensed type. These combined analyses indicate that the percentage of syringyl units in the hardwood lignins having a phenolic hydroxyl group was quite small (~5%), being about one-fourth that of the uncondensed guaiacyl units (20%). This finding fully confirms a previous observation[23] that the phenolic hydroxyl group content of hardwood lignins decreased proportionally with an increase in the content of syringyl units.

It is anticipated that the combined PO, NO, and NE techniques would be useful for analyzing the nature of the residual lignin in kraft pulps, especially the DPM-type condensed structures. This subject is being investigated further.

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