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Phenolic Structure of *in situ* Lignins

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Abstract

The influence of periodate oxidation on structural changes of Norway spruce lignin was examined, and the distribution of the phenolic hydroxyl groups among the non-condensed guaiacyl and syringyl units for aspen and white birch wood lignins *in situ* was analyzed by a combination of the nucleus exchange, nitrobenzene oxidation, and periodate oxidation techniques.

The results showed that periodate oxidation was relatively specific toward phenolic units and could be used along with the nucleus exchange and nitrobenzene oxidation methods to estimate the proportion of the phenolic and etherified structures of lignin. The percentage of the syringyl units in hardwood lignins having a phenolic hydroxyl group was quite small (−5%), being about one-fourth that of the guaiacyl units (20%). This finding fully confirmed a observation that the phenolic hydroxyl group content of wood lignins decreased proportionally with an increase in the content of syringyl units.

Key words: lignin · phenolic hydroxyl group · periodate oxidation · nucleus exchange nitrobenzene oxidation

Introduction

The phenolic hydroxyl group is one of the most important functionalities affecting the physical and chemical properties of lignin polymers[1]. It plays a prominent role in commercial pulping and bleaching processes by virtue of its ability to promote the base-catalyzed cleavage of interunit ether linkages, and the oxidative degradation of lignin[2,3]. The chemical reactivity of lignin in various modification processes is also profoundly influenced by its phenolic hydroxyl content[4]. On the other hand, the phenolic hydroxyl group significantly contributes to the poor brightness stability of lignin-containing pulps which seriously limits their more widespread utilization[5]. Quantitative measurement (quantity and distribution) of phenolic hydroxyl groups thus provides pertinent information relating to the structure and reactivity of lignin as well as to the mechanism and extent of lignin degradation.

Both physical and chemical methods, or a combination of both, have been used to estimate the free phenolic hydroxyl content of lignin[1,6]. Potentiometric and conductometric titration[7,8], ionization UV spectroscopy[9,10], and NMR spectroscopy[11−13] are typical of physical methods. A pyrolytic gas chromatographic technique based on the difference in yield of phenol and guaiacol resulting from the thermal degradation of lignin before and after

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methylation has also been used to estimate the phenolic hydroxyl content of softwood lignin[14]. Furthermore, the phenolic hydroxyl group content has been estimated through the determination of the increase in methoxyl content resulting from diazomethane methylation[15], of the phenolic acetyl group by an NMR spectroscopic technique[16] or by a selective deacetylation in pyrrolidine (aminolysis)[17] after acetylation. Although these conventional techniques can be used to provide quantitative measurements on the total phenolic hydroxyl group content of lignin, they generally do not reveal the structural environment in which they occur.

There are thioacidolysis and permanganate oxidation as chemical methods that can provide information on the nature of lignin phenolic hydroxyl groups. Thioacidolysis[18–20], a solvolysis of lignin in ethanethiol with boron trifluoride etherate, selectively degrades the non-condensed β-O-4 type structures to yield the corresponding phenyl 1, 2, 3-(tristhioethyl) propane derivatives. The phenolic non-condensed β-O-4 type units can be determined by the yield of the methyl derivative produced from the thioacidolysis of premethylated

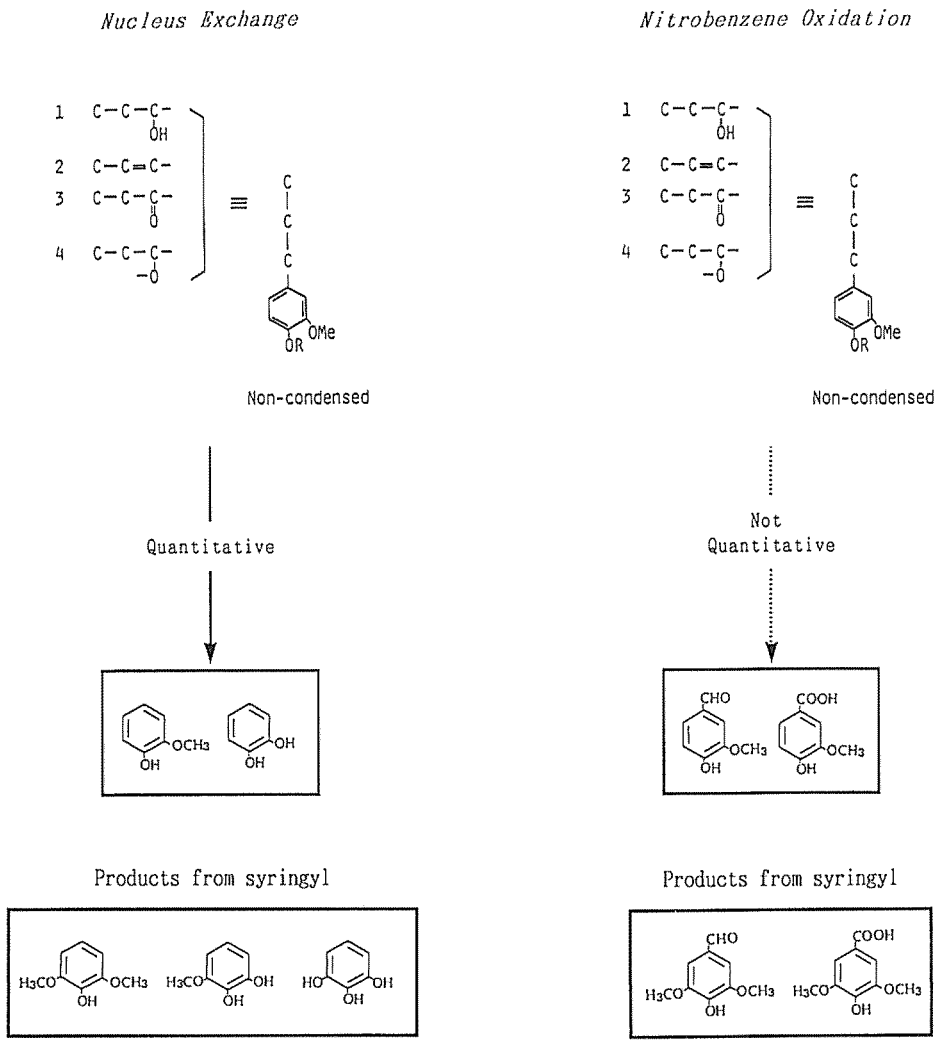

Fig. 1. Nucleus exchange and nitrobenzene oxidation products of lignin and their originating structures.

samples. Permanganate oxidation[21-24], 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, 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 is not quantitative.

On the other hand, the phenyl nucleus exchange technique[25-28] is based on the degradation of lignin by boron trifluoride in the presence of excess phenol. Through this treatment, non-condensed units in the wood lignins are converted initially to guaiacol and pyrogallol-1,3-dimethyl ether from the guaiacyl and syringyl units, respectively. Under typical nucleus exchange conditions conducted at 180°C, guaiacol and pyrogallol-1,3-dimethyl ether are partially demethylated to give catechol and pyrogallol-1-methyl ether, plus pyrogallol, respectively (Fig. 1). The yield of these nucleus exchange products (NEP) has been shown to be nearly quantitative. Therefore, this method might be the most direct procedure for determining the content of non-condensed units in the wood lignins. However, the NEP are formed from both phenolic and etherified units because of the cleavage of ether linkages during the treatment, and consequently, the phenolic structures in lignins can not be estimated, based on NEP yields. It has recently been shown[29-31] that the phenolic hydroxyl groups of lignin in wood or pulp samples can be conveniently measured *in situ* by a periodate oxidation method, which appears to be relatively specific toward the degradation of phenolic units (Fig. 2). Conceptually, the nucleus exchange reaction when combined with the periodate oxidation may be used to estimate the proportion of phenolic units in non-condensed lignin structures. That is, the NEP must be formed from only etherified non-condensed units after phenolic units are destroyed by periodate oxidation.

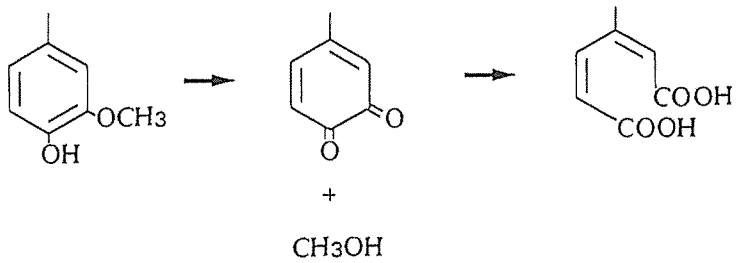

Fig. 2. Periodate oxidation of lignin.

The present paper examines the influence of periodate oxidation on structural changes of Norway spruce lignin as revealed by the nucleus exchange and nitrobenzene oxidation techniques. In addition, the proportion of phenolic units among non-condensed guaiacyl and syringyl units is estimated for aspen and birch lignins *in situ*.

Materials and Methods

Wood samples

Extractive-free wood meals (passed through 80 mesh) from Norway spruce (*Picea abies*), 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 hr. Borohydride-reduced samples were prepared by treating the extractive-free wood meal with an excess of $NaBH_4$ at ambient temperature overnight. The reduction of a

periodate-treated Norway spruce sample was conducted by using a 10% charge of sodium hydrosulfite in 0.1 M NaOH at ambient temperatures for one day. Prior to chemical analysis, the air-dried samples were throughly 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 periodate oxidation of Norway spruce, the sample (3 g o.d.) was treated with a saturated sodium periodate solution (45 ml) at 4°C in an Erlenmeyer flask. The suspension was homogenized and placed in a refrigerator at 4°C with occasional stirring for the prescribed time. After treatment, the sample was filtered, washed with cold distilled water, and then air-dried. The oxidation of aspen and white birch samples was conducted in a similar fashion for 48 hr.

Nucleus exchange reaction

The nucleus exchange reagent was prepared by mixing phenol, boron trifluoride-phenol complex, and xylene in a volume ratio of 19 : 4 : 10, respectively.

Wood samples (56 mg) placed in an autoclave were treated with the nucleus exchange reagent (2 ml) in an oil bath at 180°C for 4 hr. The content after cooling was carefully transferred into a beaker with ethyl ether. The reaction mixture, after adding a known amount of the internal standard (bibenzyl in benzene), was filtered on a glassfiber filter paper, and washed with ethyl ether. The combined filtrates in a separatory funnel were shaken vigorously with a NaCl-saturated water to deactivate the residual boron trifluoride. The separated ether layer was then concentrated to about 20 ml and dried over Na_2SO_4. The products (NEP) were converted into their trimethylsilyl derivatives with N, O-bis(trimethylsilyl)acetamide at ambient temperature and analyzed by gas chromatography.

Alkaline nitrobenzene oxidation

Wood samples (40 mg), 2 M sodium hydroxide (3.2 ml), and nitrobenzene (0.2 ml) were placed in an autoclave and heated in an oil bath at 170°C for 3 hr. The reaction mixture after cooling was transferred quantitatively into a separatory funnel and extracted 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. After the evaporation of ethyl ether, the products (Nitrobenzene oxidation products; NOP) were derivatized with N,O-bis(trimethylsilyl)acetamide at ambient temperature in pyridine and analyzed by gas chromatography.

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 packed with an 007 series methyl silicone (50 m × 0.25 mm × 0.25 μm) was used for analyses of the NEP and NOP. Nitrogen was used as the carrier gas. 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°C 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.

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°C. The final temperature was maintained for 30 min. The molar yield of vanillin plus vanillic acid was determined for the guaiacyl units while the yield of syringaldehyde plus syringic acid was measured for syringyl units.

Results and Discussion

Periodate oxidation of Norway spruce

Table 1 shows the yields in periodate oxidation of Norway spruce. It is evident that periodate treatments (at 4°C) primarily removed the carbohydrate components as indicated by a gradual increase in the lignin content of treated samples. Although periodate is known to degrade the lignin phenolic nuclei with a simultaneous release of methanol, the amount of lignin dissolved during the reaction (at 4°C) was quite small being less than 2% even after a four-day treatment.

Table 1. Periodate oxidation of Norway spruce at 4°C

Treatment time (hr)	Yield (%)	Lignin (%)
0	100	28.6
0.3	95.0	30.1
0.5	94.4	30.1
1	94.2	30.0
2	93.4	30.2
4	93.6	30.3
6	93.3	30.7
12	92.5	30.8
24	90.0	31.5
48	90.0	31.5
72	90.2	32.1
96	85.9	32.7

Significant changes in the composition of the lignin were reflected in the reduction in yields of monomeric products from the nucleus exchange (guaiacol and catechol), and from the nitrobenzene oxidation (vanillin and vanillic acid), which were exclusively attributed to non-condensed units of wood lignins (Fig. 1). As shown in Fig. 3, the curves of both the nucleus exchange products (NEP) and the nitrobenzene oxidation products (NOP) display a similar pattern indicating an initial rapid decrease in non-condensed units. This rapid phase, which accounted for about 70% of the total reduction, was complete within one hour while the maximum reduction was obtained after 6 hr.

The kinetic patterns for the periodate oxidation of Norway spruce obtained by the methanol formation (Fig. 4) and by the NEP and NOP yields (Fig. 3) were quite similar, but with discernible differences. Both patterns

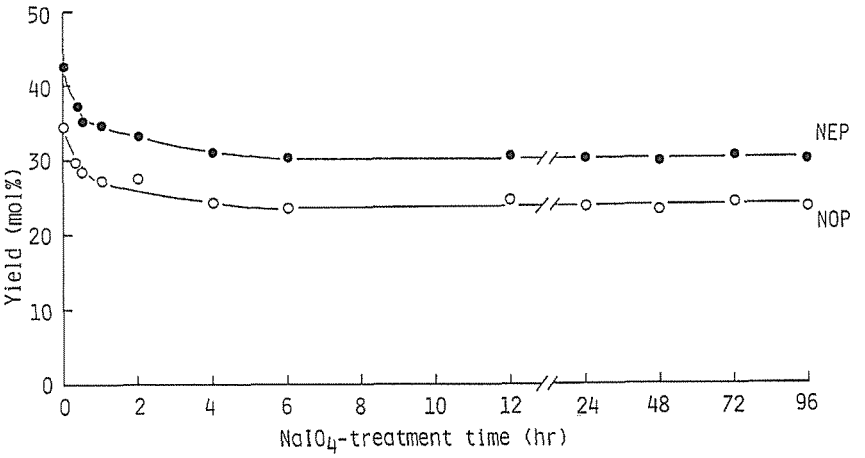

Fig. 3. Yields of nucleus exchange (NEP) and nitrobenzene oxidation products (NOP) from periodate-treated Norway spruce.

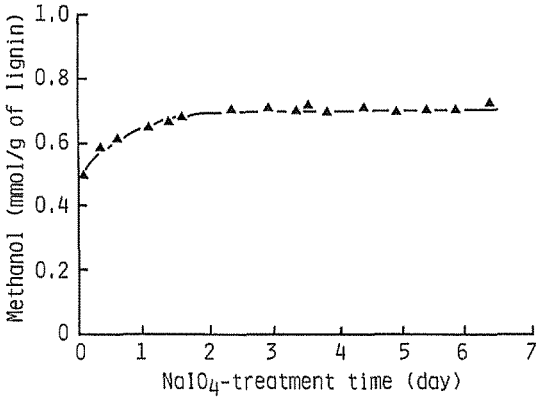

Fig. 4. Methanol formed by periodate oxidation of Norway spruce.

indicate a two-stage process. The methanol formation, however, was a much slower process. For example, the initial rapid phase of methanol formation, which accounted for about 80% of the total, extended to about 6 hr (as compared to 1 hr for the NEP). In addition, the maximum methanol formation occurred only after 48 hr of treatment as compared to 6 hr for the NEP formation. However, periodate oxidation of phenolic lignin model compounds is generally thought of as proceeding through the *o*-quinone intermediate with a simultaneous release of methanol[1,32,33] (Fig. 2). Since wood meal (40–60 mesh) was used in the periodate oxidation experiments, it is reasonable to assume that diffusion of the methanol from the reaction sites to bulk solution would not be a critical factor. Thus, the release of methanol from lignin by the periodate oxidation may involve some mechanisms other than the quinone intermediate shown in Fig. 2.

The possibility that the *o*-quinone intermediates might be present in periodate-treated samples was examined by incorporating a hydrosulfite reduction prior to the nucleus exchange reaction. This would convert the *o*-quinones to 3,4-dihydroxy phenylpropane units. The latter unit can be readily detected as catechol by

Table 2. Nucleus exchange treatment of Norway spruce at 80 and 180°C

Sample	Nucleus exchange products, NEP (mol% of lignin)			
	80°C		180°C	
	Guaiacol	Catechol	Guaiacol	Catechol
Original	18.7	Trace	13.9	28.6
Periodate-treated	11.3	Trace	8.1	22.5
Periodate/$Na_2S_2O_4$-treated	—	Trace	9.6	21.1

nucleus exchange treatment below 80°C at which the demethylation of methoxyl groups can be negligible[28]. The nucleus exchange analysis at 80°C of a periodate-treated sample (72 hr) indicated that only a trace of catechol was present and the yield was not affected by a hydrosulfite treatment (Table 2). Similarly, hydrosulfite treatments had no influence on the total yield of NEP obtained at 180°C. Thus, these results imply that the periodate-treated samples contained only traces of *o*-quinone structures.

The influence of periodate treatments on the reactivity of oxidized samples may be indicated by the relative yield of NOP to NEP obtained at 180°C, which remained approximately the same as indicated in Fig. 5. Furthermore, the formation pattern of NEP and NOP remains constant with increasing treatment temperature (Fig. 6). Thus, periodate oxidation of lignin appears to be a relatively selective process affecting primarily phenolic units.

The extent to which the carbonyl groups of lignin might play a role in periodate oxidation was investigated by comparing the behavior of untreated and borohydride-reduced Norway spruce samples. As indicated in Table 3, the influence of borohydride reduction on the yield of NOP and NEP as well as on the ratio of NOP and NEP was very small. Thus, carbonyl groups would have little influence on the periodate oxidation of lignin as revealed by the NEP and NOP.

The foregoing discussion suggests that periodate oxidation can be used for a selective degradation of phenolic units which can be readily achieved by treatments at 4°C for 48 hr (Fig. 3).

The nucleus exchange analysis indicates that Norway spruce lignin contains about 43% of non-condensed

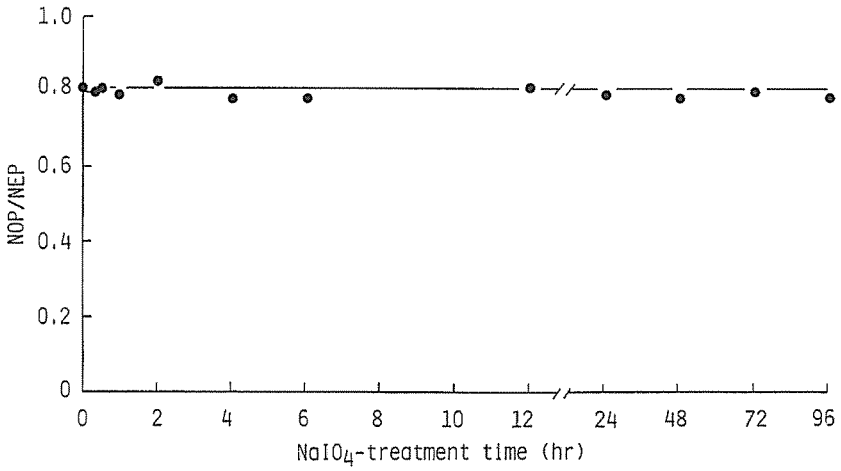

Fig. 5. Relationship between NOP/NEP values and periodate-treatment times.

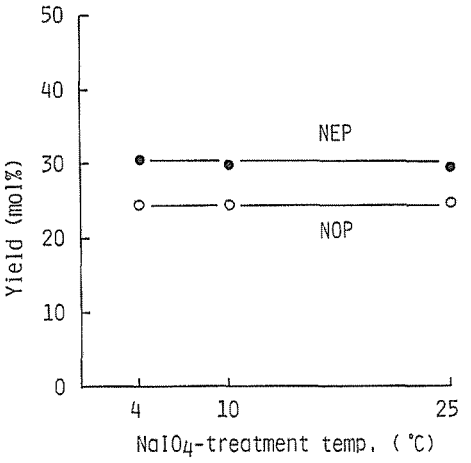

Fig. 6. Relationship between nucleus exchange (NEP) and nitrobenzene oxidation products (NOP) and periodate-treatment temperatures.

Table 3. Influence of borohydride reduction on periodate oxidation* of Norway spruce in terms of the yields of the nucleus exchange (NEP) and nitrobenzene oxidation products (NOP)

Sample	Periodate treatment*	NEP yield (mol% of lignin)			NOP yield (mol% of lignin)			NOP/NEP
		Guaiacol	Catechol	Total	Vanillin	Vanillic acid	Total	
Original	−	13.9	28.6	42.5	32.2	2.3	34.5	0.81
	+	8.1	22.5	30.6	22.4	2.1	24.5	0.80
Reduced	−	11.5	30.8	42.3	32.3	3.4	35.7	0.84
	+	8.9	21.6	30.5	23.3	2.2	25.5	0.84

* at 4°C for 72 hr.

units, while the combined nucleus exchange analyses of original and periodate-treated sample indicate that the non-condensed units contain about 28% phenolic units. It follows that Norway spruce lignin has approximately 12% phenolic units of the non-condensed type.

Phenolic property of hardwood lignins

Table 4 summarizes the NOP yields from the original and periodate-treated wood samples. For both aspen and birch wood lignins, the reduction of NOP yield resulting from the periodate 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.

Table 4. Yields of nitrobenzene oxidation products (NOP) from the aspen and white birch wood lignins

Sample	Periodate treatment	NOP yield (mol% of lignin)					
		Guaiacyl (NOP_G)			Syringyl (NOP_S)		
		Vanillin	Vanillic acid	Total	Syringaldehyde	Syringic acid	Total
Aspen	−	15.3	1.6	16.9	33.1	4.3	37.4
	+	11.2	1.3	12.5	30.1	3.4	33.5
Birch	−	11.8	1.1	12.9	34.9	4.6	39.5
	+	8.6	0.9	9.5	31.1	3.5	34.6

As shown in Table 5, the periodate oxidation of the aspen and birch wood lignins resulted in a 20–22% reduction in the NEP 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 periodate oxidation, which may have been caused by a slight modification of the side-chain structures of etherified units.

The content of the total syringyl units in hardwood lignins was estimated from the NOP (syringaldehyde and syringic acid) yield (Table 4), which was divided by the conversion factor (the NOP- and NEP-yield ratio) shown in Table 5. The assumption that the conversion factor is about the same for both the non-condensed guaiacyl and syringyl units is probably valid because of their similarity in the response to the nucleus exchange reaction[28]. Such analyses indicate that the birch wood lignin contains a higher quantity of the syringyl units (55%) than the aspen wood lignin (45%). Musha and Goring[34] also reported essentially identical values from infrared analyses of the thioglycolic lignin samples.

Similarly, the proportion of etherified syringyl units was estimated from analyses of the periodate-treated samples (Tables 4 and 5). The content of the phenolic syringyl units was then estimated. As indicated in Fig. 7, only about 5% of the syringyl units in the aspen and birch wood lignins possesses a phenolic hydroxyl group.

Table 5. Yields of nucleus exchange products (NEP_G) and the ratios of NOP_G and NEP_G for the guaiacyl units of aspen and white birch wood lignins

Sample	Periodate treatment	NEP_G yield (mol% of lignin)			NOP_G/NEP_G
		Guaiacol	Catechol	Total	
Aspen	−	5.5	14.6	20.1	0.84
	+	4.0	11.8	15.8	0.79
Birch	−	4.8	13.2	18.0	0.72
	+	4.2	10.3	14.5	0.66

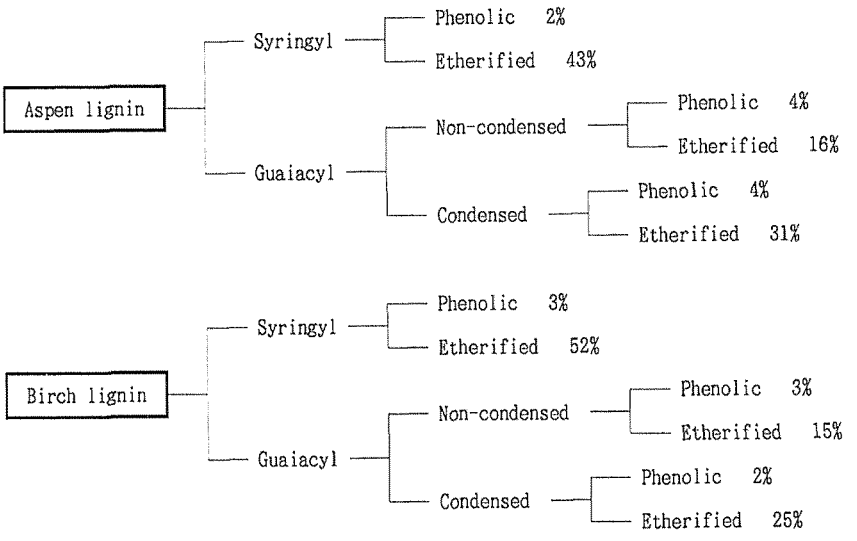

Fig. 7. Compositions of the aspen and white birch wood lignins.

Lapierre *et al.*[18,19] obtained a similar finding based on the thioacidolysis technique. They estimated that about 3–4% of the syringyl β-O-4 type structures in the poplar wood lignin was of the phenolic type.

The content of the total guaiacyl units in hardwood lignins, estimated from the difference between 100 and the syringyl content, was higher for the aspen (55%) than for the birch (45%) wood lignin. The percentage of the non-condensed guaiacyl units, obtained directly from the NEP (guaiacol and catechol) yield (Table 5), was approximately the same for both the aspen (20%) and birch (18%) wood lignins. Similarly, the content of etherified non-condensed guaiacyl structures, obtained from the NEP yield of periodate-treated samples, showed little difference between the two species. It follows that the proportion of phenolic non-condensed guaiacyl units was about 20%.

Fig. 7 summarizes the structural information for the aspen and birch wood lignins obtained by the combined nitrobenzene oxidation, nucleus exchange, and periodate oxidation techniques. It is clear that the proportion of phenolic units in the syringyl structures (5%) is considerably lower than that of the non-condensed guaiacyl units (20%). Lapierre *et al.*[18,19] also reported a similar finding that the percentage of phenolic units in the non-condensed 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, approximately 30% of the phenolic units in hardwood lignins were associated with the condensed guaiacyl structures, based on the determination[30] of the total phenolic hydroxyl group by a periodate oxidation method.

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プロトリグニンのフェノール核構造

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過ヨウ素酸酸化，核交換およびニトロベンゼン酸化を併用する新しいリグニンフェノール核構造の解析法を提案した。本法は単離リグニンのみならずリグノセルロース系複合体中のリグニンに直接適用可能であり，しかも各構成単位におけるフェノール核の分布に関する定量的知見を与える。Norway spruce を用い適正分析条件を検討し，さらに広葉樹（Aspen, Birch）プロトリグニンのフェノール核構造を解析した。過ヨウ素酸飽和溶液，4°C，48時間処理によりリグニンフェノール核は定量的に破壊されること，および広葉樹プロトリグニンのシリンギル単位におけるフェノール核分布率は極めて低く（約5%），グアイアシル単位の約1/4であることを認めた。