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## Quantitative $^{13}\text{C}$ NMR of Lignins – Methoxyl : Aryl Ratio

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Dedicated to D.A.I. Goring on the occasion of his retirement

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### Summary

A  $^{13}\text{C}$  nuclear magnetic resonance method was used to determine the methoxyl:aryl ratios of softwood and hardwood lignins, and to calculate the syringyl:guaiacyl ratio of hardwood lignins. The data indicate that the middle lamella lignin of hardwoods is a syringyl-guaiacyl copolymer. However, there were quantitative differences among species: white birch and sweetgum appeared to have guaiacyl-rich middle lamella lignin and syringyl-rich fiber cell wall lignin, whereas red oak and American elm had a more uniform syringyl-guaiacyl distribution. The morphological origin of milled wood lignin is discussed.

### Introduction

Typically, softwood (gymnosperm) lignins are composed almost entirely of guaiacylpropane units (Obst and Landucci 1986). However, hardwood (angiosperm) lignins are more complex in that they contain varying ratios of syringylpropane (S) and guaiacylpropane (G) units. The p-hydroxyphenylpropane content of hardwood lignins is generally less than that of normal softwood lignins, and typical hardwood lignins may be treated as being composed of syringylpropane and guaiacylpropane units (Sarkanen and Hergert 1971). It is possible, then, that hardwood lignin is:

- 1) a S and G copolymer,
- 2) that it is composed of discrete S polymer and discrete G polymer (these may either be intimately mixed together, or may occur individually in specific morphological regions), or
- 3) something in between.

Numerous analytical methods have been used to determine the composition of hardwood lignins. Recently, hardwood lignin heterogeneity has been examined by carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectroscopy (Obst and Ralph 1983). However, the conditions for precise and accurate quantitative analysis were not rigorously established. A reproducible method for precise quantitative NMR measurements has since been developed (Landucci 1985), and it is now applied to the question of hardwood lignin characterization.

### Experimental

Wood pulps, tissue fractions, milled wood lignins (MWL) extracted with 90% aqueous p-dioxane, and milled wood enzyme lignins (MWEL) were prepared as previously described (Obst 1982; Obst and Ralph 1983). Some of the samples were those used in the previous studies. MWLs were acetylated with acetic anhydride:pyridine (1:1) overnight at room temperature. The MWELs were also acetylated, and the chloroform soluble portion, which was usually one-fourth to one-half of the total, was used for the NMR experiments. The higher molecular weight insoluble portion was not investigated further.

Sweetgum MWEL was extracted with 96% aqueous dioxane to give a soluble lignin fraction (7% yield based on the MWEL) which was then acetylated.

To investigate the S:G nature of milled wood lignin from birch wood, several MWLs were prepared. Birch wood, which had been extracted with acetone:water, was subsequently extracted with dioxane:water (9:1) before ball milling to remove low molecular weight, accessible lignin, and extractives. The Klason lignin value for this extracted wood was 0.5% less than that extracted only with acetone:water. The dioxane:water-extracted wood was vibratory ball milled and extracted once with 96% dioxane and then once with 90% dioxane. The resulting crude MWLs, termed 96-MWL-A and 90-MWL-A, were obtained in 4.6% and 5.3% yields, respectively.

The  $^{13}\text{C}$  NMR spectra of the acetylated hardwood MWLs were obtained using the acquisition conditions established previously (Landucci 1985). The NMR experiments were run either in duplicate or triplicate, and each spectrum was integrated three times. The method of integration was modified by setting the methoxyl area measurement equal to one. By normalizing in this manner, the computer-derived aryl area measurement directly gives the aryl:methoxyl integral value. The methoxyl group:aryl group ratio (hereafter referred to simply as the methoxyl:aryl ratio) was calculated from the NMR data as previously (Landucci 1985). Except as noted in the discussion, it is assumed that the methoxyl:aryl ratios correspond to methoxyl:C9 values. The weight percent methoxyl values were calculated from the methoxyl:aryl ratios assuming that all aryl moieties are either S or G (Sarkanen and Hergert 1971), and

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that the methoxyl content of G units is 15.90% and that of S units is 27.56%, based on C9 formula weights of 195 and 225, respectively. For the softwood MWLs, the aryl integration range used was 164–108 ppm to eliminate interferences due to any contaminating polysaccharides. The range used for phase adjustments was unchanged. Methoxyl analyses were done as previously (Obst 1982).

## Results and Discussion

### Effect of polyphenolic extractives and carbohydrates on quantitative determinations

It had been demonstrated, for a birch MWL isolated from a high-yield kraft pulp, that the methoxyl:aryl value obtained by a  $^{13}\text{C}$  NMR method could be precisely determined (Landucci 1985). To test the utility of the method and extend it to lignin characterization, the methoxyl:aryl and S:G ratios of a number of different acetylated hardwood lignins were determined (Table 1). The results showed that other hardwood MWLs give methoxyl:aryl ratios typical of temperate zone hardwood lignins. However, there is a notable exception in the case of MWLs isolated from heartwood.

The methoxyl:aryl ratios of the sapwood MWLs from both black cherry and white oak were significantly greater than those from their corresponding heartwoods. Generally, most hardwood lignins are composed only of S and G units, containing fewer p-hydroxyphenyl units than softwoods (Sarkanen and Hergert 1971). In the NMR method, the calculation of the S:G ratio assumes that all aryl groups are either S or G. Errors in the S:G ratios would be large if the isolated lignin were contaminated with aromatic extractives or polyphenolics. It is reasonable to conclude that lignins isolated from heartwoods, and even some sapwoods, could contain appreciable amounts of nonlignin aromatics. The NMR determined methoxyl:aryl values would be correct, but not necessarily reflective of methoxyl:C9 values. The S:G ratios would be erroneous.

The  $^{13}\text{C}$  NMR determined methoxyl:aryl ratios of softwood MWLs could be influenced not only by contamination with nonlignin aromatic extractives, but also by compression wood lignin which contains a large amount of p-hydroxyphenyl units (Nimz *et al.* 1981). The methoxyl:aryl ratios of MWLs from loblolly pine, Sitka spruce, and white spruce were 0.93, 0.91, and 0.93 (Table 1), respectively, which compare favorably to values obtained by conventional chemical analysis (Sarkanen and Hergert 1971). The MWL from ginkgo, which is formed predominantly from the precursor coniferyl alcohol (Obst and Landucci 1986), had a methoxyl:aryl ratio of 0.94.

It is also critical to be certain that carbohydrates do not interfere with the accuracy of the  $^{13}\text{C}$  NMR determined methoxyl:aryl values. Unless purified, which often means yield loss and lignin fractionation, MWLs

generally contain polysaccharide contaminants. It had been previously shown through a double resonance experiment (Obst and Landucci 1986) that the signals observed at approximately 106 ppm in the spectra of typical softwood MWLs are not due to syringyl 2 and 6 aromatic carbons. It is likely that these signals arise from carbohydrates, specifically the C-1 arabinofuranosides in pectic arabinan contaminants (Minor 1984). Therefore, for softwood MWLs, the range used for integration of aromatic lignin carbons was changed to 164 to 108 ppm. Carbohydrate signals were thereby omitted, and these contaminants had no effect on quantitative measurements.

However, hardwood MWLs, some of which may contain appreciable amounts of carbohydrates, especially xylan, must be integrated over the full aryl range of 164 to 102 ppm in order to include the lignin syringyl carbons. To determine the effect of carbohydrate signals on the aryl integral in the 106- to 104-ppm region, two-dimensional carbon-proton correlation (CHCORR) experiments (Bax 1984) were conducted. Fig. 1A displays the partial CHCORR spectrum of loblolly pine MWL. The aliphatic signal at about 106 ppm is probably due to the C-1's of arabinofuranosides (Minor 1984). The aliphatic signal at about 101 ppm is due to the C-1's of xylan\*. The CHCORR partial spectrum of a special MWL from loblolly pine, which had been purified to remove carbohydrate and had elm MWL added to give a known syringyl content of about 1.5% (Obst and Landucci 1986), is shown in Fig. 1B. In the 106- to 104-ppm region, no aliphatic signals are observed (no, or very little hemicellulose which contains arabinose), but the syringyl 2 and 6 aromatic carbon signals due to the addition of the elm MWL are easily detected. These results are in agreement with those obtained from double resonance experiments (Obst and Landucci 1986).

The partial CHCORR spectrum of a crude sweetgum MWL, which contains about 18% carbohydrate-

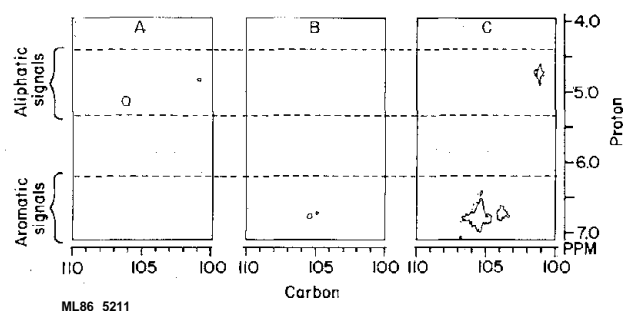


Fig. 1. Partial carbon-proton correlation spectra of acetylated MWLs: A) loblolly pine MWL; B) low carbohydrate loblolly pine MWL with elm MWL added to it to give a 1.5% syringyl content; C) high carbohydrate containing sweetgum MWL.

\* Minor, J.L. 1983. Unpublished results.

Table 1. Methoxyl : aryl and syringyl : guaiacyl (S:G) ratios and methoxyl contents of isolated lignins.

Sample	<sup>13</sup> C NMR		% Methoxyl	
	Methoxyl : aryl	Syringyl : guaiacyl	<sup>13</sup> C NMR	Chemical analysis
American elm wood MWL ( <i>Ulmus americana</i> )	1.31 (0.01) <sup>a</sup>	0.44	19.5	n.d. <sup>b</sup>
American elm kraft fiber MWL	1.35 (0.02)	0.56	20.0	19.8
American elm kraft crill MWL	1.39 (0.02)	0.64	20.4	19.5
Aspen wood MWL ( <i>Populus tremuloides</i> ) (CDCl <sub>3</sub> solvent)	1.45 (0.03)	0.89	21.1	21.4
Aspen wood MWL (Acetone-d <sub>6</sub> solvent)	1.47 (0.03)	0.89	21.4	21.4
Basswood MWL ( <i>Tilia americana</i> )	1.48 (0.03)	0.92	21.5	n.d.
Beech wood MWL ( <i>Fagus silvatica</i> )	1.52 (0.02)	1.09	21.9	20.9
Black cherry sapwood MWL ( <i>Prunus serotina</i> )	1.22 (0.07)	0.29	18.3	n.d.
Black cherry heartwood MWL	0.85 (0.02)	–	13.5	n.d.
Birch wood MWL ( <i>Betula papyrifera</i> )	1.44 (0.02)	0.78	21.0	n.d.
Birch wood 96-MWL-A	1.64 (0.05)	1.78	23.3	n.d.
Birch wood 90-MWL-A	1.59 (0.04)	1.43	22.8	n.d.
Birch kraft fiber MWL	1.58 (0.02)	1.38	22.6	21.6
Birch kraft fiber “MWEL”	1.49 (0.04)	0.96	21.6	n.d.
Birch kraft crill MWL	1.41 (0.04)	0.70	20.7	21.1
Birch ray cell MWL	1.52 (0.03)	1.09	21.7	20.9
Birch ray cell “MWEL”	1.23 (0.02)	0.31	18.6	n.d.
Mountain ash wood MWL ( <i>Pyrus americana</i> )	1.53 (0.04)	1.13	22.1	n.d.
Red oak kraft fiber MWL ( <i>Quercus rubra</i> )	1.52 (0.06)	1.09	21.9	21.3
Red oak kraft crill MWL	1.50 (0.04)	1.00	21.7	21.2
White oak sapwood MWL ( <i>Quercus alba</i> )	1.44 (0.04)	0.78	21.0	19.1
White oak heartwood MWL	1.18 (0.06)	0.22	18.0	n.d.
Sweetgum wood MWL ( <i>Liquidambar styraciflua</i> )	1.55 (0.03)	1.22	22.3	21.5
Sweetgum wood “purified” MWL	1.49 (0.03)	0.96	21.6	n.d.
Sweetgum wood s-MWEL	1.65 (0.03)	1.85	23.4	22.0
Sweetgum kraft fiber MWL	1.64 (0.03)	1.77	23.3	22.8
Sweetgum kraft crill MWL	1.46 (0.03)	0.84	21.2	21.6
Ginkgo wood MWL ( <i>Ginkgo biloba</i> )	0.94 (0.01)	–	15.0	n.d.
Loblolly pine wood MWL ( <i>Pinus taeda</i> )	0.93 (0.01)	–	14.8	14.3
Sitka spruce wood MWL ( <i>Picea sitchensis</i> )	0.91 (0.02)	–	14.5	14.7
White spruce wood “MWEL” ( <i>Picea glauca</i> )	0.93 (0.02)	–	14.8	n.d.

<sup>a</sup> Values in parentheses indicate the error range of the method, e.g. 1.35 (0.02) = 1.33 to 1.37. The error in calculating the S:G ratio is six times that of the methoxyl aryl value.

<sup>b</sup> n.d. = not determined.

mainly xylan, clearly shows the large signals due to the syringyl carbons in the 106- to 104-ppm region (Fig. 1C) Importantly, there are no aliphatic signals observed in this region. As in Fig. 1A, the signal at 101 ppm is due to the C-1 of the contaminating xylan. These results are consistent with the fact that hardwood xylans are free of arabinose side chains (Timell 1964). Therefore, the integral values of the entire aromatic region (164 to 102 ppm) of hardwood MWLs should not be influenced by the presence of carbohydrates. If an isolated lignin contains pectic substances, their effect on the integral value must be checked by two-dimensional or double-resonance experiments.

That the carbohydrate contaminants do not compromise the quantitative data from hardwood lignins is further supported. The methoxyl:aryl ratios of aspen MWL were measured using two different solvents for the NMR experiment (Table 1). The crude aspen MWL contained about 20% carbohydrate, again, mainly xylan. When acetylated, this MWL was soluble in chloroform. But acetone was a poor solvent for the acetylated carbohydrate contaminants, and a simple fractionation occurred. However, the methoxyl : aryl ratios were about the same regardless of solvent. Also, when the crude sweetgum lignin was purified to give a nearly carbohydrate-free MWL, the methoxyl:aryl ratio did not increase, as would be expected if carbohydrate contributed to the aryl integral (Table 1).

#### The Origin of Milled Wood Lignin

The morphological origin of MWL initially had been suggested as being the middle lamella (Björkman 1957). But, more recently, it was proposed that most of the MWL originates from the fiber cell wall (Whiting and Goring 1981). However, the methoxyl content of hardwood MWLs is about the same, or only slightly lower, than that of the whole lignin (Adler 1977). The implications of these conflicting views to the nature of hardwood lignin in wood are varied: 1) MWL originates from the middle lamella, and the middle lamella lignin is a S-G copolymer with about the same composition as the whole lignin; 2) MWL originates from the secondary wall of the fibers, and fiber lignin is a S-G copolymer with about the same composition as the whole lignin; 3) MWL originates from all morphological regions, and all the lignin is a relatively uniform S-G copolymer; 4) the lignin in hardwoods is S-rich or G-rich in certain morphological regions, and MWL originates from all or only certain morphological regions, but in proportionate yields to give a MWL with about the average S-G composition of the total lignin in the wood.

The different methoxyl:aryl values of the various MWLs isolated from birch wood are of particular interest. The methoxyl/C9 value of white birch lignin

has been estimated to be about 1.55 (Musha and Goring 1975). In our study, the  $^{13}\text{C}$  NMR value, determined on a crude MWL extracted with 90% dioxane, was only 1.44 (Table 1). It had been shown for birch (exact species not reported) (Lee *et al.* 1981), that the first portions of MWL, obtained in low yields, are guaiacyl-rich; it was then concluded that MWL initially arises mainly from a middle lamella composed of guaiacyl lignin. Subsequently, it was suggested that birch wood (*Betula verrucosa*) contains a low molecular weight, reactive, guaiacyl-rich lignin fraction which is distributed in all morphological regions (Kolar *et al.* 1982).

To test whether a guaiacyl-rich fraction could be removed prior to MWL isolation, a sample of Wiley-milled birch wood was extracted with 90% dioxane before vibratory ball milling. After milling, two MWLs were obtained: the first was isolated by extraction with 96% dioxane, the other by a second extraction of the residue with 90% dioxane (giving samples 96-MWL-A, and 90-MWL-A). The methoxyl:aryl ratios of these two birch lignins were about the same (1.64,  $\pm$  0.05 and 1.59,  $\pm$  0.04), but both had a much higher syringyl content than that of the MWL (1.44) prepared in the usual manner. These results support the interpretation that a guaiacyl-rich MWL was removed by the initial 90% dioxane extraction of the wood, and that this fraction is probably the "reactive" fraction identified earlier. The distribution of this lower methoxyl content MWL fraction can not be deduced from this experiment.

It can be seen from Table 2 that the yields of the MWLs from the birch pulp fractions are similar. The yields of MWL from elm kraft fibers and crill are comparable to each other, but lower than those from birch. These data support the conclusion that MWL originates from fiber cell walls, the middle lamella, and ray cells. However, the data do not reveal whether the yield of MWL from various morphological regions in ball-milled wood parallels the yields from ball-milled pulp fractions, because of the effects of chemical and physical changes resulting from pulping.

Table 2. Lignin content and yield of milled wood lignin of birch and elm kraft pulp fractions.

Pulp fraction	Klason lignin %	Yield of MWL (based on Klason lignin) %
White birch		
Fiber	10.6	36
Crill	34.8	41
Ray cells	28.3	45
American elm		
Fiber	20.3	28
Crill	34.0	30

### Syringyl:Guaiacyl Ratio of Lignin in Different Morphological Regions of Hardwoods

Because the present  $^{13}\text{C}$  NMR data show that a reliable methoxyl:aryl value can be determined, a number of NMR spectra of isolated lignins were obtained to extend and refine the previous NMR study of hardwood lignins (Obst and Ralph 1983). The methoxyl:aryl and syringyl:guaiacyl ratios of acetylated MWLs, isolated from birch kraft pulp fiber, crill (enriched in middle lamella), and ray cell fractions were determined (Table 1). Also reported are the ratios obtained from the chloroform soluble portion of acetylated milled wood enzyme lignin ("MWEL") (Obst and Ralph 1983) from the fiber and ray cell fractions. Of the MWLs, the birch crill gave the lowest methoxyl:aryl value, whereas the fiber gave the highest. However, the difference between these two was only 12%.

Comparing methoxyl:aryl values to S:G ratios immediately shows that the latter are much more sensitive to changes in monomer composition. The S:G ratio of the birch crill MWL was 0.70, whereas the fiber MWL was 1.38, nearly twice as great. However, the relative deviation of the calculated ratios is not the same as that of the NMR peak ratio (Landucci 1985). The relative deviation of the S:G ratios is six times greater than that of the methoxyl:aryl ratios. Thus, within known error limits, the S:G ratio of the crill MWL could be as high as 0.94 and that of the fiber MWL as low as 1.26, a difference of 34%.

The S:G ratio of the birch ray cell lignin, 1.09, was approximately midway between that of the fiber and crill. These results are very similar to those from a previous  $^{13}\text{C}$  NMR comparative method (Obst and Ralph 1983). The S:G ratio of the birch fiber "MWEL", 0.96, was less than that of the corresponding MWL, and suggests a fractionation in the preparation of MWL. The S:G ratio of the ray cell "MWEL" was much lower than that of the corresponding MWL, and may be a result of nonlignin aromatic or olefinic substances deposited in ray cells.

The trend of the S:G ratios of MWLs isolated from sweetgum kraft pulp fractions was similar to that of the birch samples. The fiber MWL had a S:G ratio more than twice that of the crill. However, the S:G ratios of the MWLs from red oak fiber and crill were similar, 1.09 and 1.00, respectively. Also, the S:G ratio of the fiber MWL from American elm kraft pulp was 0.56, whereas that of the crill MWL was 0.64.

The distribution of hardwood lignin, and its S:G nature, has been studied by ultraviolet and electron microscopic methods. However, critical assumptions were required and, as progress was made, newer studies did not always agree with the previous ones. For example, for white birch, it was first proposed that the middle lamella lignin between fibers had a S:G ratio of unity (Fergus and Goring 1970). Data obtained

later indicated that the middle lamella lignin of some hardwoods consisted exclusively of guaiacyl units (the normalized ultraviolet absorbance of cell corners from one sample of white birch was slightly greater than that of Douglas-fir and black spruce cell corners) (Musha and Goring 1975). More recently, it was reported that most of the white birch middle lamella lignin was a syringyl-guaiacyl copolymer, but guaiacyl units predominated (S:G = 0.1, between fibers) (Saka and Goring 1985). Improvements in experimental techniques, new procedures, and refined assumptions may yet lead to a different description of hardwood lignin distribution and character. Indeed, the state-of-art technique of measuring lignin distribution on softwoods by derivatization with bromine, and then determining bromine concentration by electron microscopy-energy dispersive x-ray analysis, is being questioned (Malcolm 1986; Westermarck 1985).

In the case of birch and sweetgum, the present results support the concept of a guaiacyl-rich middle lamella lignin and a syringyl-rich lignin in the fiber cell wall. For both American elm and red oak, the present data strongly sustain the conclusion of the presence of a more uniform S:G lignin in these regions. However, the assumptions made to allow these conclusions, as well as some qualifications, must be recalled. First, the crill fraction, possibly modified by kraft pulping, is assumed to represent a fraction enriched in middle lamella. Microscopic scrutiny has indicated the likelihood of this assumption, but some ray cells (up to about 5%) and fragments, as well as fiber cell wall pieces, are present in the crill samples. It has been reported that the lignin concentration of white birch middle lamella between fibers is 0.36 g/g and that of cell corners is 0.45 g/g, whereas the lignin concentration of the fiber cell wall is about 0.14 g/g (Saka and Goring 1985). Thus, the lignin concentration of the middle lamella/cell corner regions is about 2.6 to 3.2 times greater than that of the fiber wall. The Klason lignin content of the white birch crill is 3.3 times more than that of the fiber fraction from which it is isolated (Table 2). If the birch fiber MWL (S:G ratio 1.38) is representative of the lignin in the cell wall, and if the crill fraction contains 90% middle lamella lignin, then the middle lamella lignin, after some kraft pulping, is calculated to have a S:G ratio of 0.63. The sweetgum crill contained 3.6 times more lignin than the fiber fraction from which it was isolated, indicating a middle lamella lignin S:G of 0.74, if the crill contains 90% middle lamella lignin.

The elm crill fraction was only 1.7 times richer in lignin than the fiber from which it was isolated. The elm crill must then be considered to contain a lower proportion of middle lamella than the crill from sweetgum and birch, assuming the lignin distribution reported for birch is the same for other hardwoods. However, the S:G ratios of the elm fiber and crill

MWLs were similar, and the middle lamella lignin must have about the same monomer composition as the cell wall lignin. The red oak crill contained 2.2 times more lignin than its ray cell-free pulp fraction. Within experimental error, the oak crill and fiber MWLs had the same S:G ratio.

Furthermore, because the fractions were isolated from high-yield kraft pulps, it is possible that some syringyl-rich lignin may have been removed. Another consideration is whether the MWL isolated from the crill represents the middle lamella lignin and whether the MWL isolated from the fiber fraction represents the cell wall lignin of fibers. There is no clear understanding of the origin of MWL from sound, untreated wood; therefore the source of MWL isolated from pulp fractions remains speculative. The conclusions drawn from these data must be considered indicative, but not absolute, of the S:G nature of the lignin in the hardwood samples studied.

At this point it is interesting to comment on the syringyl-rich lignin isolated as a soluble fraction from sweetgum MWEL (s-MWEL). Small amounts of syringyl-rich lignin have been isolated; for example, about 1.3% of the total dioxane lignin from beech wood was reported to be composed predominantly of syringylpropane units (Yamasaki *et al.* 1978). In the current work, it would appear that the 96% dioxane soluble portion of s-MWEL is also syringyl-rich (S:G = 1.85; Table 1). However, the S:G ratios for sweetgum MWL, and a low carbohydrate fraction isolated from it, were considerably less. Because most of the polysaccharides were enzymatically removed in the preparation of the s-MWEL, it is probable that the high S:G value reflects solvent fractionation of the MWEL and not preferential lignin-type removal from a specific type of cell or cell region. If hardwood lignin is a random mixture of S and G units, a normal distribution of the types of monomer units is likely. Thus, there would be some portions of the copolymer which would be S-rich and others which would be G-rich.

## Conclusions

For soluble, isolated lignins, quantitative  $^{13}\text{C}$  NMR spectroscopy provides a measure of the methoxyl:aryl ratio in both hardwood and softwood lignins. It also permits calculation of a syringyl:guaiacyl ratio, assuming that the lignin is composed of only syringyl and guaiacyl units, and is uncontaminated by aromatic extractives.

Although no definitive experiments were devised to unambiguously determine the origin of milled wood lignin, it is suggested that, following high-yield kraft pulping of wood, MWL arises from all morphological regions in approximate proportion to its distribution in each. Based on the NMR data from milled wood lignins isolated from hardwood kraft pulp fractions,

the middle lamella lignin of birch and sweetgum is a syringyl-guaiacyl copolymer enriched in guaiacyl units, whereas the cell wall lignin is a syringyl-rich copolymer. The analogous NMR data for American elm and red oak strongly suggest that the middle lamella lignin and the cell wall lignin in each have a more uniform syringyl : guaiacyl composition.

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