

LIGNIN STRUCTURE AND WOOD PROPERTIES

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ABSTRACT

The objective of this study was to understand the relationship between lignin structural organization and certain wood properties. Lignin, which constitutes 20–30% of the weight of all woody plants, functions as a binding and encrusting material in the cell wall, giving rigidity to the overall plant structure. More than 60% of all linkages in lignins isolated (Björkman) from *Aspidosperma macrocarpum*, *Lophanthera lactescens*, *Gallesia gorazema*, *Peltogyne paniculata*, and *Aspidosperma polyneuron* were of the β -O-4 alkyl aryl ether type. This unit plays an important role in the physical and mechanical properties of wood. Percentages of β -O-4 unit were estimated by infrared spectroscopy. An Index of Molecular Flexibility (IMF) was introduced in order to hypothetically estimate the contribution of this unit toward wood flexibility, (under the assumption that the β -O-4 linkage is positively correlated with flexibility). Lignins from *Aspidosperma macrocarpum* (AM) and *Aspidosperma polyneuron* (AP) show the highest and lowest structural complexity (diversity of linkage types β - β , β -5, β -O-4, etc.) with IMF values of 2.02 and 3.00, respectively. In this case, lignins AM and AP are supposedly contributing toward lowest and highest grade of wood flexibility, respectively, which demonstrates the hypothesis that β -O-4 linkages correlate well with flexibility.

Keywords: Lignin, infrared, wood, methoxyl group, index of molecular flexibility (IMF), guaiacyl-glycerol- β -aryl ether (β -O-4).

INTRODUCTION

Lignin can be described as a three-dimensional macromolecule with high molecular weight in the range of 100 KD. It originates from phenylpropanoid precursors such as coumaryl, coniferyl, and sinapyl alcohol C_6C_3 (Fig. 1) and is present in vascular plants. In the woody tissue of angiosperms, it is found in tracheids, fiber, vessels, and parenchyma cells (Sarkanen and Ludwig 1971). In spite of technology's progress at the end of this century, it has not been possible to determine ex-

actly the inter- and intra-molecular bonds involving lignin and other polymers in the cell wall (Carpita and Gibeau 1993). Additionally, its heterogeneity has been a struggle for all wood researchers worldwide. Furthermore, the mechanism of lignin formation has not been established completely. Some evidence about enzymatic interactions (Lewis and Yamamoto 1990; Whetten and Sederoff 1995; Higuchi et al. 1977; Nose et al. 1995; Davin and Lewis 1995), lignin-carbohydrate interaction (Houtman and Atalla 1995), and gene expression

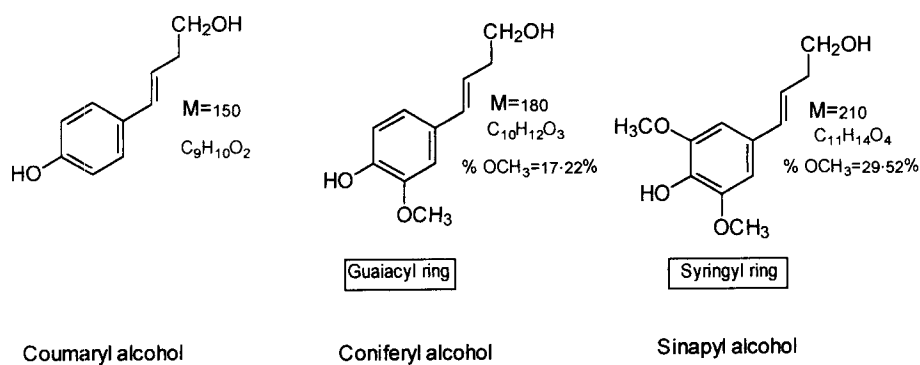


FIG. 1. Phenylpropanoid lignins precursors.

(Tirumalai et al. 1996) are also being investigated. Its formation in the cell wall has previously been investigated (Freudenberg and Neish 1968; Higuchi 1985; Eraso and Hartley 1989; Fukuda 1996; Hahlbrock and Scheel 1989; Lewis and Yamamoto 1990; Whetten and Sederoff 1995).

According to Cassab and Varner (1988), the first concepts of elastic properties and tensile strength of sclerenchyma cells and their correlation with the lignification of the cell wall date back to the last century. Since then, research on the relationship between lignin and wood properties has been carried out. However, in most cases wood properties are related to the shape, orientation, size, and frequency of the structural elements in the wood. It is known that lignin is considered to be a material that contains the highest content of carbon atoms and methoxyl groups in wood. In this context, lignin structural organization must also contribute significantly to the physical and mechanical properties of wood. The net of intra-carbon-carbon and carbon-oxygen (ether bond) bonds may confer more or less flexibility to the cell-wall system. In this regard, it is interesting to evaluate the flexibility of the lignin molecule and its role in wood. Figure 2 shows two different systems of molecular organization, one with more and the other with less flexibility.

It was observed recently that cellulose microfibrils, hemicellulose, and pectic compounds in the cell-wall matrix play a role as

templates for lignin deposition (Terashima and Atalla 1995). According to their observation, these substances determine the size and shape of the lignin macromolecules. The relative concentration of the lignin-to-cellulose varies considerably between ML (middle lamella) and CC (cell corner) (Tirumalai et al. 1996). These new considerations of lignin to cellulose ratio, ML and CC regions must be also taken into account. Recently it was observed by computation that the intermolecular bond involving α and β hydroxyl groups (side chain) to the ether oxygen creates a shift in electron density toward ether oxygen at the expense of the AR-O bond order (Simon and Eriksson 1996). According to this opinion, it reduces the rotational barrier of the aromatic ring in the β -O-4 linkage, producing considerably more flexibility in the ring orientation. In addition, methoxyl groups on the aromatic ring create an entirely different intermolecular hydrogen-bonding environment. Evidence does exist showing that middle lamellae (ML) of birch wood contain lignin of *p*-hydroxyphenylpropane and guaiacylpropane composition (Tirumalai et al. 1996). This suggests a strong probability of finding condensed lignin in this region. Lignin of this type was also detected in the S2 layer of vessels (Table 1).

MATERIALS AND METHODS

From the wood of *Aspidosperma macrocarpum*, *Lophanthera lactescens*, *Gallesia gora-*

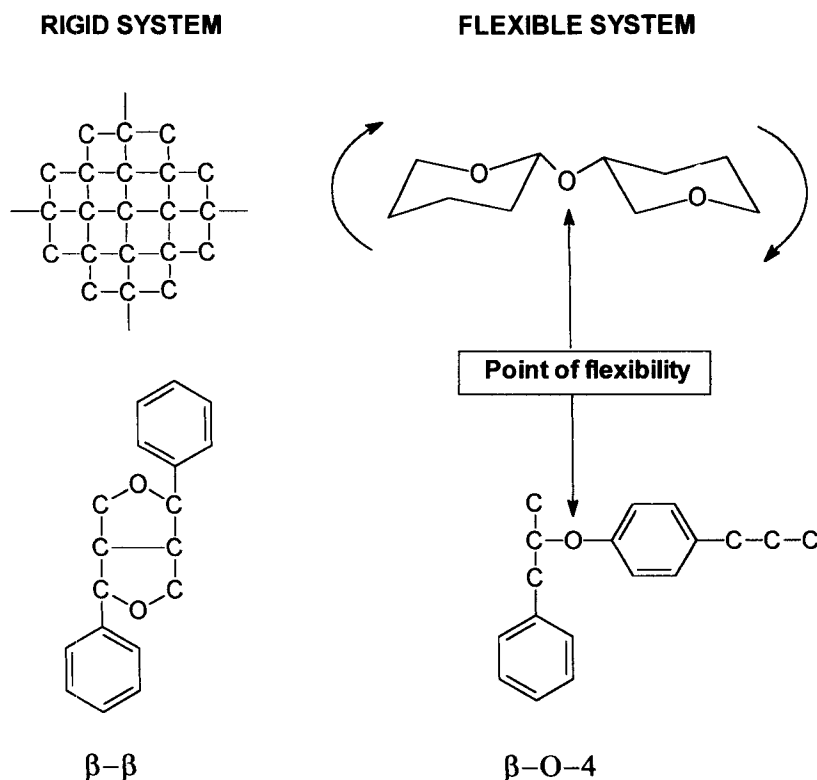


FIG. 2. Systems of molecular organization.

zema, *Peltogyne paniculata*, and *Aspidosperma polyneuron* (AM, LL, GG, PP, and AP), respectively, milled wood lignin (MWL) was isolated by Björkman's method (Björkman 1956). Samples of wood (100 g of the dry wood dust, 40-80 mesh), extracted with acetone and in 1% NaOH, were ground in a ball rotational planetary mill (Fritzch) for 168

hours; then the milled wood was extracted with dioxane and water (95:5) (Björkman 1956). Treatment with 1% NaOH was carried out to extract polyphenolic compounds from tropical woods. The determination of the methoxyl content was based on the modified Seizel's method as described elsewhere (Vieböck and Schwappach 1930).

TABLE 1. Distribution of guaiacyl-syringyl lignins in birch cells (Higuchi 1985).

Morphological regions	Guaiacyl:syringyl ratio	Probable types of lignin structure
Fiber S2	12:88	No condensed
Vessel S2	88:12	Condensed
Ray parenchyma	49:51	Semi-condensed
MLcc (F/F)	91:9	Condensed
MLcc (F/V)	80:20	Condensed
MLcc (F/R)	100:0	Condensed
MLcc (R/R)	88:12	Condensed

S = secondary wall. ML = middle lamellae. cc = cell corner. F = fiber.

Infrared

Fourier transformation infrared (FT-IR) spectra were recorded from 2 mg of each lignin sample in 300 mg of KBr. Spectra were acquired after 64 scans in a Biorad Digilab FT 54 FTIR spectrometer. A detector DTGS (Deuterated Triglycine Sulfate), Diffuse Reflected Infrared Fourier Transformer (DRIFT), and a reflectometer with hemiellipsoidal mirrors were used. The comparative analysis was possible due to similar conditions of spectrum

TABLE 2. Theoretical Number of Intermonomeric Bonds (TNIB).

Lignin types	TNIB	Peroxide number excluded	Theoretical OCH ₃ %
H	24	01	0
G	15	01	17.22
S	8	01	29.52
HG	78	03	15.90
GS	46	03	19.40
HGS	138	06	11.48

acquisition. The 1,126 cm⁻¹ absorption signal was considered a reference for normalization of spectra. The content of β-O-4 linkage was calculated in percent per mol. This calculation was based on the 5b and 5 signal intensities (100% of absorbance). They are originated from deconvolution on the 1,600 cm⁻¹ band.

RESULTS AND DISCUSSION

It is known that lignin structural organization is a consequence of the type of combination involving phenoxy radicals formed

from coumaryl (H), coniferyl (G), and sinapyl (S) alcohol precursors (Freudenberg and Neish 1968). The first of them (coumaryl alcohol) sustains five reactive sites, including ring and side chains. They are located on C-1, C-3, C-5 (aromatic ring), HO-Phe, and C-β in side chain. The coniferyl alcohol has four possibilities of linking on C-1, C-5 (aromatic ring), HO-Phe, and C-β, while the sinapyl alcohol has only three free sites, located on C-1 (aromatic ring), HO-Phe, and C-β. This means that the lignin from coumaryl alcohol supposedly has the highest number of cross links, so that a high degree of complexity may be found in it, while lignin from a sinapyl alcohol precursor has a low number of cross links. The maximum number of combinations among phenoxy radicals at a (1:1) ratio is called TNIB (Theoretical Number of the Intermonomeric Bonds) (Table 2). The TNIB decreases from coumaryl to sinapyl alcohol precursors (Fig. 3). The structural unit from combination between Ra × Ra (a peroxide) was excluded

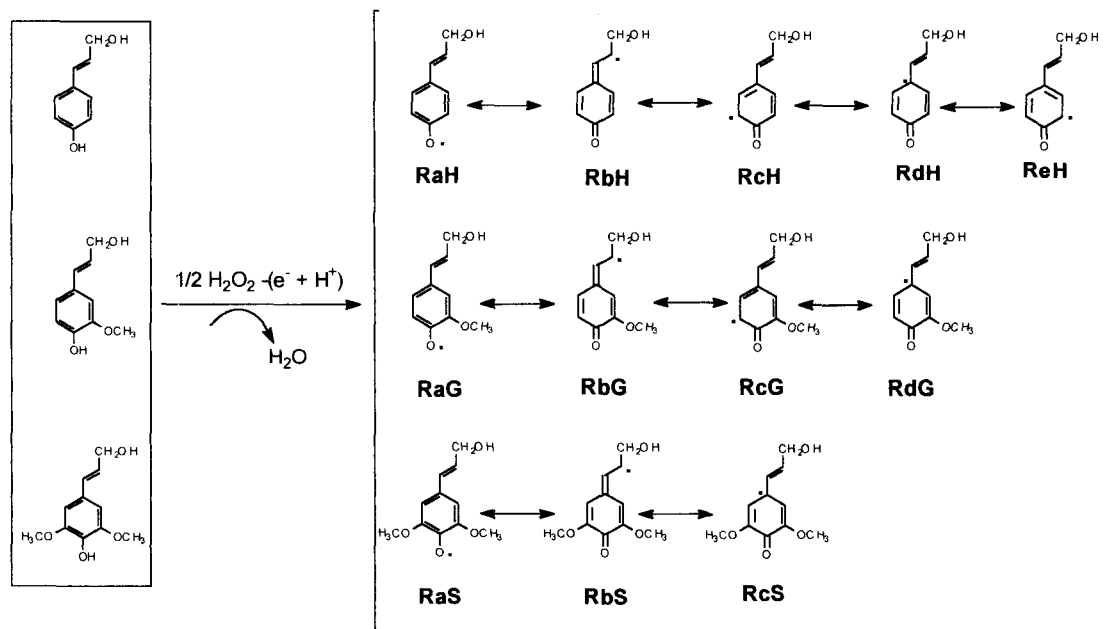


Fig. 3. Predicated phenoxy radicals from coumaryl (H), coniferyl (G), and sinapyl (S) alcohols (Freudenberg and Neish 1968).

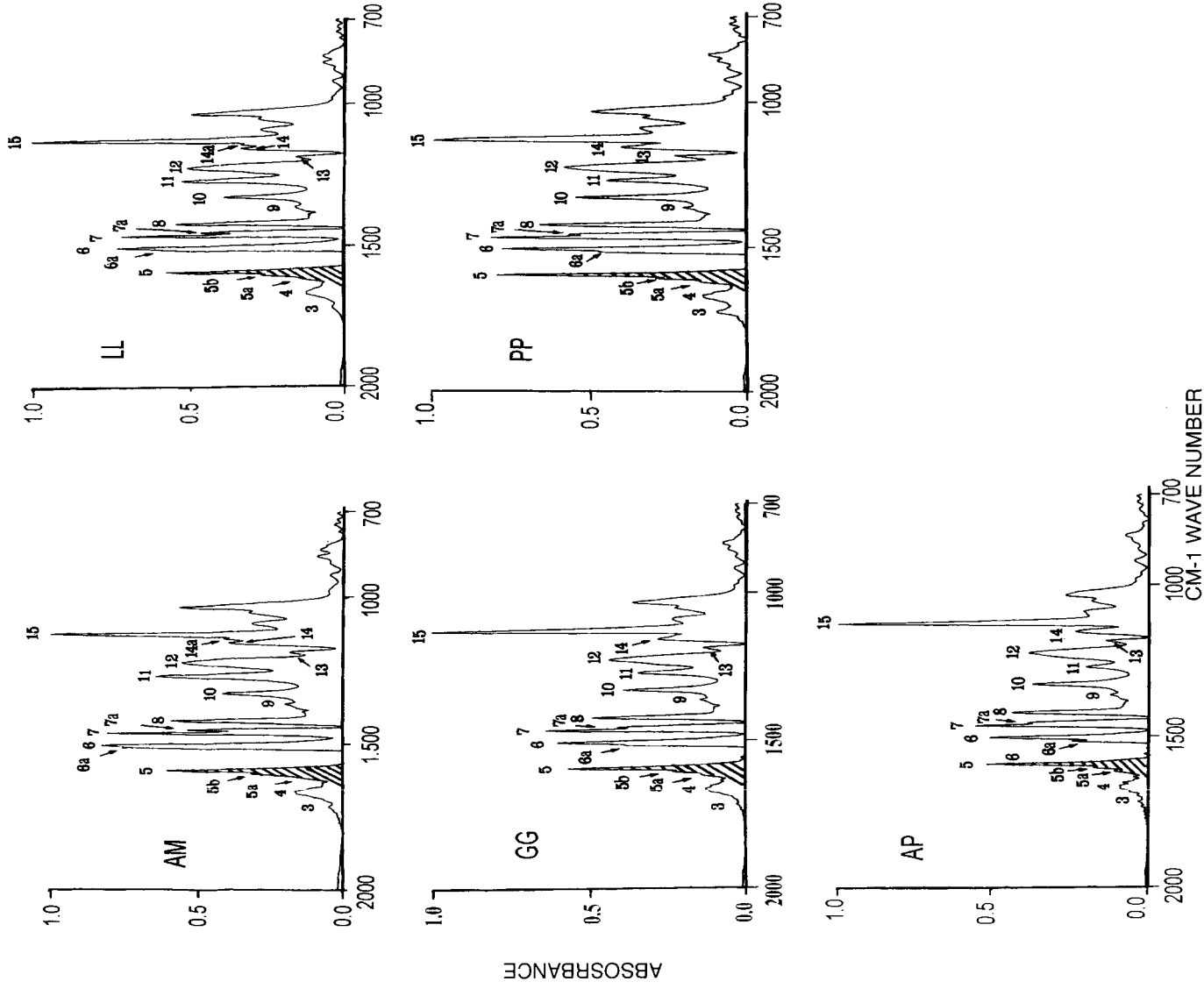


FIG. 4. Deconvolution infrared spectra of AM, LL, GG, PP, and AP lignins.

TABLE 3. Percentage of the β -O-4 structural unit in AM, LL, GG, PP, and AP lignins estimated by infrared (Abreu 1997).

Structural unit/functional group	Lignins				
	AM	LL	GG	PP	AP
β -O-4	65.5%	68.0%	71.0%	73.4%	75.0%
OCH ₃ /C ₉	1.23	1.28	1.36	1.45	1.55

from TNIB estimation (Table 2). It has been considered an extremely unstable product.

Infrared

For decades infrared spectroscopy has been a very useful tool in lignin investigations. The use of computational methods in infrared spectroscopy has been a revolution in lignin analysis. The deconvolution technique is available for visualization of complex and multiple bands of infrared and other spectroscopic methods. In the deconvoluted infrared spectra of DHPs and lignin models, various dismembered bands are shown. The band at 1,593 cm⁻¹ for example in the DHP and lignin model spectra is broken into three components

1,616, 1,602, and 1,592 cm⁻¹. The second component at 1,602 cm⁻¹ was attributed to the β -5, β - β , 4-O-5 and the third at 1,592 cm⁻¹ to β -O-4 (guaiacylglycerol- β -aryl ether) structural unit (Lin and Dence 1992; Faix and Beinhoff 1988). Both components at 1,602 and 1,592 cm⁻¹ probably originate from their aromatic ring vibrations, respectively. The assignment of the original signals was done, according to the literature data (Lin and Dence 1992; Faix and Beinhoff 1988). The β -O-4 percentages in lignins isolated from *Aspidosperma macrocarpum* (AM), *Lophanthera lactescens* (LL), *Gallesia gorazema* (GG), *Peltogyne paniculata* (PP), and *Aspidosperma polyneuron* (AP) (Fig. 4) were estimated; then

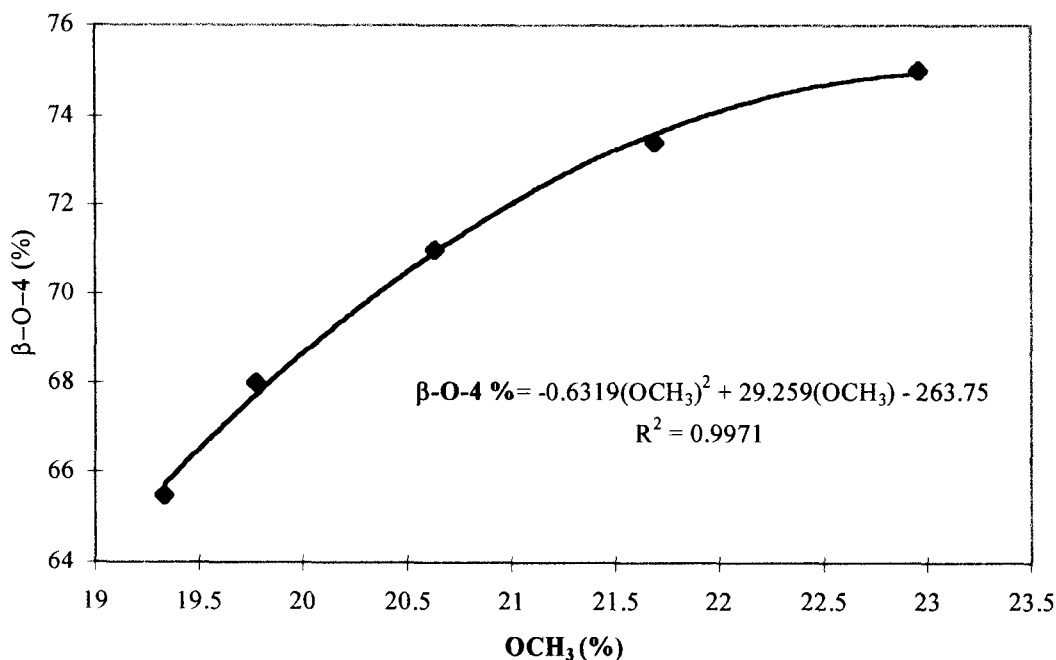


FIG. 5. Comparison between values of β -O-4 estimated by infrared and OCH₃ percentage.

TABLE 4. β -O-4% and IMF calculated for AM, LL, GG, PP, and PA lignins.

Lignin	OCH ₃ %	β -O-4% (original) by infrared	Type of lignin	TNIB G:S (1:1)	Estimated β -O-4%	Original IMF	Estimated IMF
AM	19.33	65.5	GS	46	65.67	2.02	1.91
LL	19.77	68	GS	46	67.67	2.12	2.10
GG	20.63	71	GS	46	70.88	2.43	2.43
PP	21.69	73.4	GS	46	73.54	2.75	2.77
AP	22.96	75	GS	46	74.86	3.00	2.97

G = Guaiacyl, S = Syringyl.

the values of the relative intensity played by components 5b and 5, respectively, at 1,602-1,592, 1,600-1,592, 1,603-1,592, 1,606-1,592, 1,604-1,592 cm⁻¹ (Fig. 4). The 5 component (1,592 cm⁻¹) in all spectra showed higher intensity than 5b component. The following order of β -O-4 percentage is suggested AP>PP>GG>LL>AM (Abreu 1997) (Table 3).

The regression analysis showed that the methoxyl group was strongly correlated to the β -O-4 formation. The best fit was a quadratic model with $R^2 = 0.9971$ (Fig. 5). The theoretical percentage of β -O-4 linkage could be estimated with 95% confidence. Observations are also represented graphically (Fig. 5).

In this context, an Index of Molecular Flexibility (IMF) was suggested. It was shown to increase with increasing β -O-4 linkages, according to the sequence AM>LL>GG>PP>AP (Table 4). Based on this concept, IMF was also estimated for angiosperms and gymnosperms plants.

$$\text{IMF} = \frac{\text{no. of } \beta\text{-O-4/mol}}{\text{TNIB} - \text{no. of } \beta\text{-O-4/mol}} \quad (1)$$

$$\begin{aligned} &\text{Number of } \beta\text{-O-4/mol} \\ &= \frac{\beta\text{-O-4\%} \times \text{TNIB}}{100} \end{aligned} \quad (2)$$

The data in Table 5 suggest contribution of the methoxyl group toward β -O-4 formation. It reinforces the opinion that gymnosperm lignins sustain higher structural complexity than angiosperms lignins. It also means that lignin with low methoxyl content has low IMF. The average values indicated in Table 5 were calculated according to data available in the literature.

CONCLUSIONS

It is important to note that this work is speculative. Naturally, we are not sure about the relationship between lignin structural organization and wood properties. However, this work encourages future discussions on structural organization and its role in wood properties. Based on this hypothetical result, it was concluded that:

1. There is a relationship between lignin and wood properties that must be investigated.
2. The IMF increases from the middle lamella (ML) to the inner part of the cell wall.
3. Of the lignins examined, *Aspidosperma macrocarpum* (AM) and *Aspidosperma polyneuron* (AP) lignins show the highest and lowest structural complexity, respectively.
4. The concept attributed to TNIB and IMF is entirely original.

TABLE 5. Estimated IMF for Björkman lignin of gymnosperm and angiosperm plants.

Botanical group	OCH ₃ % average (MWL)	TNIB G:S (1:1)	β -O-4% average	IMF average	Type of lignin
Gymnosperms	15.74	78	40.23	0.67	HG
Angiosperms (tree)	20.68	46	71.08	2.45	GS
Angiosperms (shrub)	22.01	46	74.12	2.86	GS

5. The percentage of β -O-4 may be associated with methoxyl content variation.

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