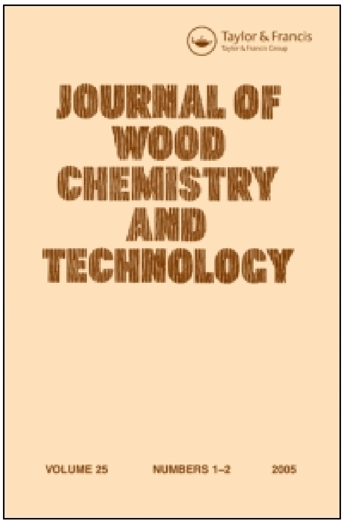

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ASSESSMENT OF LIGNIN MODEL QUALITY IN LIGNIN CHEMICAL SHIFT ASSIGNMENTS -- SUBSTITUENT AND SOLVENT EFFECTS[1]

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ABSTRACT

Typical solution-state ^{13}C NMR spectra of lignins obtained with relatively modern instrumention contain well over 100 signals. The use of classical lignin model compounds is no longer sufficient for accurate interpretation of these spectra. Ultimately, the only valid models for etherified C_9 units in lignin (which account for about 80% of the lignin polymer) must be at least trimeric or tetrameric, depending on the linkages involved. One approach that can be used involves NMR substituent effects. This approach avoids tedious syntheses while retaining the much-needed accuracy of chemical shift correlations between models and natural lignins. Appropriate substituent effects have been calculated by the use of an extensive NMR database of dimeric, trimeric and tetrameric lignin model compounds. Effects related to acetylation and solvent have also been determined. For example, accurate chemical shift data for an underivatized milled-wood lignin (MWL) in DMSO-d_6 can be determined on the basis of the chemical shifts of the corresponding acetylated MWL in acetone-d_6.

INTRODUCTION

In one-dimensional solution-state ^{13}C NMR spectra of lignins, there is no increase in the number of signals beyond 50 to 60 MHz ^{13}C (200-250 MHz ^{1}H) field strength.[2] At this optimal level, typical lignin spectra contain well over 100 signals. Generally, signals about 0.1 ppm apart can be resolved without resolution enhancement; with some enhancement, signals about 0.05 ppm apart can be resolved with a concomitant increase in the number of signals in a given spectrum. However, due to the limitations of conventional monomeric and dimeric lignin model compounds, the dramatic increase in the number of observable signals in lignin spectra in the past several years has not been accompanied by a corresponding increase in their interpretability.

We have been compiling an extensive NMR database of lignin and cell-wall model compounds[3] to overcome some of these limitations. Presently, the database includes over 300 compounds, most of which were analyzed in three deuterated solvents: acetone, chloroform, and dimethylsulfoxide (DMSO). The inclusion of monomers, dimers, trimers, and tetramers in these solvents, and in many cases in both underivatized and acetylated forms, allows calculation of very reliable substituent, acetylation, and solvent effects.

Determination of solvent effects is particularly important because of the widespread use of chloroform in the analysis of lignin model compounds. This is somewhat unfortunate as chloroform is generally a poor choice (as will be shown) for higher oligomers and lignin. With accurate solvent conversion factors, extensive chemical shift (CS) listings of lignin model compounds, such as those of Nimz and coworkers,[4,5] Morck and Kringstad,[6,7] Chen and coworkers,[8] and Sipila and Syrjanen,[9] can be compared and fully utilized.

Ideally, with a limitless database, determination of substituent effects would not be necessary as there would always be a trimeric or tetrameric fragment represented by a specific model in a specific solvent. A more realistic situation requires the use of substituent effects to fill the gaps when a specific structural detail is absent, when the compound was analyzed in the "wrong" solvent, or when the target compound is not available in the desired form (underivatized or acetylated). However, the compounds used to determine substituent effects must be very close to the target structure; otherwise, the deviations become unacceptable. A useful substituent effect is one that has a deviation no greater than ±0.2 ppm, but preferably less. The working assumption in specifying such low tolerances is that, in liquid state NMR spectra, the CS of a particular carbon in a suitable model is within ±0.1 ppm of the corresponding CS in the polymer providing that the solvent is the same in both cases.

It should be noted that the concept of substituent effects in lignin model compounds was previously explored quite extensively.[10-12] However, the CS data were limited to underivatized material in DMSO–d_6. Also, the "substituent chemical shifts" could not generally be applied directly to lignin spectra because of excessively large deviations due to limitations in many of the parent compounds. However, the information is extremely valuable in the prediction of CSs of model structures, particular those of the β-5 type.[12] To obtain the accuracy necessary for assigning signals in lignin spectra, parent compounds are typically dimeric or trimeric "duplicates" of actual C9 units in the lignin polymer.

In this study, we assess the quality of various lignin dimeric model compounds based on substituent effects dealing with changes in the character of the aryl-ether substituent (B-ring) both in terms of methoxyl substitution and sidechain substitution. Substituent effects due to derivitization and solvent changes are also included to enable conversions of literature data to common ground.

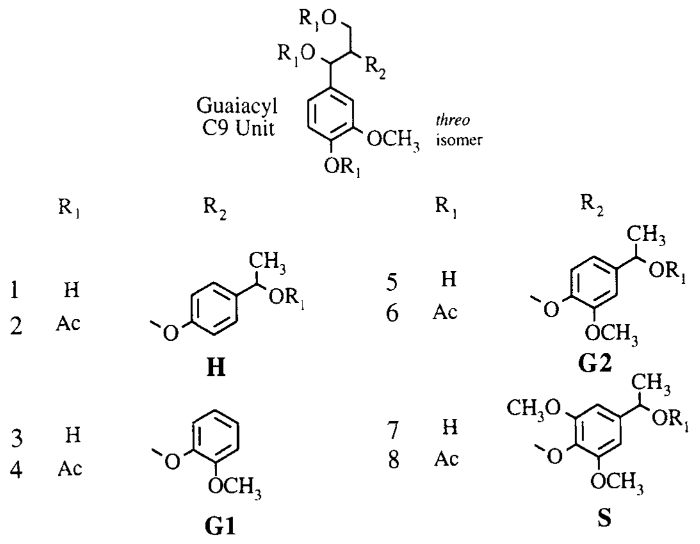


Figure 1. Dimeric model compounds.

RESULTS AND DISCUSSION

Free Phenolic C9 Units

Free phenolic C9 units in lignin can be represented by numerous dimeric models, four of which are shown in Figure 1 as both the underivatized and acetylated forms of the *threo* isomer. These compounds represent free phenolic guaiacyl C9 units in lignin attached to p-hydroxyphenyl (**1**,**2**), guaiacyl (**3**,**4**,**5**,**6**), and syringyl (**7**,**8**) rings. Substituent effects (Δ), referred to the p-hydroxyphenyl compound (R_2=**H**) of the carbons in the underivatized and acetylated guaiacyl C9 unit (Ring A and β-O-4 linkage), are compiled in Tables 1 and 2, respectively (Δ must be added to the corresponding CS value of the reference compound). As indicated from the standard deviations (Std Dev) in Tables 1 and 2, there is a negligible effect of the B-ring on the CSs of the A-ring carbons of the C9 unit. In contrast, the effect of the

TABLE 1.
Substituent Effects (Δ) of B-ring in Underivatized Free Phenolic C9 Unit[a] in Structures **1**, **3**, **5**, and **7** (Figure 1).

R_2[b]	α	β	γ	1	2	3	4	5	6
H(CS)	73.4	84.2	61.7	134.2	111.4	147.9	146.6	115.2	120.3
G1(Δ)	0.5	4.4	0.2	-0.4	0.0	0.1	0.2	0.0	0.3
G2(Δ)	0.6	4.6	0.2	-0.3	0.1	0.1	0.2	0.0	0.2
S(Δ)	0.7	5.7	-0.3	-0.5	0.1	0.0	0.2	0.0	0.4
Average Δ	**0.6**	**4.9**	**0.0**	**-0.4**	**0.1**	**0.1**	**0.2**	**0.0**	**0.3**
Std Dev	**0.1**	**0.7**	**0.3**	**0.1**	**0.1**	**0.0**	**0.0**	**0.0**	**0.1**

[a]*threo* isomer, [b] R_2 (B-ring) substituent in Figure 1

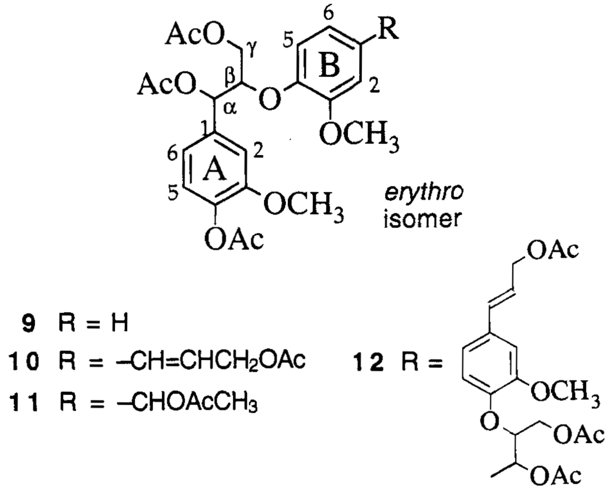
TABLE 2.
Substituent Effects (Δ) of B-ring in Acetylated Phenolic C9 Unit[a] in Structures **2**, **4**, **6**, and **8** (Figure 1).

R_2[b]	α	β	γ	1	2	3	4	5	6
H(CS)	75.1	79.1	63.2	136.4	112.6	152.2	141.0	123.6	120.4
G1(Δ)	0.3	1.6	0.3	0.3	0.0	-0.1	-0.1	-0.1	0.0
G2(Δ)	0.3	1.6	0.3	0.2	0.0	-0.1	-0.1	-0.1	0.0
S(Δ)	1.2	2.3	0.9	0.5	0.0	-0.2	-0.3	-0.3	-0.1
Average Δ	**0.6**	**1.8**	**0.5**	**0.3**	**0.0**	**-0.1**	**-0.1**	**-0.2**	**0.0**
Std Dev	**0.5**	**0.4**	**0.3**	**0.2**	**0.0**	**0.1**	**0.1**	**0.1**	**0.0**

[a]*threo* isomer, [b] R_2 (B-ring) substituent in Figure 1

B-ring on the sidechain CSs is generally quite substantial.

One of the most commonly used lignin models is guaiacylglycerol-β-guaiacyl ether. The acetylated form of this model is compound **9** in Figure 2. This model type is intended to represent two guaiacyl C9 units in lignin connected by a β-O-4 linkage. Generally, the second ring or "B-ring" is unsubstituted (R=H) with the exception of the methoxyl group. Although this model is usually adequate for studies involving



9 R = H
10 R = –CH=CHCH$_2$OAc
11 R = –CHOAcCH$_3$
12 R =

Figure 2. Guaiacyl β-O-4 model compounds with different B-ring sidechains.

chemical reactions such as β-O-4 bond cleavage, it is a rather poor model for NMR studies because the B-ring does not accurately reflect an internal (etherified) lignin C9 unit. This is clearly seen from the data in Table 3. In the calculation of the substituent effects (Δ) trimer **12** was used as the reference compound since it would be expected to give the most accurate CS values for two C9 units connected by a β-O-4 linkage in lignin. In contrast, it is clearly seen, from the relatively large deviations in the B-ring CSs, that this ring in compounds **9**, **10**, and **11** would not be expected to accurately represent corresponding etherified C9 units in lignin. This is particularly true for the *ipso* (B1), *ortho* (B2,6), and *para* (B4) positions. As expected, the R group has no significant effect on the CSs of the A-ring and associated sidechain. This confirms that ring A is a valid and accurate model of free phenolic β-O-4 C9 units in lignin.

TABLE 3.

Effect of B-ring Sidechain on β-O-4 Dimeric Units.[a]

	Compound				**Substituent Effect**				
Carbon	**9**	**10**	**11**	**12**	**Δ9–12**	**Δ10–12**	**Δ11–12**	**Ave**	**Std Dev**
α	74.6	74.5	74.5	74.5	0.1	0.0	0.1	0.1	0.1
β	80.4	80.3	80.2	80.2	0.2	0.1	0.0	0.1	0.1
γ	63.0	63.0	63.0	63.0	0.0	0.0	0.0	0.0	0.1
A1	136.7	136.6	136.6	136.6	0.1	0.0	0.0	0.0	0.1
A2	112.8	112.7	112.7	112.8	0.0	–0.1	–0.1	-0.1	0.1
A3	152.1	152.1	152.0	152.1	0.0	0.0	–0.1	0.0	0.1
A4	140.8	140.8	140.8	140.8	0.0	0.0	0.0	0.0	0.0
A5	123.4	123.4	123.3	123.3	0.1	0.1	0.0	0.1	0.1
A6	120.5	120.4	120.4	120.4	0.1	0.0	0.0	0.0	0.1
B1	124.1	132.6	138.0	136.5	-12.1	-3.9	1.5	-4.8	6.8
B2	113.9	111.4	111.7	113.1	0.8	-1.7	0.8	-0.1	1.4
B3	152.1	152.0	151.7	151.6	0.5	0.4	0.1	0.3	0.2
B4	148.3	148.3	147.7	152.2	-3.9	-3.9	-4.5	-4.1	0.3
B5	119.9	119.4	119.2	118.9	1.0	0.5	0.3	0.6	0.4
B6	121.7	120.5	119.3	120.5	1.2	0.0	-1.2	0.0	1.2

[a]*erythro* isomers.

Etherified C9 Units

In the past it has been common practice to use veratryl (4-methoxy) models to represent etherified C9 units. To test the validity of using such models for NMR studies, the CSs of the models shown in Figure 3 were compared under identical conditions. In this test **12** is the reference structure as its internal C9 unit (B-ring and associated sidechain) would be expected to accurately represent an analogous β–O–4 etherified C9 unit in lignin. The simpler dimeric models are then compared directly with **12**. The A-ring of **11** represents the free phenolic end of **12**; ring B of **13** represents the internal etherified C9

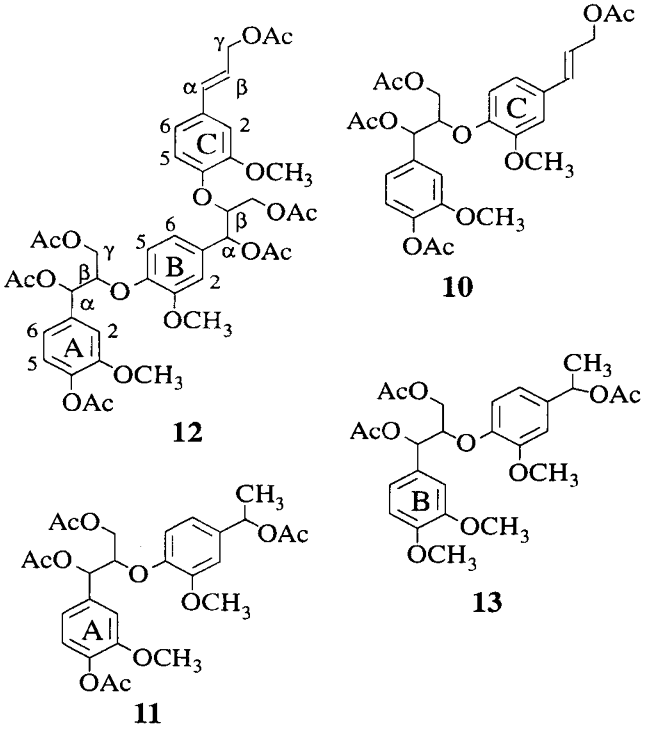


Figure 3. β-O-4/β-O-4 Trimer and representative β-O-4 dimers.

unit of **12**; and ring C of **10** represents the terminal etherified C9 unit of **12**. Selected CSs and substituent effects are summarized in Table 4.

From the absence of significant effects in the comparison of the two A-rings (**11** and **12**), one can infer that the dimeric model **11** is a good representation of free phenolic C9 units in lignin (as was also inferred from the data in Table 3). In contrast, the very large differences in the CSs of the B-rings (**12** and **13**) indicate that the veratryl model **13** is generally unsuitable and does not accurately represent corresponding etherified C9 units in lignin. Finally, comparison of the C-rings (**10** and **12**) indicate that the dilignol **10** is a

TABLE 4.

Comparison of Chemical Shifts of β-O-4 Dimers with a β-O-4 Trimer

Carbon	**11**	**12**	ΔCS	**13**	**12**	ΔCS	**10**	**12**	ΔCS
	(A-rings)			(B-rings)			(C-rings)		
α	74.5	74.5	0.0	74.8	74.6	-0.2	134.1	134.1	0.0
β	80.2	80.2	0.0	80.2	80.3	0.1	123.4	123.3	-0.1
γ	63.0	63.0	0.0	63.3	63.2	-0.1	65.3	65.3	0.0
1	136.6	136.6	0.0	130.2	136.5	6.3	132.6	132.6	0.0
2	112.7	112.8	0.1	112.3	113.1	0.8	111.4	111.3	0.1
3	152.0	152.1	0.1	150.5	151.6	1.1	152.0	151.9	0.1
4	140.8	140.8	0.0	150.2	152.2	2.0	148.3	148.4	0.1
5	123.3	123.3	0.0	112.5	118.9	6.4	119.4	119.1	-0.3
6	120.4	120.4	0.0	120.9	120.5	-0.4	120.5	120.4	0.1

good representation of the corresponding C9 unit in **12**. However, this terminal C9 unit is only important in guaiacyl dehydrogenated polymers (DHPs) as it is not present in more than a trace in natural lignin.[13]

The unsuitability of veratryl model compounds as representative of etherified aromatic rings in lignin can also be demonstrated with a C9 unit of the β-5 (coumaran) type. The compounds that were compared are shown in Figure 4. The trimer **14** represents both a β-O-4 linked C9 unit and a β-5 linked C9 unit. As in the previous case, the A-ring of **11** represents the free phenolic β-O-4 linked C9 unit. The B-ring of the veratryl model **15** represents the etherified internal unit of **14** and the C-ring of **16** represents the etherified terminal C9 unit of **14**.

Again, as shown in Table 5, there is little difference in the CSs of the two A-rings, significant difference between the B-rings, and little difference between the C-rings. It is noteworthy that both of the previous comparisons (Tables 4 and 5) indicate that veratryl model

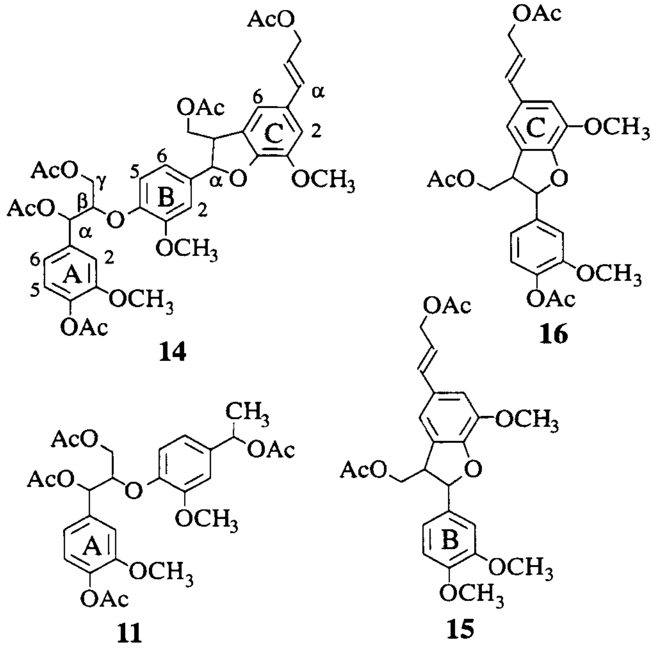


Figure 4. β-O-4/β-5 Trimer and representative β-O-4 and β-5 dimers.

TABLE 5.

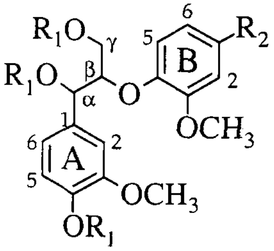
Comparison of Chemical Shifts of β-O-4/β-5 Dimers with a β-O-4/β-5 Trimer

Carbon	11	14	ΔCS	15	14	ΔCS	16	14	ΔCS
	(A-rings)			(B-rings)			(C-rings)		
α	74.5	74.5	0.0	88.8	88.5	-0.3	134.7	134.7	0.0
β	80.2	80.3	0.1	51.1	51.2	0.1	122.4	122.2	-0.2
γ	63.0	63.0	0.0	65.9	66.0	0.1	65.5	65.5	0.0
1	136.6	136.6	0.0	134.4	137.1	2.7	131.7	131.5	-0.2
2	112.7	112.7	0.0	110.8	111.5	0.7	112.4	112.2	-0.2
3	152.0	152.1	0.1	150.4	152.0	1.6	145.4	145.4	0.0
4	140.8	140.8	0.0	150.4	148.1	-2.3	149.3	149.3	0.0
5	123.3	123.3	0.0	112.7	119.4	6.7	128.9	129.0	0.1
6	120.4	120.5	0.1	119.3	119.1	-0.2	116.4	116.3	-0.1

compounds can be reasonably good representatives of etherified C9 units if only the sidechain CSs are of interest.

Derivatization and Solvent Effects

In the analysis of lignin by NMR spectroscopy, solutions of underivatized lignin in DMSO-d_6 or solutions of acetylated lignin in acetone-d_6 are commonly used. Chloroform is also used for acetylated lignins, and it is very commonly used for lignin model compounds. Unfortunately, these various conditions of analysis hinder comparisons and interpretation when data are extracted from different sources as there are appreciable derivatization and solvent effects on CSs. In an effort to quantify these effects the series of compounds illustrated in Figure 5 were analyzed in both their underivatized and acetylated forms and in the three deuterated solvents: acetone, chloroform, and DMSO. A previous publication on the systematic synthesis of several *erythro* dimeric β-O-4 model compounds was very useful in confirming the stereochemistry of our corresponding models.[9] The CSs are tabulated in Tables 6 and 7 and the corresponding solvent CS effects and precision are tabulated in Tables 8 and 9. The $\Delta CDCl_3$ and ΔDMSO rows in Tables 8 and 9 are the solvent CS effects, which are the corrections (relative to acetone-d_6) that must be applied to obtain the correct CSs. When these values are averaged within each set of *erthro* or *threo* compounds and a standard deviation calculated, it can be seen that the chloroform standard deviations are excessively high, especially with underivatized models, whereas with DMSO the values are generally within experimental error with the exception of carbons B4, B5, and B6. It should be emphasized that a single "overall" value for the solvent chemical shift effect would be relatively useless as a predictive tool as the values cover a range of over 2 ppm in the case of chloroform and over 4 ppm with DMSO. The relative errors on converting from acetone CSs to chloroform and DMSO CSs for the twelve compounds shown in Figure 5 are



Compound Type	Isomer	R_1	R_2
G-b-G1	*threo*	H	H
G-b-G2	*threo*	H	$-CHOHCH_3$
G-b-G3	*threo*	H	$-CH=CHCH_2OH$
G-b-G1	*threo*	Ac	H
G-b-G2	*threo*	Ac	$-CHOAcCH_3$
G-b-G3	*threo*	Ac	$-CH=CHCH_2OAc$
G-b-G1	*erythro*	H	H
G-b-G2	*erythro*	H	$-CHOHCH_3$
G-b-G3	*erythro*	H	$-CH=CHCH_2OH$
G-b-G1	*erythro*	Ac	H
G-b-G2	*erythro*	Ac	$-CHOAcCH_3$
G-b-G3	*erythro*	Ac	$-CH=CHCH_2OAc$

Figure 5. Compounds used for calculating derivatization and solvent effects.

summarized graphically in Figure 6. Each data bar represents the standard deviation of the solvent effect (ΔCS) among six different underivatized β-O-4 dimers (upper chart) and six acetylated dimers (lower chart).

In addition to correcting for substituent and solvent effects, the data in Tables 6 and 7 provide the capability to combine the effects of both acetylation and solvent. This results in a useful predictive tool to convert data obtained with underivatized material in DMSO-d_6 to

TABLE 6.
Chemical Shifts of Underivatized Lignin Model Compounds in Acetone-d6, Chloroform-d, and DMSO-d6[a].

Solv.[b]	Model	Iso.[c]	α	β	γ	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5	B6
A	G-b-G1	*e*	73.8	86.7	61.8	134.2	111.4	147.9	146.6	115.1	120.5	123.3	113.5	152.0	149.0	119.7	121.8
C	G-b-G1	*e*	72.8	87.0	60.6	132.0	108.8	146.6	145.1	114.3	120.6	124.0	112.2	151.4	146.9	119.1	121.6
D	G-b-G1	*e*	71.6	83.7	60.0	133.2	111.4	146.9	145.4	114.5	119.4	120.9	112.6	149.7	148.0	115.9	120.6
A	G-b-G1	*t*	73.9	88.6	61.9	133.8	111.4	148.0	146.8	115.2	120.6	123.4	113.4	151.8	149.7	120.1	122.0
C	G-b-G1	*t*	74.0	89.5	61.1	131.5	109.5	146.7	145.6	114.4	121.0	124.2	112.2	151.3	147.6	120.3	121.7
D	G-b-G1	*t*	70.9	84.4	60.0	132.9	111.0	146.9	145.3	114.6	118.9	121.0	112.5	149.6	148.3	115.8	120.6
A	G-b-G2	*e*	73.8	86.6	61.8	134.3	111.4	148.0	146.7	115.1	120.5	132.8	111.0	151.9	148.6	119.3	120.2
C	G-b-G2	*e*	73.0	87.3	60.9	133.1	110.1	145.3	144.0	114.4	120.8	131.9	108.8	151.6	146.8	119.1	120.1
D	G-b-G2	*e*	71.7	83.8	60.2	133.2	111.5	147.0	145.5	114.6	119.5	130.1	109.9	149.8	147.6	115.6	119.1
A	G-b-G2	*t*	73.8	88.4	61.9	133.8	111.4	148.0	146.8	115.2	120.5	133.0	110.9	151.7	149.2	119.6	120.3
C	G-b-G2	*t*	74.1	89.5	61.2	133.2	110.0	145.7	144.8	114.4	120.8	131.6	108.9	151.3	147.5	120.2	120.3
D	G-b-G2	*t*	71.0	84.4	60.2	133.0	111.1	147.0	145.5	114.7	119.1	130.2	109.8	149.7	147.9	115.5	119.1
A	G-b-G3	*e*	73.8	86.9	61.9	134.3	111.5	147.6	146.6	115.2	120.5	142.8	110.8	151.4	148.3	118.7	119.3
C	G-b-G3	*e*	72.8	86.9	60.8	132.0	109.5	146.7	145.3	114.4	120.2	141.7	108.9	151.2	146.8	119.1	120.2
D	G-b-G3	*e*	71.6	83.9	60.0	133.2	111.3	146.5	145.3	114.6	119.4	140.3	109.9	149.3	146.5	115.6	117.2
A	G-b-G3	*t*	74.0	88.7	61.9	133.9	111.5	148.0	146.8	115.2	120.6	142.9	110.7	151.4	148.3	118.7	119.7
C	G-b-G3	*t*	73.9	89.0	61.1	131.6	109.5	146.7	145.6	114.4	120.2	141.9	109.4	151.0	146.8	118.4	120.2
D	G-b-G3	*t*	70.9	84.7	60.0	132.9	111.0	146.9	145.3	114.6	118.9	140.4	109.8	149.3	146.9	115.6	117.2

[a]Referred to internal TMS. [b]A=acetone-d_6, C=chloroform-d, D=DMSO-d_6. [c]*e* = *erythro*, *t* = *threo*.

TABLE 7.

Chemical Shifts of Acetylated Lignin Model Compounds in Acetone-d6, Chloroform-d, and DMSO-d6[a].

Solv.[b]	Model	Iso.[c]	α	β	γ	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5	B6
A	G-b-G1	*e*	74.6	80.4	63.0	136.7	112.8	152.1	140.8	123.4	120.5	124.1	113.9	152.1	148.3	119.9	121.7
C	G-b-G1	*e*	73.8	80.2	62.6	135.4	112.0	151.1	139.8	122.5	119.7	123.6	112.7	151.0	147.2	119.5	121.0
D	G-b-G1	*e*	73.1	78.4	61.8	135.3	111.6	150.5	139.1	122.4	119.3	122.8	112.9	150.3	146.6	117.9	120.6
A	G-b-G1	*t*	75.4	80.6	63.6	136.7	112.7	152.2	140.9	123.5	120.3	123.8	113.8	151.8	149.1	119.2	121.7
C	G-b-G1	*t*	74.5	80.3	63.1	135.4	111.8	151.1	139.9	122.8	119.6	123.3	112.6	150.8	148.0	118.8	121.0
D	G-b-G1	*t*	74.3	79.1	62.5	135.4	111.6	150.7	139.2	122.6	119.4	122.6	112.8	150.1	147.5	117.5	120.6
A	G-b-G2	*e*	74.5	80.3	63.0	136.6	112.7	152.1	140.8	123.4	120.4	132.6	111.4	152.0	148.3	119.4	120.5
C	G-b-G2	*e*	73.7	80.2	62.5	135.3	111.9	151.0	139.8	122.6	119.7	131.9	110.2	151.0	147.2	119.1	119.8
D	G-b-G2	*e*	73.1	78.3	61.9	135.3	111.7	150.6	139.1	122.6	119.4	130.9	110.4	150.3	146.6	117.5	119.6
A	G-b-G2	*t*	75.3	80.6	63.6	136.6	112.6	152.2	140.9	123.6	120.3	132.4	111.3	151.8	149.1	118.7	120.5
C	G-b-G2	*t*	74.4	80.2	63.0	135.2	111.7	151.1	139.9	122.8	119.5	131.5	110.2	150.7	148.0	118.3	119.8
D	G-b-G2	*t*	74.3	79.0	62.5	135.4	111.7	150.7	139.2	122.7	119.5	130.6	110.2	150.1	147.6	117.0	119.6
A	G-b-G3	*e*	74.5	80.2	63.0	136.6	112.7	152.0	140.8	123.3	120.4	138.0	111.7	151.7	147.7	119.2	119.3
C	G-b-G3	*e*	73.7	80.1	62.5	135.3	112.0	151.0	139.8	122.5	119.7	137.0	110.7	150.9	146.7	118.6	119.0
D	G-b-G3	*e*	73.1	78.3	61.8	135.3	111.6	150.5	139.1	122.5	119.4	136.3	110.8	150.0	146.1	117.5	118.1
A	G-b-G3	*t*	75.3	80.7	63.5	136.6	112.6	152.2	140.9	123.5	120.3	137.8	111.7	151.6	148.5	118.8	119.2
C	G-b-G3	*t*	74.4	80.1	63.0	135.2	111.7	151.1	139.9	122.8	119.5	136.7	110.7	150.6	147.5	118.3	118.6
D	G-b-G3	*t*	74.2	79.1	62.4	135.3	111.6	150.7	139.2	122.6	119.4	136.1	110.6	149.9	147.0	117.2	118.1

[a]Referred to internal TMS. [b]A=acetone-d_6, C=chloroform-d, D=DMSO-d_6. [c]*e* = *erythro*, *t* = *threo*.

TABLE 8.
Solvent Chemical Shift Effects[a] and Precision for Underivatized Lignin Model Compounds.

	Model	Isomer[b]	α	β	γ	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5	B6
$\Delta CDCl_3$	G-b-G1	*e*	-1.0	0.3	-1.2	-2.2	-2.6	-1.3	-1.5	-0.8	0.1	0.7	-1.3	-0.6	-2.1	-0.6	-0.2
$\Delta CDCl_3$	G-b-G2	*e*	-0.8	0.7	-0.9	-1.2	-1.3	-2.7	-2.7	-0.7	0.3	-0.9	-2.2	-0.3	-1.8	-0.2	-0.1
$\Delta CDCl_3$	G-b-G3	*e*	-1.0	0.0	-1.1	-2.3	-2.0	-0.9	-1.3	-0.8	-0.3	-1.1	-1.9	-0.2	-1.5	0.4	0.9
Average			-0.9	0.3	-1.1	-1.9	-2.0	-1.6	-1.8	-0.8	0.0	-0.4	-1.8	-0.4	-1.8	-0.1	0.2
StdDev			0.1	0.4	0.2	0.6	0.7	0.9	0.8	0.1	0.3	1.0	0.5	0.2	0.3	0.5	0.6
$\Delta CDCl_3$	G-b-G1	*t*	0.2	0.4	0.3	1.0	1.3	-1.4	-1.2	0.1	0.2	-1.6	-0.9	0.3	0.3	0.4	0.1
$\Delta CDCl_3$	G-b-G2	*t*	0.3	1.1	-0.7	-0.6	-1.4	-2.3	-2.0	-0.8	0.3	-1.4	-2.0	-0.4	-1.7	0.6	0.0
$\Delta CDCl_3$	G-b-G3	*t*	-0.1	0.3	-0.8	-2.3	-2.0	-1.3	-1.2	-0.8	-0.4	-1.0	-1.3	-0.4	-1.5	-0.3	0.5
Average			0.1	0.6	-0.4	-0.6	-0.7	-1.7	-1.5	-0.5	0.0	-1.3	-1.4	-0.2	-1.0	0.2	0.2
StdDev			0.2	0.4	0.6	1.7	1.8	0.6	0.5	0.5	0.4	0.3	0.6	0.4	1.1	0.5	0.3
ΔDMSO	G-b-G1	*e*	-2.2	-3.0	-1.8	-1.0	0.0	-1.0	-1.2	-0.6	-1.1	-2.4	-0.9	-2.3	-1.0	-3.8	-1.2
ΔDMSO	G-b-G2	*e*	-2.1	-2.8	-1.6	-1.1	0.1	-1.0	-1.2	-0.5	-1.0	-2.7	-1.1	-2.1	-1.0	-3.7	-1.1
ΔDMSO	G-b-G3	*e*	-2.2	-3.0	-1.9	-1.1	-0.2	-1.1	-1.3	-0.6	-1.1	-2.5	-0.9	-2.1	-1.8	-3.1	-2.1
Average			-2.1	-2.9	-1.8	-1.1	0.0	-1.0	-1.2	-0.6	-1.1	-2.5	-1.0	-2.2	-1.3	-3.5	-1.5
StdDev			0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.5	0.4	0.6
ΔDMSO	G-b-G1	*t*	-3.0	-4.2	-1.9	-0.9	-0.4	-1.1	-1.5	-0.6	-1.7	-2.4	-0.9	-2.2	-1.4	-4.3	-1.4
ΔDMSO	G-b-G2	*t*	-2.8	-4.0	-1.7	-0.8	-0.3	-1.1	-1.3	-0.5	-1.4	-2.8	-1.1	-2.0	-1.3	-4.1	-1.2
ΔDMSO	G-b-G3	*t*	-3.1	-4.0	-1.9	-1.0	-0.5	-1.1	-1.5	-0.6	-1.7	-2.5	-0.9	-2.1	-1.4	-3.1	-2.5
Average			-3.0	-4.1	-1.8	-0.9	-0.4	-1.1	-1.4	-0.6	-1.6	-2.6	-1.0	-2.1	-1.4	-3.8	-1.7
StdDev			0.2	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.6	0.7

[a] Relative to acetone-d_6; [b] *e* = *erythro*, *t* = *threo*.

TABLE 9.
Solvent Chemical Shift Effects[a] and Precision for Acetylated Lignin Model Compounds.

	Model	Isomer[b]	α	β	γ	A1	A2	A3	A4	A5	A6	B1	B2	B3	B4	B5	B6
ΔCDCl3	G-b-G1	*e*	-0.8	-0.2	-0.4	-1.3	-0.8	-1.0	-1.0	-0.9	-0.8	-0.5	-1.2	-1.1	-1.1	-0.4	-0.7
ΔCDCl3	G-b-G2	*e*	-0.8	-0.1	-0.5	-1.3	-0.8	-1.1	-1.0	-0.8	-0.7	-0.7	-1.2	-1.0	-1.1	-0.3	-0.7
ΔCDCl3	G-b-G3	*e*	-0.8	-0.1	-0.5	-1.3	-0.7	-1.0	-1.0	-0.8	-0.7	-1.0	-1.0	-0.8	-1.0	-0.6	-0.3
Average			-0.8	-0.1	-0.5	-1.3	-0.8	-1.0	-1.0	-0.8	-0.7	-0.7	-1.1	-1.0	-1.1	-0.4	-0.6
StdDev			0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.3	0.1	0.2	0.1	0.2	0.2
ΔCDCl3	G-b-G1	*t*	-0.9	-0.3	-0.5	-1.3	-0.9	-1.1	-1.0	-0.7	-0.7	-0.5	-1.2	-1.0	-1.1	-0.4	-0.7
ΔCDCl3	G-b-G2	*t*	-0.9	-0.4	-0.6	-1.4	-0.9	-1.1	-1.0	-0.8	-0.8	-0.9	-1.1	-1.1	-1.1	-0.4	-0.7
ΔCDCl3	G-b-G3	*t*	-0.9	-0.6	-0.5	-1.4	-0.9	-1.1	-1.0	-0.7	-0.8	-1.1	-1.0	-1.0	-1.0	-0.5	-0.6
Average			-0.9	-0.4	-0.5	-1.4	-0.9	-1.1	-1.0	-0.7	-0.8	-0.8	-1.1	-1.0	-1.1	-0.4	-0.7
StdDev			0.0	0.2	0.1	0.1	0.0	0.0	0.0	0.1	0.1	0.3	0.1	0.1	0.1	0.1	0.1
ΔDMSO	G-b-G1	*e*	-1.5	-2.0	-1.2	-1.4	-1.2	-1.6	-1.7	-1.0	-1.2	-1.3	-1.0	-1.8	-1.7	-2.0	-1.1
ΔDMSO	G-b-G2	*e*	-1.1	-1.6	-1.1	-1.3	-1.1	-1.5	-1.7	-0.9	-0.9	-1.2	-1.0	-1.7	-1.6	-1.7	-1.1
ΔDMSO	G-b-G3	*e*	-1.4	-2.0	-1.1	-1.3	-1.0	-1.5	-1.7	-0.8	-1.0	-1.7	-1.0	-1.7	-1.7	-1.9	-0.9
Average			-1.3	-1.9	-1.1	-1.3	-1.1	-1.5	-1.7	-0.9	-1.0	-1.4	-1.0	-1.7	-1.7	-1.9	-1.0
StdDev			0.2	0.3	0.1	0.1	0.1	0.1	0.0	0.1	0.2	0.3	0.0	0.1	0.1	0.2	0.1
ΔDMSO	G-b-G1	*t*	-1.0	-1.6	-1.1	-1.2	-0.9	-1.5	-1.7	-0.9	-0.8	-1.8	-1.1	-1.7	-1.5	-1.7	-0.9
ΔDMSO	G-b-G2	*t*	-1.4	-1.9	-1.2	-1.3	-1.1	-1.5	-1.7	-0.8	-1.0	-1.7	-0.9	-1.7	-1.6	-1.7	-1.2
ΔDMSO	G-b-G3	*t*	-1.1	-1.6	-1.1	-1.3	-1.0	-1.5	-1.7	-0.9	-0.9	-1.7	-1.1	-1.7	-1.5	-1.6	-1.1
Average			-1.2	-1.7	-1.1	-1.3	-1.0	-1.5	-1.7	-0.9	-0.9	-1.7	-1.0	-1.7	-1.5	-1.7	-1.1
StdDev			0.2	0.2	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.2

[a]Relative to acetone-d_6; [b]*e* = *erythro*, *t* = *threo*.

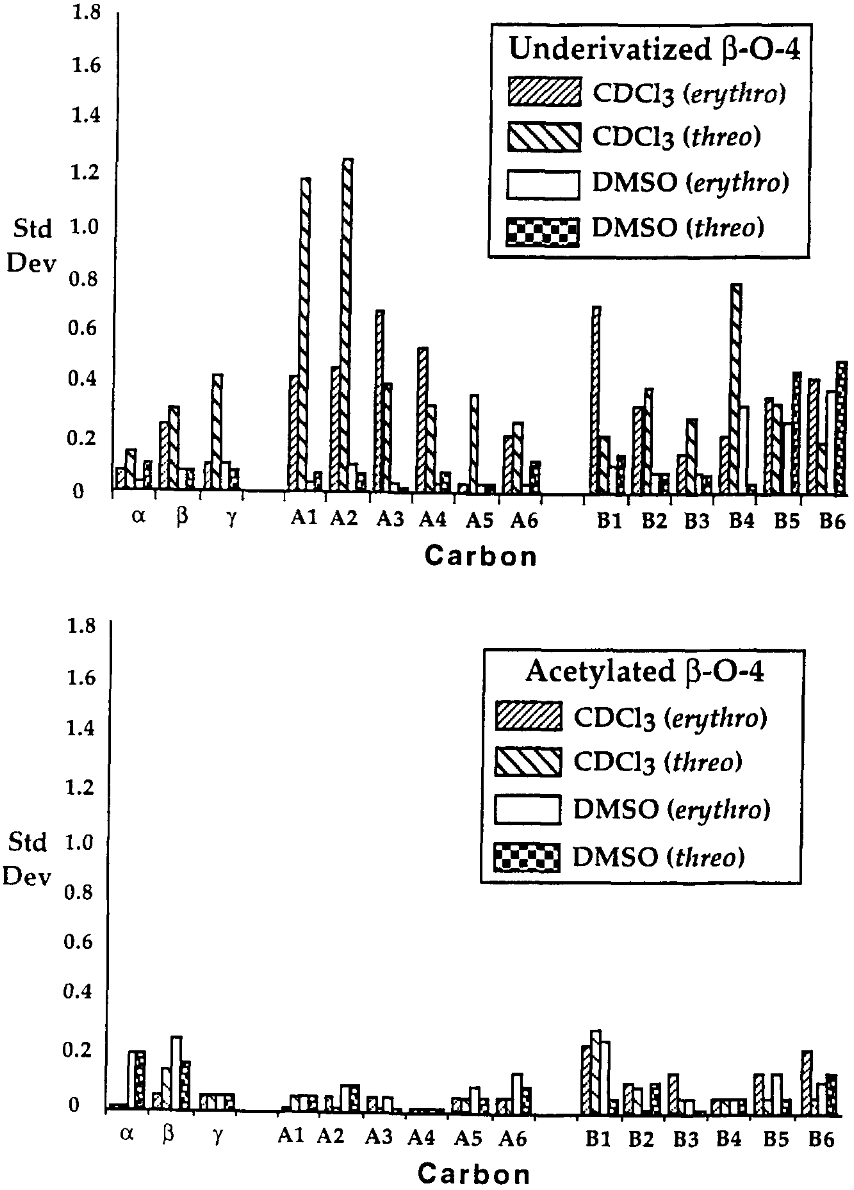
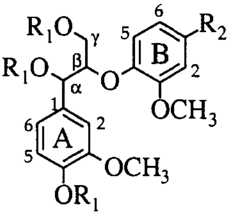


Figure 6. Relative errors in the conversion of chemical shifts in acetone to chemical shifts in chloroform or dimethyl sulfoxide .

Chemical shifts of underivatized material in DMSO-d6 $\xrightarrow{\Delta}$ **Chemical shifts of acetylated material in acetone-d_6**

(Data is based on 3 sets of *erythro* and three sets of *threo* model compounds)



R_1 = H or Ac
R_2 = H or –CH=CHCH$_2$OH or –CHOHCH$_3$

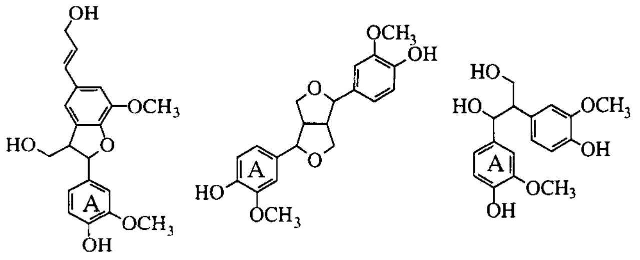
	erythro		*threo*	
C	Ave Δ	Std Dev	Ave Δ	Std Dev
α	2.9	0.1	4.4	0.1
β	-3.5	0.2	-3.9	0.1
γ	2.9	0.1	3.5	0.1
A1	3.4	0.0	3.7	0.1
A2	1.3	0.1	1.6	0.1
A3	5.2	0.2	5.3	0.1
A4	-4.6	0.1	-4.5	0.1
A5	8.8	0.1	8.9	0.0
A6	1.0	0.1	1.3	0.1
B1	1.1	3.0	0.8	3.0
B2	1.5	0.3	1.6	0.3
B3	2.3	0.1	2.2	0.1
B4	0.7	0.5	1.2	0.4
B5	3.8	0.2	3.3	0.1
B6	1.5	0.6	1.5	0.5

Example Calculation

If the chemical shift of the α carbon (erythro) in underivatized material in DMSO is 71.6, then the calculated value of α in the acetylated material in acetone is:

71.6 + 2.9 = 74.5 ± 0.1 (the actual value = 74.6.

Figure 7. Corrections (Δ) for the conversion of the CSs of underivatized material in DMSO-d_6 to CSs of acetylated material in acetone-d_6.



β-5 β-β β-1

Carbon	Δ	Δ	Δ
α	1.0	1.0	3.6
β	-1.7	1.8	-3.7
γ	3.0	1.7	2.7
A1	8.6	7.9	6.4
A2	0.7	0.7	1.8
A3	5.3	4.8	7.7
A4	-5.7	-4.1	-6.1
A5	8.8	3.4	5.7
A6	0.1	4.9	5.0

Figure 8. Conversion factors for CSs of underivatized material in DMSO-d_6 to CSs of acetylated material in acetone-d_6.

those of acetylated material in acetone-d_6 – the two most common data types in the lignin NMR literature. The ΔCSs required for this conversion for β-O-4 C9 units are summarized in Figure 7. The very low standard deviations for the sidechain and A-ring attest to the validity of this method for free phenolic β-O-4 C9 units in lignin. In contrast, the ΔCSs for the B-ring are too variable (with the exception of B3,5) to be of any value as predictive tools. However, values for etherified C9 units could be calculated when appropriate sets of trimeric model compounds are synthesized and analyzed.

Analogous conversions for the A-ring and sidechain of β–5, β–β, and β–1 structures are summarized in Figure 8. In this case, standard deviations are not given as the data are based on only one set of compounds.

CONCLUSIONS

The A-ring C9 unit in simple dimeric lignin model compounds accurately represents corresponding unetherified C9 units in lignins, regardless of the type of terminal sidechain on ring B. In contrast, the B-ring of dimeric compounds does not accurately model lignin aryl structures and should not be used for ^{13}C chemical shift correlations.

The best models for etherified lignin C9 units are tri- or tetralignols. If unavailable, the next best are dilignols with a B-ring side chain such as $-CH(OH)CH_3$. Veratryl (3,4-dimethoxy) structures are very poor models for etherified lignin aryl units, although they are acceptable models for lignin sidechains.

With acetylated model compounds and acetylated lignins, solvent substituent effects can be used for relatively precise predictions among acetone, chloroform, and dimethyl sulfoxide (DMSO). However, with underivatized models and lignins, only acetone and DMSO give acceptable conversions. Because of this and the relatively weak deuterium lock signal, chloroform is best avoided if correlations between lignins and model compounds are desired.

EXPERIMENTAL

Lignin Model Compounds

All of the lignin model compounds referred to herein have been authenticated and are included in the NMR Database of Lignin and Cell-Wall Model Compounds.[3] The dimeric compounds **1-11** and **13** were synthesized from acetovanillone according to published procedures.[14,15] Substituting p-hydroxy acetophenone, acetovanillone, or acetosyringone for guaiacol (dimer **3**) yielded the sidechain substituted (B-ring) models **1**, **5**, and **7**, respectively. The major stereochemical isomer depended largely on the method of reduction of the α-carbonyl.[16] Compounds **10, 12, 14,** and **16** were obtained from enzymatic dehydropolymerization reactions,[17] and more recently by metal salt intitiated dehydropolymerization reactions.[18,19] Dimer **15** was prepared by diacetylation of the corresponding veratryl compound with a 1/1 acetic anhydride/pyridine mixture.

NMR Experiments

In general ^{13}C data in acetone-d_6, chloroform-d, and DMSO-d_6 were obtained with the same sample, with a standard set of acquisition parameters to assure against differences due to sample concentration or instrument parameters. The data were obtained with a Bruker WM250 or DPX-250 spectrometer (62.9 MHz ^{13}C). All CSs are referred to tetra- methysilane as internal standard and the reported substituent effects are differences (Δ) in ppm.

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