

Correlation Analysis of ^{31}P NMR Chemical Shifts with Substituent Effects of Phenols

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Over 60 lignin-related model compounds were phosphitylated with 2-chloro-4,4,5,5-tetramethyldioxaphospholane, a sterically hindered analogue of 2-chloro-1,3,2-dioxaphospholane used in earlier work, and their ^{31}P chemical shifts were recorded. Excellent resolution between the chemical shifts of phosphitylated carboxylic acids, phenols and aliphatic alcohols was obtained. The correlations of the phosphorus chemical shifts with the chemical environments of lignin-related phenols using the Hammett principles provided an excellent linear relationship between the resonance substituent constant, σ_{R} , and the corresponding ^{31}P NMR chemical shift values for *para*-substituted lignin-related phenols. In addition, a correlation between ^{31}P NMR chemical shifts for *ortho*- and *para*-substituted phosphitylated phenols was obtained. A set of empirical parameters that permits the accurate prediction of ^{31}P NMR chemical shifts of lignin-related phenolic compounds derivatized with 2-chloro-4,4,5,5-tetramethyldioxaphospholane was thus obtained.

KEY WORDS NMR; ^{31}P NMR; chemical shifts; correlation analysis; lignins; phenols; substituent constants; symmetry

INTRODUCTION

Correlation analysis has been extensively practised in chemistry since the early 1930s after Hammett¹ discovered that for a number of systems linear relationships apply between the logarithms of rate and equilibrium constants. Such analyses have also been applied to demonstrate that correlations exist between substituent effects and chemical shifts in nuclear magnetic resonance spectroscopy, mainly involving ^1H or ^{19}F nuclei.² Several reviews of such treatments have been published^{3–5} and the theories governing the shielding mechanisms and substituent effects have been reviewed by Gorenstein.^{6,7}

Our laboratory's needs to identify and quantify functional groups in lignins have prompted us to examine NMR-active nuclei other than proton and carbon which, when covalently linked to lignin by appropriate derivatization procedures, may provide novel and rapid routes to new structural information for these heterogeneous biopolymers. In a series of papers with the general title ' ^{31}P NMR in Wood Chemistry' we have been examining the potential of ^{31}P NMR spectroscopy toward the characterization of model compounds,⁸ carbohydrates⁹ and lignins,^{10–13} after derivatizing their labile protons with 2-chloro-1,3,2-dioxaphospholane **I**. This reaction was proved to be a novel and powerful means to determine quantitatively the three principal types of phenolic hydroxyls, the primary hydroxyls, carboxylic acids and the *erythro* and *threo* forms of arylglycerol β -O-4-ether structures present in lignins. Prior to using this method quantitatively, we investigated the ^{31}P spin-lattice relaxation behaviour of phosphitylated

lignins and certain solvent effects known to operate in ^{31}P NMR.¹⁰ Further work using two-dimensional ^{31}P NMR spectroscopic techniques clarified the assignments of one-dimensional ^{31}P NMR spectra of lignins.¹¹ Extensive evidence was obtained confirming the absence of ^{31}P – ^{31}P and ^{31}P – ^1H through-bond and through-space couplings from within a ^{31}P NMR spectrum of phosphitylated lignins.¹¹ All signals in such spectra are clear singlets arising in their respective positions in accordance with earlier reports on model compounds and lignins.^{8,9,12} Detailed measurements of the phosphorus spin-lattice and spin-spin relaxation times at various static magnetic fields and temperatures allowed the detailed analysis of the spin relaxation mechanism of ^{31}P nuclei to be made. The predominant spin relaxation mechanism of phosphorus in phosphitylated lignins was thus found to be due to chemical shift anisotropy.¹¹ This background information was then used to design an experimental protocol for obtaining quantitative ^{31}P NMR spectra of phosphitylated lignins.¹³ The quantitative reliability of our methodology was recently verified by participating in an international round robin analytical effort with lignin standards.¹⁴

However, early efforts, examining about 80 lignin-related model compounds including phenols, alcohols, aldehydes and carboxylic acids,⁸ for their structure– ^{31}P chemical shifts relationships, after their labile protons were phosphitylated with **I**, revealed no systematic trends that would permit any detailed correlation analyses to be carried out. In this paper we present ^{31}P NMR chemical shift data of over 60 lignin-related model compounds phosphitylated with 2-chloro-4,4,5,5-tetramethyldioxaphospholane **II**, a sterically hindered analogue of reagent **I**. It is demonstrated that simple and significant empirical parameters exist which allow the accurate calculation of ^{31}P chemical shifts for

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lignin-related phenolic compounds phosphitylated with **II**.

EXPERIMENTAL

Phosphitylating reagent

2-Chloro-4,4,5,5-tetramethyldioxaphospholane **II** was prepared from pinacol (Aldrich) and phosphorus trichloride (Aldrich) in the presence of triethylamine (Aldrich) according to the method of Zwierzak.¹⁵ The yield after distillation was 34% and the product had a ³¹P chemical shift at 176.0 ppm in CDCl₃.

Solution preparation

A solvent mixture composed of pyridine and deuterated chloroform (Isotec) in a 1.6:1 (v/v) ratio was prepared based on considerations outlined by Argyropoulos.¹³ The solution was protected from moisture with molecular sieves 3A and kept in a sealed container under nitrogen.

NMR spectroscopy

The ³¹P NMR spectra were obtained in 5 mm sample tubes on a Varian XL-300 or a Varian XL-500 NMR spectrometer (operating at 121.5 and 202.3 MHz, respectively), by using methods identical with those described previously.^{8,13} All chemical shifts reported are relative to the reaction product of water with **II**, which has been observed to give a sharp signal in

pyridine-CDCl₃ at 132.2 ppm. For each spectrum 128 transients were acquired with a pulse width corresponding to a 45° flip angle and a pulse delay of 0.5 s. Acquisition and processing parameters for the spectrum in Fig. 1 were concentration 3.6%, spectral width. 70052.5 Hz, number of data points. 70080 and line broadening 1.00 Hz; zero filling and decoupling were not used.

Lignin model compounds

β-Aryl ether models 1–5 were synthesized from β-aryl ether quinonemethides using base-catalyzed condensations.¹⁶ 2-(4-Hydroxy-3-methoxybenzyl)-6-methoxy-4-methylphenol (model 6) was synthesized using the method of Harkin.¹⁷ 2,2'-(6,6'-Dimethoxy-4,4'-dimethyl)diphenylmethane (model 7), 2,2'-(6,6'-dimethoxy-4,4'-dimethyl)diphenol (model 13) and 3,3'-(6,6'-dimethoxy-4,4'-dimethyl)diphenylmethane (model 14) were prepared according to the method of Kratzl and Vierhopper.¹⁸ Stilbenes 8–12 were obtained by the method of Gierer and Nilvebrant.¹⁹ 3,4-Dihydroxyphenylethanol (model 15) was commercially available.

RESULTS AND DISCUSSION

The phosphitylation reaction of labile protons in model compounds employing reagents **I** and **II** is depicted in Scheme 1.

The ³¹P NMR spectrum of a mixture of model compounds 4 and 5 is shown in Fig. 1.

A variety of lignin-related model alcohols, carboxylic acids and phenols were derivatized with **II** and their ³¹P NMR chemical shifts were recorded (Tables 1 and 2). The actual structures of lignin-like model compounds whose ³¹P NMR chemical shifts are identified as numbered models in Tables 1 and 2 are shown in Fig. 2.

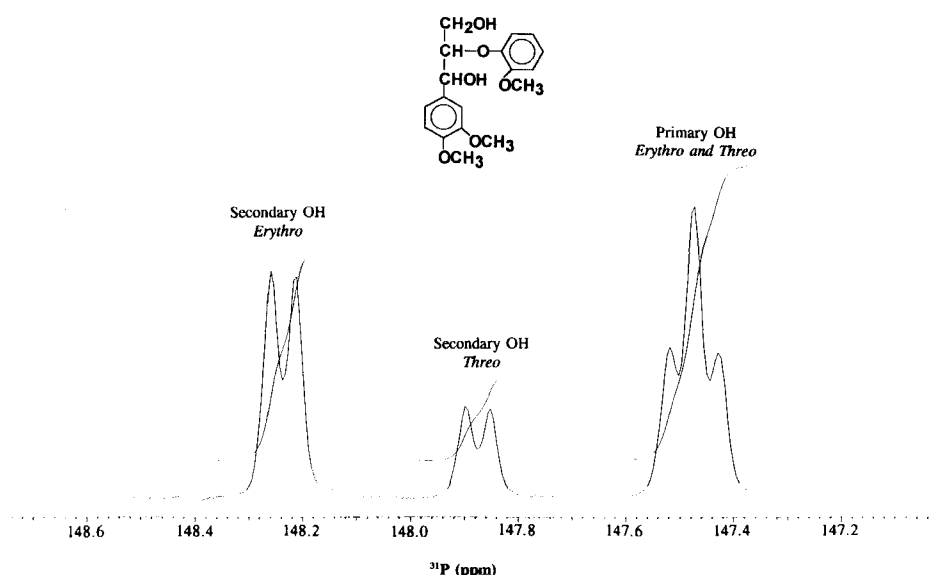
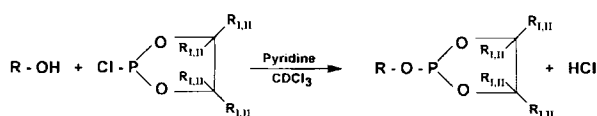


Figure 1. ³¹P NMR spectrum of a mixture of model compounds 4 and 5 obtained at 500 MHz on a Varian XL-500 NMR spectrometer.



Scheme 1. Where R-OH the labile protons of the examined model compounds. $R_1 = \text{H}$, 2-chloro-1,3,2-dioxaphospholane **I**; $R_{1,II} = \text{CH}_3$, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane **II**.

It is apparent that for the three classes of compounds shown in Tables 1 and 2 the use of reagent **II** allows an excellent separation between the chemical shifts of carboxylic acids, phenols and aliphatic alcohols. These shifts are positioned in the ranges 134.6–135.2, 137.6–144.0 and 145.1–148.4 ppm, respectively. It is also apparent that an excellent signal separation exists (of about at least 2 ppm) between disubstituted *ortho*-phenols and the chemical shifts of other phenols. An overlap between primary and secondary aliphatic hydroxyls is apparent in the region 147.8–148.0. Therefore, reagent **II** does not allow the distinction of primary and secondary hydroxyls present in arylglycerol β -aryl ether structures. Such structures are the most frequent links of the phenylpropane units in lignin. In this respect reagent **I** is of considerable value since it can resolve these environments and their *erythro* and *threo* diastereomers in model compounds and actual lignin samples.^{8,13,20}

Similar observations have been reported by Wroblewski and co-workers,^{21,22} who used this technique to

examine the functional group distributions of coal-derived materials. They discovered that 100% of the ^{31}P chemical shifts of acids, about 95% of those of phenols and approximately 90% of those of alcohols derivatized with reagent **II** were free of mutual overlap. The corresponding overlap statistics for reagent **I** were 80%, 90% and 95%, respectively.²² These observations demonstrate that reagent **II** has the potential to be an additional phosphitylation reagent that can provide well resolved structural information for lignin samples containing syringyl phenolic (2,6-dimethoxy), condensed (diphenylmethane, diaryl ether, biphenolic 5–5') and unhindered phenolic structural units. However, the ^{31}P signals for tertiary alcohols phosphitylated with **II** are located in the range of phenols.²² Despite the fact that such environments are unlikely to occur in lignins, one must be aware that such a possibility exists.

para Substitution patterns on phenols were found to influence the ^{31}P NMR chemical shifts of their 4,4,5,5-tetramethyldioxaphospholanyl derivatives in the range –0.64 to 0.70 ppm. Amongst these, the value for various typical lignin side-chain groups (including their different diastereomeric forms, i.e. models 1–3, 6, 11, 12 and 15) is close to zero.

The difference of 0.23 ppm in the ^{31}P chemical shifts obtained between models 6 and 7, i.e. 2,4,6-trisubstituted phenols (Table 2 and Fig. 2) may be due to the symmetrical nature of model 7 in which both OH groups are of identical chemical environments after phosphitylation. Such symmetry effects were also apparent in our earlier investigation.⁸ However, the ^{31}P chemical shift values of phosphitylated lignins are likely to be free of such effects owing to their irregular and rigid features.

Correlation analysis of ^{31}P chemical shifts in phenols

Linear relationships between substituent constants and ^1H and ^{19}F chemical shifts in phenols are not unusual.^{23–25} Linear or nearly linear correlations have been documented between Hammett and/or Taft substituent constants and ^{31}P chemical shifts for phosphinyl compounds, such as substituted phenylphosphonic acids,²⁶ phenylphosphonic dichlorides²⁷ and difluorides,²⁸ alkyl diphenylphosphonates,²⁹ aryl diphenylphosphinates³⁰ and $(\text{C}_6\text{H}_5)_2\text{P}^+\text{YX}$ [$\text{Y} = \text{O}^-$, $\text{N}(\text{CH}_3)_2$] compounds.³¹

The availability of a significant number of ^{31}P chemical shift data for phosphitylated phenolic compounds coupled with the availability of substituent constants allowed the following correlation analysis to be made for phenolic environments related to lignins. Despite the fact that linear relationships have been demonstrated to exist between σ_p^- and ^1H and/or ^{19}F chemical shift for various phenolic systems,⁵ in this work it was discovered that the resonance substituent constant (σ_R^0) is the one that displayed an excellent linear relationship with ^{31}P NMR chemical shift values for *para*-substituted lignin-related phenols.

Table 3 summarizes the ^{31}P NMR chemical shifts and the corresponding resonance substituent constants, obtained for substituted lignin-related phenolic model compounds phosphitylated with **II**. The plot of relative

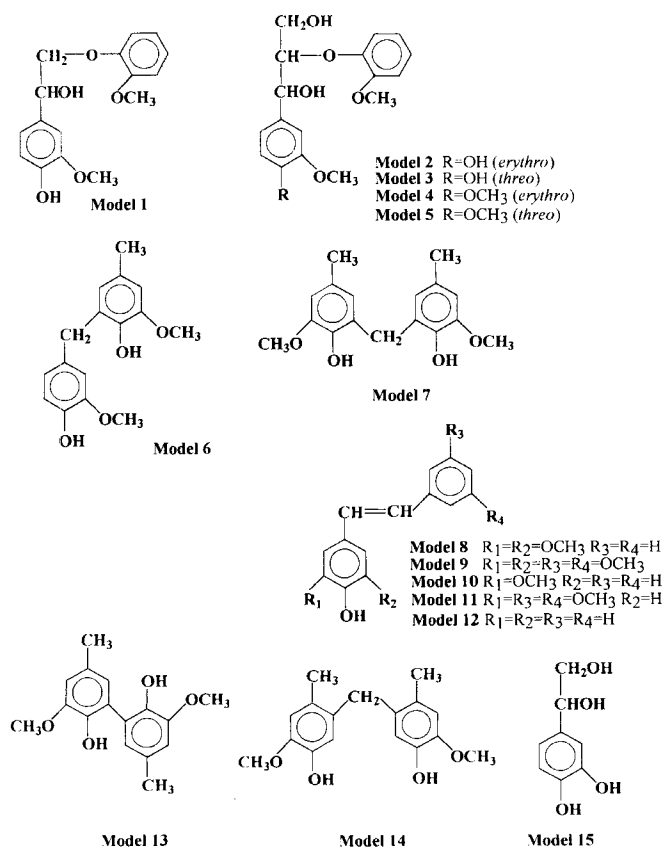


Figure 2. Structures of typical lignin-related model compounds. The numbers correspond to the compound numbers shown in Table 2.

Table 1. ^{31}P chemical shifts of alcohols and carboxylic acids phosphitylated with II

Compound		^{31}P chemical shift (ppm)
Alcohols		
1	4-Hydroxy-3-methoxybenzyl alcohol	148.40
2	Model 2	148.23(2°) ^a , 147.47(1°) ^b
3	<i>p</i> -Isopropylbenzyl alcohol	148.22
4	Model 4	148.20(2°) ^c , 147.50(1°) ^f
5	Ethanol	147.99
6	<i>L</i> -Malic acid ($\text{COOHCHOHCH}_2\text{COOH}$)	147.96
7	Model 3	147.87(2°) ^c , 147.47(1°) ^d
8	Model 5	147.80(2°) ^e , 147.50(1°) ^h
9	Model 1	147.30
10	<i>L</i> -Menthol ($\text{C}_{10}\text{H}_{18}\text{OH}$)	146.25
11	Cyclohexanol	145.15
Acids		
12	4-Hydroxy-3-methoxycinnamic acid [$\text{CH}_3\text{OC}_6\text{H}_3(\text{OH})\text{CH}=\text{CHCOOH}$]	135.15
13	Salicylic acid ($\text{HOC}_6\text{H}_4\text{COOH}$)	135.13
14	4-Hydroxy-3-methoxybenzoic acid	135.09
15	3,5-Dimethoxybenzoic acid	135.06
16	<i>L</i> -Malic acid	134.98(1°), 134.79(3°)
17	<i>o</i> -Methoxyphenyl acetic acid	134.80
18	Muconic acid ($\text{COOHCH}=\text{CHCH}=\text{CHCOOH}$)	134.78
19	Phenylsuccinic acid ($\text{COOHCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{COOH}$)	134.79, 134.69
20	(+)-3-Methyladipic acid [$\text{COOH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}_2\text{COOH}$]	134.78, 134.73
21	Acetic acid	134.63

^a $^3J_{\text{P,H}} = 9.4$ Hz.
^b $^3J_{\text{P,H}} = 9.5$ Hz.
^c $^3J_{\text{P,H}} = 9.6$ Hz.
^d $^3J_{\text{P,H}} = 9.5$ Hz.
^e $^3J_{\text{P,H}} = 9.5$ Hz.
^f $^3J_{\text{P,H}} = 9.0$ Hz.
^g $^3J_{\text{P,H}} = 9.7$ Hz.
^h $^3J_{\text{P,H}} = 9.0$ Hz.

chemical shift ($\Delta\delta$) as a function of substituent constant (σ_{R}^0) is shown in Fig. 3. The data points of this correlation are well described by a straight line whose slope is equal to -1.769 and with an intercept of -0.0843 (correlation coefficient 0.996).

This correlation suggested that the ^{31}P chemical shifts of substituted phenols phosphitylated with II may provide a means for probing the electronic effects caused by a *para* substituent on various phenols. This

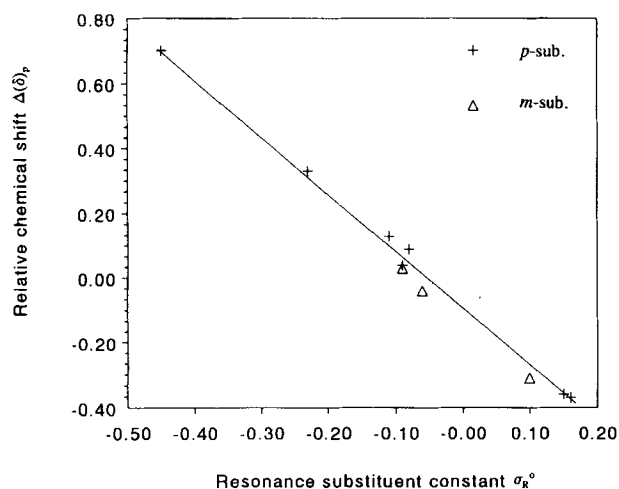


Figure 3. Relative ^{31}P chemical shifts ($\Delta\delta$) as a function of resonance substituent constants (σ_{R}^0).

led to the calculation of some new resonance substituent constants (σ_{R}^0) for substituents whose σ_{R}^0 values have not been reported to data. These constants are given in Table 4.

When the chemical shift data for phenols possessing electron-releasing *meta* substituents were correlated with the substituent constant (σ_{m}) obtained from the data set for *para*-substituted phenols (Table 3 and Fig. 3), another linear correlation (correlation coefficient 0.991) was obtained. Although a limited number of data points were available for *meta*-substituted phenols and despite the fact that the deviations apparent in Fig. 3 are associated with the electron-withdrawing *meta*-substituted phenols (i.e. *m*- NO_2 and *m*- COCH_3), this work may suggest that *meta* shifts are influenced by both the inductive and resonance effects and that *para* shifts are predominantly affected by the resonance effect.

In a study dealing with the substituent effects of fluorobenzenes on their ^{19}F chemical shifts, Taft *et al.*²⁴ considered that the *meta* shifts are predominantly affected by the inductive effect and the *para* shifts by the resonance effect. In an attempt to study the substituent effects on the ^{31}P NMR chemical shifts of phenylphosphonic acids, Mitsch *et al.*²⁶ discovered that for these chemical shifts, the inductive effect was operative for *meta* substituents whereas both inductive and resonance effects were operative for *para* substituents.

The data in Table 3 demonstrate that *ortho* substitution on the aromatic ring of phenols has a considerably

Table 2. ^{31}P chemical shifts of various phenols phosphitylated with II

No.	Compound	^{31}P chemical shift (ppm)		
		Observed	Calculated	Obs. - Calc.
1	Model 6	143.94, 139.82	143.94, 139.82	0.00
2	Model 7	143.71	143.71	0.00
3	2,6-Dimethoxyphenol	142.87	142.87	0.00
4	Model 8	142.82	142.83	-0.01
5	Model 9	142.80	142.83	-0.03
6	3-Methoxycatechol[3-OCH ₃ C ₆ H ₃ -1,2-(OH) ₂]	142.72, 138.60	142.72, 138.72	0, -0.12
7	Model 13	141.87	141.87	0.00
8	Model 14	139.80	139.80	0.00
9	2-Methoxyphenol (guaiacol)	139.78	139.78	0.00
10	4-Hydroxy-3-methoxybenzyl alcohol	139.78	139.78	0.00
11	Model 10	139.73	139.74	-0.01
12	Model 11	139.70	139.74	-0.04
13	Model 1	139.60	139.60	0.00
14	Model 3	139.55	139.60	-0.05
15	Model 2	139.49	139.60	-0.11
16	4-Hydroxy-3-methoxycinnamic acid	139.43	139.43	0.00
17	4-Hydroxy-3-methoxybenzoic acid	139.14	139.14	0.00
18	Model 15	139.00, 138.85	139.00, 139.85	0.00
19	Catechol [C ₆ H ₄ -1,2(OH) ₂]	138.92	139.03	-0.08
20	4-Methoxyphenol	138.72	138.72	0.00
21	2,5-Dimethylphenol	138.66	138.59	0.07
22	2-Nitrophenol	138.61	138.61	0.00
23	3-Hydroxyacetophenone	138.53	138.52	0.01
24	3,4-Dichlorophenol	138.40	138.40	0.00
25	4-Chlorophenol	138.35	138.35	0.00
26	4-Methylphenol	138.15	138.15	0.00
27	3,4-Dimethoxyphenol	138.29	138.41	-0.12
28	4- <i>tert</i> -Butylphenol	138.11	138.11	0.00
29	2-Chlorophenol	138.07	138.07	0.00
30	4-Ethylphenol	138.06	138.06	0.00
31	Phenol	138.02	138.02	0.00
32	3- <i>tert</i> -Butylphenol	138.02	138.02	0.00
33	2,2'-Biphenol	138.00	138.00	0.00
34	Model 12	137.98	137.98	0.00
35	3-Methylphenol	137.98	137.98	0.00
36	3,5-Di- <i>tert</i> -butylphenol	137.92	138.02	-0.10
37	3-Ethoxyphenol	137.83	137.82	0.01
38	3-Methoxyphenol	137.72	137.71	0.01
39	Salicylic acid	137.74	137.72	0.02
40	4-Nitrophenol	137.66	137.66	0.00
41	4-Hydroxyacetophenone	137.65	137.65	0.00

greater effect on the magnitude of the ^{31}P NMR chemical shifts than that of *para* and/or *meta* substitution patterns. Hence it was of interest to correlate the ^{31}P NMR chemical shift values with the substituent constants for

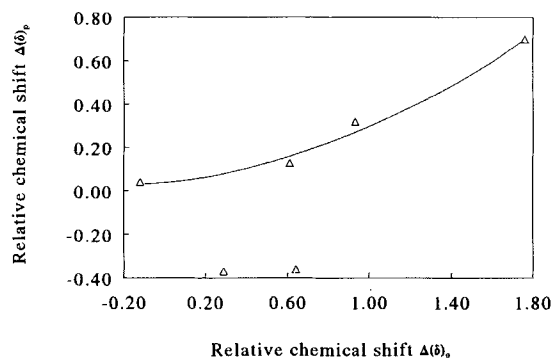


Figure 4. Relative ^{31}P chemical shifts of *para*-substituted phenols as a function of those obtained for the corresponding *ortho*-substituted phenols.

ortho-substituted lignin-related phenols. Despite the fact that for *ortho*-substituted phenols no linear relationship was apparent between the Hammett or Taft substituent constants and the corresponding ^{31}P NMR chemical shift data, a plot of $\Delta(\delta)_p$ versus $\Delta(\delta)_o$ for some *ortho*-substituted phenols resulted in the curve in Fig. 4. The deviation from linearity is in the direction of large $\Delta(\delta)_o$ values. Similar results were reported by Traynham and Knesel²³ and Thomas and Traynham³⁵ in an attempt to correlate the relative proton chemical shifts of the hydroxyl groups in *para*-substituted phenols with those of the corresponding *ortho*-substituted phenols. In accord with our results, extreme deviations for the cases of *o*-NO₂ and *o*-COCH₃ substituents were apparent.²³

Calculation of the ^{31}P chemical shifts of phenols after phosphitylation with II

The successful correlation analyses illustrated so far demonstrated the potential of using such an approach

Table 3. ^{31}P chemical shift data for a variety of substituted phenols after phosphitylation with II and the corresponding substituent constants

No.	Substituent	Relative chemical shift, $\Delta\delta^a$ (ppm)	Substituent constants, σ_R^b or σ_m^c
1	<i>p</i> -COMe	-0.37	0.16
2	<i>p</i> -NO ₂	-0.36	0.15
3	<i>p</i> -Et	0.04	-0.09 ³⁴
4	<i>p</i> - <i>t</i> -Bu	0.09	-0.08 ³⁴
5	<i>p</i> -CH ₃	0.13	-0.11
6	<i>p</i> -Cl	0.33	-0.23
7	<i>p</i> -OMe	0.70	-0.61
8	<i>p</i> -OH	0.32	— ^e
9	<i>m</i> - <i>t</i> -Bu	0.03	-0.09 ³⁴ (-0.07) ^d
10	<i>m</i> -Me	-0.04	-0.06 (-0.05)
11	<i>m</i> -OMe	-0.31	0.10 (0.27)
12	<i>m</i> -COMe	0.50	0.36 (0.20)
13	<i>m</i> -NO ₂	0.59	0.71 (0.65)
14	<i>m</i> -OH	-0.26	— ^e
15	<i>o</i> -Phenol	-0.02	
16	<i>o</i> -Et	-0.12	
17	<i>o</i> -COMe	0.29	
18	<i>o</i> -CH ₃	0.61	
19	<i>o</i> -NO ₂	0.64	
20	<i>o</i> -OH	0.93	
21	<i>o</i> -OMe	1.76	

^a Obtained by subtracting the ^{31}P chemical shift value of the examined phosphitylated compound from that of phosphitylated phenol.

^b For *para* substituent (from Ref. 32).

^c For *meta* substituent (from Ref. 33).

^d Numbers in parentheses are σ_1 (from Ref. 33).

^e Not available.

toward calculating the ^{31}P NMR chemical shifts of various phenolic environments for a variety of substitution patterns as they may be present in lignins. The following account describes our efforts to specify the various parameters that will allow such detailed calculations to be made. This effort allowed the development of a set of empirical parameters that permits the accurate prediction of ^{31}P chemical shifts of lignin-related phenolic environments phosphitylated with 2-chloro-4,4,5,5-tetramethyldioxaphospholane. These parameters are given in Tables 5 and 6.

Table 5 lists the parameters that can be used for the calculation of the substitution on the ^{31}P chemical shift of phenol, derivatized with reagent II. These parameters were obtained directly from the data in Table 2, although they can also be calculated from the corre-

Table 5. Parameters for the calculation of the substitution effect on the ^{31}P chemical shift of phenolic hydroxyls phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

Substituent	<i>ortho</i>	<i>meta</i>	<i>para</i>
OH ^a	1.01	-0.26	0.32
OCH ₃	1.76	-0.31	0.70
OC ₂ H ₅	—	-0.20	0.44
CH ₃	0.61	-0.04	0.13
C ₂ H ₅	-0.12	—	0.04
<i>t</i> -Bu	—	0.00	0.09
CH ₂ OH ^a	—	—	-0.02
CHOHCH ₂ OH ^a	—	—	-0.11
CHOHCH ₂ OPh ^a	—	—	-0.18
CH ₂ Ph	—	-0.11	0.04
CH=CHPh	—	—	-0.04
CH=CHCOOH ^a	—	—	-0.35
Phenol ^a	-0.02	—	—
COOH ^a	-0.30	—	-0.64
COCH ₃	0.29	0.50	-0.37
Cl	—	0.05	0.33
NO ₂	0.64	0.59	-0.36

^a The OH groups in these substituents were all phosphitylated with reagent II.

lation equation shown in Table 4 and the Taft substituent constants (σ_R^0), when available. These parameters are valid only for phenols which do not possess substituents at both *ortho* positions. For such a case the parameters listed in Table 6 may be used, i.e. the effect of a variety of second *ortho* substituents on the ^{31}P chemical shift of guaiacolic hydroxyls (2-methoxyphenol) derivatized with reagent II may be calculated. For example, for model 6 (Fig. 2), which contains two kinds of phenolic environments, the following calculation may apply. The ^{31}P NMR chemical shift of the 2,4-disubstituted phenolic environment will be equal to 138.02 (value for phenol) + 1.76 (value for *o*-OCH₃ substituent from Table 5) + 0.04 (value for *p*-CH₂Ph substituent from Table 5). The ^{31}P NMR chemical shift of the phenolic environment with two *ortho* substituents will be equal to 138.02 (value for phenol) + 1.76 (value for *o*-OCH₃ substituent from Table 5) + 0.13 (value for *p*-CH₃ substituent from Table 5) + 4.03 [value for the second *ortho* substituent of 4-hydroxy-3-methoxybenzyl [$-\text{CH}_2(4\text{-OH})(3\text{-OCH}_3)$] from Table 6].

Such calculations were carried out for all phenolic model compounds examined in this work and the results are given in Table 2. The calculated ^{31}P NMR chemical shifts are in excellent agreement with the observed values within an error margin of about ± 0.12 ppm. These results indicate that the ^{31}P NMR chemical shifts of phenolic hydroxyls for various lignin-related phenols depend strongly on the nature of the substituent and their substitution patterns. Further, these substituent effects seem to obey the additivity principle.^{1,36}

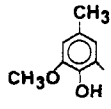
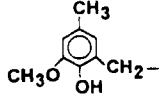
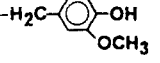
Although the parameters described in Tables 5 and 6 allow the prediction of the ^{31}P chemical shifts for various lignin-related phenolic environments with reasonable accuracy, our conclusions are based on a relatively limited amount of experimental data. This work has laid the foundations for similar future efforts that

Table 4. New σ_R^0 constants derived from the data in Table 2 and the equation $\Delta\delta = -1.769\sigma_R^0 - 0.0843$

Substituent	σ_R^0
<i>p</i> -CH=CHC ₆ H ₅	-0.03
<i>p</i> -CH=CH(3,5-OCH ₃) ₂ C ₆ H ₃	0.00
<i>p</i> -CHOHCH ₂ OH	0.01
<i>p</i> -CHOHCH ₂ O(2-OCH ₃)C ₆ H ₄	0.05
<i>p</i> -CHOHC(CH ₂ OH)(H)O(2-OCH ₃)C ₆ H ₄ (<i>erythro</i>)	0.08
<i>p</i> -CHOHC(CH ₂ OH)(H)O(2-OCH ₃)C ₆ H ₄ (<i>threo</i>)	0.11

^a The OH groups in these substituents were all phosphitylated with reagent (II).

Table 6. Substituent effects of a second *ortho* substituent on the ^{31}P chemical shift of guaiacol (2-methoxyphenol) phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

Substituent ^a	Effect
OH	2.94
CH ₃	3.18
OCH ₃	3.09
	1.96
	3.80
	4.03
CH ₂ N(CH ₂) ₅	4.55

^a The OH groups in these substituents were all phosphitylated with reagent II.

are needed to obtain other parameters aimed at exploring more structural features in lignins.

CONCLUSIONS

2-Chloro-4,4,5,5-tetramethyldioxaphospholane is another useful phosphitylating reagent for the quantitative ^{31}P NMR analysis of lignins and related compounds. It permits the excellent resolution of the various hydroxylic environments, especially those belonging to lignin-related phenolic hydroxyls. The ^{31}P chemical shifts of phenolic hydroxyls with various sub-

stitution patterns depend strongly on the nature of the substituents and can be calculated using the parameters developed herein.

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REFERENCES

1. L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York (1940).
2. O. Exner, in *Advances in Linear Free Energy Relationships*, edited by N. B. Chapman and J. Shorter. Plenum Press, London (1972).
3. J. Shorter, *Correlation Analysis in Organic Chemistry*. Clarendon Press, Oxford (1973).
4. M. T. Tribble, in *Advances in Linear Free Energy Relationships*, edited by N. B. Chapman and J. Shorter. Plenum Press, London (1972).
5. N. B. Chapman and J. Shorter, *Correlation Analysis in Chemistry: Recent Advances*. Plenum Press, London (1978).
6. D. G. Gorenstein, in *Phosphorus-31 NMR, Principles and Applications*, edited by D. G. Gorenstein. Academic Press, London (1984).
7. D. G. Gorenstein, *Prog. Nucl. Magn. Reson. Spectrosc.* **16**, 1 (1983).
8. Y. Archipov, D. S. Argyropoulos, H. I. Bolker and C. Heitner, *J. Wood Chem. Technol.* **11**, 137 (1991).
9. Y. Archipov, D. S. Argyropoulos, H. I. Bolker and C. Heitner, *Carbohydr. Res.* **220**, 49 (1991).
10. D. S. Argyropoulos, Y. Archipov, H. I. Bolker and C. Heitner, *Holzforschung* **47**, 50 (1993).
11. M. Mazúr and D. S. Argyropoulos, *Cellulose Chem. Technol.* in press.
12. D. S. Argyropoulos, H. I. Bolker, C. Heitner and Y. Archipov, *J. Wood Chem. Technol.* **13**, 187 (1993).
13. D. S. Argyropoulos, *J. Wood Chem. Technol.* **14**, 45 (1994).
14. D. S. Argyropoulos, *J. Wood Chem. Technol.* **14**, 65 (1994).
15. A. Zwierzak, *Can. J. Chem.* **45**, 2501 (1967).
16. H. L. Chum, D. K. Johnson, P. D. Palasz, C. Z. Smith and J. H. P. Utley, *Macromolecules* **20**, 2698 (1987).
17. J. M. Harkin, in *Lignin Structure and Reactions*, edited by R. F. Gould. American Chemical Society, Washington, DC, pp. 65–74, (1966).
18. K. Kratzl and F. W. Vierhopper, *Monatshe. Chem.* **102**, 425 (1971).
19. J. Gierer and N. Nilvebrant, *J. Wood Chem. Technol.* **11**, 171 (1991).
20. Z. H. Jiang and D. S. Argyropoulos, *J. Pulp Paper Sci.* **20**, J183 (1994).
21. A. E. Wroblewski, R. Markuszewski and J. G. Verkade, *Am. Chem. Soc. Div. of Fuel Chem. Prepr.* **32**, 202 (1987).
22. A. E. Wroblewski, C. Lensink, R. Markuszewski and J. G. Verkade, *Energy Fuels* **2**, 765 (1988).
23. J. G. Traynham and G. L. Knesel, *J. Org. Chem.* **31**, 3350 (1966).
24. R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen and G. T. Davis, *J. Am. Chem. Soc.* **85**, 709, 3146 (1963).
25. L. A. Cohen and W. M. Hones, *J. Am. Chem. Soc.* **85**, 3402 (1963).
26. C. C. Mitsch, L. D. Freedman and C. G. Moreland, *Org. Magn. Reson* **3**, 446 (1970).
27. L. Maier, *Phosphorus* **4**, 41 (1974).

28. L. L. Szafraniec, *Org. Magn. Reson.* **6**, 565 (1974).
29. P. A. Manninen, *Acta Chem. Scand., Ser. B* **35**, 2 (1981).
30. S. Hoz, E. J. Dunn, E. Buncl, R. A. B. Bannard and J. G. Purdon, *Phosphorus Sulfur* **24**, 321 (1985).
31. A. Schmidpeter and H. Brecht *Z. Naturforsch., Teil B* **23**, 1529 (1968).
32. T. H. Lowry, *Mechanism and Theory in Organic Chemistry*, p. 157. Harper and Row, New York (1987).
33. J. March, *Advanced Organic Chemistry*, pp. 2143–247. Wiley, New York (1985).
34. O. Exner, in *Advances in Linear Free Energy Relationships*, edited by N. B. Chapman and J. Shorter, pp. 37–38. Plenum Press, London (1972).
35. M. Thomas and J. G. Traynham, *J. Am. Chem. Soc.* **91**, 379 (1969).
36. L. A. Cohen and W. M. Hones, *J. Am. Chem. Soc.* **85**, 3397 (1963).