Semiquantitative Determination of Quinonoid Structures in Isolated Lignins by ^{31}P Nuclear Magnetic Resonance

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A semiquantitative analytical method has been developed for the determination of the total quinonoid content (*o*-benzoquinones and *p*-benzoquinones) of soluble lignins. The method is based on detailed measurements and observations made with model *o*- and *p*-quinones, which in dry organic solvents were shown to form adducts with trimethyl phosphite in quantitative yield. These adducts gave ^{31}P NMR signals for *o*- and *p*-quinones at around −46 and −2 ppm, respectively. In the presence of moisture and lignin the adducts from *o*-quinones were shown to be hydrolyzed to the open ring product, dimethylphenyl phosphate (−2 ppm), at an overall yield of ∼70%. Similarly, the hydrolysis yields of *p*-quinone adducts with trimethyl phosphite were ∼70%. Consequently, a number of important issues in relation to the use of trimethyl phosphite toward the quantitative analysis of quinonoid groups in lignins have been investigated, which permitted the development of an experimental semiquantitative protocol recommended for spectral acquisition.

Keywords: *Adducts; analysis; determination; lignins; nuclear magnetic resonance (NMR); phosphorus; quinones; spectroscopy*

INTRODUCTION

The color of paper has been an issue of major concern in many research endeavors including those of the pulping of wood, the bleaching of pulp, and the yellowing of paper. Chromophoric lignin structures have long been considered responsible for causing most of the color in pulp and paper products. Despite numerous research efforts, the state of our knowledge about the origin of color in different wood pulps is still relatively limited. Among the possible chromophoric structures suggested, quinonoids are by far the most mentioned (Pew and Connors, 1971; Leary, 1967; Imsgard et al., 1971). Therefore, the detection and quantification of quinonoids in pulp and soluble lignins is of considerable significance from both a theoretical and a practical point of view.

The formation of quinonoid structures in lignin during photoyellowing has been qualitatively verified by model compound (Zhang and Gellerstedt, 1994b), UV−visible (Zhang and Gellerstedt, 1994a), fluorescence (Zhu et al., 1995; Konya and Scaiano, 1994), and ^{31}P NMR studies (Lebo et al., 1990; Argyropoulos et al., 1992, 1995; Argyropoulos and Heitner, 1994). Imsgard et al. (1971) developed a colorimetric method, in which *o*-quinones were reduced to the corresponding catechols followed by analysis of the intensely colored, catechol−ferric complexes in a DMSO/cellosolve mixture. About 0.7 mol/100 lignin C_9 units of *o*-quinonoids was thus estimated to be present in spruce milled wood lignin. An important limitation of this technique, however, is the fact that *p*-quinonoid chromophores cannot be detected. Furthermore, the steps of quantitative reduction and recovery of the reduced lignin samples are relatively cumbersome. Zakis et al. (1987) have developed a method for determining such functional groups in soluble lignins based on the ability of quinones to oxidize hydrazine and release a stoichiometric amount of nitrogen. The number of quinone groups present in a sample of Björkman spruce lignin was thus determined to be 0.26 wt % or 0.8/100 lignin C_9 units. *o*-Quinone detection has become possible for solid pulp samples (Lebo et al., 1990; Argyropoulos et al., 1992, 1995; Argyropoulos and Heitner, 1994) by oxyphosphorylation followed by elemental analysis of the phosphorus content of the treated pulps. This gave an *o*-quinone estimation of 0.7/100 C_9 units for black spruce mechanical pulp (Argyropoulos and Heitner, 1994) in agreement with those of Imsgard et al. (1971) and Zakis et al. (1987). Phosphorus elemental analysis on freshly oxyphosphorylated pulp samples, however, requires tedious sample preparation, which introduces significant complications.

The present work attempts to introduce a convenient semiquantitative analytical method for the detection of both *o*- and *p*-quinones in soluble lignins based on quantitative ^{31}P NMR. More specifically, this work examines the potential of trimethyl phosphite toward being a derivatizing reagent that can provide quantitative information on quinonoid groups in soluble lignins. Initially, we examined various salient features of the reactions of *o*- and *p*- quinones with trimethyl phosphite to fully comprehend the suitability of the proposed derivatization system toward the quantitative analysis of quinones. We then turned our attention to the stability of the adducts, internal standard, and spin−lattice relaxation considerations for model compounds and lignins oxyphosphorylated with trimethyl phosphite to arrive at a set of recommended spectral acquisition conditions. Finally, we applied this technique to the quantitative analysis of quinones in various lignins and discuss the results in light of the actual lignin sample and the method of preparation.

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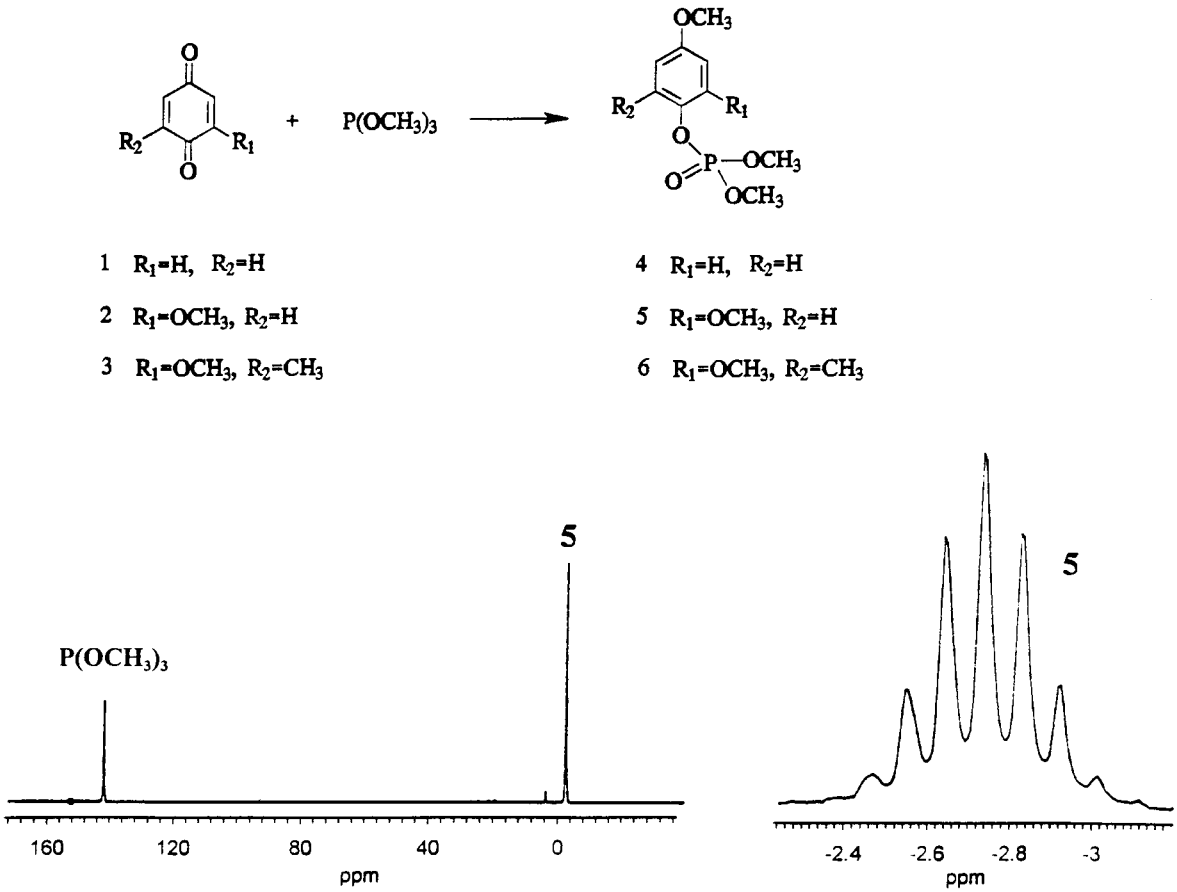


1 R_1=H, R_2=H
2 R_1=OCH_3, R_2=H
3 R_1=OCH_3, R_2=CH_3
4 R_1=H, R_2=H
5 R_1=OCH_3, R_2=H
6 R_1=OCH_3, R_2=CH_3

Figure 1. Reaction of *p*-benzoquinones with trimethyl phosphite and ^{31}P NMR spectra of compound **5**. Its proton-coupled spectrum gives seven lines (right).

EXPERIMENTAL PROCEDURES

Compounds **1** and **9** are commercially available (Aldrich Chemical Co.); all other quinone models were prepared in a previous effort (Zhang and Gellerstedt, 1994).

Model Compound Studies. *Internal Standard Solution.* Triphenyl phosphate (327.6 mg) and chromium acetylacetonate (27.7 mg) were dissolved in dry dioxane, and the volume of the solution was adjusted to 5 mL.

Reactions of Model Compounds with Trimethyl Phosphite. Approximately 20 μmol of a quinone model compound was dissolved in the selected solvent [chloroform-*d* ($CDCl_3$), dioxane, dimethylformamide (DFM)], alone or together with 50 mg of dioxane lignin in a 2 mL vial. Trimethyl phosphite (50 μL) was added to the vial, and the solution was stirred in the dark at room temperature overnight. Internal standard solution (100 μL) was then added to the vial. The whole mixture was finally transferred to a 5 mm NMR tube together with 60 μL of deuterated acetone for the purpose of providing the deuterium lock.

Lignin Isolation and Reactions. Milled wood lignin was prepared in accordance with the method of Bjorkman (1956). Kraft lignin was isolated form spent liquor in accordance with previously published procedures (Jiang and Argyropoulos, 1994), whereas the treatment of the kraft lignin with dimethyldioxirane was carried out in accordance with the procedure described by Sun and Argyropoulos (1996). Finally, the oxygen treatment of the kraft pulp and the isolation of the lignin was carried out in accordance with the earlier effort described by Sun and Argyropoulos (1995).

Lignin Quinone Analyses. *Internal Standard Solution.* Triphenyl phosphate (41.6 mg) and chromium acetylacetonate (54.4 mg) were weighed in a dry 10 mL volumetric flask and were dissolved with DMF to the mark. The sharp signal of triphenyl phosphate at −16.13 ppm was thus used for accurate quantification.

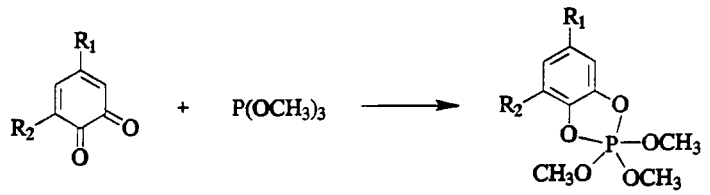
Reaction of Lignin Samples with Trimethyl Phosphite. Prior to analysis, all lignin samples were thoroughly dried in a vacuum oven set at room temperature for at least 48 h and then stored in a vacuum desiccator over Dryrite. Samples of lignin (50 mg) were accurately weighed in a dry 2 mL volumetric flask. The sample was then dissolved with ~0.8 mL of DMF, 50 μL of trimethyl phosphite was then added, and the mixture was capped and stirred in the dark for 24 h at room temperature. Internal standard solution (100 μL containing $\sim 1.3 \times 10^{-3}$ mmol of triphenyl phosphate) was finally added prior to dilution of the mixture to the mark with DMF.

^{31}P NMR Spectroscopy. ^{31}P NMR spectra were obtained on a Varian XL300 Fourier transform (FT-NMR) spectrometer, oprerating at a frequency of 121.5 MHZ. All chemical shifts are relative to 85% phosphoric acid, which was used as external standard. Quantitative spectra were acquired using a flip angle of 45°, a pulse delay of 15 s, gated decoupling, and a spectral window of 100 ppm (30 to −70 ppm).

RESULTS AND DISCUSSION

Chemical Reactions between Benzoquinones and Trimethyl Phosphite. Trimethyl phosphite is known to react under ambient conditions with both *o*- and *p*-quinones (Sun and Argyropoulos, 1995). *p*-Quinones in the presence of trimethyl phosphite are known to yield dimethylphenyl phosphates (Duthaler et al., 1984), which are quite stable and can readily be followed with ^{31}P NMR.

In an effort to further understand these reactions and to realize their quantitation potential, we used quantitative ^{31}P NMR in the presence of an internal standard (triphenyl phosphate). It was thus found that the various *p*-benzoquinones (Figure 1) formed the respec-



7 R_1=CH_3, R_2=H

8 R_1=CH_3, R_2=OCH_3

9 R_1=R_2= *t*-butyl

10 R_1=CH_3, R_2=H

11 R_1=CH_3, R_2=OCH_3

12 R_1=R_2= *t*-butyl

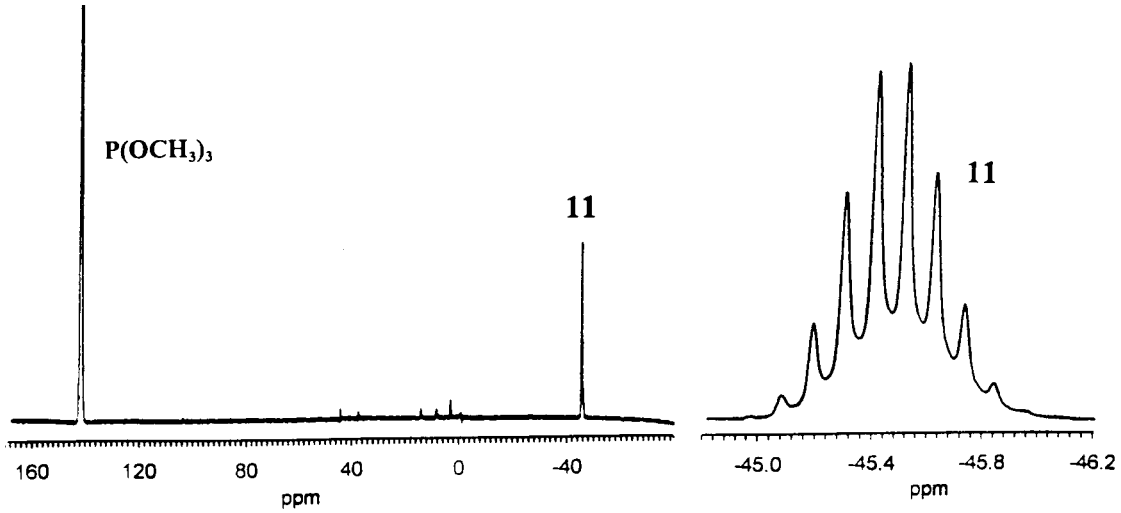


Figure 2. Reactions of *o*-benzoquinones with trimethyl phosphite and ^{31}P NMR spectra of compound **11**. Its proton-coupled spectrum gives eight well-resolved and two very weak lines (right).

tive dimethyl phosphates in quantitative yield at room temperature. These adducts give ^{31}P NMR signals between −2 and −3 ppm, (Figure 1), which allow the quantification of the starting quinones by signal integration. When their ^{31}P NMR spectra are recorded with proton coupling, the seven signals in the spectrum can clearly be seen (J = 12 Hz), indicating that there are two methoxy groups bonded to the central phosphorus atom.

However, the reactions of *o*-benzoquinones with trimethyl phosphite are more complicated. A number of reports have shown the first step in the reaction of an *o*-quinone and trimethyl phosphite is the formation of a pentoxyphosphorane, which gives ^{31}P NMR signals at ∼ −46 ppm. In fact, Ramirez (1964) has obtained several such phosphoranes in crystalline form which were stable in the absence of moisture and air. This was confirmed in our work because trimethyl phosphite on reaction with the *o*-benzoquinones of Figure 2 gave the expected cyclic oxyphosphorane adducts within minutes at room temperature. These adducts were found to be stable in chloroform solutions for several weeks. For example, pure **11** was obtained by mixing **8** with trimethyl phosphite in chloroform followed by solvent evaporation. The proton-coupled ^{31}P NMR spectrum of the pentoxyphosphorane shows 10 lines, among which only 8 can clearly be observed to have a coupling constant of 12.7 Hz, in accordance with the structure of the cyclic pentoxyphosphorane as obtained by Ramirez (1964).

In accordance with previous suggestions (Sun and Argyropoulos, 1994), cyclic pentoxyphosphoranes were found to be very sensitive to traces of water, usually present in pulp and/or lignin samples. All samples of *o*-quinone model compounds when treated with trimethyl phosphite in the presence of solvents containing low levels of water or lignin showed the formation of the cyclic oxyphosphorane as evidenced by the signal at −46 ppm, which, however, quickly disappeared with the simultaneous formation of a new signal at ∼ −2 ppm (Figure 3). Konya and Scaiano (1994) have reported that the conversion of the signal from −46 to −2 ppm can be accomplished by adding acid. The proton-coupled ^{31}P NMR spectrum of the newly formed signal was found to be split into seven lines with a coupling constant of 11.5 Hz, indicating that two methoxy groups were still bonded to the phosphorus atom while the third methoxy group was cleaved during the conversion. On the basis of these observations, one may assume that dimethylphenyl phosphate is formed during the conversion. This is also supported by the work of Kirillova and Kukhtin (1962), who have observed the formation of dialkyl phosphate esters as the predominant products of water addition to similar cyclic pentaoxyphosphoranes.

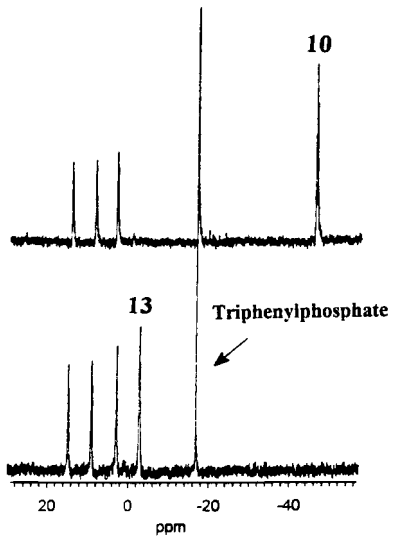


Figure 3. ^{31}P NMR spectra demonstrating the conversion of the cyclic pentoxyphosphorane **10** to dimethylphenyl phosphate **13**. The signals at 3, 9, and 15 ppm arise from the degradation of trimethyl phosphite.

Previous efforts (Lebo et al., 1990) have shown that in the presence of water, pentoxyphosphoranes are quantitatively converted to cyclic phosphate esters of the type depicted by **16** (δ at 11.1; Lebo et al., 1990). However, the proposed cyclic phosphate esters have only one methoxy group bonded to the phosphorus atom, which should show a characteristic quartet. Such a signal was indeed detected at 13.9 ppm, in trace amounts, when **12** was converted to **15** by the addition of water (Figure 4). However, pentoxyphosphoranes **10** and **11** did not give rise to any such signals when treated with water under the conditions used in this effort. In contrast, the formation of dimethyphenyl phosphates (**13**−**15**) was continuously observed as the predominant products of this work, in agreement with the accounts of Kirillova and Kukhtin (1962). The latter group studied the formation of a similar cyclic phosphate by hydrolysis of its pentoxyphosphorane precursor. Low temperatures (0 °C) were essential for isolating the cyclic phosphate at a maximum of 30% yield, whereas the open ring dimethylphenyl phosphate (−2 ppm) was always the predominant product at a yield of >70%.

The products of hydrolysis of pentoxyphosphoranes **10**−**12** can give two sets of isomers as shown in Figure 4. However, we found that **12** gave only one isomer of **15** with a clean characteristic septet in its proton-coupled ^{31}P spectrum (Figure 4). This may be due to the steric effect of the neighboring *tert*-butyl group, which favors the formation of only one of the isomers. Compound **11**, on the other hand, after hydrolysis gave the two isomers of **14**, which displayed two well-resolved ^{31}P signals at −1.37 and − 2.33 ppm, respectively. The ^{31}P NMR signals of the two isomers from compound **13** could not be resolved.

Trimethyl phosphite was also found to slowly react with air and moisture, giving three characteristic signals at 3, 9, and 15 ppm, respectively (see Figures 3 and 4). Such impurities cannot be avoided because they spontaneously form within trimethyl phosphite. These signals did not cause significant interference during our model compound study. They are, however, of greater concern when lignin samples are examined. This is because the quinonoid content of most lignin samples is extremely low and the reaction between lignin and trimethyl phosphite requires at least 24 h. During this period a very large signal (compared to the quinonoid adducts) caused by these byproducts can be formed. The large intensity of this signal causes proper phasing and integration a rather cumbersome task. The signal at 3 ppm was due to trimethyl phosphate, which is an oxidation product of trimethyl phosphite by air. In fact, this is the signal that causes the major interference to integration and phasing due to its proximity to the signals derived from quinones (−1 to −3 ppm). The formation of trimethyl phosphate may be minimized by excluding the air in the system or by carrying out the reaction at lower temperatures. Such effects are to be examined in our future efforts. The identities of the other two signals at 9 and 15 ppm have not been determined, although their proton-coupled ^{31}P NMR spectra were both composed of seven lines (Figure 4), indicating that there are two methoxy groups bonded to the central phosphorus atoms in these structures.

Table 1. ^{31}P NMR Chemical Shift and Yield Data for a Variety of Model Quinones Reacted with Trimethyl Phosphite

	in high-purity $CDCl_3$			in DMF in the presence of dioxane lignin		
starting compd	product	δ	yield %	product	^{31}P NMR δ	yield %
1	**4**	−2.74	86.6	**4**	−2.32	52.5
2	**5**	−2.33	84.8	**5**	−1.90	64.6
3	**6**	−2.35	96.8	**6**	−1.92	73.8
7	**10**	−46.08	92.0	**13**	−2.16	68.7
8	**11**	−45.42	90.0	**14**	−2.33 −1.37	63.8
9	**12**	−46.45	97.5	**15**	−1.78	78.3

Factors That Influence the Quantitation of Quinones. *Reaction Yields.* Table 1 shows the ^{31}P NMR chemical shift and yield data for a variety of model quinones reacted with trimethyl phosphite. When the reaction was carried out in high-purity $CDCl_3$, the yields were in the range of 85−97%. However, when the same reactions were carried out in DMF in the presence of dioxane lignin (50 mg), the yields of the expected dimethylphenyl phosphates **4**, **5**, and **6** from *p*-quinones **1**, **2**, and **3** decreased to the range of 52−74%. Because model quinone **3** is of the structure most likely to be present in lignin, one may assume that lignin *p*-quinones will yield **6** at ∼70%. (The low yield may be entirely due to hydrolysis arising from H_2O in DMF and not from lignin itself.)

In accordance with the preceding discussion, *o*-quinones **7**, **8**, and **9** initially formed the cyclic pentoxyphosphoranes **10**, **11**, and **12**, displaying signals between −45.42 and −46.45 ppm. These were rapidly converted to dimethylphenyl phosphates **13**, **14**, and **15** when the oxyphosphorylation was carried out in DMF in the presence of dioxane lignin at an average overall yield of ∼70%.

On the basis of the overall preceding discussion and the data of Table 1, one may assume that quinones in lignin will react with trimethyl phosphite to give ^{31}P NMR signals in the range −1.0 to −3.0 ppm at a yield of ∼70%.

Relaxation Time Considerations. Our efforts to establish a quantitative analytical method necessitated the need to measure the spin−lattice relaxation times (T_1) of the ^{31}P NMR signals that are to be eventually

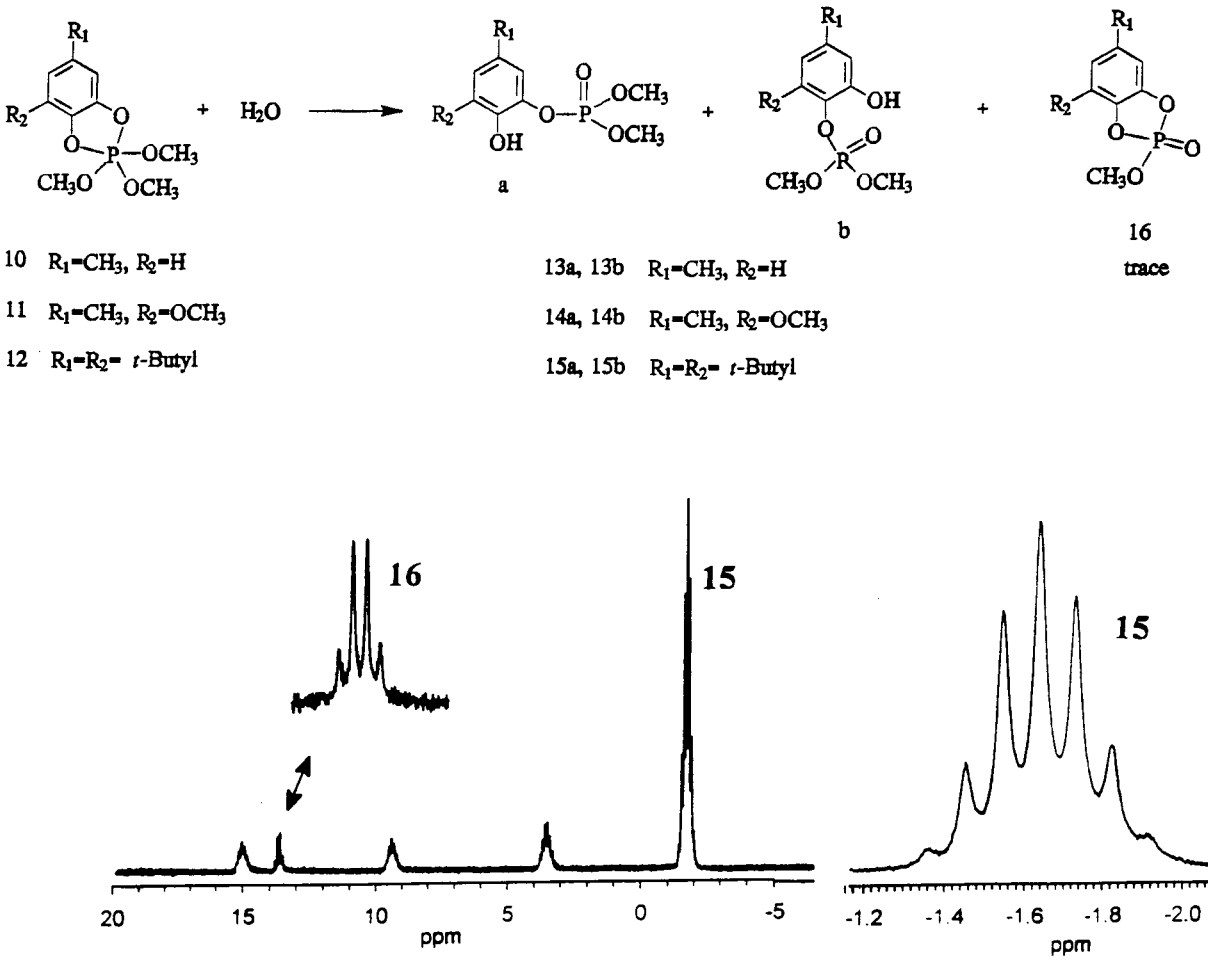


Figure 4. Formation of dimethylphenyl phosphates by hydrolysis of pentoxyphosphoranes and the ^{31}P NMR spectra showing trace amounts of cyclic phosphate ester **16** derived from **12**.

Table 2. ^{31}P Spin−Lattice Relaxation Time (T_1) Values for Adducts of Quinones and Trimethyl Phosphite in the Presence and Absence of Chromium Acetylacetonate

	spin−lattice relaxation time (T_1) (s)	
structure	in the absence of Cr(acac)$_3$	in the presence of Cr(acac)$_3$
5	2.7	1.5
10	6.5	3.0
13	2.9	1.6
triphenyl phosphate	4.2	2.1

integrated. This is because to obtain accurate signal areas under Fourier transform NMR conditions, sufficient delay time between pulses should be used. In our earlier work (Argyropoulos et al., 1993), the phosphorus-31 spin−lattice relaxation times for a variety of model tricoordinated phoshites were determined and found to range between 5 and 10 s. However, we had no relaxation information for pentacoordinated phosphorus compounds similar to those examined in this work. As such, the spin−lattice relaxation times for selected model quinones derivatized with trimethyl phosphite and that of the internal standard (triphenyl phosphate) were measured. As shown in Table 2, the T_1 of such systems may vary between 3 and 7s. Such high T_1 values are not unusual in ^{31}P NMR spectroscopy (Dale and Hobbs, 1971). Therefore, a delay time of at least 40 s needs to be applied between pulses if quantitative claims are to be made from the obtained spectra. Under conditions of relatively low quinone concentrations, such acquisition protocols will be unacceptable. Kasler and Tierney (1978) have demonstrated that quantitative ^{31}P NMR spectra of organic compounds may be obtained in the presence of a compound bearing a paramagnetic metal center [chromium(III) acetylacetonate; Cr(acac)$_3$], and this approach has successfully been applied in our earlier lignin work (Argyropoulos, 1994; Granata and Argyropoulos, 1995).

The resulting relaxation data in the presence of Cr^{3+} for the model compounds of this work are also shown in Table 2. All T_1 values are seen to significantly decrease, thus reducing the time needed for quantitative measurements. The cyclic pentoxyphospholane (**10**) was found to have the longest T_1. However, it is the final products, dimethylphenyl phosphates (**5** and **13**), that are to be analyzed for quantification. Both of these compounds were found to have shorter T_1 values than that of the internal standard, triphenyl phosphate. In the presence of Cr^{3+} triphenyl phosphate showed a T_1 of 2.1 s. Therefore, a relaxation delay of 15 s was selected for quantification purposes. This should be sufficiently long, considering the fact that quinones in lignin are bound on a polymer which moves more slowly and therefore is of shorter T_1 than those of the examined model compounds. Furthermore, a pulse flip angle of 45° would further ensure that conditions of complete relaxation are met prior to the next pulse.

Quantification of Quinones in Lignin. The experimental conditions employed for the quantification of quinones in lignin were chosen according to the data

Table 3. Total Quinone Content of Different Lignin Samples Measured in This Work

lignin sample	quinone content (mmol/g)
black spruce MWL	0.020
softwood solubilized kraft lignin	0.029
indulin (commercial kraft lignin)	0.023
dimethyldioxirane-treated hardwood residual kraft lignin	0.24
oxygen-treated kraft lignin	0.055

and the emerging discussion that has already been made. Because both *o*-and *p*-benzoquinones give signals at the same chemical shift region (~ -2 ppm), this method can provide information only on the total amount of quinones in lignin, possibly with some qualitative conclusions in relation to the relative contributions of each.

The weight of the lignin sample should be at least 50−70 mg because the quinone content in lignin is usually rather low. DMF was chosen as the solvent because it can easily dissolve such amounts of lignin in 1−2 mL. The DMF used in this work had a water content of 0.5%. Therefore, the pentoxyphosphoranes, which were derived from *o*-quinones, were immediately converted to dimethyl phosphate esters. In our model compound study, it was observed that the reactions between quinones and trimethyl phosphite were complete mostly within minutes, or hours in some cases. An overnight reaction period is thus sufficiently long for lignin samples. No yield increases were observed by extending the reaction period to 2 days or even a week. The quinone content of a given lignin sample can be calculated by taking into account that the yield of the reactions between trimethyl phosphite and quinones is 70%:

$$Q = \frac{1000}{50} \times 0.001275 \times \frac{A_1}{A_0} \times \frac{100}{70} = 0.0364 \times \frac{A_1}{A_0}\,(\text{mmol/g})$$

where A_0 is the area integration for signal from quinones at -1 to -3 ppm and A_1 is the area integration for the internal standard.

A number of lignin samples were analyzed for their quinone content using the procedure developed in this work. The accumulated data are given in Table 3. Assuming that the repeat unit in milled wood lignin (MWL) has a molecular weight of 194, the quinone content of black spruce MWL obtained in this work (0.02 mmol/g) is equal to 0.4/100 C_9 units, which is somewhat lower than the results obtained in other previous studies (Imsgard et al., 1971; Argyropoulos and Heitner, 1994). Furthermore, oxygen delignification was found to increase the quinone content within kraft lignin, possibly via demethylation reactions as recently demonstrated by Asgari and Argyropoulos (1997). Finally, a treatment of a hardwood (aspen) solubilized kraft lignin with dimethyldioxirane resulted in a dramatic increase in its quinone, as expected from its actual reactivity with lignin model compounds (Argyropoulos et al., 1996).

Conclusions. Trimethyl phosphite reacts with *p*-benzoquinones to form dimethylphenyl phosphate in high yield in dry organic solvent at room temperature. If moisture or lignin is present in the reaction mixture, the yield of dimethylphenyl phosphate will be ~70%. *o*-Benzoquinone forms pentoxyphosphorane quantitatively when it reacts with trimethyl phosphite in dry organic solvent. In the presence of moisture or lignin, the initially formed pentoxyphosphorane hydrolyzes to give dimethylphenyl phosphate in a yield of ~70%. Dimethylphenyl phosphate shows a unique signal at ~ -2 ppm in the ^{31}P NMR spectrum, which allows the semiquantitative estimation of the total quinone content of lignin samples.

LITERATURE CITED

Argyropoulos, D. S. Quantitative Phosphorus-31 NMR Analysis of Lignins; A New Tool for the Lignin Chemist. *J. Wood Chem. Technol.* **1994b**, *14* (1), 45−63.

Argyropoulos, D.; Heitner, C. ^{31}P NMR Spectroscopy in Wood Chemistry. *Holzforschung* **1994**, *48* (Suppl.), 112.

Argyropoulos, D. S.; Heitner, C.; Morin, F. ^{31}P NMR Spectroscopy in Wood Chemistry, Part III. Solid State NMR of Trimethyl Phosphite Derivatives of Chromophores in Mechanical Pulps. *Holzforschung* **1991**, *46* (3), 211−218.

Argyropoulos, D. S.; Archipov, Y.; Bolker, H. I.; Heitner, C. ^{31}P NMR Spectroscopy in Wood Chemistry. Part IV Lignin Models: Spin Lattice Relaxation Times and solvent Effects in ^{31}P NMR. *Holzforschung* **1993**, *47* (1), 50−56.

Argyropoulos, D. S.; Heitner, C.; Schmidt, J. A. Observation of Quinonoid Groups during the Light-Induced Yellowing of Softwood Mechanical Pulp. *Res. Chem. Intermediates* **1995**, *21* (3−5), 263−274.

Argyropoulos, D. S.; Sun, Y.; Berry, R. M.; Bouchard, J. Reactions of Dimethyldioxirane with Lignin Model Compounds. *J. Pulp Paper Sci.* **1996**, *22* (3), J84−J90.

Asgari, F.; Argyropoulos, D. S. Fundamentals of Oxygen Delignification, Part II, Kinetics of Functional Group Formation/Elimination in Residual Kraft Lignin. *Pulping Conf., Proc.* **1997**, *2*, 951−961.

Björkman, A. Studies on Finely Divided Wood (Part I) Extraction of Lignin with Neutral Solvents. *Svensk Papperstidn.* **1956**, *59* (13), 477−485.

Dale, S. W.; Hobbs, M. E. *J. Phys. Chem.* **1971**, *75*, 3537.

Duthaler, R. O.; Lyle, P. A.; Heuberger, C. Preparation of Regioselectively Protected Hydroquinones by Phosphorylation of p-Benzoquinones with Triakyl Phosphites. *Helv. Chem. Acta* **1984**, *67*, 1406.

Granata, A.; Argyropoulos, D. S. 2-Chloro-4,4,5,5-Tetramethyl-1,3,2-Dioxaphospholane a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* **1995**, *43* (6), 1538−1544.

Imsgard, F.; Falkehag, S. I.; Kringstad, K. P. On Possible Chromphoric Structures in Spruce Wood. *Tappi* **1971**, *54* (10), 1680.

Jiang, Z.; Argyropoulos, D. S. The Stereoselective Degradation of Arylglycerol-*β*-Aryl Ethers during Kraft Pulping. *J. Pulp Paper Sci.* **1994**, *20* (7), J183−J188.

Kasler, F.; Tierney, M. *Microchim. Acta* **1978**, *411*.

Kirillova, K. M.; Kukhtin, V. A. Some New Forms of the Arbuzov Rearrangement, XVI. Addition of Trialkyl Phosphites to 1,2-Naphthoquinone. *Zh. Obshch. Khim.* **1962**, *32* (7), 2338.

Konya, K. G.; Scaiano, J. C. Development and Applications of Pyrene-Containing Fluorescent Probes for Monitoring the Photodegradation of Lignin-Rich Products. *Chem. Mater.* **1994**, *6* (12), 2369.

Leary, G. J. The Yellowing of Wood by Light. *Tappi* **1967**, *50* (1), 17.

Lebo, S. E.; Lonsky, W. F. W.; McDonough, T. J.; Medvecz, P. J.; Dimmel, D. R. The Occurrence and Light-Induced Formation of *Ortho*-Quinonoid Lignin Structures in White Spruce Refiner Mechanical Pulp. *J. Pulp Paper Sci.* **1990**, *16* (5) J139.

Pew, J. C.; Connors, W. J. Color of Coniferous Lignin. *Tappi* **1971**, *54* (2), 245.

Ramirez, F. Condensation of Carbonyl Compounds with Phosphite Esters. *Pure Appl. Chem*. **1964**, *9*, 337.

Sun, Y.; Argyropoulos, D. S. Fundamentals of High-Pressure Oxygen and Low-Pressure Oxygen-Peroxide (Eop) Delignification of Softwood and Hardwood Kraft Pulps; A Comparison. *J. Pulp Paper Sci.* **1995**, *21* (6), J185−J190.

Sun, Y.; Argyropoulos, D. S. A Comparison of the Reactivity and Efficiency of Ozone, Chlorine Dioxide, Dimethyldioxirane and Hydrogen Peroxide with Residual Kraft Lignin. *Holzforschung* **1996**, *50* (2), 175−182.

Zakis, G. F.; Melkis, A. A.; Nieberte, B. Ya. Methods for Determination of Quinone Carbonyl Groups in Lignins. *Khim. Drev.* **1987**, *3*, 82−86.

Zhang, L.; Gellerstedt, G. Reactive Structures in Wood and High-Yield Pulps. IV. Daylight-Induced Oxidation of Stilbene Structures in the Solid State. *Acta Chem. Scand.* **1994a**, *48*, 490.

Zhang, L.; Gellerstedt, G. Quinoid lignin chromophores and their contribution to photoyellowing. *Proceedings of the Third European Workshop on Lignocellulosics and Pulp*, Stockholm; 1994b.

Zhu, J. H.; Olmstead, J. A.; Gray, D. G. Fluorescent Detection of *o*-Quinones Fomed in Lignin- Containing Pulps during Irradiation. *J. Wood Chem. Technol.* **1995**, *15* (1), 43.

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