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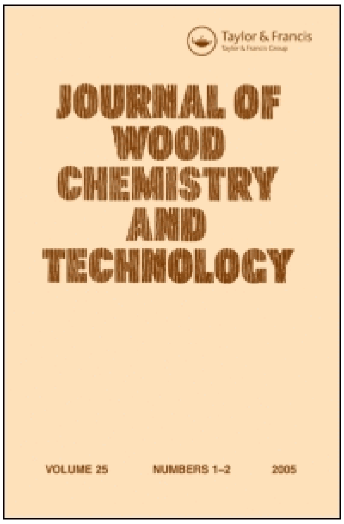

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# Improvements in the Structural Investigation of Lignins by $^{19}$F NMR Spectroscopy

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# IMPROVEMENTS IN THE STRUCTURAL INVESTIGATION OF LIGNINS BY $^{19}F$ NMR SPECTROSCOPY.

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## ABSTRACT

Derivatization of lignins samples by p-fluorobenzyl groups (etherification of phenolic groups) leads to the distinction between G and G-S-lignin, and to analyze approximately the G/S ratio and the ($\alpha$ -C=O) content of the studied samples by integration of the $^{19}F$ NMR spectra.

## INTRODUCTION

In previous papers [1,2] we showed the use of lignin fluoroderivatives (analyzed by $^{19}F$ NMR spectroscopy) for the quantitative analysis of the O-H groups ratios: hydroxylic, phenolic and carboxylic groups. Various fluoro-aromatic compounds were tested as blocking groups of the lignin hydroxyl groups. As a result of these works, other investigations seem possible.

In this report, we describe the usefulness of the specific parafluorobenzylation of free phenolic groups to improve the structural knowledge in lignins.

With the aid of the $^{19}F$ NMR spectroscopy we can :

– distinguish between a guaïacyl lignin (G-lignin) and a guaïacyl-syringyl lignin (G-S lignin).

- determine the syringyl/guaïacyl ratio of structural units with phenolic groups.
- approximately determine the (α-C=O) content in the same structural units.

The fluorine nucleus give chemical shifts sensitive to the interactions with other groups through space or through bonds. This is an advantage when investigating small structural changes in complex molecules.
To ascertain the results obtained with lignins, a preliminary study on fluorobenzylated lignin model compounds was necessary and the $^{19}$F chemical shifts of models functionalized in various ways were established.

## RESULTS AND DISCUSSION

### $^{19}$F NMR study of fluorobenzylated model compounds

Table 1 lists $^{19}$F chemical shifts, (δF) for various fluorobenzylated lignin models and chemical shifts differences.

### Study of δF and ΔδF

The δF values are different for the α- G–ketones and α-S–ketones and ΔδF differences are between 0.20 and 0.27 ppm. Moreover we noted the δF values for the two compounds FBzl-OG and FBzl-OS of δ = 24.88 and 24.63 ppm respectively with Δδ = 0.25 ppm, is consistent with Δδ observed in the keto series.

In a same series (S or G), the δF values are different for the (α-C=O)–compounds and the (α–C–OR)–compounds and the ΔδF differences are between 0.43.and 0.58 ppm.Clearly, δF is subject to the electronic effects of one or two methoxy-groups through space and through bonds, or only through bonds : and is influenced by conjugated or non conjugated groups on the S–or–G–aromatic ring.

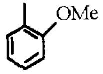
In the (α–C–OR) series (entries 5 to 8 only), the ΔδF (G–S) differences (no included in table 1) become important and therefore increases with the complexity of the model. Indeed, the knowledge of ΔδF, on various models, as showed in table 1, gives us a tool to elucidate the G/S ratio or (α–C=O) content in structural units with phenolic groups.

TABLE 1
Assignment of Signals in the $^{19}$F NMR Spectra of Model Compounds

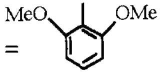
| | α-(C=O) compounds | δ | Δδ<br>G – S(C=O) | α–(C-OR) compounds | δ | Δδ<br>α-(C=O )- α-(C-OR) |
|---|---|---|---|---|---|---|
| 1 | FBz1-O-G-CHO | 25.34 | 0.27 | FBz1-O-G-CH$_2$OH | 24.77 | 0.57 |
| | | | | FBz1-O-G-CH$_2$OG | 24.92 | 0.42 |
| | | | | FBz1-O-G-CH$_2$OS | 24.93 | 0.41 |
| 2 | FBz1-O-S-CHO | 25.07 | | FBz1-O-S-CH$_2$OH | 24.61 | 0.46 |
| 3 | FBz1-O-G-CO-CH$_3$ | 25.25 | 0.23 | FBz1-O-G-CHOH-CH$_3$ | 24.60 | 0.65 |
| 4 | FBz1-O-S-CO-CH$_3$ | 25.02 | | FBz1-O-S-CHOH-CH$_3$ | 24.58 | 0.44 |
| 5 | FBz1-O-G-CO-CH$_2$OG | 25.28 | 0.20 | FBz1-O-G-CHOH-CH$_2$OG | 24.89 | 0.39 |
| | | | | FBzl-O-G-CHOG-CH$_2$OG | 24.85 | 0.43 |
| 6 | FBz1-O-S-CO-CH$_2$OG | 25.08 | | FBz1-O-S-CHOH-CH$_2$OG | 24.65 | 0.43 |
| 7 | FBz1-O-G-CO-CHOG<br>CH$_2$OH | 25.40 | 0.20 | FBz1-O-G-CHOH-CHOG<br>CH$_2$OH | 24.87*<br>24.90 | 0.53<br>0.50 |
| 8 | FBz1-O-S-CO-CHOG<br>CH$_2$OH | 25.20 | | FBz1-O-S-CHOH-CHOG<br>CH$_2$OH | 24.65*<br>24.62 | 0.55<br>0.58 |

* Two values for two diastereoisomeric forms.

G =



S =



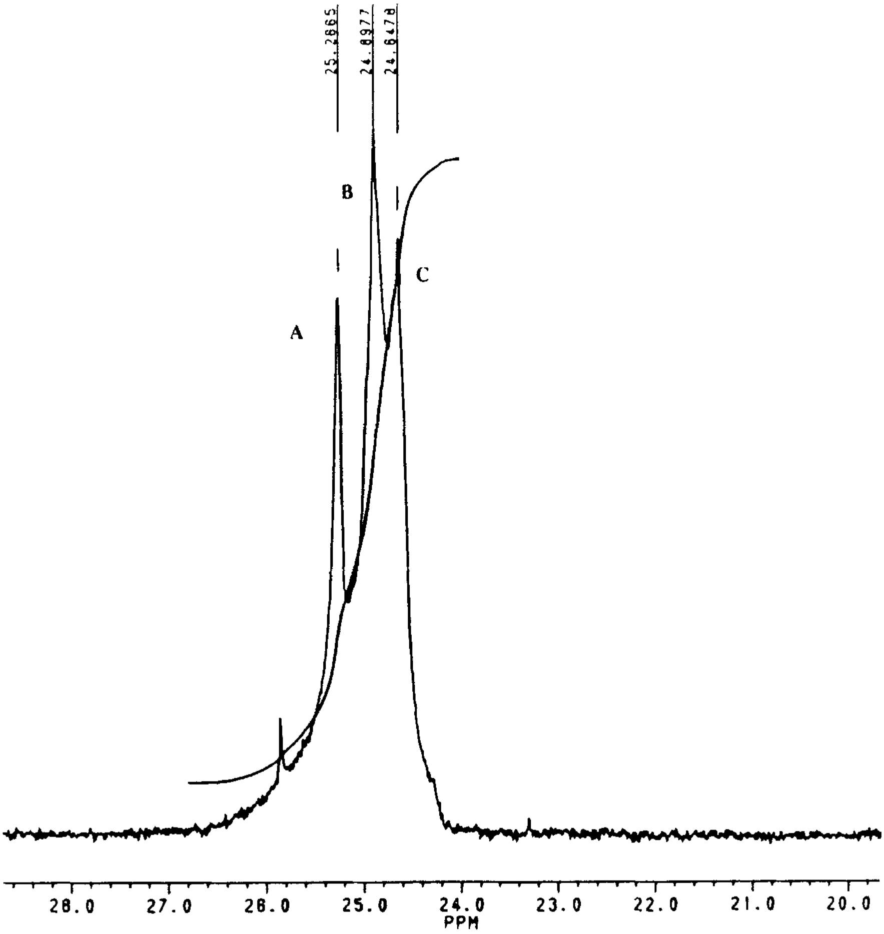


FIGURE 1. $^{19}F$ NMR spectrum of a fluorobenzylated organosolv G-S-lignin.

## Analysis of a $^{19}F$ spectrum of G/S fluorobenzylated lignin

On the $^{19}F$ spectrum shown in fig 1, we can observe three main broad resonances (noted, A, B, C). The resonances are centered at 25.26 ppm (A), 24.89 ppm (B) and 24.64 ppm (C). These values correlate well with those determined for α-ketocompounds, G-compounds and S-compounds (with α-C-

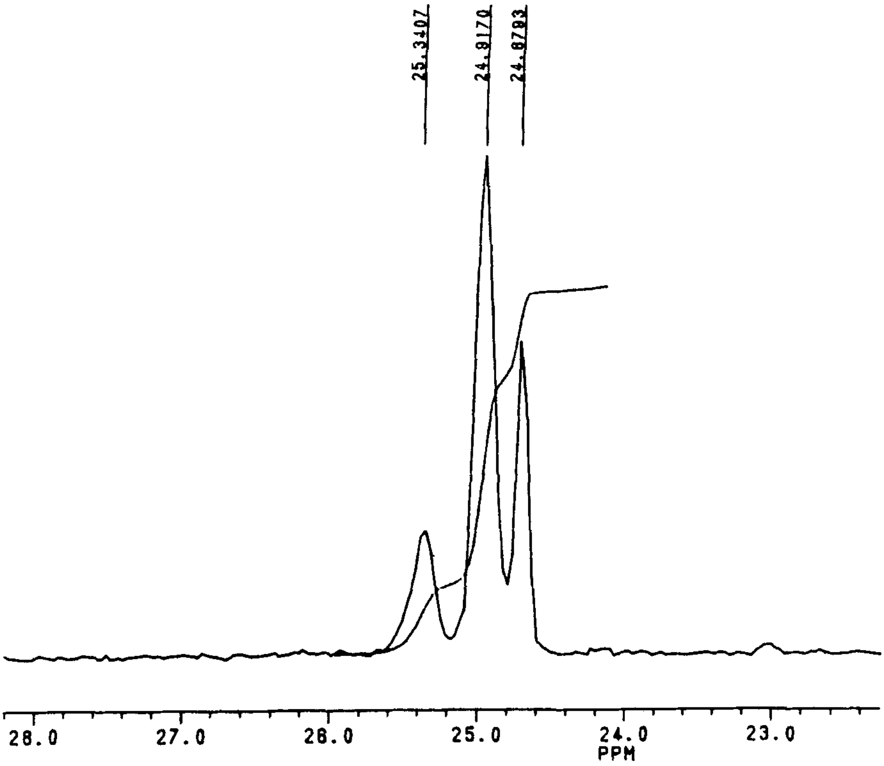


FIGURE 2. $^{19}$F NMR spectrum of a mixture of lignin model compounds (high concentration).

OR) respectively. To ascertain these correlations, we introduced in the NMR tube containing the lignin solution, a small quantity of a model (structuraly related to A, B or C) and after recording of the new spectra we observed a sharp peak superimposed on the three resonances A, B, C.

In fig. 2, we show, a spectrum obtained from a mixture of eight model compounds such as the total concentration in the NMR tube corresponds to that of a fluorobenzylated lignin solution (35-40 mg/1.5 ml). There is a good similarity between the three broad bands obtained in this experiment and the A, B, C resonances of the fluorobenzylated G–S lignin spectrum.

The experiments were carried out with three lignin samples, an exploded wood lignin, an organo solv lignin from poplar (Fig. 1) and kraft lignin. In each cases the three main resonances A, B, C were observed.

### Analysis of a $^{19}$F spectrum of a G–fluorobenzylated lignin

A commercial indulin sample (Westwaco Corp.) was studied, and after fluoro benzylation, its spectrum was recorded (Fig. 3) and showed a broad resonance at 24.80 ppm. This chemical shift correlated well with the G–δF obtained previously. In this case the (α–C=O) structural unit with phenolic groups are distinguished (shoulder at 25.20 ppm).

In a complementary experiment we mixed two solutions of fluorobenzylated G–S–lignin and G–lignin and as expected the B–resonance was enhanced (Fig.4)

As a result of this study we propose :

First; a good and versatile distinction between the G– and G–S–lignins after fluorobenzylation of phenol groups.

Secondly; an approximate determination of G/S ratio in units of G–S–lignins with phenolic groups. The peak width and their superimposition don't permit an accurate determination. However, a G/S value of 1.4–1.45 can be extracted from the integral ratio (Fig. 1 or 4 a).

Third; in the same manner we are able to give an approximate percentage of (α–C=O) content (always for the structural units with phenolic groups) and from the G–S–lignin (Fig. 1) we found a ratio of about 20 %, if, this ratio is defined as total free phenolic groups in (α–C=O) structural units/total free phenolic groups.

Other works are in progress for the determination of total (C=O)content in lignins by fluoroderivatization [5]

Finally, we are able to analyze the (α-C=O) content and G/S ratio in phenolic lignin subunits.Assuming these results are the same in etherified and phenolic lignin subunits, we possess a good tool for the functionnal analysis of lignins by the use of fluoroderivatization.

## CONCLUSION

The results obtained can be regarded as a good approach for the determination of (α–C=O) content and G/S ratio in G–S–lignins. Particularly, the

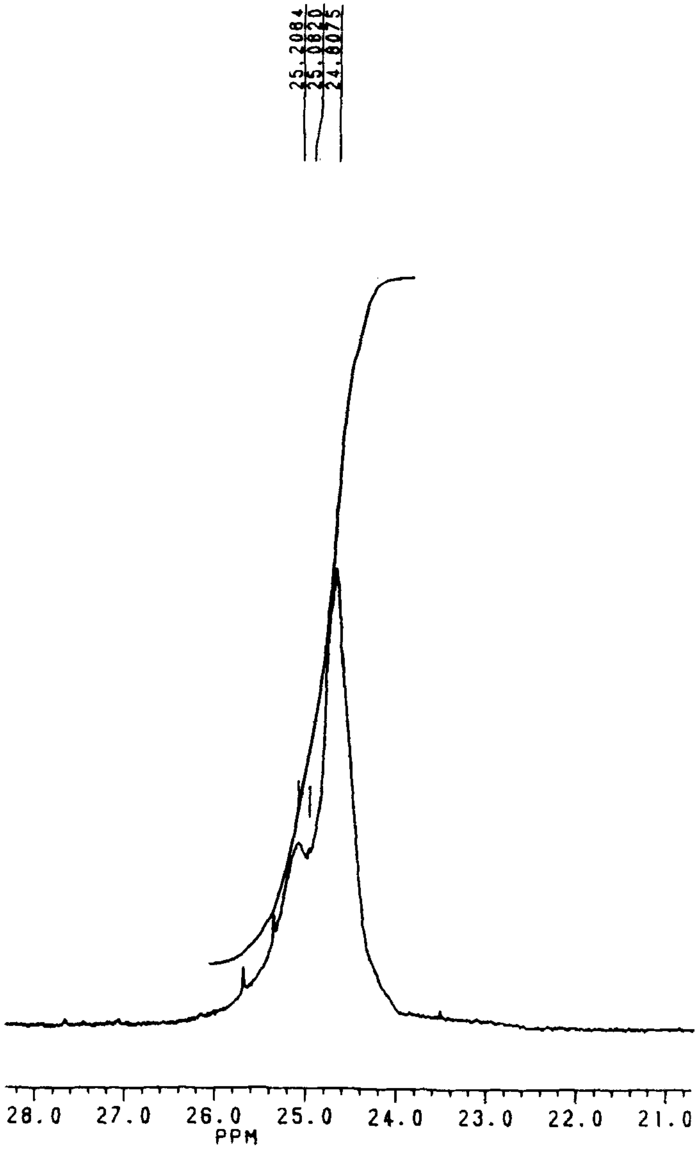


FIGURE 3. $^{19}$F NMR spectrum of a fluorobenzylated G-lignin (Indulin).

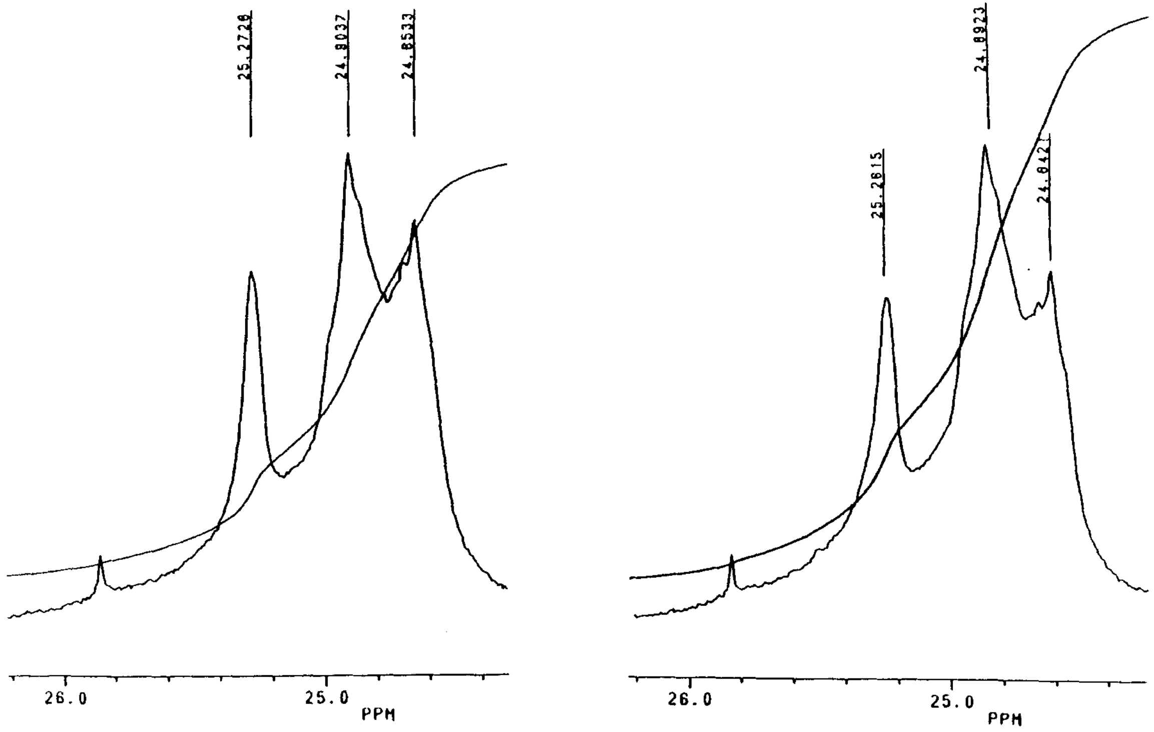


FIGURE 4. a) expanded $^{19}F$ NMR spectrum of FIG. 1.

b) expanded $^{19}F$ NMR spectrum of a mixture G-S-lignin/G-lignin (3/1) obtained from samples having their representative spectra in FIG. 1 and 3.

C=O content is difficult to analyze in lignins. It is well knowed that the variability of lignin composition is very great, following its origin and its extraction mode for instance. In this work, H–lignins (p.hydroxyphenyl unit) were not considered because they are not discernible in the studied samples. We can recall here, two lignin compositions G/S/H = 94/1/5 for spruce lignin [6] and G/S/H = 56/40/4 for a beech lignin [7] Incidentally our result G/S = 1.4 coincides with that of ref (7) : 56/40 =1.4.This coincidence is fortuitous, because our organosolv lignin comes from poplar and only the order of magnitude is to consider.It is knowned that the lignin composition varies with species and our work is limited to phenolic units alone.

## EXPERIMENTAL

### $^{19}$F NMR spectra :

The spectra were recorded with a BRUKER AC 200 spectrometer at operational frequency for $^{19}$F nuclei at 188.82 MHz. The lignin derivatives were dissolved in DMSO (30-50 mg/1.5 ml) using $C_6F_6$ as an internal reference. The measurements were carried out in a 5 mm tube at 50°C. The relaxation delay was 5 sec and the number of scans for the acquisition of the $^{19}$F NMR signals ranged from 200 to 300.

For quantitative measurements an exactly weighted standard were introduced into the solution (1.5 to 2.5 mg of guaïacyl 2-fluorobenzoate with $\delta F = 29.9$ ppm).

### Chemicals :

4-fluorobenzyl chloride was a commercial product (LANCASTER SYNTHESIS) used without purification : Lignin model compounds were synthetized according to the ref 3 and 4.

### Lignin fluorobenzylation :

As described in ref 1.

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