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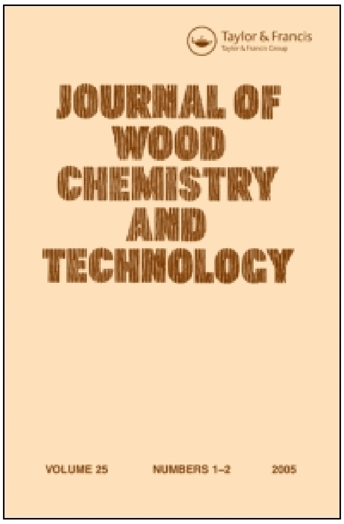

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AN APPROACH TO THE DETERMINATION OF FUNCTIONAL GROUPS IN OXIDIZED LIGNINS BY ^{19}F NMR

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Dedicated to the memory of Kyosti V. Sarkanen

ABSTRACT

Derivatization of an oxidized lignin sample by suitable fluoroaromatic compounds is described. Integration of the ^{19}F NMR spectra of the derivatives allows the determination of the carboxyl content of the sample. Three reagents were investigated : 4-fluorobenzyl chloride, 4-fluorophenacyl bromide and 4-fluorophenyldiazomethyl ketone.

INTRODUCTION

Since the development of ^{13}C NMR spectroscopy [1] of acetylated lignins for the quantitative estimation of hydroxyl groups, alternative techniques have emerged. ^{29}Si NMR have been applied to silylated lignins [2,3] and ^{31}P NMR to model substances derivatized by 1,3,2-dioxaphospholanyl chloride [4]. One of us have published recently a method for the determination of phenolic and alcoholic hydroxyl groups by ^{19}F NMR [5]. Like ^{31}P, ^{19}F has a 100% natural abundance and its chemical shifts extend over a wide range. Fluoroaromatic derivatives of lignin exhibit good stability. The chemical shifts are very sensitive to the position of the fluorine atom on the aromatic ring. It is possible by combination of several reagents to obtain well defined signals for each class of hydroxyl groups. As an example, this method was used to characterize the major functional groups and particularly the carboxyl groups of a lignin extracted from an ozone treated TMP pulp.

RESULTS AND DISCUSSION

The lignin of a TMP pulp treated with ozone was extracted by acidolysis in a dioxane/water mixture. Two samples (L1 and L2) were prepared. The ozone consumption was 3.8% and 5.1% for samples L1 and L2 respectively (see experimental for details). Side reactions occuring during the extraction were not taken into account and the samples were used without further purification. The solubility of the samples in an aqueous solution of sodium bicarbonate suggested the presence of rather strong acidic groups.

We have first determined the number of alcoholic and phenolic groups by treatment of the lignin with the 4-fluorobenzoic anhydride according to the method already published [5]. The results were :

0.10 phenolic groups and 0.09 alcoholic groups / C_9 for the sample L1

0.15 phenolic groups and 0.05 alcoholic groups / C_9 for the sample L2

assuming a molecular weight of 200 for the C_9 unit.

In experiments published elsewhere [5,6], the alcoholic to phenolic groups ratio determined by this method was found in good agreement with the ratio obtained by ^{13}C NMR. In the present study we have not checked again the fit between the two methods. A dramatic decrease of both phenolic and alcoholic groups was observed. It is the same for the methoxyl content (0.6 / C_9). These results are in agreement with the proposed mechanisms for the oxidation of lignin by ozone : formation of ortho quinone from the guaiacyl moieties, cleavage of the side chain, formation of derivatives of muconic acid by opening of the aromatic ring. However our challenge was not to confirm the mechanism of oxidation by ozone but to have a substrat enriched in carboxyl groups.

TABLE 1

Chemical Shifts of Fluoroderivatives of Several Model Compounds

Acid	Reagent				
	C2F	C3F	C4F	PhB	DZC
Benzoic	21.81			34.97	34.97
Anisic		26.35	25.32		
Cinnamic		26.30	25.18		
Syringic		25.77* 26.26**	25.10* 25.77**		
Ferulic			24.87* 25.20**	34.62* 34.85**	
Vanillic	20.25* 20.75**	25.83* 26.30**	25.27* 25.35**	34.68* 34.87**	23.55 34.97

* chemical shift corresponding to the phenolic group
** chemical shift corresponding to the carboxyl group
C2F : 2-fluorobenzyl chloride
C3F : 3-fluorobenzyl chloride
C4F : 4-fluorobenzyl chloride
PhB : 4-fluorophenacyl bromide
DZC : 4-fluorophenyldiazomethyl ketone

For the determination of the carboxyl groups, we have selected three reagents able to react with phenolic and carboxyl groups :

the 4-fluorobenzyl chloride ($FC_6H_4CH_2Cl$)

the 4-fluorophenacyl bromide ($FC_6H_4COCH_2Br$)

the 4-fluorophenyldiazomethyl ketone ($FC_6H_4COCHN_2$)

The different chemical shifts were determined from a series of model compounds bearing carboxyl groups and both phenolic and carboxyl groups. The results for the different reagents are summarized in Table 1. The chemical shifts depend mainly on the atoms in ipso of the ring bearing the fluorine atom and on the position of the fluorine on this ring. With the fluorobenzyl chlorides and the fluorophenacyl bromide the difference in chemical shifts between phenolic and carboxyl groups is about 0.5 ppm only. Of course, with lignin, these two signals overlap and only one broad peak is observed. Hence one must determine the phenolic groups in a separate experiment. It is noteworthy that the signals, even broadened are still well apart of those corresponding to alcoholic and phenolic

TABLE 2

Number of Carboxyl and Phenolic Groups / C_9 (Sample L1)

Reagent	COOH / C_9	OH_{Phenol} / C_9
C4F	0.15	0.10
DZC	0.14	0.10
PhB	0.15	0.10
DZM	0.16	0.11

DZM : diazomethane

groups esterified by 2-fluorobenzoic anhydride (δ= 29 to 31 ppm) [5]. With diazoketone the assignment of chemical shifts is more complex. This point will be discussed later.

Sample L1 was allowed to react with the three reagents mentioned above. The number of carboxyl groups was determined after substraction of the number of phenolic groups found by treatment with the 4-fluorobenzoic anhydride. For comparison, the sample was methylated with diazomethane and saponified. The number of carboxyl and phenolic groups was calculated from the methoxyl content after and before saponification. The results are summarized in Table 2. The agreement between the values found by ^{19}F NMR and the values calculated from the methoxyl content is satisfactory. The extent of the reactions appears good enough for analytical purpose. This is confirmed by the disappearance of the OH band in the infrared spectrum of the derivatives and their insolubility in sodium hydroxyde.

With the sample L2 we carried out several reaction sequences. The 4-fluorobenzyl chloride reacts on both phenolic and carboxyl groups in their ionised form.Treatment of sample L2 with 4-fluorobenzyl chloride gives 0.37 carboxyl groups / C_9 after deduction of the phenolic groups. In order to check this value, the following sequence was applied : methylation by CH_2N_2, saponification and reaction with the fluorobenzyl chloride. This procedure allows a direct determination of carboxyl groups. We obtained 0.37 with the 4-fluorobenzyl chloride and 0.39 with the 3-fluorobenzyl chloride. These two reagents give roughly the same chemical shifts and their reactivity is quite similar. The spectrum of the 3-fluoro derivative is shown in figure 1.

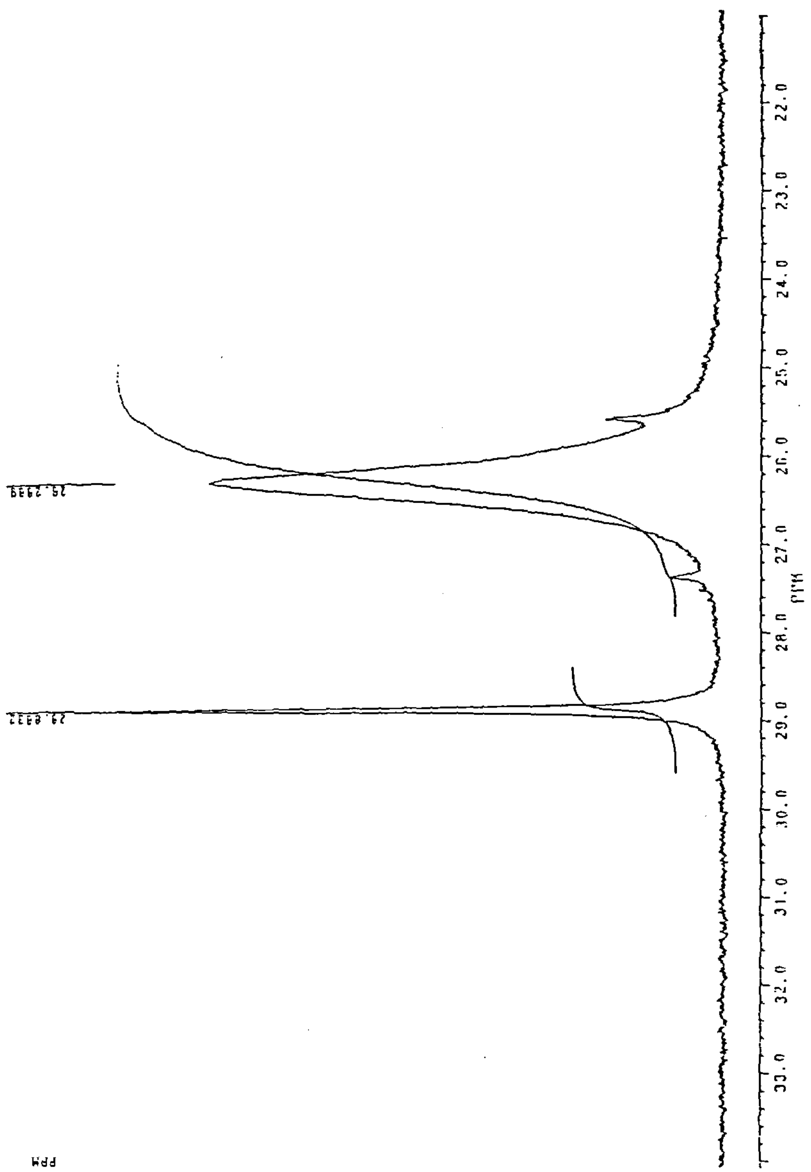

Figure 1 : ^{19}F-NMR spectrum of lignin derivatized with 3-fluorobenzyl chloride after methylation of phenols. The signal at 29 ppm coresponds to the internal standart (2-fluorobenzoic acid).

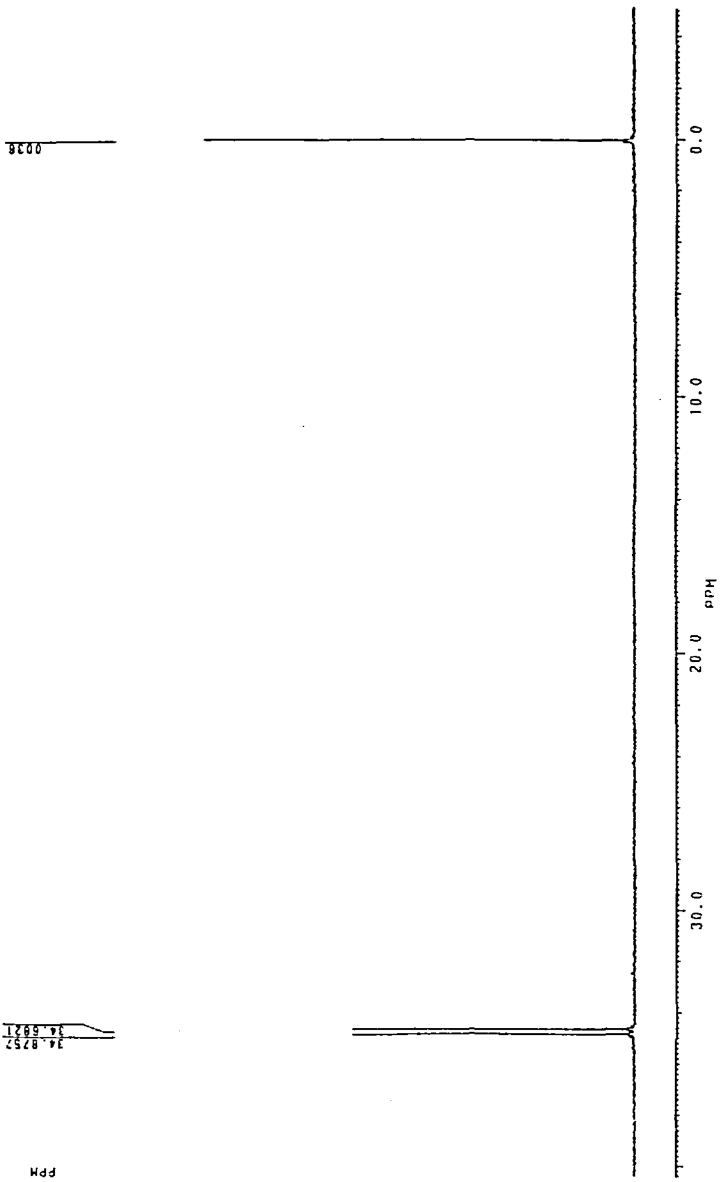

Figure 2 : ^{19}F-NMR spectrum of vanillic acid derivatized with 4-fluorophenacyl bromide.

TABLE 3

Number of Carboxyl Groups / C_9 and Chemical Shifts of the Derivatives

Treatment	COOH / C_9	δ (ppm)
C4F	0.37	25-27
DZM + S + C4F	0.37	25-27
DZM + S + C3F	0.39	25-27
A2F + PhB	0.39	
DZM + S + PhB	0.41	33-36
A2F +DZC	0.33	
DZM + S + DZC	0.23	35 and 23.5
DZM + S + DZC + PhB	0.35	

A2F : 2-fluorobenzoic anhydride
S : saponification
All other symbols as in table 1 and 2

The ^{19}F NMR spectrum of the reaction product of vanillic acid with 4-fluorophenacyl bromide is shown on figure 2. There are two peaks at 34.68 and 34.87 ppm corresponding to phenolic and carboxyl groups respectively. The reaction is carried out in mild conditions and if esters groups are present they are preserved. This is shown in the following experiments. When 4-fluorophenacyl bromide reacted with sample L2 whose phenolic groups have been methylated, the number of carboxyl groups / C_9 was found equal to 0.41. When the same sample was first treated with 2-fluorobenzoic anhydride and then allowed to react with 4-fluorophenacyl bromide the result was 0.39 (Table 3).

The previous experiments, which are all in good agreement, lead to an average of 0.39 ± 0.02 carboxyl groups / C_9 unit.

We will now discuss the results obtained with the diazoketone.The main advantage of the diazoketone is that the ionisation step is no longer needed. The reaction is carried out in dioxane without addition of base. At first sight, 4-fluorophenacyl bromide and 4-fluorophenyldiazomethyl ketone should lead to the same derivatives. However, with diazoketone the reaction can also take place according to the scheme below, known as the Wolff rearrangement :

$$RCOCHN_2 \dashrightarrow RCH{=}C{=}O + N_2 \xrightarrow[HX]{} RCH_2COX$$

This rearrangment is less likely with strong acidic groups [8]. It explains the difference between the spectra of the two derivatives of vanillic acid (figures 2 and 3). In the spectrum of the derivative of vanillic acid (figure 3) the peak at 23.55 ppm corresponds to the phenol and the one at 34.57 ppm to the carboxyl. Nevertheless, in the case of lignin, the peak near 24 ppm cannot be assigned to phenolic groups alone. Lignin, after methylation of phenolic groups, gives a signal in the same region (figure 4).Scattering of the results obtained with the diazoketone (see Table 3) shows that the reaction is incomplete employing our conditions.

EXPERIMENTAL

Extraction of Lignin.

The TMP was prepared from spruce (*Picea abies*) in a Sprout-Waldron pilot intallation at the Centre Technique du Papier in Grenoble. The following conditions were used : temperarure 120°C, pressure 1.4 bar, retention time 15 minutes. The pulp was refined in a Sprout-Bauer refiner to a freeness of 45° SR.

The pulp was treated with ozone at ambient temperature. The consistency was 35% and the pH was adjusted to 2.5 with sulfuric acid. The gas velocity was adjusted so that during the resident time the desired quantity of ozone had been added to the pulp. The residual ozone in the exit gases from the reaction vessel was determined by iodometric titration. After the reaction the treated pulp was washed with water.

After oxidation, the pulp was treated 36 hours at 80°C by a mixture dioxane, water 80 / 20 (v/v) 1 M in HCl. The pulp to liquor ratio was 0.02 (w/v). The residual pulp was washed with dioxane.The liquid phase was concentrated under reduced pressure and the lignin was recovered by precipitation in water, washed with water and dried at 50°C. The yield of extraction was 80%.

Reaction with 4-Fluorobenzyl Chloride.

Lignin (100 mg.) was dissolved in 10 ml. of 0.1 N tetrabutylammonium hydroxide in methanol. After stirring for one hour at 50°C, the volume of the

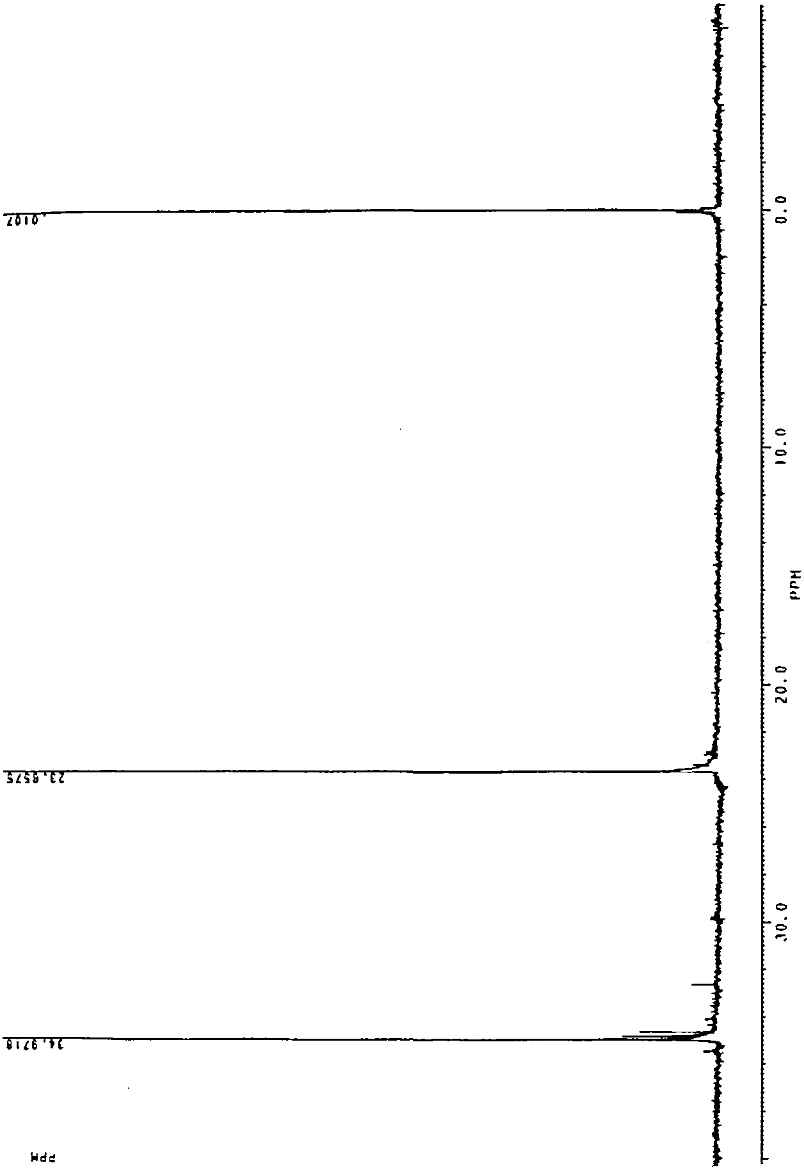

Figure 3 : 19F NMR spectrum of vanillic acid derivatized with 4-fluorophenyldiazomethyl ketone.

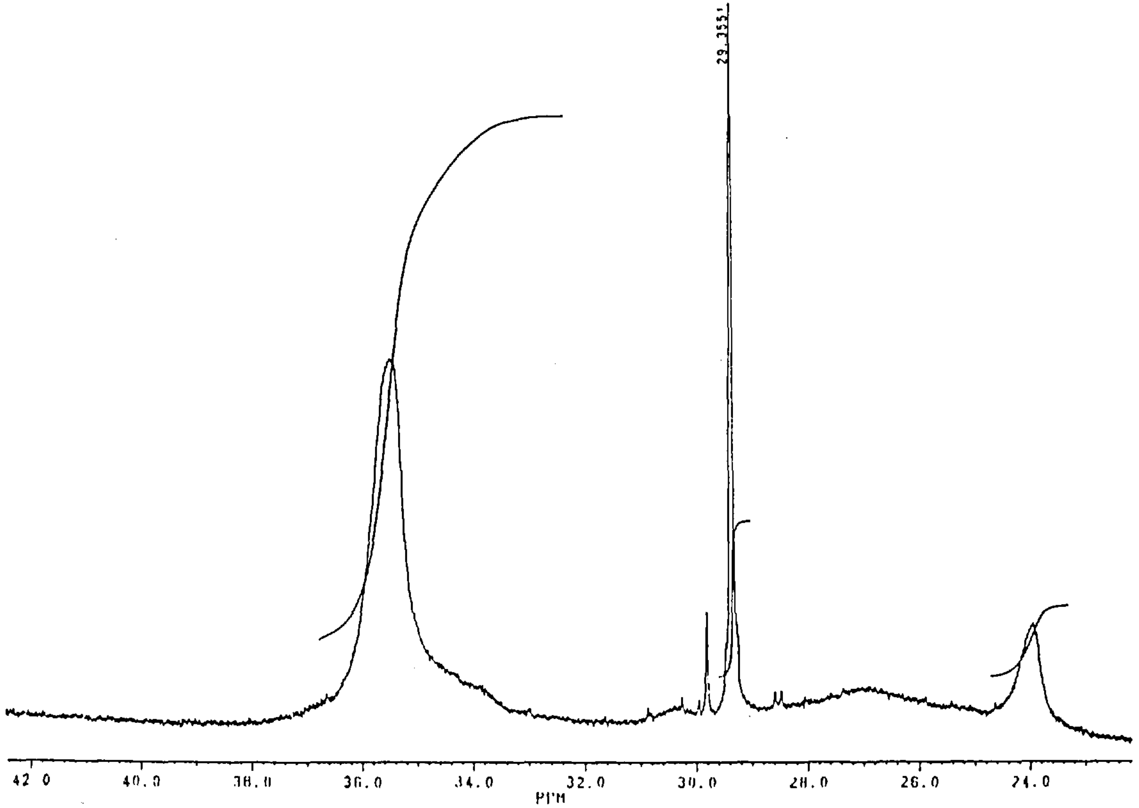

Figure 4 : ^{19}F-NMR spectrum of lignin derivatized with 4-fluorophenyldiazomethyl ketone after methylation of phenols. The signal at 29 ppm corresponds to the internal standart (2-fluorobenzoic acid).

solution was reduced to 2 ml. by evaporation under reduced pressure. After addition of 10 ml. of acetonitrile and 300 mg. of 4-fluorobenzyl chloride, the mixture was stirred ovenight at 50°C. Lignin was recovered by precipitation in ethyl ether, washed several times with ether and dried in an oven at 50°C.

For vanillic acid, the reaction was carried out at room temperature and the fluoro reagent was added in stoechiometric amount.

Reaction with 4-Fluorophenacyl Bromide.

Lignin (100 mg.) was dissolved in anhydrous DMF (2 ml.). Potassium carbonate (100 mg.), potassium iodide (20 mg.) and 4-fluorophenacyl bromide (100 mg.) were added. The mixture was stirred at room temperature during 24 hours. The derivatized lignin was precipitated by addition of 5 ml. of water and filtered under vacuo .The solid was redissolved in THF, precipitated with ethyl ether, recovered by filtration and dried in an oven at 50°C.

For vanillic acid, chloroform was used instead of THF. The solution was dried over magnesium sulfate and the derivative was recovered by evaporation of the solvent.

Reaction with 4-Fluorophenyldiazomethyl Ketone.

The diazoketone was prepared from diazomethane and 4-fluorobenzoic chloride according to the procedure described in reference 7. Lignin (100 mg.) was dissolved in dioxane together with 200 mg. of diazoketone. The solution was stirred 24 hours at 80°C. The lignin was recovered by precipitation in ethyl ether, washed with ether and dried.

For vanillic acid the procedure was similar : vanillic acid (5.10^{-4} mole) was allowed to react with 7.10^{-4} mole of diazoketone in 5 ml. of dioxane. The reaction time was reduced to 12 hours.

^{19}F NMR

The NMR spectra were recorded at 188,226 MHz on a BRUKER AC200 spectrometer. The derivatized lignin samples were dissolved in DMSO d_6 (30 to 50 mg / 1,5 ml) with C_6F_6 as a reference. The measurements were carried out in 5 mm tube at 50°C. The relaxation delay was 5 s. and the number of scans for the acquisition of the ^{19}F-NMR signals ranged from 200 to 400.

CONCLUSION

The results obtained must be regarded as a first attempt to determine the carboxyl content of oxidized lignins by ^{19}F NMR. They appear very promising. From the three reagents investigated, diazoketone must be temporarily discarded as long as its reaction pattern is not be fully elucidated. It remains to optimize the experimental conditions for the two other reagents. With phenacyl bromide, the use of K_2CO_3 as ionising agent allows the preservation of ester groups. It is thus possible to determine all the hydroxyl groups by a two steps procedure : first, treatment with 2-fluorobenzoic anhydride and second, treatment with 4-fluorophenacyl bromide.

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