PRE-SYMPOSIUM WORKSHOP TO

THE 9th INTERNATIONAL SYMPOSIUM

ON WOOD AND PULPING CHEMISTRY

ADVANCES IN MICROSCOPY AND

NMR SPECTROSCOPY OF

LIGNOCELLULOSIC MATERIALS

Québec City Hilton
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QUALITATIVE AND QUANTITATIVE ASPECTS OF PROTON NMR SPECTROSCOPY OF LIGNIN

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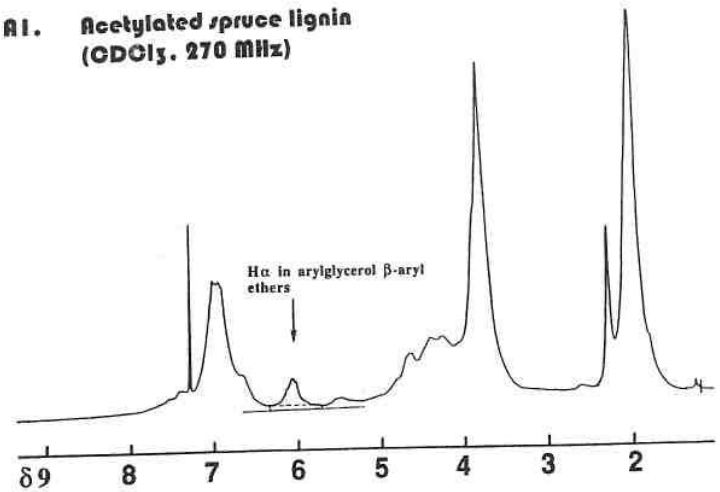
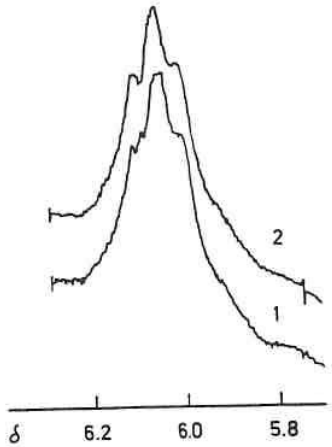
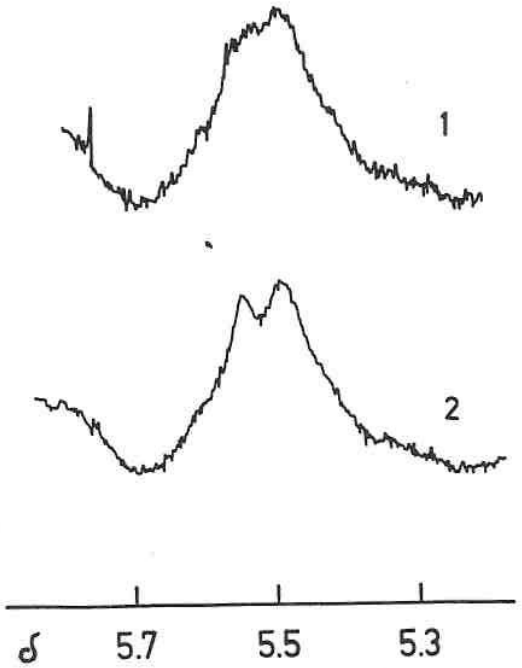
A1. Acetylated spruce lignin (CDCl3. 270 MHz)



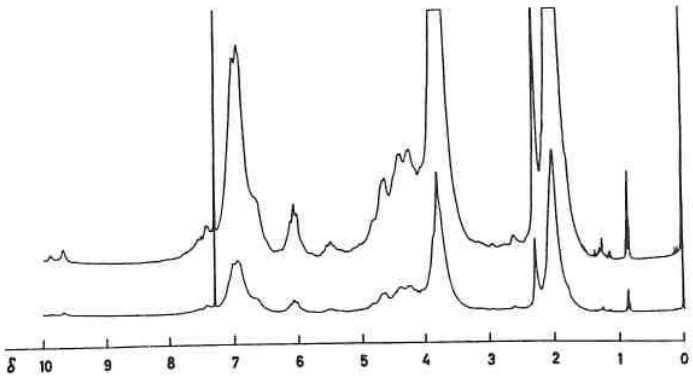
A2. Decoupling of Hα (2)



A3. Hα in phenylcoumaran structures (decoupling. 2)



A4. 500 MHz spectrum



A1-A4. Comments.

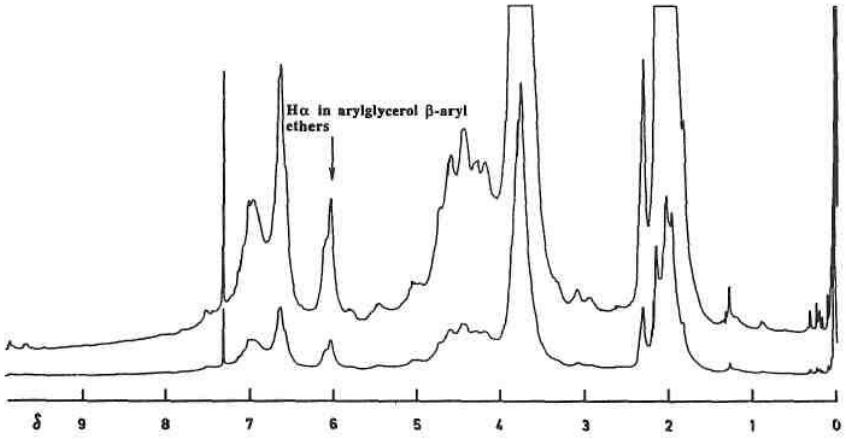
A1. Estimate of β-ethers (30-40%); the area above the dashed line corresponds to the lower figure. **Note: Baseline corrections using spectrometer commands leads to erroneous results.**

A2. Decoupling by irradiation of Hβ. Peaks due to different diastereomers appear (similar amounts of *erythro* and *threo* forms as judged from spectra of lignin samples with methylated phenolic groups).

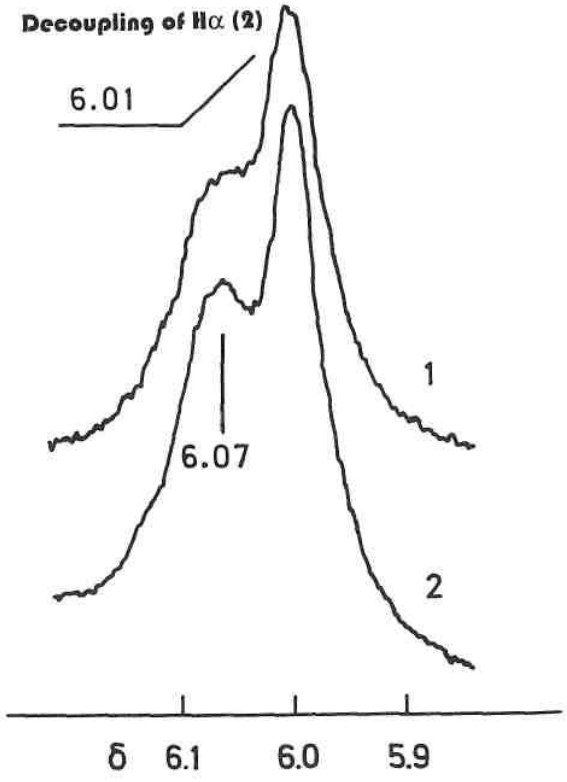
A3. Decoupling by irradiation of Hβ. Peaks due to phenolic (higher δ value) and non-phenolic units appear. Number of units attached to adjacent units by a β-5 linkage (in phenylcoumarans): ≈ 7%.

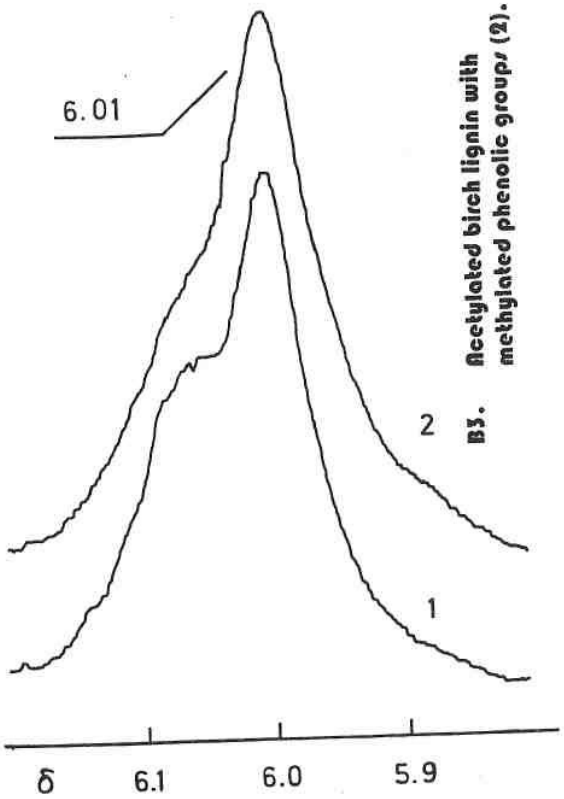
A4. Increased spectrometer frequency results in a resolution similar to that obtained by decoupling.

B1. Acetylated birch lignin (CDCl3. 270 MHz)



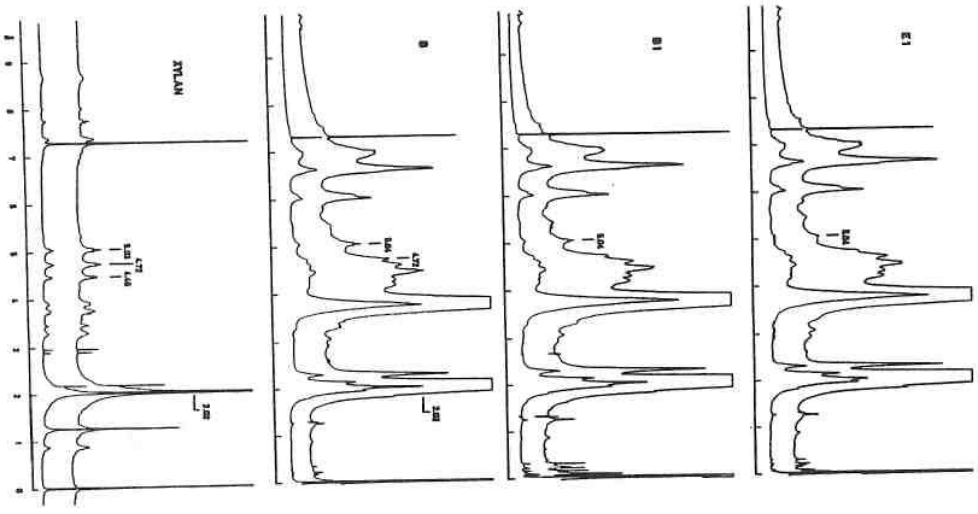
B2. Decoupling of Hα (2)





B3. **Acetylated birch lignin with methylated phenolic groups (2).**

B4. **Xylan in birch lignin**



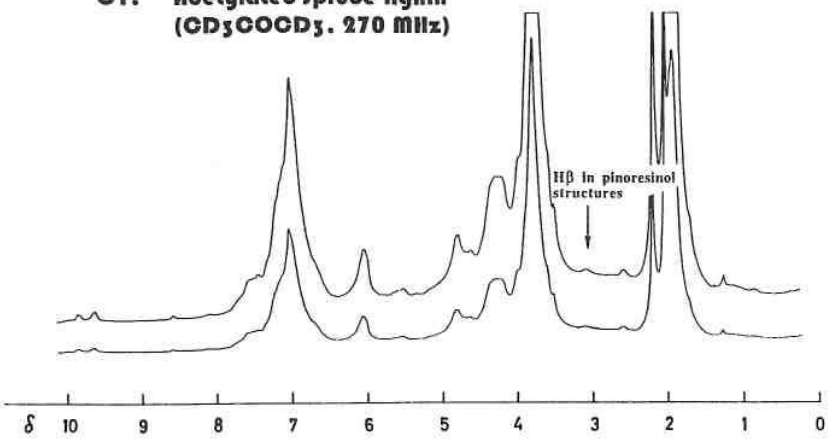
B1-B4. Comments.

B1. The number of arylglycerol units attached to an adjacent unit by β-ether bond has been estimated as 40-50 %.

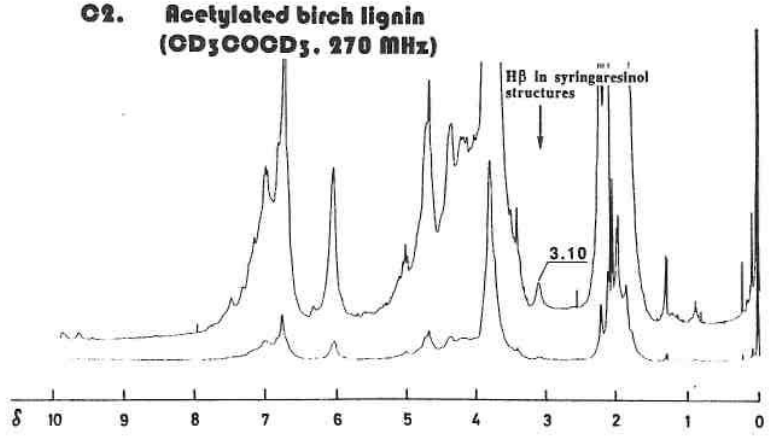
B2 and B3. From decoupling experiment (Hβ) it can be concluded that the *erythro* forms (δ - 6.01) dominate (≈ 70 %).

B4. The presence of xylan in the lignin samples is very evident from the NMR spectra (peaks at δ 5.04 and 2.02). It is possible to estimate the amounts.

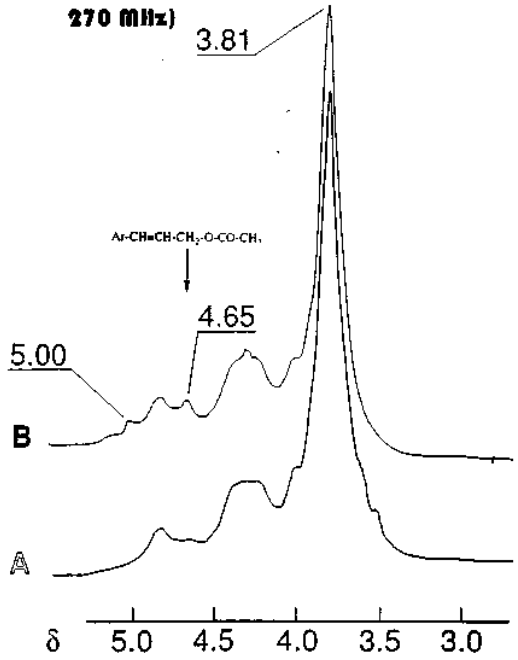
C1. **Acetylated *spruce* lignin (CD3COCD3, 270 MHz)**



C2. **Acetylated birch lignin (CD3COCD3, 270 MHz)**



C3. **Acetylated *spruce* lignin (A) and acetylated borohydride-reduced *spruce* lignin (B) (CD3COCD3, 270 MHz)**



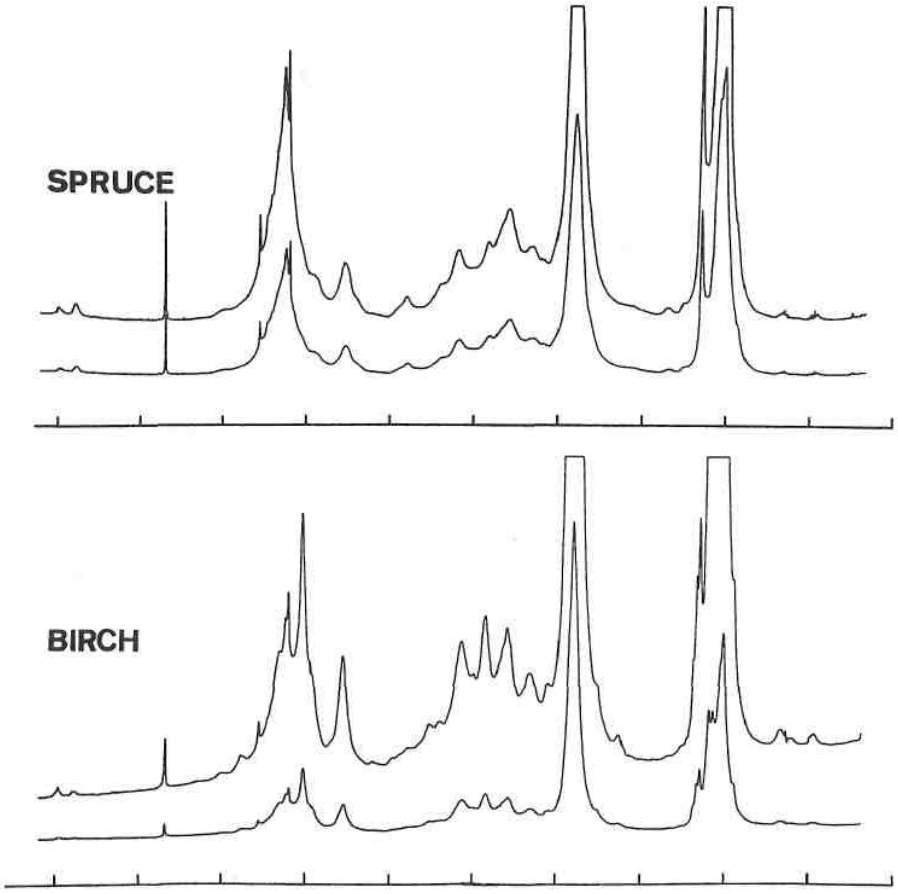
C1 - C3. Comments.

C1. Determination (based on the Hβ signal) of the number of units in pinoresinol structures in spruce lignin gives 2-3%.

C2. Determination of the number of units in pinoresinol and syringaresinol structures in birch lignin gives 7%.

C3. A very small peak at δ 4.65 (Hγ) reveals the presence of coniferyl alcohol units in spruce lignin. Their number is estimated to be ≈1%. This is supported by the fact that borohydride reduction/acetylation (spectrum B) causes a substantial increase of this peak that is explained by the conversion of coniferaldehyde units (3-4%) into acetylated coniferyl alcohol units. A peak at δ 5.00 in the reduced/acetylated lignin spectrum (B) is due to conversion of benzaldehyde units into acetylated benzyl alcohol units.

D. Acetylated lignins
(pyridine-d_5, 270 MHz)



D. Comments.

Notable in the pyridine spectrum of birch lignin (partly based on comparisons with the spruce lignin spectrum) is:

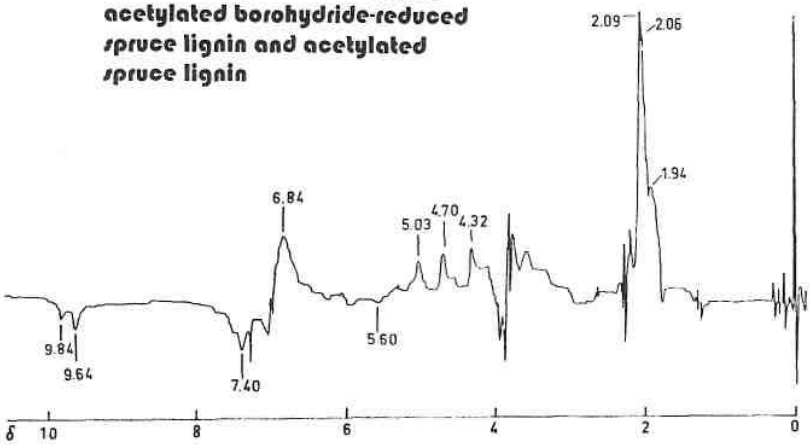
1) A resolution of the phenolic acetate peak indicating a comparatively large number phenolic guaiacyl groups.
2) The position of the Hβ signal from β-β structures shows that syringaresinol structures are the prevalent types of such structures.
3) Peaks showing that a large number of *erythro* forms of arylglycerol β-syringyl ethers are present in the lignin.

Notable in the pyridine spectrum of spruce lignin is:

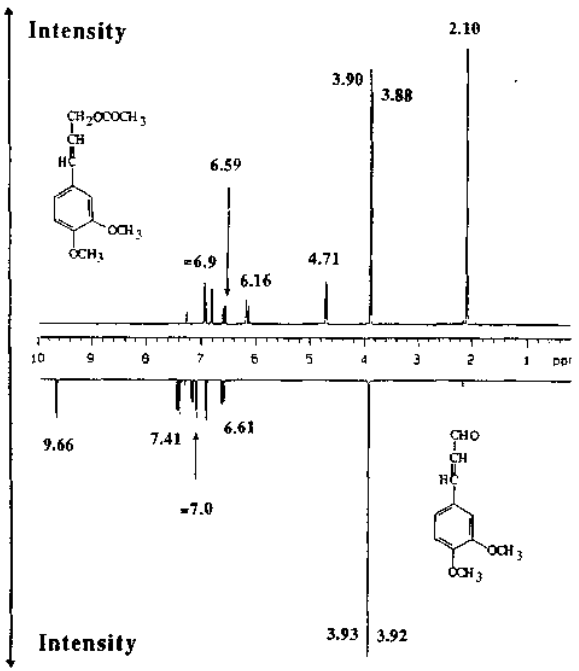
1) The absence of peaks due to β -1 structures, non-cyclic benzyl arylethers and 2-aryioxy-1-propiophenone structures (confirmation of results obtained using other solvents).

2) The peak due to methoxyl is comparatively well separated from other peaks (this is true also in the case of birch lignin) making it possible to estimate the number of methoxyl groups.

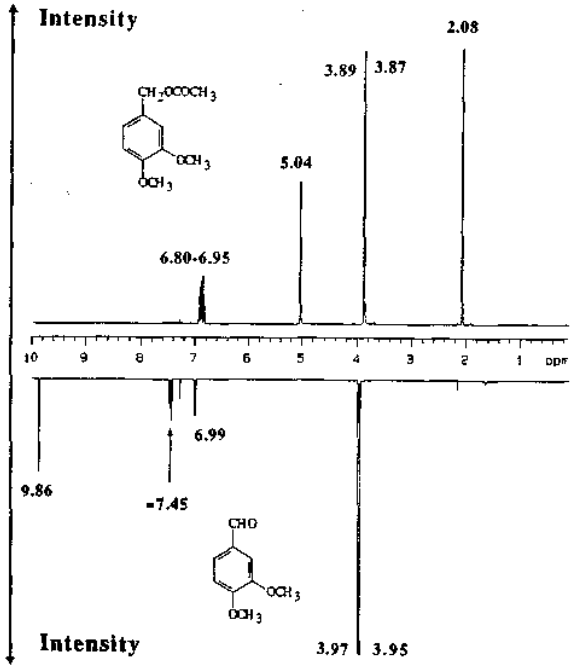
E1. Difference spectrum between acetylated borohydride-reduced spruce lignin and acetylated spruce lignin



E2. Model study



E3. Model study



E1 - E3. Comments.

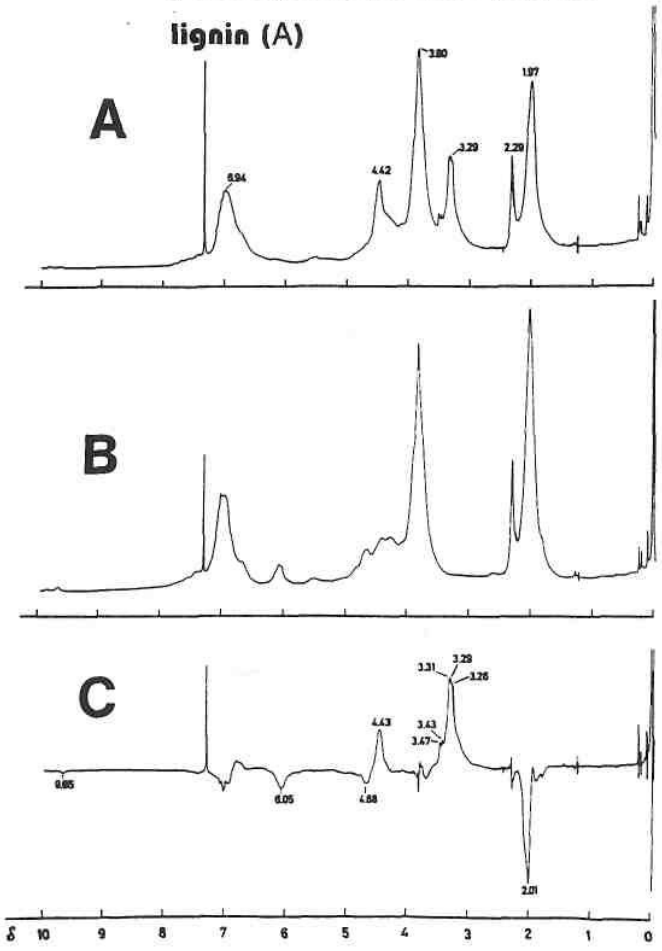
Comparisons of the difference spectrum (E1) with the model compound spectra (E2 and E3) show that almost all the details in the difference spectrum can be explained by the occurrence of coniferaldehyde units (3-4%) and vanillin units (≈ 3%) in spruce lignin. The peak at δ 4.32 in the difference spectrum can be explained by the occurrence of glyceraldehyde 2-aryl ethers *(*≈ 1%).

The results suggest that the aldehydes (a total of =8% of the units) represent the major part of the carbonyl groups in spruce lignin. Borohydride reduction of carbonyl groups gives rise to hydroxyl groups. This groups are in turn converted into acetate groups on acetylation. In accordance with this the difference spectrum E1 exhibits a positive acetate peak.

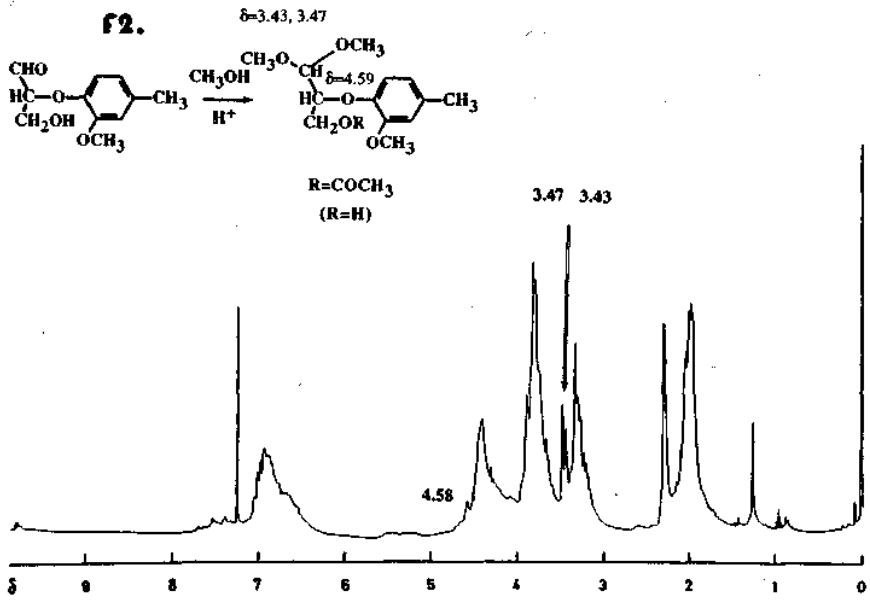
The position of this peak (=δ 2.08) corresponds to what is expected from the model compound spectra (E2 and E3) and the size of the peak indicates that the aldehydes explains about 70 % of the acetate groups formed on borohydride reduction/acetylation of spruce lignin.

It follows that the total number of units with carbonyl groups in spruce lignin can be expected to be ≈12%.

f1. Acetylated methylated (CH_3OH, *p*-toluenesulfonic acid) *spruce* lignin (A)



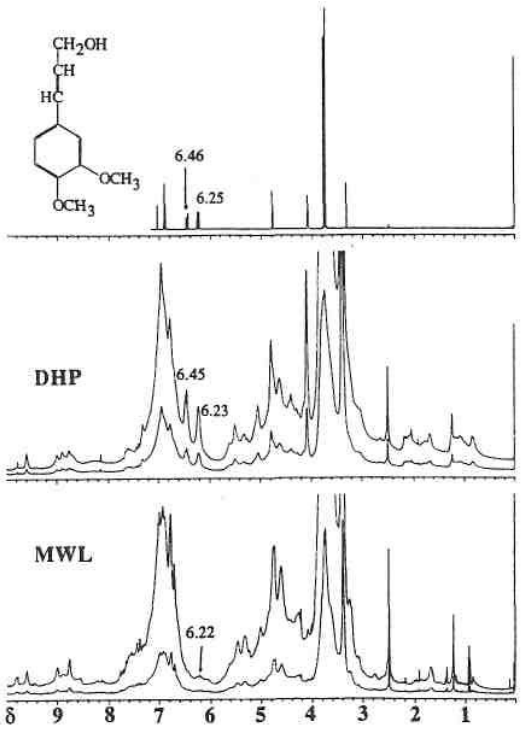
f2.



f1-f2 Comments.

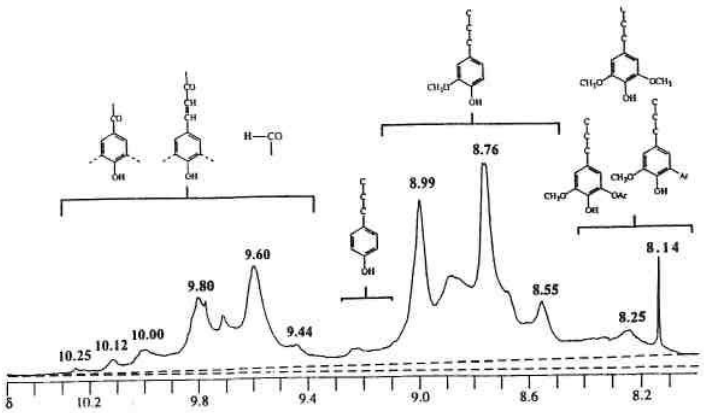
F1. Comparisons of the spectrum of methylated lignin (A) with the spectrum of non-treated lignin (B) show that benzyl alcohol groups (Hα signal at δ =6) are almost completely methylated. A methyl group is introduced in about every second lignin unit. The disappearance of benzyl alcoholic groups is reflected in the negative acetate peak at δ 2.01 in the difference spectrum (C).

F2. The spectrum shows very clearly the presence of acetals of glyceraldehyde 2-aryl ethers in a low molecular weight fraction of methylated spruce lignin. Model compound data are included in the in the fig.

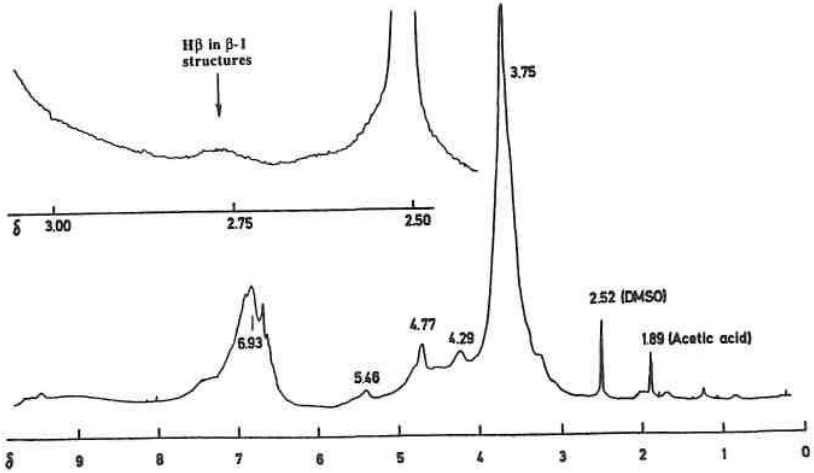


G1. Spruce lignin and models (DMSO, 500 MHz)

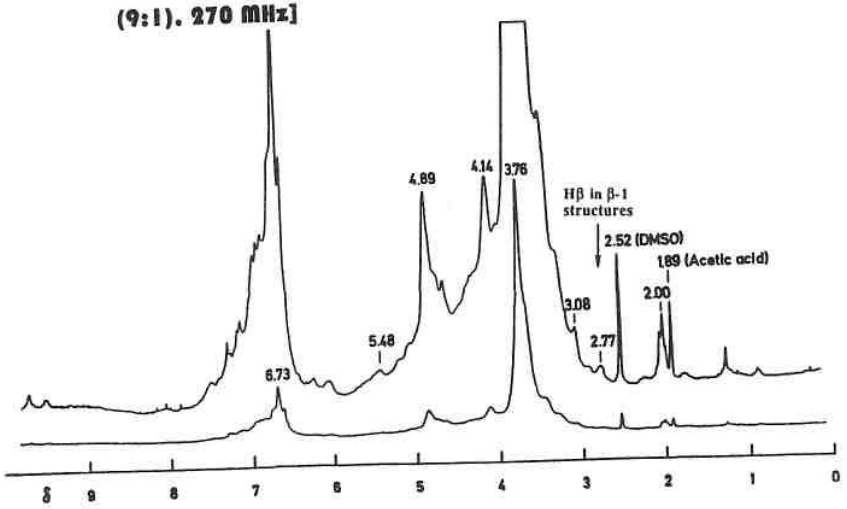
G2. Signals caused by phenolic groups and formyl groups



G3. Spruce lignin [DMSO-CD3COOD (9:1), 270 MHz]



G4. Birch lignin [DMSO-CD3COOD (9:1), 270 MHz]



G1-G4. Comments.

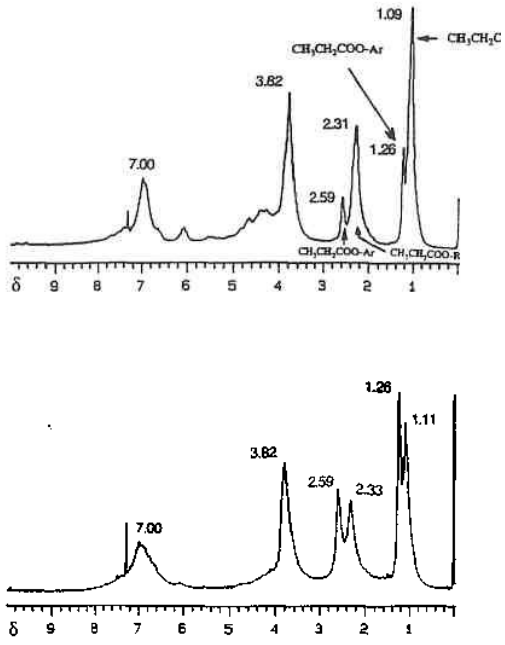
G1. Note that a small peak at δ 2.78 (Hβ in β-1 structures) is absent in the DHP spectrum.

G2. Integrations suggest that about 5% of the units are phenolic units in biphenyl structures.

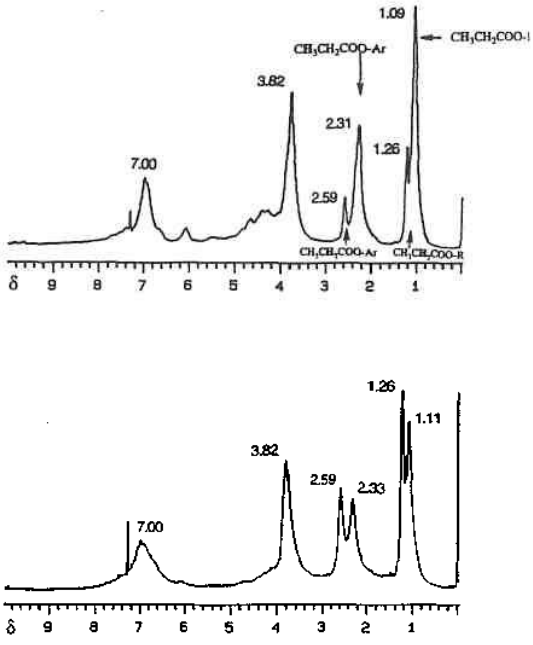
G3. The small peak at δ 2.77 corresponds to Hβ in *erythro* forms of β-1 structures. The amount of β-1 side chains is estimated to 1-2%.

G4. The peak (δ 2.77) attributed to *erythro* forms of β-1 structures is rather large (corresponds to 4-5% of the side chains).

H. Propionates of spruce lignin and kraftlignin (pine) ($CDCl_3$, 400MHz)



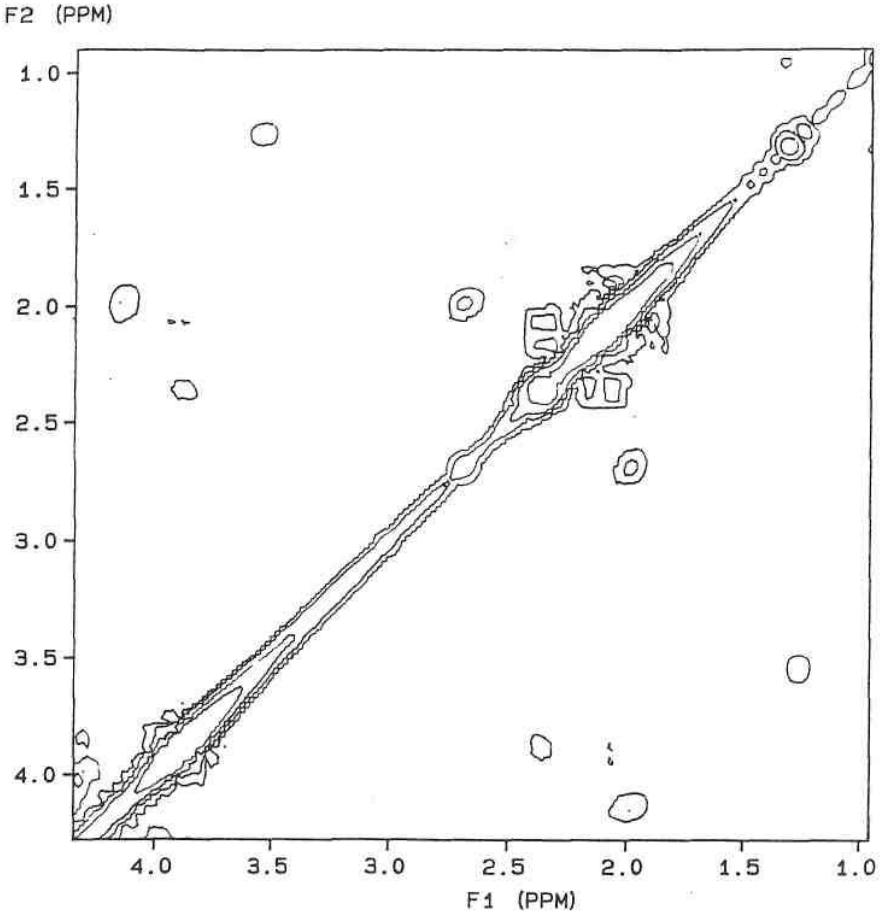
H. Propionates of spruce lignin and kraftlignin (pine) ($CDCl_3$, 400MHz)



H. Comments.

Propionates are suitable for the determination of total hydroxyl in lignins. This is particularly true in the analysis of modified lignins (e.g. kraft lignin) since such lignins often exhibit signals that interfere with acetate group signals.

I. 2D COSY *spectrum of spruce lignin*
(region δ1-4) ($CDCl_3$, 400MHz)



I. Comments.

The spectrum shows cross peaks that can be attributed to dihydroconiferyl alcohol units.