Carbon-13 NMR Spectra of Lignins, 10.[1] Comparison of Structural Units in Spruce and Beech Lignin

H. H. Nimz[a]; U. Tschirner[b]; M. Stähle[c]; R. Lehmann[c]; M. Schlosser[c]

[a] Institute of Wood Chemistry and Chemical Wood Technology, Hamburg [b] Polymer-Institute, Karlsruhe [c] Institut de Chimie Organique de Lausanne, Switzerland

PLEASE SCROLL DOWN FOR ARTICLE

CARBON-13 NMR SPECTRA OF LIGNINS, 10.[1]
COMPARISON OF STRUCTURAL UNITS IN SPRUCE AND BEECH LIGNIN

H.H. Nimz*, U. Tschirner**, M. Stähle***,
R. Lehmann***, and M. Schlosser***

*Dedicated to Prof. J.L. McCarthy on the occasion
of his 70th birthday

* Institute of Wood Chemistry and Chemical Wood
Technology
Leuschnerstr. 91, D-2050 Hamburg 80

**   Polymer-Institute
Hertzstr. 16, D-7500 Karlsruhe 21

***Institut de Chimie Organique de Lausanne
Switzerland

ABSTRACT

90.7 MHz Carbon-13 NMR spectra of spruce and beech mill-
ed wood lignins (MWLs) and comparison with the spectra
of their acetates as well as acetylated dehydrogenation
polymer (DHP) from coniferyl alcohol reveals detailed
information on the constitution of the two lignins. The
signals indicative of ß-0-4 units are split, due to the
occurrence of erythro and threo isomers. In beech lignin
erythro ß-0-syringyl ethers by far prevail in the ß-0-4-
linkages. The spectra also provide unequivocal evidence
for the occurrence of ß-5 and ß-ß linkages in both
spruce and beech lignins, while some anomalies remain in
the case of ß-1 and α,ß-bis-0-4 units. Two-dimensional
^{13}C-$J(^1H)$-NMR spectra of acetylated DHP corroborate the
assignment of signals in the spectra of acetylated MWLs.

INTRODUCTION

The first carbon-13 NMR spectra of MWLs from spruce and

beech were obtained with a Varian XL-100-15 spectrometer

at 25.2 MHz some ten years ago[2,3]. From these spectra,
it was not possible to differentiate between the main
structural units in lignin, because of severe overlap
and poor resolution of signals in the aliphatic ranges
of the spectra between 50 and 90 ppm. Acetylation of
the lignins led to a downfield shift of about 2 ppm for
most aliphatic carbon atoms linked directly to acetoxy
groups and a similar or even more pronounced upfield
shift for carbon atoms adjacent but not directly linked
to them[4]. An either upfield or downfield shift or no
shift at all after acetylation of the lignin was there-
fore indicative for the assignment of a signal in the
carbon-13 NMR spectra. Furthermore, the resolution of
the spectra from acetylated lignins was improved and
their solubility was higher, meaning higher concentra-
tions and signal intensities. The assignment of the
signals was further confirmed by comparison with the
spectra of DHPs and their acetates[4,5].

During the past years spectrometers with much higher
magnetic fields have become available, improving signal
intensities as well as signal resolutions profoundly.
This is demonstrated in Fig. 1, where nonacetylated
spruce and beech MWLs at 90.7 and 75.6 MHz, respective-
ly, give twenty to thirty separated signals while at
25.2 MHz there are only five or six[3]. Comparison of
these spectra with those of the lignin acetates, record-
ed at 90.7 MHz (Fig. 2), allows detailed insight into
the constitution and configuration of beech and spruce
lignins.

For a better understanding of the differences between
the spectra of acetylated spruce and beech lignins, we
have synthesized the ß-0-4 syringyl ether 1 (Fig. 3),
which for carbon atoms α,ß and γ gives different signals
from those for the corresponding guaiacyl ether, publish-
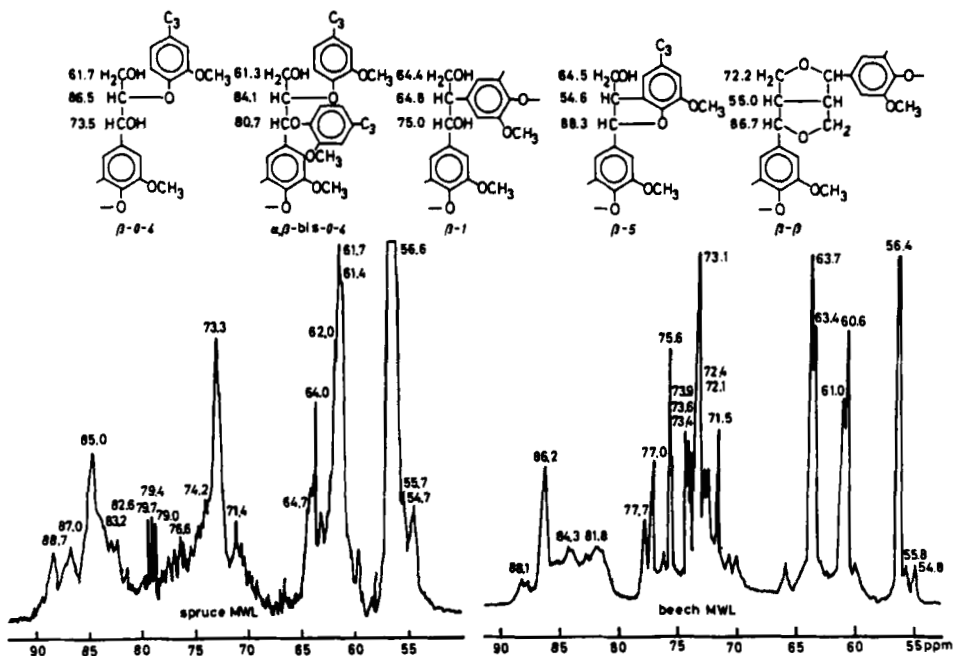
FIGURE 1: Carbon-13 NMR spectra of spruce and beech MWL.

ed earlier (cf. Fig. 2, upper left)[4]. In the same paper
the chemical shift value for the ß carbon atom in acety-
lated ß-1 units was found to be 51.2 ppm, which seems to
be surprisingly low when compared to the chemical shift
value of the ß-carbon atom in nonacetylated ß-1 units
at 64.8 ppm (df. Fig. 1). For this reason we have also
synthesized the ß-1 dilignol 2, and found a value of
51.5 ppm for the ß-carbon atom.

Due to the complexity of lignin structure, off resonance
spectra lead to a severe overlap of many multiplets
rendering their assignment nearly impossible. A recent
technique, two dimensional NMR spectroscopy[6], circum-
vents the overlap of the multiplets by displaying the
chemical shifts of the carbon atoms and their splitting
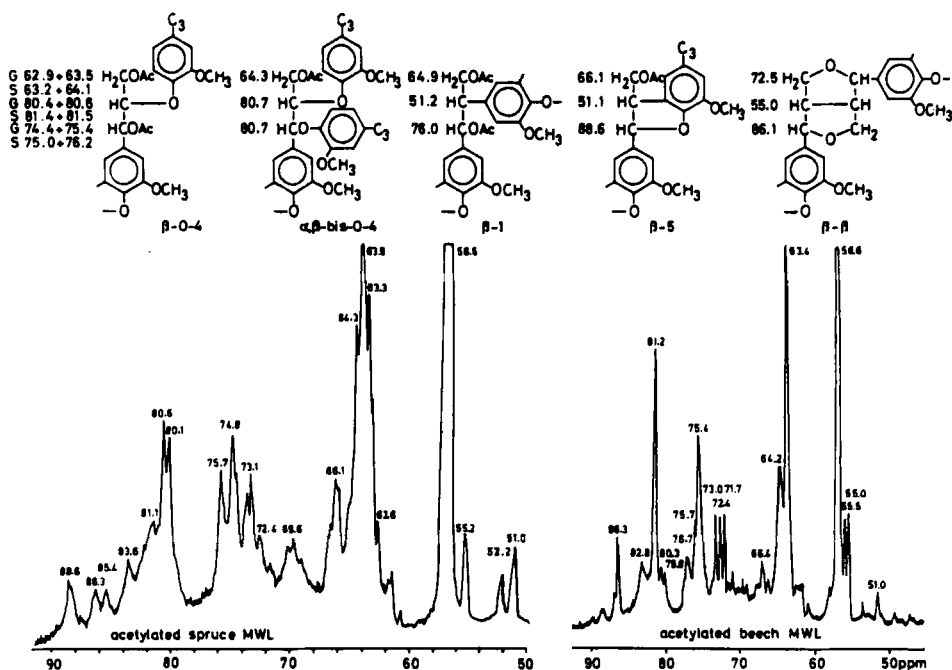
FIGURE 2:   Carbon-13 NMR spectra of acetylated spruce and beech MWL.

by spin-spin coupling with protons into two dimensions. In these 2DJ-^{13}C-PFT-NMR spectra (Fig. 5 and 6) one can distinguish between CH_3, CH_2, CH groups, and quaternary carbon atoms in acetylated DHP, which further confirms the assignment of signals in the carbon-13 NMR spectra of acetylated spruce and beech MWL.

MATERIALS AND METHODS

MWLs of beech and spruce wood were obtained according to Björkman[7] and freed from carbohydrates by dropping distinct amounts of benzene into their solutions in di-oxane/water in the presence of aluminium oxide[8]. Acety-lation of MWLs, DHP as well as model compounds 1 and 2 was carried out with pyridine/acetic anhydride.

Synthesis of model compound 1 was performed according to Nimz[9], but with syringyl alcohol instead of creosol. mp of the tetraacetate 1: 153°C. Compound 2 was synthesized according to Lundquist[10]. The nonacetylated 2 had mp 194°C (lit.: 192-193°C[11]). Tetraacetate 2: mp 130-133°C (lit. 130-133°C[11]).

DHP was obtained according to the Zutropf-procedure[12] and its solution in dioxane/water (1 : 1) was oxidized with the same amount of peracetic acid at 60°C and pH 3 for 5 hours[13]. PFT-Carbon-13 NMR spectra were obtained from 10 to 15 % solutions in hexadeuteroacetone/D_2O (9 : 1) with a Bruker WP 360 spectrometer at 90.7 MHz with the exception of beech MWL, which was recorded with a Bruker CXP 300 spectrometer at 75.6 MHz, and DHP acetate, which was recorded with a 400 MHz spectrometer. Usually some 25,000 scans were accumulated at pulse interval times between 1 and 4 sec. The technique used for obtaining the 2DJ-^{13}C-PFT NMR spectra has been described elsewhere[6].

RESULTS AND DISCUSSION

β-0-4- Structures

The abundance of β-0-4 linkages in spruce lignin has been the subject of intensive biosynthetical as well as analytical work by many authors and was estimated by both Freudenberg[14] and Adler[15] to be about 48 %. Degradation of beech lignin with thioacetic acid revealed 65 % β-0-4 plus α-0-4 ethers[16], meaning a number close to 60 % for β-0-4 structures. A similar number was recently found by Robert and Gagnaire[17] in birch lignin by quantitative carbon-13 NMR spectroscopy.

Consequently, carbon atoms α, β, and γ in β-0-4 structures give the most prominent signals between 50 and 90

ppm in the carbon-13 spectra of nonacetylated (Fig. 1)
as well as acetylated (Fig. 2) spruce and beech MWLs.
In the spectra of the nonacetylated MWLs (Fig. 1),
carbon atoms α and β in β-0-4 units give relatively
broad signals at 73.1 - 73.3 and 85.0 - 86.2 ppm, re-
spectively. The signals are not split, though one should
expect two signals, one each for the threo and erythro
diastereoisomers. As this is the case for the acetylated
MWLs (Fig. 2), one may assume that hydrogen bonding
broadens these signals. The signals of the γ carbon atom
at 60.6 - 62.0 ppm are only slightly split.

As mentioned above, acetylation shifts the signals of
the α- and γ-carbon atoms in β-0-4 units downfield by
some 2 ppm, while that of the β-carbon atom is shifted
upfield by about 5 ppm. In the spectrum of acetylated
spruce lignin (Fig. 2, left hand side), one finds two
signals each for the α-carbon (74.8 + 75.7 ppm), the
β-carbon (80.1 + 80.6 ppm), and the γ-carbon atom
(63.3 + 63.8 ppm) in β-0-4 units. These values fit well
with those of the two diastereoisomeric acetates of a
β-0-4 dilignol model compound, which we had synthesized
earlier[4]. According to the literature[18,19] the threo
isomer has the higher ppm values (lower field). From
the ratio of the signals it is difficult to estimate
which of the two diastereoisomers prevails,partly be-
cause the signal areas are not exactly proportional to
the concentrations of the carbon atoms and partly because
in this case they are similar to each other.   In model
studies, Nakatsubo et al.[18] obtained a 7 : 3 ratio of
threo : erythro guaiacylglycerol-β-guaiacylether by addi-
tion of water to the corresponding quinone methide in
dioxane. It is interesting to note that acetylated DHP
gives nearly identical signals for the β-0-4 diastereo-
isomers (cf. Fig. 5). Additional signals at 63.0 and

63.5 ppm may be assigned to γ-carbon atoms in glycerol side chains, obtained from α,β double bonds with per-acetic acid (see above).

In the case of acetylated beech MWL (Fig. 2, right hand spectrum) β-0-syringyl units give separated signals from β-0-guaiacyl moieties. For comparison, we have synthe-sized the guaiacylglycerol-β-syringyl ether 1. The crystalline compound 1 (mp 153°C) gives signals at 76.2, 81.5, and 64.1 ppm for carbon atoms α, β, and γ, re-spectively, while the noncrystalline isomer gives signals at higher field (lower ppm values): 75.0, 81.4, and 63.2 (cf. Fig. 3, compound 1). From the spectrum of acetylated beech lignin (Fig. 2) it clearly appears that the signals at 75.4, 81.2, and 63.4 ppm, which are the most prominent ones in these areas, can be assigned to the latter isomer. If we assume that this is the erythro isomer, we may conclude that in beech lignin the erythro β-0-syringyl units form the main linkages between the C_9 units. The corresponding threo β-0-syringyl units are indicated by much weaker signals at 76.7 and 63.2 ppm, assigned to the α and γ carbon atoms, while the signal of the β-carbon atom at around 81.3 ppm is overlapped by the strong signal of its erythro isomer at 81.2 ppm. β-0-guaiacyl units are indicated by very low signals at 79.8 and 80.3 ppm (cf. Fig. 2 right hand spectrum) assigned to the β-carbon atom, and a shoulder at 75.7 ppm, caused by carbon atom α in threo β-0-guaia-cyl ethers.

As a consequence it may be concluded that in beech lignin the β-0-4 units are overwhelmingly of the erythro β-0-syringyl ether type. This is in accordance with the observation that hardwood lignin can be more easily de-graded than softwood lignins. It has been shown earlier,

[20] that beech lignin can be degraded by mild hydrolysis
in 40 % yield and spruce lignin only to 10 %. In recent
model experiments we have found[21] that the rate of hy-
drolysis is four times as high with ß-O-syringyl than
with ß-O-guaiacyl ethers. It is also well known that
organosolv pulping of hardwoods proceeds more smoothly
than with softwoods[22].

α,ß-bis-O-4 Structures (noncyclic benzyl aryl ethers)

As indicated in Figs. 1 and 2, α,ß-bis-O-4 units are
expected to give signals at 80.7, 84.1 and 61.3 ppm in
the spectra of nonacetylated and at 80.7 as well as
64.3 ppm in that of acetylated lignins. These ppm
values were determined from the spectra of three oligo-
meric α,ß-bis-O-4 model compounds and checked by their
off resonance spectra[23]. Though the structure of these
compounds has been doubted by Leary recently[24], we main-
tain that the structures, given by Freudenberg and
Friedmann[25], are correct (cf. also Nimz[26]).

On the other hand, we have to assume that these struc-
tures in lignin would be sterically very restricted,
leading to line broadening and some change of the chemi-
cal shift values in the carbon-13 spectra. In Fig. 1
there exist broad signals in the beech MWL spectrum be-
tween 81 and 85 ppm, which possibly may be assigned to
carbon atoms α and ß in α,ß-bis-O-4 units, while the
γ carbon atom, which is sterically less restricted, may
contribute to the signal at 61.0 ppm.

In the spectrum of spruce MWL (Fig. 1, left hand side),
possible signals of carbon atoms ß and γ are completely
overlapped by the signals of carbon atoms ß and γ in
ß-O-4 units. At 80.7 ppm there exists only a very small
signal which could be assigned to the α-carbon atom in

α,β-bis-0-4 units. It seems, however, possible that the
signals at 82.6 and 83.2 ppm could be due to carbon atom
α in sterically restricted α,β-bis-0-4 units.

The situation is even more uncertain in the spectra of
acetylated spruce and beech MWLs (cf. Fig. 2), where
carbon atoms α and β in α,β-bis-0-4 units are expected
to give the same signal at 80.7 ppm. In the spectrum of
acetylated beech MWL (Fig. 2, right hand side) both
signals, at 80.7 for carbon atoms α and β and at 64.3
ppm for C-γ, are completely overlapped by the strong
signals for carbon atoms β and γ (threo isomer) in β-0-
4 units. Only in the spectrum of acetylated spruce MWL
(Fig. 2, left hand side), do we find a relatively strong
and broad signal at 81.1 ppm, which could be assigned to
carbon atoms α and β in α,β-bis-0-4 units. The same
signal, though less pronounced, is also present in the
spectrum of acetylated DHP (cf. Fig. 5). More characteri-
stic is the sharp signal of the stericly not restricted
carbon atom γ in α,β-bis-0-4 units at 64.3 ppm in Fig.5.

It is therefore so far not possible to provide unambigu-
ous evidence for the occurrence of α,β-bis-0-4 struc-
tural units in lignin from their carbon-13 NMR spectra.
There exists the possiblity that the above discussed
signals may be assigned to α-alkyl ethers and more work
with appropriate model compounds is needed (cf. also
Leary et al.[27]).

It is, however, interesting to note that the signal at
84.3 ppm in beech MWL (Fig. 1) disappears on acetyla-
tion (Fig. 2) but not the signal at 81.8, which is ex-
actly expected when the former is assigned to carbon β
and the latter to α in α,β-bis-0-4 units. It is also
possible to assign the signal at 61.0 ppm in the spec-
trum of beech MWL (Fig. 1) to the γ carbon atom of

α,β-bis-O-4 units rather than to the γ carbon atom in threo β-O-syringyl ethers. The same is true for the signal at 64.2 ppm in the spectrum of acetylated beech lignin (Fig. 2).

β-1 units

β-1 dilignols were first obtained from beech and spruce lignins by mild hydrolysis [28]. Independently Lundquist and Miksche[29] provided evidence for the occurrence of β-1 units in spruce lignin by isolation of the corresponding acidolysis products. From the yields of the corresponding lignin degradation products obtained with thioacetic acid, the amount of β-1 units in beech lignin was calculated to be about 15 %[16,30].

In the spectrum of nonacetylated beech MWL (Fig. 1, right hand side) we find three strong signals at 75.6, 63.7, and 63.4 ppm, which may be assigned to carbon atoms α, β, and γ in β-1 units, respectively. The fact that the γ-carbon atoms in β-5 units also absorb at 64.5 ppm (cf. Fig. 1) is of little importance, because β-5 units do not occur frequently in beech lignin (see below). However, beech MWL is always contaminated by xylans, which cannot be separated completely. For this reason we recorded the carbon-13 NMR spectrum of xylan in hexadeuteroacetone/D_2O (1 : 1) and obtained signals at 102.1 (C-1), 73.0 (C-2), 74.1 (C-3), 76.7 (C-4), and 63.3 (C-5). From these values we have to assume that carbon atom 5 in xylans also contributes to the signals at 63.4 and 63.7, which might explain the fact that the intensity of the latter is higher than that of carbon atom γ in β-O-4 units at 60.6 ppm.

In the spectrum of spruce MWL (Fig. 1, left hand side) the signals at 64.0 - 64.7 and at 75.0 ppm indicate the

presence of ß-1 structures, though their amount must be less than in beech lignin.

It had been found previously[4] that acetylation of 1,2-disyringyl-propanediol- (1,3) shifts the signals of carbon atoms α and γ only slightly downfield, while that of carbon atom ß was shifted upfield by 13.6 ppm. An explanation might be that the signal of carbon atom ß in the nonacetylated ß-1 dilignol is overlapped by that of the methoxy group at 56.6 ppm[31]. We have synthesized the acetate 2, which confirmed the previously found δ values of the aliphatic carbon atoms in acetylated ß-1 units (Fig. 3).

The expected signals for carbon atoms α and γ in acetylated ß-1 units, at 76.0 and 64.9 ppm, seem to be overlapped by the signals of carbon atoms α and γ in ß-0-4 units. More surprisingly, the signal of carbon atom ß at 51.2 ppm is very weak in beech lignin. The reason for this is presently unknown. Perhaps the signal is shifted downfield for some sterical reasons, or the relaxation time of the ß-carbon atom is extremely long.

ß-5 and ß-ß units

All six signals of the ß-5 and ß-ß units in the 25.2 MHz-carbon-13 spectra of nonacetylated MWLs from spruce and beech [2,3] were completely overlapped by the strong signals of ß-0-4 units and the methoxyl groups. Increasing the magnetic field by a factor of 3.6 leads to fairly well separated signals at 88.7 and 54.7 ppm for carbon atoms α and ß in ß-5 units as well as at 87.0 and 55.7 for carbon atoms α and ß of ß-ß units in the carbon-13 spectrum of spruce MWL (Fig. 1, left hand side). In beech MWL, which was recorded at 75.6 MHz (Fig. 1, right hand side) ß-5 units are clearly indicat-
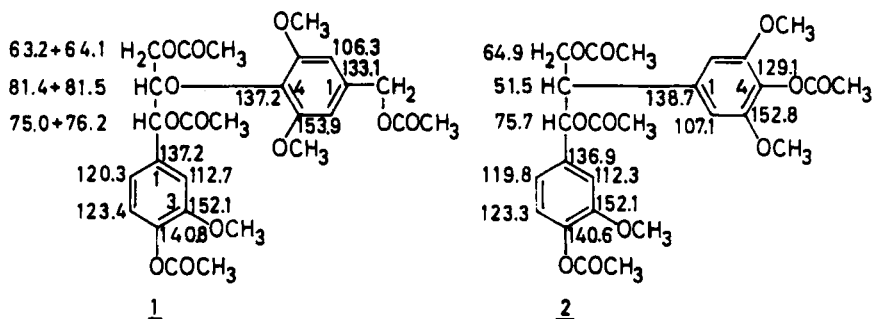
FIGURE 3: Chemical shift values of model compounds 1 and 2.

ed by signals at 88.1 and 54.8, and ß-ß units by signals
at 55.8 and 72.4 ppm.

Acetylation leads to an upfield shift of 3.5 ppm for
the signal of carbon atom ß and a downfield shift of
1.6 ppm for the signal of carbon atom γ in ß-5 struc-
tures, while the signals of ß-ß units remain constant.
This results in separated signals for carbon atomsα
(88.6 ppm), ß (51.0 ppm), and γ (66.4 ppm) in ß-5 units
as well as for carbon atoms α (86.3 ppm), ß (55.2 ppm)
and γ (72.4 ppm) in ß-ß units of acetylated spruce and
beech MWLs (cf. Fig. 2).

From the relative intensities of these signals it may
be concluded that in spruce lignin ß-5 units prevail
over ß-ß units, while the reverse is the case in beech
lignin. It has recently been concluded[32] from the
20 MHz carbon-13 NMR spectra of Pinus radiata lignins
that the presence of ß-ß units "in significant amounts
appears unlikely", which is certainly not the case for
spruce lignin.

Comparison of Spruce Lignin with DHP

Comparison of the spectrum of acetylated spruce MWL in
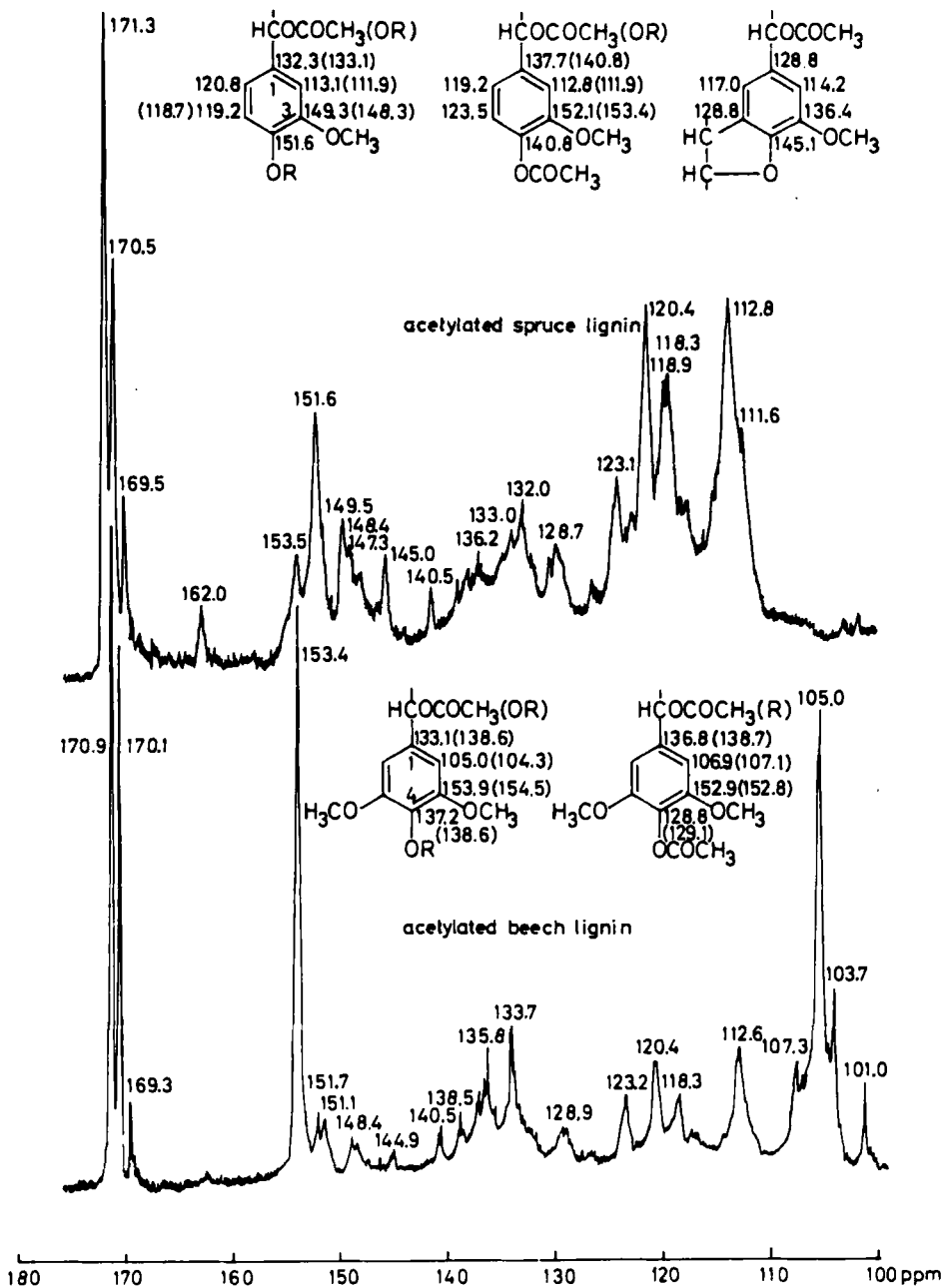Fig. 2 with the "one-dimensional" spectrum of acetylated

FIGURE 4: Aromatic part of the carbon-13 NMR spectra
of acetylated spruce and beech MWL.

DHP in Fig. 5 reveals that the main difference of the
two spectra is the higher intensity of signals assigned
to ß-5 and ß-ß units in acetylated DHP. A more detailed
explanation for this discrepancy has already been given
earlier[5]. On the other hand, there is only one broad
signal missing in the DHP spectrum at 69.6 ppm, which
may be assigned to carbohydrates in spruce MWL. Most
interestingly, there are three signals in both spectra,
that cannot be assigned so far, at 85.4, 83.6, and 73.1
ppm, in the spectrum of acetylated spruce lignin(Fig.2),
corresponding to the signals at 85.1, 83.2, and 73.1 ppm
in the spectrum of acetylated DHP (Fig. 5). The splitting
of the signals in the two-dimensional spectrum of acety-
lated DHP is in accordance with the assignments to
quaternary, tertiary, and secondary carbon atoms we have
given earlier[4].

Aromatic Carbon Atoms

Figs. 4 and 6 display the assignment of signals of
aromatic carbon atoms in acetylated spruce and beech MWL
as well as DHP. The chemical shift values are influenced
by the substitution patterns at the aromatic carbon atoms
as well as at the phenolic oxygen and α-carbon atoms.
Thus,for example, carbon atoms 2 and 6 in syringyl resi-
dues give three signals, at 103.7, 105.0, and 107.3
(cf. Fig. 4, lower spectrum) for Se(α-OR), Se(α-OAc), and
Sa, respectively, where "S" means syringyl, "a" acetylat-
ed, and "e" etherified. The difference in relative inten-
sities of the signals in the spectra of acetylated spruce
MWL (Fig. 4, upper spectrum) and DHP (Fig. 6) reveals the
assignment of aromatic carbon atoms in "condensed" aro-
matic rings of ß-5 units (cf. upper right formula in
Fig. 4). Signals 9, 11a, 16a, and 17a in Fig. 6 seem to
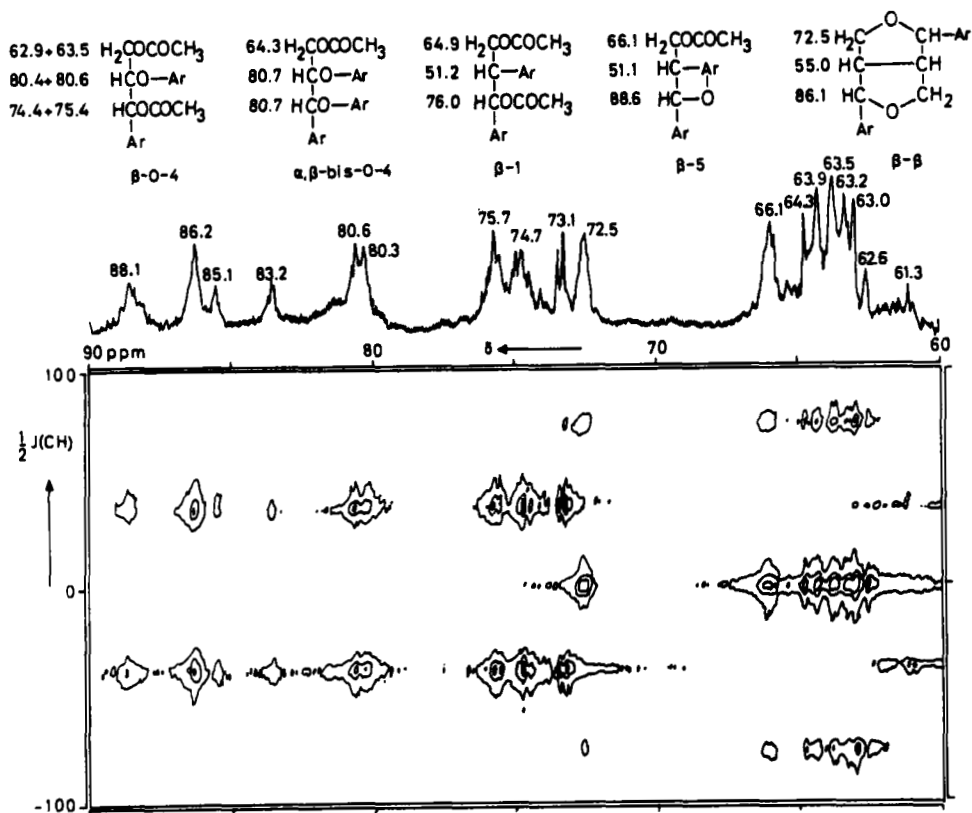be artifacts from CH groups. The two-dimensional spectrum

FIGURE 5: Aliphatic part of 2DJ-^{13}C-NMR spectrum of acetylated DHP.

in Fig. 6 clearly shows that besides these mentioned exceptions there is a border between quaternary aromatic carbon atoms, absorbing below 125 ppm (higher ppm values) and nonsubstituted, tertiary aromatic carbon atoms, absorbing above 125 ppm (lower ppm values). The olefinic carbon atoms in acetylated coniferyl alcohol groups, primarily present in DHP and absorbing at 134.5 ppm (C-α) and at 123.3 ppm (C-β) have been completely oxidized by peracetic acid (see above).
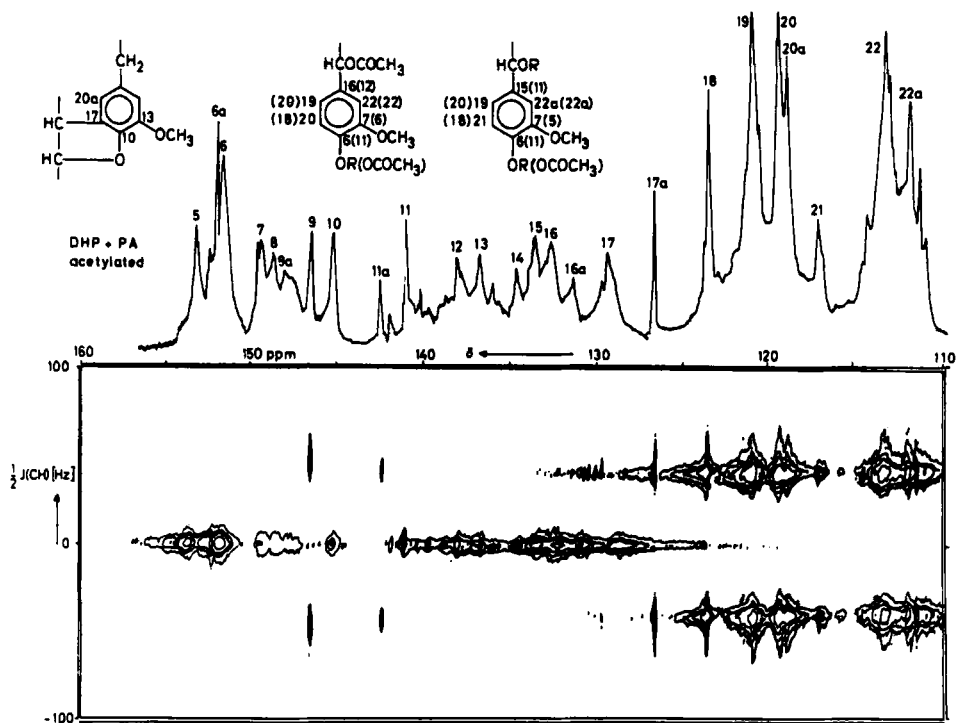
FIGURE 6: Aromatic part of 2DJ-^{13}C-NMR spectrum of acetylated DHP.

CONCLUSIONS

It has been shown that the improvement in signal reso-
lution gained by increasing the magnetic field leads
to fairly well separated signals for ß-0-4, ß-5, and
ß-ß units in spruce as well as in beech lignin (Fig. 1).
ß-1 units are also indicated in the spectrum of beech
MWL by two intense signals, while the corresponding
signals in the spectrum of spruce lignin are less clear
and partly overlapped. In the case of α,ß-bis-0-4 units,
broad absorption areas exist at the ppm values expected
for carbon atoms α and ß. One also finds relatively

broad signals for the same carbon atoms in ß-0-4
structures, which are actually expected to give two
signals for the threo and erythro isomers, as they
actually do in the spectra of their acetates (Fig. 2).
Also, the signal of the ß-carbon atom in ß-0-4 units
of spruce MWL is shifted upfield by 1.5 ppm, when com-
pared to that of ß-0-4 dilignols (Fig. 1, upper left
formula). These findings are indications for restricted
conformations caused by hydrogen bonding or steric
hindrance. Acetylation removes the hydrogen bonding but
not steric hindrance by bulky groups existing in α,ß-
bis-0-4 ethers.

In the spectra of acetylated MWLs (Fig. 2) and DHP (Fig.5,
one dimensional spectrum) carbon atoms α and ß in ß-0-4
structures give separated signals for their threo and
erythro isomers. In the case of spruce MWL and DHP the
areas of the corresponding signals, at 75.7 and 74.8 ppm
for C-α and at 80.6 and 80.1 ppm for C-ß, are similar to
each other, so that no conclusion can be drawn, which
one of the two isomers prevails over the other one. In the
case of acetylated beech MWL (Fig. 2, right hand spectrum)
four signals are to be expected for each, the α- and the
ß-carbon atom in ß-0-4 structures, belonging to the
erythro and threo isomers of ß-0-guaiacyl and ß-0-syrin-
gyl structures. From the relative signal areas of these
eight signals it can be concluded that in beech lignin
the ß-0-4 structures are mainly of the erythro ß-0-
syringyl ether type.

There is no doubt that a branched macromolecule like
lignin having a nonregular structure will never give a
completely resolved carbon-13 NMR spectrum. It is, how-
ever, desirable to apply high magnetic fields and use
more sophisticated techniques in order to gain further

insight into lignin structure. Also more appropriate
lignin model compounds are needed for comparison.

ACKNOWLEDGEMENTS

REFERENCES

1. Carbon-13 NMR spectra of lignins, 9. H.H. Nimz,
   M. Nemr. P. Schmidt, C. Margot, B. Schaub, and
   M. Schlosser, J.Wood Chem. Technol. 2, 371 (1982).

2. H.-D. Lüdemann and H. Nimz, Biochem.Biophys.Res.
   Comm. 52, 1162 (1973).

3. H.-D. Lüdemann and H. Nimz, Makromol.Chem. 175,
   2409 (1974).

4. H. Nimz and H.-D. Lüdemann, Holzforschung 30, 33
   (1976).

5. H. Nimz, J. Mogharab and H.-D. Lüdemann, Makromol.
   Chem. 175, 2563 (1974).

6. L. Müller, A. Kumar and R.R. Ernst. J.Chem.Phys. 63,
   5490 (1975); G. Bodenhausen, R. Freeman, R. Nieder-
   meyer and D.L. Turner, J.Magn.Res. 26, 133 (1977).

7. A. Björkman, Svensk Papperstidn. 59, 477 (1956).

8. K. Freudenberg, In Constitution and Biosynthesis of
   Lignin, p. 52, K. Freudenberg and A.C. Neish (ed.),
   Springer-Verlag, Berlin-Heidelberg-New York, 1968.

9. H. Nimz, Chem.Ber. 102, 3803 (1969).

10. P. Kristersson and K. Lundquist, Acta Chem.Scand. 34,
    213 (1980).

11. H. Nimz, Chem.Ber. 99, 469 (1966).

12. H. Nimz, J. Mogharab and H.D. Lüdemann, Makromol.
    Chem. 175, 2563 (1974).

13. H. Schwind, thesis, University of Karlsruhe, 1981.

14. K. Freudenberg, ref. 8, p. 73.

15. E. Adler, Wood Sci.Technol. 11, 169 (1977).

16. H. Nimz, Tappi 56 (5), 124 (1973).

17. D. Robert and D. Gagnaire, Proc. Ekman-Days 1981,
    Vol. 1, p. 86.

18. F. Nakatsubo, K. Sato and T. Higuchi, Mokuzai Gakka-
    ishi 22, 29 (1976).

19. J. Ralph, L.L. Landucci and R.A. Young, 1982 Canadian
    wood Chem.Symp. Extended Abstracts, p. 153.

20 H.Nimz, Holzforschung 20, 106 (1966).

21. H.H. Nimz, U. Tschirner and M. Roth, Proc. 1983
    ISWPC, Tsukuba, Japan, Vol. 1, p. 90.

22. B.D. Bogomolov and A.S. Groscev, Chim.Drev. 3, 3
    (1980).

23. H. Nimz and H.-D. Lüdemann, Makromol.Chem. 175,
    2577 (1974).

24. G.J. Leary, Wood Sci.Technol. 14, 21 (1980).

25. K. Freudenberg and M. Friedmann, Chem.Ber. 93, 2138
    (1960).

26. H.H. Nimz, Wood Sci.Technol. 15, 311 (1981).

27. G.J. Leary, D.A. Sawtell and H. Wong, Holzforschung
    37, 213 (1983).

28. H. Nimz, Chem.Ber. 98, 3160 (1965); 99, 469, 2638
    (1966).

29. K. Lundquist and G.E. Miksche, Tetrahedron Letters
    1965, 2131.

30. H. Nimz, Angew. Chem. 86, 336 (1974); Angew. Chem.
    internat. Edit. 13, 313 (1974)

31. Y. Sano, private communication.

32. J.A. Hemmingson, J.Wood Chem.Technol. $\underline{3}$ (3), 289
    (1983).