

^1H NMR spectral studies of lignins

Results regarding the occurrence of β -5 structures, β - β structures, non-cyclic benzyl aryl ethers, carbonyl groups and phenolic groups

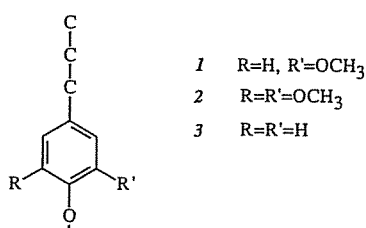
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SUMMARY: Spruce and birch lignin have been examined using ^1H NMR spectral methods. About 7% of the units may be attached to adjacent units by β -5 linkages in spruce lignin; only a few percent β -5 linked units are present in birch lignin. A large percentage of the lignin units in β - β structures of the pinoresinol type may be "condensed". Minor amounts of lignan-related structural elements other than those of the syringaresinol and pinoresinol types may be present in birch lignin. The distribution of various types of lignin units with carbonyl groups is treated. The major part of the hydroxyl groups introduced on borohydride reduction of spruce lignin originates from units of the cinnamaldehyde and benzaldehyde types. The occurrence of various types of phenolic groups is discussed.

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It is possible to study the occurrence of and distribution of various types of structural elements in lignins by ^1H NMR spectrometric methods. A previous paper (Lundquist 1991) describes quantitative estimates of a series of lignin structures in spruce lignin and birch lignin. The present paper summarizes and/or complements earlier ^1H NMR spectral studies on the occurrence of β -5 structures, β - β structures, non-cyclic benzyl aryl ethers, phenolic groups and carbonyl groups. Guaiacylpropane units (1) predominate in spruce lignin while birch lignin is composed of nearly



equal amounts of guaiacylpropane and syringylpropane (2) units; minor amounts of *p*-hydroxyphenylpropane units (3) are present in both lignins. Only results derived from examinations of milled wood lignins and model compounds are reported in this paper. However, it is possible in many cases to analyse technical lignins or lignin products in pulping liquors for the aforementioned types of structural elements by the same methods or modifications thereof.

Results and discussion

β -5 Structures (4)

Spruce lignin. ^1H NMR spectra of acetylated spruce lignin in chloroform solution exhibit a peak at $\delta \approx 5.5$ [fig. 1]; the complete spectrum has been published previously (Lundquist 1980, Lundquist and Stern 1989)] which on the basis of model compound studies

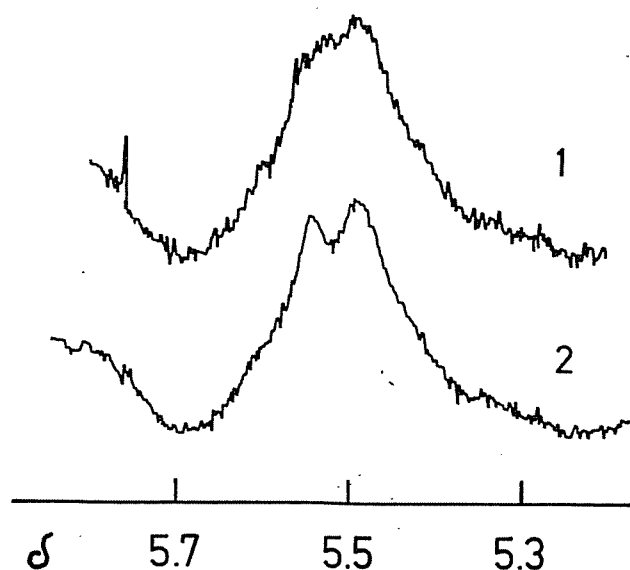


Fig. 1. Range δ 5.3-5.7 of the ^1H NMR spectrum (270 MHz) of acetylated spruce lignin. Spectrum 2 appeared on irradiation at $\delta \approx 3.76$ (the peak position for $\text{H}\beta$ in β -5 structures); the peaks in spectrum 2 are attributed to $\text{H}\alpha$ in etherified (4a) (δ 5.49) and phenolic (4b) (δ 5.54) β -5 structures.

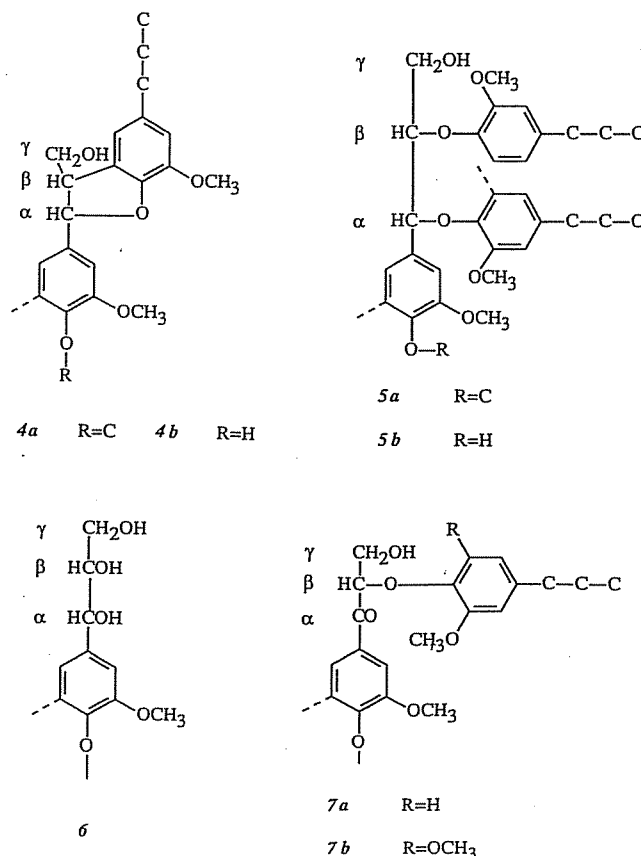


Table 1. H^1 NMR data for acetate derivatives of lignin model compounds representative of arylglycerol units (6) and structural elements involving non-cyclic benzyl aryl ethers (5).

Compound	δ units/ppm; J values in Hz are given in parentheses (m = multiplet)					
	H α	H β	H γ	OCH ₃	CH ₃ CO	Ar-H
8 (erythro)	5.93 (6.0)	5.40 (m)	4.23 (m) ^a	3.87, 3.89	1.98, 2.04, 2.11	≈ 7
8 (threo)	5.90 (7.6)	5.43 (m)	3.79 (5.8, 12.1) 4.24 (3.4, 12.1)	3.87, 3.89	2.05, 2.07, 2.08	≈ 7
9 (erythro)	6.00 (5.7)	5.38 (m)	4.24 (m) ^a	3.84	1.99, 2.03, 2.12, 2.30	≈ 7
9 (threo)	5.96 (7.5)	5.43 (m)	3.82 (5.6, 12.1) 4.28 (3.8, 12.1)	3.84	2.04, 2.06, 2.08, 2.30	≈ 7
10 (erythro)	6.00 (6.0)	5.39 (m)	4.26 (m) ^a	3.83 ^b	2.00, 2.04, 2.14, 2.32	6.61
10 (threo)	5.92 (7.6)	5.43 (m)	3.83 (5.6, 11.8) 4.28 (3.6, 11.8)	3.83 ^b	2.05, 2.07, 2.09, 2.32	6.61
11 (erythro)	5.38 (6.2)	4.70 (m)	4.66 (m) 4.57 (2.8, 11.4)	3.71, 3.75, 3.82	1.94, 2.27	≈ 7
11 (threo)	5.42 (4.8)	4.79 (m)	4.14 (6.6, 11.8) 4.48 (4.2, 11.8)	3.76, 3.77, 3.81	1.94, 2.28	≈ 7
12 (erythro)	5.43 (6.1)	4.69	4.65 (m) 4.55 (3.0, 11.4)	3.72, 3.76, 3.85	1.95, 2.06, 2.27	≈ 7
12 (threo)	5.47 (5.1)	4.77 (m)	4.13 (6.4, 11.8) 4.46 (4.1, 11.8)	3.77, 3.80, 3.81	1.97, 2.07, 2.29	≈ 7
13 (erythro)	5.33 (6.6)	4.71 (m)	4.65 (m) 4.56 (3.2, 11.6)	3.73, 3.82, 3.83 ^b	1.95	≈ 7
14 (erythro)	5.38 (6.3)	4.71 (m)	4.6 (m) ^a	3.71, 3.76, 3.83	1.94, 2.28	≈ 7

^a2H. ^b6H.

can be attributed to β -5 structures (4). There are other types of lignin structures which can be expected to give signals at $\delta \approx 5.5$, namely non-cyclic benzyl aryl ethers (5) [etherified such structures (5a) are assumed to predominate (Adler et al. 1968) and are expected to give rise to a signal close to δ 5.4 (H α), table 1; see also Brunow et al. 1989], arylglycerol units (6) [expected to give rise to a signal close to δ 5.4 (H β), table 1 (stereoselective syntheses of the diastereomers of 8 (Adler and Gustafsson 1963) provide a basis for the

stereochemical assignments of 8-10 given in table 1)] and 2-guaiacoxypropylphenones (7a) (expected to give rise to a signal at $\delta \approx 5.6$ (H β), table 2). However, the position of the $\delta \approx 5.5$ peak, decoupling experiments (fig. 1), examinations of methylated lignin and 2D experiments clearly evidence that the $\delta \approx 5.5$ peak essentially is due to H α in β -5 structures (Lundquist and Stern 1989, Ede et al. 1990). Support for this is also obtained from spectra recorded using other solvents than chloroform and spectra of underivatized lignin, since in all these instances peaks appear in the spectra, which can be attributed to H α in β -5 structures. It follows that the number of arylglycerol units (6), non-cyclic benzylaryl ethers (5) and 2-guaiacoxy-

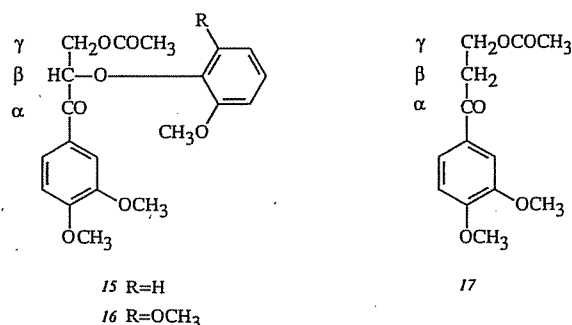
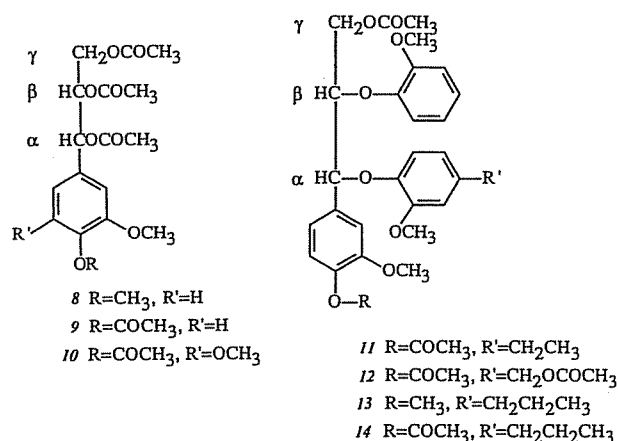


Table 2. H^1 NMR data for acetate derivatives of lignin model compounds representative of lignin units with an arylconjugated keto group. Spectra of 15 have been recorded at 293 K, 300 K and 311 K to illustrate the temperature dependence of peak positions. Recording of spectra of a series of acetate derivatives of lignin models (solvent, CDCl₃) showed that moderate temperature changes only slightly affected the peak positions [the location of acetate signals and some other signals (e.g. the signal from H β in 15) are comparatively sensitive to temperature changes].

Compound	δ units/ppm; J values in Hz are given in parentheses (m = multiplet)					
	H β	H γ	OCH ₃	CH ₃ CO	Ar-H	
15 ^a	5.63 (m)	4.52 (7.3, 12) 4.68 (3.8, 12)	3.78, 3.93, 3.95	2.06	$\approx 6.9^d$, 7.68 (2.1), 7.85 (2.1, 8.5)	
15 ^b	5.62 (m)	4.52 (6.8, 12) 4.67 (3.8, 12)	3.78, 3.93, 3.95	2.05	$\approx 6.9^d$, 7.68 (1.6) 7.85 (1.6, 8.4)	
15 ^c	5.59 (m)	4.53 (6.8, 12) 4.66 (3.8, 12)	3.77, 3.92, 3.94	2.03	$\approx 6.9^d$, 7.68 (1.7), 7.84 (1.7, 8.5)	
16	5.43 (5.5)	4.56 (5.5)	3.73 ^e , 3.93, 3.95	1.95	6.5-7.1 ^f , 7.72 (2.0), 7.86 (2.0, 8.5)	
17	3.28 (6.4)	4.52 (6.4)	3.94, 3.96	2.04	6.9 (8.4), 7.58 (m) ^g	

^aTemperature, 293 K. ^bTemperature, 300 K. ^cTemperature, 311 K. ^d5H. ^e6H. ^f4H. ^g2H.

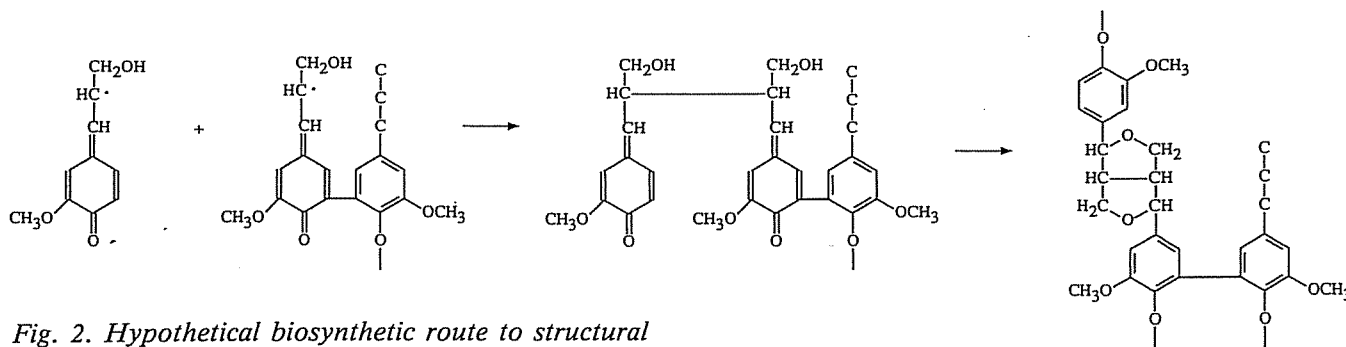
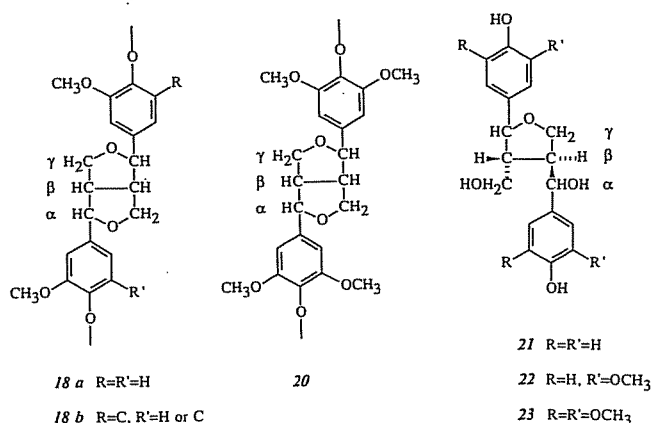


Fig. 2. Hypothetical biosynthetic route to structural elements of the pinoresinol type attached to an adjacent unit by a biphenyl linkage (19).

propiophenone structures (7a) must be small as compared with the number of units attached to an adjacent unit with a β -5 linkage (the occurrence of structure of types 5 and 7 in lignins is treated below).

Nevertheless the occurrence of these types of structures causes an uncertainty in connection with quantitative evaluations of the $\delta \approx 5.5$ peak. It was found that this peak represents 6-16% of the side chains calculated as $H\alpha$ in β -5 structures (Lundquist 1980; regarding the definition of the upper and lower value, cf. Lundquist 1991). An attempt to summarize results from runs performed under various conditions (different solvents, derivatized and underivatized lignin) indicated that the proportion of units attached to an adjacent unit by a β -5 linkage may be about 7%. This figure is somewhat lower than those obtained by independent methods [acidolysis (Adler and Lundquist 1963), permanganate oxidation (Erickson et al. 1973), ozonolysis (Habu et al. 1990)]; results obtained by these last methods include, however, to a greater or lesser extent structural elements other than those of type 4.

Birch lignin. Spectra of birch lignin recorded under various conditions exhibit a signal which can be attributed to $H\alpha$ in β -5 structures. Quantitative evaluation of this signal is difficult because of the structural complexity of birch lignin owing to the presence of large amounts of guaiacyl units (1) as well as syringyl units (2) [results from examinations of model compounds representative of arylglycerol units (table 1) and 2-aryloxypropiophenone structures (table 2) are of interest in this context]. It seems, however, that only a few percent of the units are linked to an adjacent unit by a β -5 linkage in birch lignin (possibly as much as 5% of the units, a figure obtained in an evaluation of results from permanganate oxidation studies, Larsson and Miksche 1971).



β - β Structures

Spruce lignin. The occurrence of β - β structures of the pinoresinol type (18) in spruce lignin has been discussed recently (Lundquist and Stomberg 1988). No pinoresinol was found in acidolysis mixtures from spruce lignin (Lundquist 1970). Thioacidolysis and subsequent Rayney nickel treatment of spruce lignin gave only trace amounts of degradation products originating from pinoresinol structures (Lapierre et al. 1991). However, NMR studies clearly evidence that a few percent of the units in spruce lignin are present in pinoresinol structures (Lundquist and Stomberg 1988 and references therein). These findings may be interpreted as indicating that a large proportion of the units in pinoresinol structures are attached to adjacent units by linkages which are stable to solvolytic treatments (primarily structures of type 18 b). A hypothetical biosynthetic route to one type of such structural elements (19) is shown in fig. 2. The biosynthetic route shown in fig. 2 is in accordance with lignin biosynthesis in an "end-wise" manner; this has been discussed previously (Lundquist and Hedlund 1971).

Evidence for the occurrence of an additional type of β - β structures in spruce lignin has accumulated during the past few decades, namely those of the 3,4-divanillyltetrahydrofuran or 2,3-divanillyl-1,4-butanediol types (Lundquist and Stomberg 1988, Lapierre et al. 1991).

Birch lignin. The occurrence of β - β structures in birch lignin has been discussed in recent papers (Lundquist and Stomberg 1988, Lundquist 1991). It seems that such structural elements in hardwood lignins are primarily of the syringaresinol type (20) (Lundquist and von Unge 1986, Bardet et al. 1986, Lapierre et al. 1987a). Small amounts of the β - β linked dimer 21 are formed on oxidation of *p*-coumaryl alcohol (Nakatsubo and Higuchi 1975). The analogous compounds (22 and 23) are not known to form on oxidation of coniferyl alcohol and sinapyl alcohol but the isolation of a lignan with structure 22 has been reported (Andersson et al. 1975, Ozawa et al. 1988). The ¹H NMR spectrum of the acetate of this compound shows a signal at δ 5.79 ($H\alpha$). A hitherto unassigned signal at δ 5.76 in the spectrum of acetylated birch lignin (Lundquist 1979, Lundquist et al. 1980) might reflect the presence of minor amounts of structural elements corresponding to dimers 22 or 23. Alternatively, the δ 5.76 peak could be due to other types of lignin units carrying benzyl alcoholic groups of the type present in 22 and 23. It is noteworthy in this context that the occurrence of small amounts of β - β structures of dibenzyltetrahydrofuran

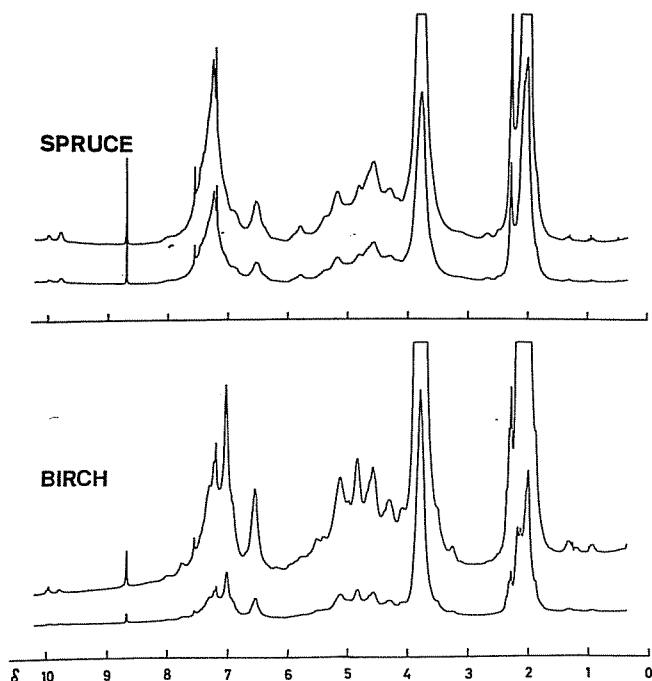


Fig. 3. ^1H NMR spectra of spruce and birch lignin in pyridine- d_5 solution.

type in beech lignin has been suggested by Nimz and Lüdemann (1976).

Non-cyclic benzyl aryl ethers (5)

According to ^1H NMR spectral studies at most a few percent arylglycerol β -aryl ether structures carry an aryl ether group at the α -position (structures of type 5) (see, e.g., Lundquist and von Unge 1986 and Ede et al. 1990). Most studies have been performed with lignin acetates in chloroform solution. It can be derived from the model compound data compiled in table 1 that the signal from $\text{H}\alpha$ under these conditions can be expected to appear close to δ 5.4 (Brunow et al. 1989 and unpublished data). Acetylated spruce lignin does not exhibit any peak at this δ value (fig. 1). It is notable that recent hydrolysis studies of lignin in wood (in situ) also give small figures for the frequency of non-cyclic benzyl aryl ethers (Lai and Guo 1991).

Carbonyl groups

Spruce lignin. In a previous paper the occurrence of aldehyde groups in spruce lignin was studied using ^1H NMR spectrometric methods (Lundquist and Olsson 1977). The results suggested the presence of 4% cinnamaldehyde groups, 3% benzaldehyde units and, possibly, 1-2% glyceraldehyde-2-aryl ethers. A variety of approaches have been used to determine the frequency of this last type of structure in spruce lignin and results in the range 1-3 % have been reported; the large figures are possibly related to a partial liberation of such structures on mild acid treatment (Brunow and Lundquist 1991). Degradation studies [acidolysis (Lundquist 1970), thioacidolysis (Lapierre et al. 1987b)] suggest the presence of 2-aryloxypropylphenone units in lignins. Their number seem to be small (<2%) according to ^1H NMR studies. Thus examinations of spruce lignin acetates in different solvents did not provide clear-cut evidence for the presence of such units. $\text{H}\beta$ in 2-guaiacoxypropylphenones should for instance according to

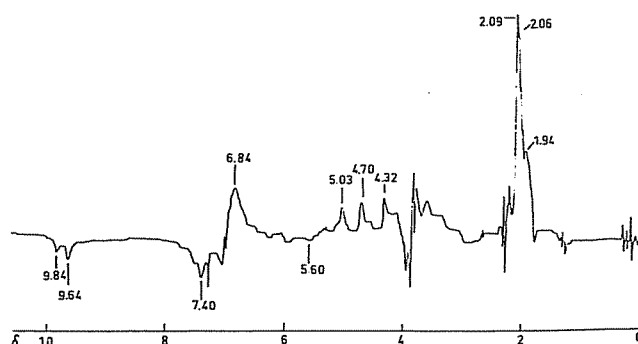


Fig. 4. Difference spectrum obtained by subtraction of the spectrum of acetylated spruce lignin from the spectrum of spruce lignin subjected to borohydride reduction/acetylation.

model compound data give rise to a peak at about δ 6 in pyridine solution (Lundquist and von Unge 1986). As is evident in fig. 3 no such peak appear in the spruce lignin spectrum. Further, no pronounced negative peak appears at $\delta \approx 5.6$ ($\text{H}\beta$ in 7a, table 2) in a difference spectrum showing changes caused by borohydride reduction (fig. 4, see below); structures of type 7a would give rise to such a negative peak since 2-aryloxypropylphenone groups are eliminated on borohydride reduction.

Fig. 4 shows a difference spectrum obtained by subtraction of the spectrum of acetylated spruce lignin from the spectrum of borohydride-reduced and subsequently acetylated spruce lignin. Most of the features of the difference spectrum has been interpreted previously (Lundquist and Olsson 1977) and the discussion in this presentation is therefore restricted to the peak at δ 2.09 which can be attributed to methyl protons in acetate groups ($>\text{CHOCOCH}_3$) formed from carbonyl groups ($>\text{CO}$) on reduction and subsequent acetylation. Reduction/acetylation of benzaldehyde units (24) and cinnamaldehyde units (26) produces acetate groups with signals located at $\delta \approx 2.09$ (table 3). Integrations show that the δ 2.09 peak largely ($\approx 70\%$) can be explained by conversion of benzaldehyde units and cinnamaldehyde units into units of types 25 and 27, respectively. Accordingly, there are only a few carbonyl groups in spruce lignin other than those in units of types 24 and 26 which give rise to acetate groups on reduction/

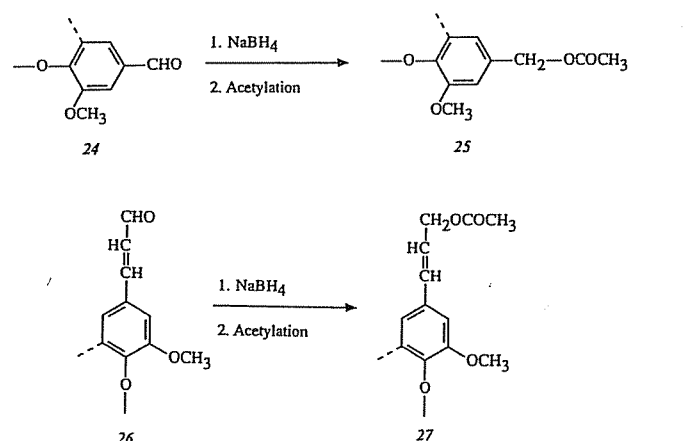
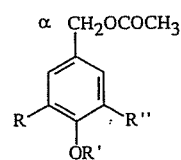
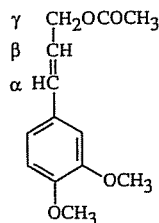


Fig. 5. Conversion of benzaldehyde units (24) and cinnamaldehyde units (26) into units of type 25 and of type 27, respectively by borohydride reduction/acetylation.



- 28 R=R'=H, R'=COCH₃
 29 R=H, R'=R''=OCH₃
 30 R=H, R'=COCH₃, R''=OCH₃
 31 R=R''=R'''=OCH₃
 32 R=R''=OCH₃, R'=OCH₃



33

acetylation. Although the quantitative results from difference spectra should be treated with caution this rises the question as to whether the number of carbonyl groups in spruce lignin is smaller than usually assumed [$\approx 20\%$ units with carbonyl groups are reported by Adler and Marton (1959) while a smaller figure (12%) is given by Gierer and Wallin (1966); see also Kirk and Chang (1975)]. Lignins may contain some carbonyl groups in quinoid units and units of cyclohexadienone type. This may explain the discrepancy regarding the carbonyl content, since it is at least in some cases uncertain if reduction of these types of structures results in an increase of the number of hydroxyl groups and, consequently, acetate groups in the acetylated sample.

Birch lignin. It was concluded in a previous paper that birch lignin contained 1-2% of benzaldehyde units (24) as well as of cinnamaldehyde units (26) (Lundquist 1979). From the spectrum of acetylated birch lignin in pyridine (fig. 3) and model compound data it can be concluded that the number of 2-aryloxypropiophenone structures must be small in birch lignin: H β in such structures should give rise to a signal at $\delta \approx 6$ (Lundquist and von Unge 1986), no such signal is discernible in the birch lignin spectrum (fig. 3).

Phenolic groups

Acetylated lignins in chloroform exhibit a peak at $\delta \approx 2.3$ which is attributed to phenolic acetate. This is supported by examination of a wide variety of lignin model compounds. Phenolic acetate in biphenyl structures does not contribute to the $\delta \approx 2.3$ peak; signals from such structures are located at $\delta \approx 2.1$ (Lundquist 1991). As illustrated by examples in table 3, phenolic acetate groups in guaiacyl, syringyl as well as *p*-hydroxyphenyl units contribute to the lignin peak at $\delta \approx 2.3$. Although *p*-hydroxyphenylpropane units usually are present in small numbers they are of importance in this context since a large fraction of these units are phenolic; this has been shown in recent thioacidolysis studies of methylated lignins (Lapierre and Rolando 1988, Lapierre et al. 1988).

As judged from the composition of degradation products formed on thioacidolysis of methylated aspen lignin it can be concluded that the number of phenolic groups of the guaiacyl type is larger than the number of phenolic groups of the syringyl type (Lapierre et al. 1988). Similarly permanganate oxidation studies (Larsson and Miksche 1971) as well as ^1H NMR examinations (Lundquist and von Unge 1986)

Table 3. ^1H NMR data for acetylated model compounds representative of lignin units formed on borohydride reduction of aldehydic lignin units (25 and 27).

Compound	δ units/ppm; J values in Hz are given in parentheses		
	H α	CH ₃ CO	Ar-H
28	5.09	2.09, 2.30	7.0-7.2
29 ^a	5.04	2.08	≈ 7
30	5.07	2.10, 2.31	
31	5.03	2.11	
32	5.05	2.11, 2.32	
33 ^b	6.60 (16)	2.08	≈ 7

^a δ for OCH₃ 3.87, 3.88.

^b δ (J) for H β 6.16 (6.5, 16), for H γ 4.71 (6.5) and for OCH₃ 3.89, 3.90.

suggest a comparatively large number of phenolic groups of the guaiacyl type in birch lignin. Thus it seems that the proportion of free phenolic groups in the *p*-hydroxyphenylpropane moiety of lignins is considerably larger than the proportion of such groups in the guaiacylpropane moiety; guaiacylpropane units in turn carry free phenolic groups more frequently than syringylpropane units do. This may reflect the relative ability of units of types 1-3 to undergo oxidative phenol coupling during the biosynthesis of lignin. Such a difference in reactivity could explain why a comparatively large proportion of the *p*-hydroxyphenylpropane units is phenolic.

It is in this connection of some interest to note that it has been shown in recent unpublished studies (Lapierre and Lundquist) that a low molecular mass fraction (yield $\approx 50\%$) separated from purified spruce lignin exhibited a comparatively high phenol content.

Experimental

^1H NMR spectra of acetylated lignins and most of the model compounds were recorded at 270 MHz with a Bruker WH270 instrument (temperature ≈ 300 K). Spectra of some of the model compounds (10, 15, 17, 28) were recorded at 400 MHz with a Varian VXR-5000 instrument (temperature 300 K unless otherwise stated). Deuteriochloroform was used as solvent unless otherwise stated. TMS was used as internal reference. When lignin spectra were recorded the number of scans was ≈ 1000 and the pulse interval was ≈ 4 seconds. Quantitative estimates of structural elements in lignins are based on the assumption that the peak at $\delta \approx 7$ corresponds to 2.7 H/phenylpropane unit in the case of spruce lignin and 2.3 H/phenylpropane unit in the case of birch lignin (cf. Lundquist 1991). It was found that peak positions were essentially independent of sample concentration as far as spectra of acetate derivatives in chloroform solution are considered. Spectral data for 15 obtained at different temperatures are given in table 2 to illustrate the temperature dependence of the peak positions.

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