^{1}H NMR spectral studies of lignins
Quantitative estimates of some types of structural elements

Knut Lundquist, Department of Organic Chemistry, Chalmers University of Technology, Göteborg, Sweden

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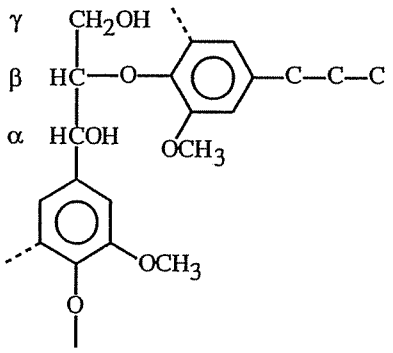
SUMMARY: Spruce and birch lignin have been examined using ^{1}H NMR spectral methods. The results suggest that spruce milled wood lignin contains some 30% arylglycerol units with a β-aryl ether substituent together with certain types of derivatized structural elements of this type and birch milled wood lignin about 40% of the corresponding types of units. Extended model compound studies confirmed earlier results regarding the distribution of *erythro* and *threo* forms of arylglycerol-β-aryl ethers. Trace amounts of cinnamyl alcohol units (<1%) were detected in spruce lignin samples. Examination of model compounds of the biphenyl type showed that phenolic groups in biphenyls are not included in estimates of phenolic groups in lignins made on the basis of the signal from aromatic acetate ($\delta \approx 2.3$). The number of units in syringaresinol and related structures in birch lignin was estimated as 7%. Problems relating to quantitative estimation of structural elements in lignins by ^{1}H NMR spectrometric methods are discussed.

ADDRESS OF THE AUTHOR: Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden.

^{1}H NMR spectrometry offers a possibility to estimate the frequency of some types of structural elements in lignins. Results from such estimates are reported in this paper. To obtain a wider basis for the examinations, spectra of a series of model compounds have been recorded. Problems associated with determinations of the quantitative contribution of structural elements in lignins on the basis of ^{1}H NMR spectrometry are discussed. Only milled wood lignins have been examined in this paper but the methods developed are also largely applicable for the structural elucidation of technical lignins and lignin products in pulping liquors.



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Structural elements of the β-O-4 type

Spruce lignin. Fig. 1 shows the ^{1}H NMR spectrum of acetylated spruce lignin (solvent, $CDCl_3$). The signal at $\delta \approx 6$ is primarily caused by H_α in acetylated arylglycerol-β-aryl ethers (*1*). Integration of this signal constitutes a comparatively direct method for the quantitative estimation of the number of arylglycerol-β-aryl ethers in lignins (figures obtained by this method include some types of "derivatized" structures of type *1*, see below). Ludwig et al. (1) found in studies of the ^{1}H NMR spectrum of acetylated milled wood lignin (MWL) from spruce (solvent, $CDCl_3$) that the integral of the spectral range δ 5.74-6.28 corresponded to 39% arylglycerol units with a β-aryl ether substituent. Signals from H_β in coniferyl alcohol units (*2*) are also located in this range. Ludwig et al. (1) assumed the presence of 6% units of this type in spruce lignin. Subtraction of the coniferyl alcohol

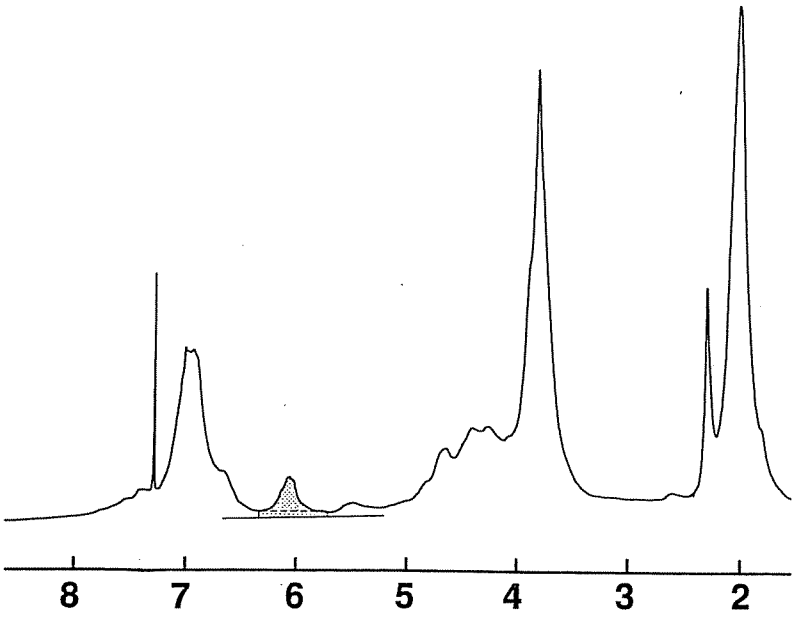
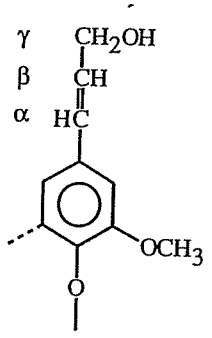


Fig. 1. ^{1}H NMR spectrum (range δ 1-9) of acetylated spruce lignin (solvent, $CDCl_3$). The figure shows the definition of the peak areas used in quantitative estimates. The dotted area gives the upper value and the area above the dashed line gives the lower value.



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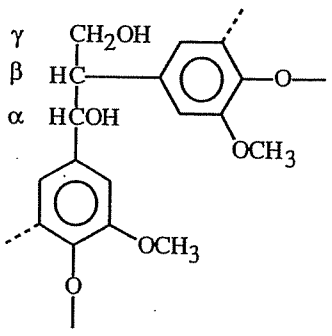

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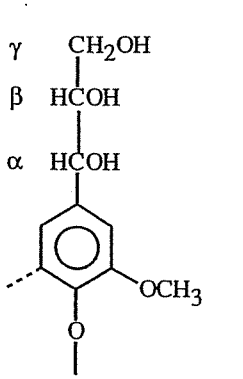
units gave the figure 33% for the frequency of arylglycerol units with a β-aryl ether group. In the light of later researches one has to consider that β-1 structures (*3*) and arylglycerol units (*4*) also contribute to the integral of the topical spectral range. According to ^{1}H NMR studies there are $\approx$1% coniferyl alcohol units (2, 3) and 1-2% β-1 structures (4) in spruce lignin. Recent ^{1}H NMR work (5) suggests the presence of arylglycerol units in spruce lignin. According to periodic acid oxidation experiments (6) there may be as much as 3% arylglycerol units in spruce lignin. Thus a correction of the magnitude assumed by Ludwig et al. (1) (6%) may still be adequate. Lignin structures of the β-O-4 type can be divided into three categories: arylglycerol-β-aryl ethers, derivatized arylglycerol-β-aryl ethers and additional types of β-O-4 structures (7). As far as is known the contribution of "additional types of β-O-4 structures" to the $\delta \approx 6$ peak is small. Derivatized arylglycerol-β-aryl ethers with an ether group in the α-position (*5*) do not contribute to the $\delta \approx 6$ peak (8, 9) while other types of esterified and etherified β-O-4 structures largely do (10). To summarize arylglycerol-β-aryl ethers, derivatized arylglycerol-β-aryl ethers (those with an ether group in the α-position and perhaps some other types of structures belonging to this category excluded) and a few percent other types



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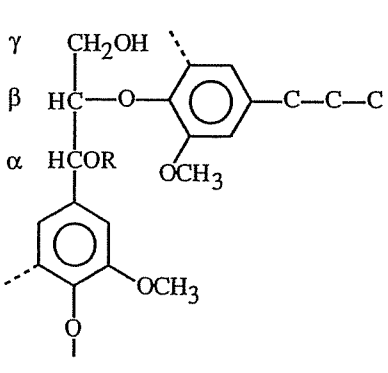

R= aryl or alkyl

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of side chains (specified above) would be responsible for the peak at $\delta \approx 6$ in the ^{1}H NMR spectrum of acetylated spruce lignin.

In a ^{1}H NMR spectral reexamination of acetylated spruce lignin using a modern high-frequency pulse Fourier instrument the $\delta \approx 6$ peak was found to correspond to 30-50% of the side chains (11). The lower figure (30%) was obtained by integration of the very peak at $\delta \approx 6$ while the upper figure (50%) was obtained by an integration which approximately corresponds to the integration of the spectral range δ 5.76-6.28 according to Ludwig et al. (1) (see fig. 1). In connection with later studies on the influences of instrumental parameters and recording conditions, it was found that the upper value was rather dependent on the appearance of the baseline; this is always the case when broad peaks of small to moderate size are located in the neighbourhood of large peaks. Thus the appearance of the baseline have to be considered when such peaks are quantitatively evaluated. Results from reinvestigations suggest that the range 30-40% is more adequate for the number of side chains corresponding to the $\delta \approx 6$ peak. This is in agreement with recent examinations of acetylated spruce lignin using pyridine-d_5 as a solvent (12). The ^{1}H NMR spectral results seem to be compatible with recent ^{13}C NMR studies (13, 14).

Errors in quantitative determinations may be related to the polymeric nature of the sample or interferences due to unfavorable location of signals from unidentified structures. Recordings using a series of solvents should provide an idea about the importance of such errors. Examination of acetylated spruce lignin using deuterioacetone as solvent gave the figure 33 ± 5% for the number of side chains corresponding to the $\delta \approx 6$ peak. Similar or slightly higher values were obtained with dimethyl sulfoxide-d_6 as solvent.

Another type of errors is associated with the derivatization which may be incomplete or cause unwanted chemical modifications. We have therefore also examined underivatized spruce lignin. In this case pyridine-d_5/deuterioacetic acid (1:1) was used as solvent since the peak due to H_α in arylglycerol-β-aryl ethers ($\delta \approx 5.27$) is comparatively well separated from other peaks in this solvent (*fig. 2*). Model experiments showed that not only signals from H_α in β-O-4 structures (*1* and possibly some types of derivatized structures of type *1*) but also signals from H_α in β-1 structures (*3*) are located at about δ 5.27. It appears in fig. 2 that the δ 5.27 peak is not completely separated from other peaks. Thus we have integrated the spectral range δ 5.15-5.6 and the integral is therefore expected to give an upper figure for the number of side chains in arylglycerol-β-aryl ethers (*1*). It was found that the integral corresponded to about 40% of the total of the side chains.

Birch lignin. The $\delta \approx 6$ peak in spectra of birch lignin acetates has also been studied. Examinations using chloroform (15) or pyridine (12) as solvent gave integrals of the $\delta \approx 6$ peak corresponding to 40-50%

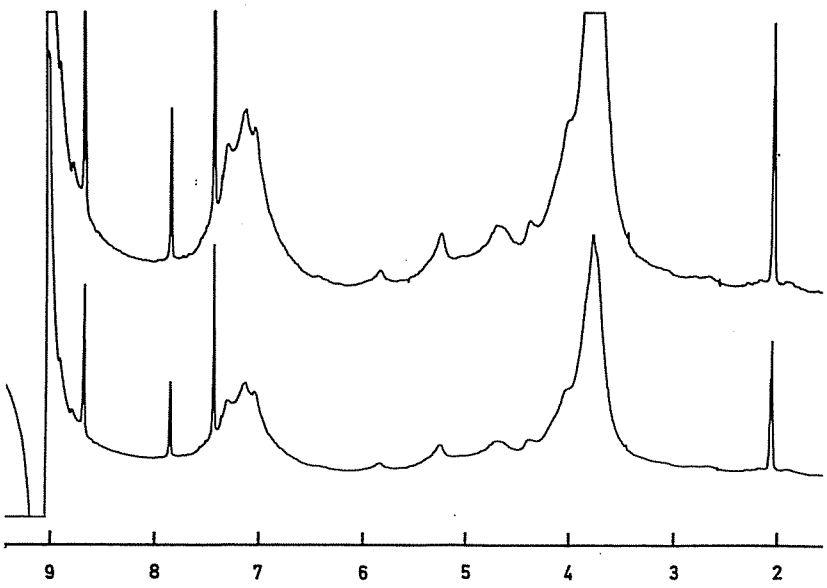


Fig. 2. ^1H NMR spectrum of spruce lignin. Solvent, pyridine-d_5/CD_3COOD (1:1). The appearance of the spectrum at $\delta \approx 9$ is due to infolding of the signal from hydroxyl protons.

of the side chains which is in accordance with earlier ^1H NMR studies (16). Deuterioacetone solution gave a somewhat higher figure (about 50%); the spectrum of acetylated birch lignin in this solvent is shown in *fig. 3*. The $\delta \approx 6$ peak in the spectrum of acetylated birch lignin can be expected to comprise the same types of side chains as in the case of spruce lignin, but the correction for "other side chains" (cf. the above discussion regarding such side chains in spruce lignin) should be somewhat larger since there may be as

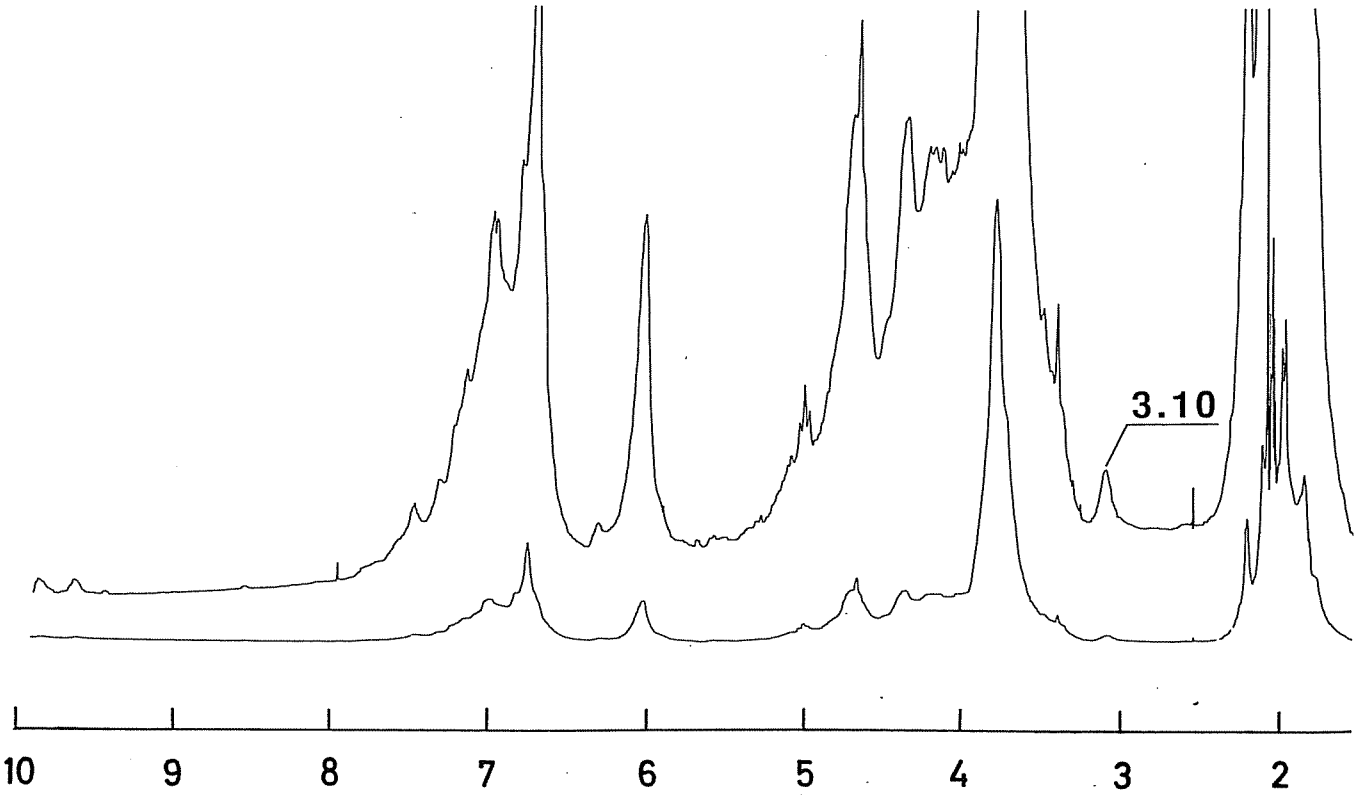
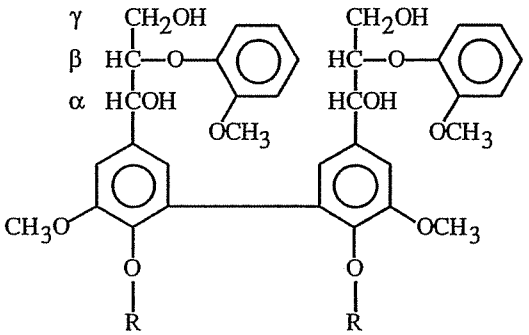


Fig. 3. ^1H NMR spectrum of acetylated birch lignin. Solvent, deuterioacetone. The peak at δ 3.10 is attributed to H_β in syringaresinol (16) and related structures.

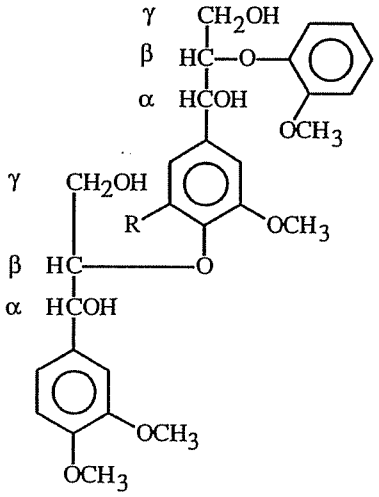
much as 5% β-1 structures (*3*) (4), about 1% cinnamyl alcohol groups (*2*) (2) and, according to periodic acid oxidation experiments (6), about 2% arylglycerol units (*4*) in birch lignin. The sum of "other side chains" may thus be of the order of 8%. It should be pointed out that there is an uncertainty regarding the occurrence of β-1 structures in spruce lignin as well as birch lignin since degradation studies [see, e.g., Lapierre et al. (17)] suggest larger amounts of β-1 structures in lignins than spectral studies do (4). Further, it should be kept in mind when hardwood lignins are examined that there may be a correlation between the number arylglycerol-β-aryl ethers and methoxyl content: a higher methoxyl content can be expected to be accompanied with a larger number of arylglycerol-β-aryl ethers.

Erythro *and* threo *forms of* β-O-4-*structures.* The fine structure of the peak at $\delta \approx 6$ in ^{1}H NMR spectra of spruce lignin and birch lignin acetates has been subjected to detailed studies aiming at an elucidation of the distribution of *erythro* and *threo* forms of structural elements of the arylglycerol-β-aryl ether type (18). The evaluation of the fine structure was based on extensive model compound studies. So far only data of dimeric model compounds have been used. It is therefore of interest to complement with data from examinations of oligomeric model compounds. Biphenyl *6* was prepared by peroxidase catalysed oxidation of *erythro*-guaiacylglycerol-β-guaiacyl ether. As judged from the ^{1}H NMR spectrum of the acetate derivative of the product about equal amounts of the possible diastereomeric forms (a *meso*-form and a (±)-form) had been produced. The signals from H_α are located at δ 6.06 and δ 6.07; these positions are very close to the position for H_α in the dimeric model *erythro*-guaiacylglycerol-β-guaiacyl ether (δ 6.08).

^{1}H NMR spectra of the acetates of samples of trimers *8* and *9* (synthesis in ref. 19) have been recorded. Although the samples were mixtures of diastereomers it could be concluded from comparisons with ^{1}H NMR spectra of acetylated dimeric



6 . R=H
7 . R=CH_3

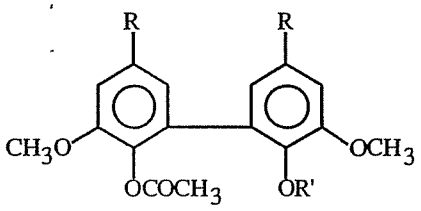


8 . R=H
9 . R=OCH_3

model compounds that the *threo* configuration of the arylglycerol-β-aryl ether groups strongly dominated in the samples of the trimers *8* and *9* examined. In acetylated *8* the predominating signals from H_α were located at δ 6.073 (d, J=6.1 Hz) and δ 6.057 (d, J=6.7 Hz). In the sample of acetylated *9* the predominating signals from H_α were located at δ 6.10 (d, J=7.3 Hz) and δ 6.05 (d, J=6.3 Hz). In the case of *8* as well as *9* the signal positions are close to what is expected from results from examinations of dimeric model compounds. Thus the results from the examinations of the trimers support the conclusions drawn from ^{1}H NMR spectrometric studies of the distribution *erythro* and *threo* forms of β-O-4 structures in lignins (18). To our knowledge an evaluation of the fine structure of the signal from H_α in terms of the distribution of *erythro* and *threo* forms is only possible when acetate derivatives are examined in chloroform solution. Hawkes et al. (20) have attempted to perform such evaluations on the basis of the signal from H_α in arylglycerol-β-aryl ethers in spectra of underivatized lignins. It is questionable whether this is possible since the signals from H_α in the spectra of the *threo* and *erythro* forms of the adequate model compound veratrylglycerol-β-guaiacyl ether (solvent, dimethyl sulfoxide-d_6) are located very close to each other (δ 4.77 *erythro*; δ 4.79 *threo*).

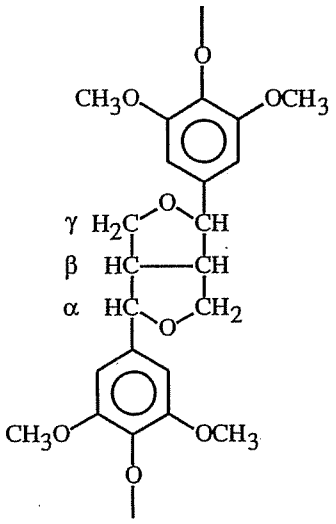
Phenolic groups

The signal from phenolic acetate ($\delta \approx 2.3$) is fairly well separated from signals caused by aliphatic acetate ($\delta \approx 2.0$) in spectra of lignin acetates in $CDCl_3$ (fig. 1). Ludwig et al. (21) examined the diacetate of dehydrodicoerulignol (*10*) and found that the signal from phenolic acetate was located at about δ 2.1. We have recorded spectra of a number of acetylated model compounds representative of biphenyl structures (the



10. R=$CH_2CH_2CH_3$, R'=$COCH_3$
11. R=CH_3, R'=$COCH_3$
12. R=$C(CH_3)_3$, R'=$COCH_3$
13. R=$C(CH_3)_3$, R'=CH_3
14. R=CH_2OCOCH_3, R'=$COCH_3$
15. R=CH_2OCOCH_3, R'=$PhCH_2$

acetate derivative of *6* and *11-16*). The results show that the signals from phenolic acetate in biphenyls are generally found at comparatively low δ values; in the examined compounds the signals are located in the range δ 2.08-2.11. Since the biphenyl structure is one of the major types of structural elements in softwood lignins (22) this causes a noticeable error when the phenol content in such lignins is determined on the basis of the δ 2.3 peak in acetate derivatives. Nevertheless we think ^{1}H NMR spectrometric analysis of lignin acetates in $CDCl_3$ constitutes a comparatively facile and useful method for rough estimates of the number of phenolic groups in lignins, particularly in connection with studies of changes of the frequency of such groups. Since there are few biphenyl structures in hardwood lignins, the ^{1}H NMR spectrometric method is comparatively well suited in that case. In a previous paper it was assumed that biphenyls exhibited signals from aromatic protons at comparatively high field ($\delta \approx 6.6$) (11). This is true in some cases but it appears from the data given in Experimental that most of the biphenyl model compounds examined do not show any signals from aromatic protons at relatively low δ values. In addition, a mixture of stereoisomers of acetylated *7* (23) was examined and it was found that no aromatic proton signals appeared below δ 6.7 (the signals from aromatic protons were centered at $\delta \approx 6.9$). Thus the generalization made in ref. 11 regarding signals from aromatic protons in biphenyls is not justified in the light of later model compound studies.



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Cinnamyl alcohol units (2) in lignins

It is possible to estimate the number of cinnamyl alcohol side chains (*2*) on the basis of the signals from H_β in such units ($\delta \approx 6$) in spectra of underivatized lignins. Such analyses suggest the presence of about 1% cinnamyl alcohol units in spruce and birch lignins (2). Another possibility for the analysis of units of type *2* in spruce lignin represents examinations of spectra of acetate derivatives in deuterioacetone solution. A small peak at δ 4.65 in such spectra is

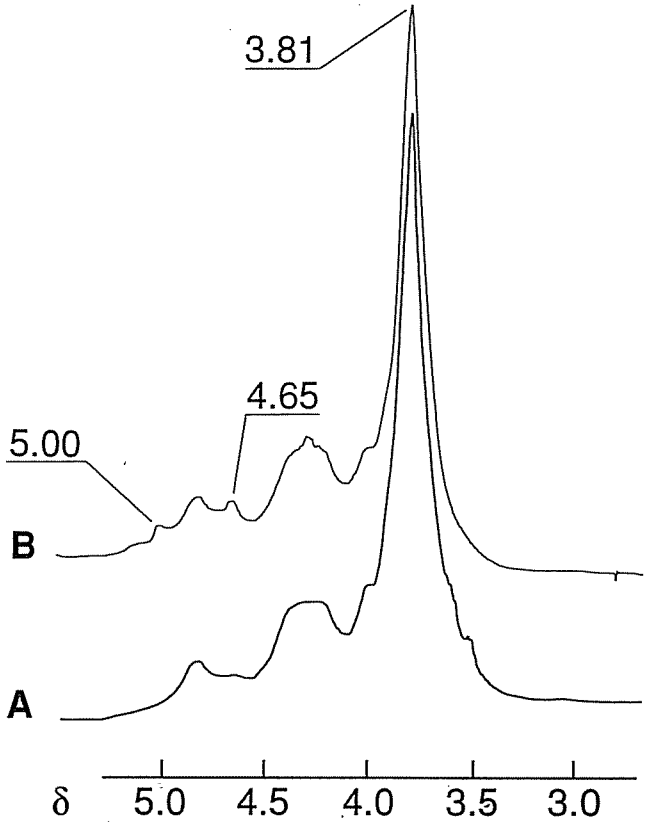

Fig. 4. The range δ 3-5 of the ^{1}H NMR spectrum of acetylated spruce lignin (A) and borohydride reduced/acetylated spruce lignin (B). The peaks at δ 4.65 and δ 5.00 are due to coniferyl alcohol units (2) and vanillyl alcohol units, respectively.

attributed to H_γ in cinnamyl alcohol side chains (*2*) (*fig. 4,* ref. 3). The topical signal is located in a spectral area where large signals due to other types of groups are found (fig. 4). It is, however, clearly discernible. Analysis of units of type *2* on the basis of the δ 4.65 peak is favored by the facts that the signal is caused by two hydrogen atoms and is only moderately splitted by coupling. That the small δ 4.65 peak actually is due to such units is supported by the fact that its intensity increases dramatically when the lignin is pretreated by borohydride reduction (see below).

Borohydride reduction/acetylation converts coniferaldehyde units into acetylated coniferyl alcohol units. The peak at δ 4.65 is comparatively large in borohydride reduced/acetylated spruce lignin (fig. 4). Since there are 3-4% coniferaldehyde units in untreated lignin, this implies that the number of coniferyl alcohol units in the original spruce lignin is considerably smaller than 3-4%. As judged from fig. 4, the number of coniferyl alcohol units in the original lignin can hardly be more than 1%. Examinations of a series of lignins samples gave varying results with respect to the size δ 4.65 peak. However, the δ 4.65 peak was small in all the untreated samples investigated as compared with the δ 4.65 peak exhibited by borohydride reduced lignin. Thus the number of cinnamyl alcohol units is substantially smaller than the number of coniferaldehyde units in the lignin samples investigated. Lindgren and Mikawa (24) studied the number of cinnamyl alcohol units and coniferaldehyde units in freshly cut spruce wood using a color reaction and found that the lignin moiety of the wood contained similar amounts of these two types of units. The number of cinnamyl alcohol units was found to be of the magnitude of 2%. Lindgren and Mikawa (24) also examined a Brauns lignin sample from spruce and found that coniferyl alcohol units were not present in detectable amounts. According to the present studies milled wood lignins from spruce contain small but detectable amounts of cinnamyl alcohol units.

Syringaresinol (16) and related structures in birch lignin

In lignin acetates in acetone solution the signal from H_β in "resinol" structures (δ 3.10) is well separated from other signals; this is true also for birch lignin (fig. 3). Quantitative estimates suggest that about 7% of the units in birch lignin are present in structural elements of the "resinol" type. This is in agreement with earlier estimates of the frequency of such units (15).

Experimental

NMR spectra

^{1}H NMR spectra of acetylated lignins, lignins and some model compounds were recorded at 270 MHz with a Bruker WH270 instrument. Spectra of model compounds were in most cases recorded at 400 MHz with a Varian VXR-5000 instrument. Deuteriochloroform was used as solvent if not stated otherwise. Temperature, 300 K. TMS was used as internal reference. When lignin spectra were recorded the number of scans was $\approx$1000 and the pulse interval was $\approx$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. refs. 8 and 15).

^{1}H NMR spectral data for model compounds

Acetylated mixture of diastereomers of *6* obtained by enzymic oxidation (25) of *erythro*-guaiacylglycerol-β-guaiacyl ether: 400 MHz; $\delta \approx 2.06$ (12H, aliphatic acetate in both diastereomers), $\approx$2.10 (6H, aromatic acetate in both stereoisomers), 3.75 (6H, s; OCH_3), 3.83 (6H, s; OCH_3), 4.24 (2H, J=4.0 and 11.8 Hz; $H_{\gamma 1}$), 4.65 (2H, m; H_β), 4.47 ($\approx$1H, dd, J=3.7 and 11.8 Hz; $H_{\gamma 2}$ in one of the diastereomers), 4.49 ($\approx$1H, dd, J=3.7 and 11.8 Hz; $H_{\gamma 2}$ in one of the diastereomers), 6.06 ($\approx$1H, d, J=5.4 Hz; H_α in one of the diastereomers), 6.07 ($\approx$1H, d, J=5.4 Hz; H_α in one of the diastereomers), 6.7-7.5 (14H, m; aromatic protons).

11: 400 MHz; δ 2.09 (6H, s; CH_3CO), 2.34 (6H, s; CH_3-Ar), 3.83 (6H, s; CH_3O), 6.65 (2H, approx. s; aromatic protons), 6.77 (2H, approx. s; aromatic protons).

12: 400 MHz; δ 1.32 (18H, s; CH_3-C-Ar), 2.08 (6H, s; CH_3CO), 3.86 (6H, s; CH_3O), 6.89 (2H, d, J=2.1 Hz; aromatic protons), 6.98 (2H, d, J=2.1 Hz; aromatic protons).

13:400 MHz; δ 1.31 (9H, s; CH_3-C-Ar), 1.34 (9H, s; CH_3-C-Ar), 2.09 (3H, s; CH_3CO), 3.54 (3H, s; CH_3O), 3.88 (3H, s; CH_3O), 3.91 (3H, s; CH_3O), 6.8-7.1 (4H, m; aromatic protons).

14: 270 MHz; δ 2.10 (6H) and 2.11 (6H) (aliphatic and aromatic acetate), 3.86 (3H, s; OCH_3), 5.08 (CH_2), 6.85 (2H, d, J= 1.8 Hz) and 6.97 (2H, J= 1.8 Hz) (aromatic protons).

15: 270 MHz; δ 2.06 (3H, s; aliphatic acetate), 2.08 (3H, s; aliphatic acetate), 2.11 (3H, s; aromatic acetate), 3.87 (3H, s; OCH_3), 3.89 (3H, s; OCH_3), 4.74 (2H, s; CH_2 in the benzyl ether group), 5.03 (3H, s; CH_2 in benzyl acetate), 5.06 (2H, s; CH_2 in benzyl acetate), $\approx$6.9 (4H, m; aromatic protons in the biphenyl group), $\approx$7.1 (5H, m; aromatic protons in the phenyl group).

Erythro-veratrylglycerol β-guaiacyl ether in DMSO-d_6/HAc (9:1): 270 MHz; δ 3.6 (2H, m; H_γ), 3.71 (3H, s; OCH_3), 3.719 (3H, s; OCH_3), 3.724 (3H, s; OCH_3), 4.33 (1H, m; H_β), 4.77 (1H, d, J=5.3 Hz; H_α), $\approx$7 (7H, m; aromatic protons).

Threo-veratrylglycerol β-guaiacyl ether in DMSO-d_6/HAc (9:1): 270 MHz; δ 3.28 (1H, dd, J= 6.2 and 11.6 Hz), 3.62 (1H, dd, 4.1 and 11.6 Hz), 3.73 (6H,

s; OCH_3), 3.77 (3H, s; OCH_3), 4.30 (1H, m; H_β), 4.79 (1H, d, J= 4.6 Hz; H_α), ≈7 (7H, m; aromatic protons).

Preparation of borohydride reduced spruce lignin
Milled wood lignin from spruce (5.0 g; OCH_3, 15.4%) was suspended in dioxane/water (1:1) (150 mL). $NaBH_4$ (2.0 g) and 0.1 M NaOH (50 mL) were added to the mixture. After three days the pH was adjusted to 5 with 2 M HCl and the volume reduced to ≈10 mL by film evaporation. Precipitated materials were washed with water (2×100 mL) and were thereupon dried in vacuo. (Further washing with water will result in substantial losses because the lignin forms a colloid (26). Washing with dilute aqueous acetic acid might reduce the amount of residual inorganic impurities.) The residue was leached with 75 mL dioxane containing 3% water. The solution was filtered and added dropwise to ether (3 L) under stirring. The precipitated lignin was centrifuged off and washed twice with ether and once with petroleum ether. The product was dried in vacuo. Yield: 4.1 g (OCH_3, 15.2%). Ash content: 3.5%. No signals owing to aldehyde protons were discernible in the ^1H NMR spectrum of the acetate derivative of the product. Procedures for borohydride reduction of lignin have been described previously (27, 28).

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