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Comparison of a Synthetic Dehydrogenation Polymer of Coniferyl Alcohol with Milled Wood Lignin from Spruce, using ^{1}H NMR Spectroscopy

ABSTRACT

The structural differences between a dehydrogenation polymer (DHP) from coniferyl alcohol and a milled wood lignin (MWL) from spruce were investigated by ^{1}H NMR, using a 270 MHz instrument. The DHP contained more β-5, β-β and cinnamyl alcohol groups, while the amount of β-0-4 and hydroxyl groups was lower than in the MWL.

TIIVISTELMÄ

(Synteettisen, koniferyylialkoholista valmistetun dehydrogenaatiopolymeerin vertailu kuusen puunjauhatusligniiniin ^{1}H NMR spektroskopiaa käyttäen)

Koniferyylialkoholista valmistetun dehydrogenaatiopolymeerin (DHP) ja kuusen puunjauhatusligniinin (MWL) välisiä rakenne-eroja on tutkittu 270 MHz NMR-laitteella. DHP todettiin sisältävän enemmän β-5, β-β ja kanelialkoholiryhmiä, sekä vähemmän β-0-4 ja hydroksyyliryhmiä kuin MWL.

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The use of dehydrogenation polymers (DHP) as model systems in lignin research makes it possible in many cases to bridge the gap between studies made on low molecular model compounds and on different lignin preparations, such as milled wood lignin (MWL). Recent applications of this approach are the preparations of isotopically labelled dehydrogenation polymers used in biodegradation studies (1).

As a part of a study of the structure of DHP we have carried out spectroscopic comparison of a typical "Zutropf" DHP with MWL from spruce using recently developed ^{1}H NMR spectral techniques (2).

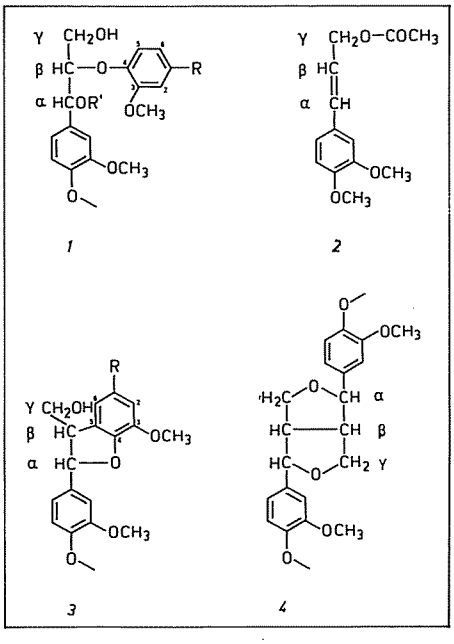
RESULTS AND DISCUSSION

The 270 MHz spectrum of acetylated DHP is shown in Fig. 1. Peak positions together with an interpretation of the spectrum are given in Table 1. The spectrum of acetylated MWL from spruce is given in Fig. 2 (for an interpretation of the spectrum, see Ref. 3). In order to make the spectral differences more clearly visible, the MWL spectrum in Fig. 2 was subtracted from the DHP spectrum in Fig. 1. The difference is shown in Fig. 3. Peak positions are given in Table 2 and the peak designations in that table are used in the following discussion. Using data from published ^{1}H NMR studies on lignins and on model compounds (2—4), the following main structural differences were deduced from the spectra.

Cinnamyl alcohol end groups (*1* or *3*, R = —CH = CH—CH_2OH). The appearance of the difference spectrum is largely determined by the comparatively large number of cinnamyl alcohol end groups in the DHP (peaks 2, 7, 12, 13, 14, and 15). Integrations suggest that such end groups constitute ca 10 % of the units in the DHP. Their frequency in MWL is small (3).

This could be very clearly demonstrated by an examination of a non-derivatised MWL in dioxane-d_8-D_2O (5:1). In this medium the signal from H_β in coniferyl alcohol end groups should appear at δ 6.2 ppm (the signal from H_β in 3,4- dimethoxycinnamyl alcohol is located at δ 6.23, J = 5.5 and 16 Hz). No signal was found at this δ-value and it was concluded that the number of coniferyl alcohol units was less than 1 %. A corresponding spsectrum of DHP exhibited a peak at α 6.2, showing the presence of cinnamyl alcohol end goups (*cf.* Ref. 5).

Units with fromyl groups. The amount of benzaldehyde units in DHP



1 *2* *3* *4*

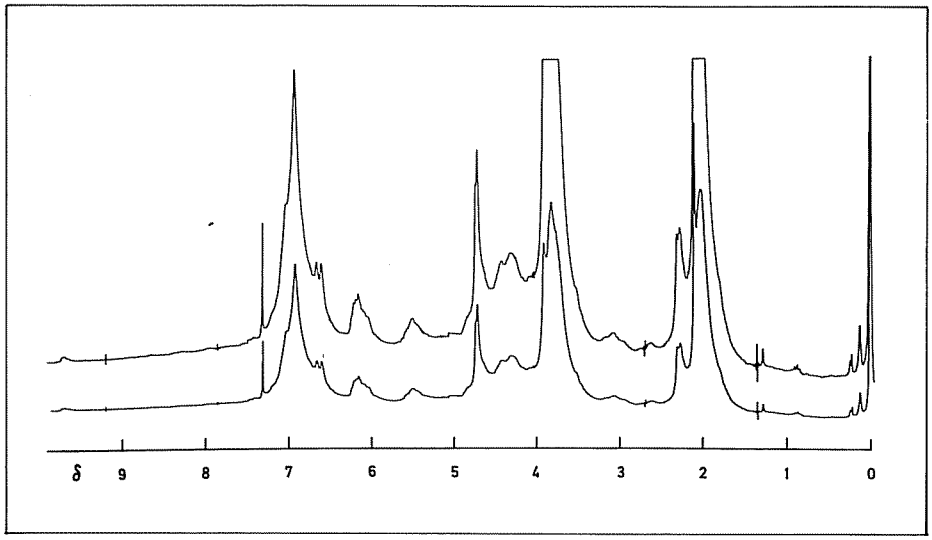


Fig. 1. ^1H NMR spectrum of acetylated DHP.

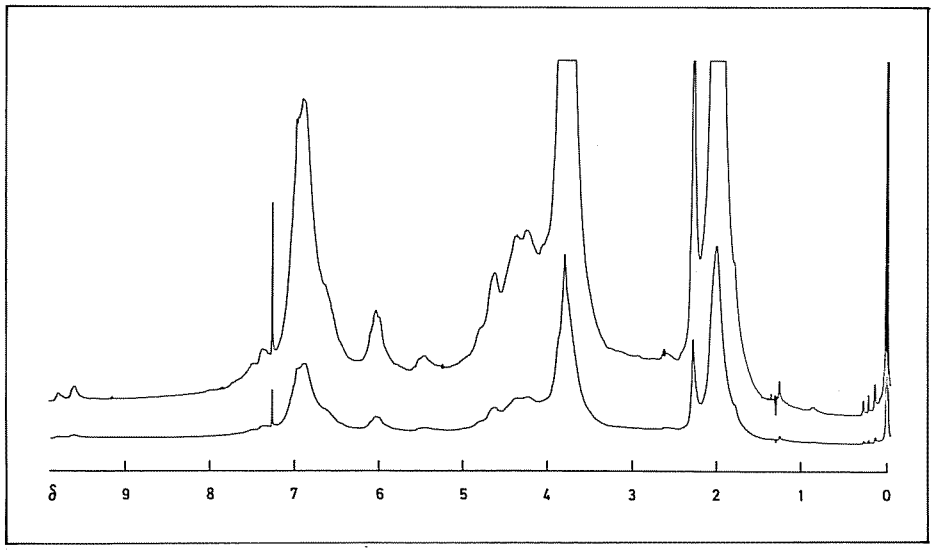


Fig. 2. ^1H NMR spectrum of acetylated milled wood lignin from spruce.

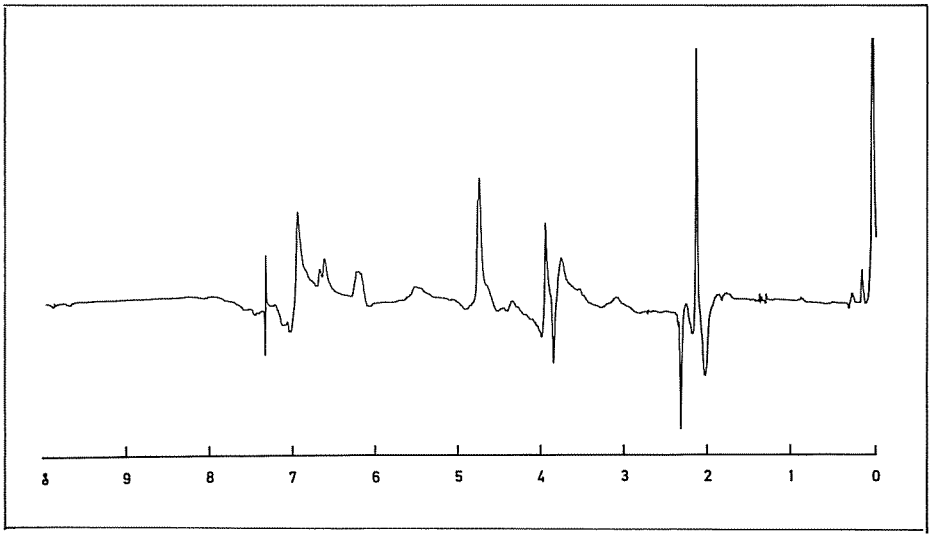


Fig. 3. Difference spectrum obtained by subtraction of the spectrum of spruce lignin (Fig. 2) from the spectrum of DHP (Fig. 1).

is negligible; the number of cinnamaldehyde units in DHP is smaller than in MWL (peaks 8, 16, 18—21, *cf.* Ref. 2).

β-β structures (*4*). The number of β-β structures in DHP is larger than in MWL (peak 4). Attempts to detect such structures in MWL by ^1H NMR have failed (Ref. 3, *cf.* Fig. 2).

β-5 structures (*3*). Peak 10 can be explained by an excess of β-5 and/or β-0-4 structures (*1*, R' = Ar) in DHP.

β-0-4 structures (*1*, R' = H). Peak 11 indicated a smaller frequency of β-0-4 structures in DHP. The interference of the signal from H_β in cinnamyl alcohol units made it difficult to make a quantitative estimation of this difference.

Hydroxyl groups. The difference spectrum suggested a somewhat lower content of phenolic groups (peak 3) and alcohol groups (peak 1) in DHP.

The results concur with the structural differences observed in comparative studies of DHP and MWL made by ^{13}C NMR spectroscopy (*6*). Both ^1H and ^{13}C NMR examinations point to a higher content of β-β structures (*4*), β-5 structures (3), and cinnamyl alcohol end groups (*1* or *3*, R = —CH=CH—CH_2OH) in DHP. Furthermore, the absence of benzaldehyde units and a lower content of β-0-4 (*1*, R' = H) and hydroxyl groups in DHP are evident in both ^1H and ^{13}C NMR studies.

The structural differences between DHP and MWL can be caused by:

1. The presence of other materials than those derived from coniferyl alcohol in MWL.
2. Chemical "ageing" of the lignin in wood.
3. Modification of MWL during isolation from wood.
4. A different mode of polymerisation during the formation from coniferyl alcohol.

Since the guaiacyl type of units strongly predominate in spruce lignin and since a lignin preparation with very low carbohydrate content was used in this study, the presence of "other materials" must be of minor importance. Modification during isolation and "ageing" may involve oxidative conversion of coniferyl alcohol end groups into units with formyl groups and this may explain the differences regarding these types of units. The polymerisation of coniferyl alcohol during lignin formation can be envisioned to proceed *via* an oxidative dimerisation of coniferyl alcohol or in an "end-wise" manner. It is possible that dimerisation of coniferyl alcohol occurs to a relatively large extent during DHP synthesis (in spite of precautions to avoid this). This would explain the differences in the frequen-

Table 1. Assignments of signals in the ^{1}H NMR spectrum of acetylated DHP (Fig. 1). Several peaks are broad and have irregular shapes; δ-values given always refer to the highest point of the peak. ^{1}H NMR data for acetylated 3,4-dimethoxycinnamyl alcohol (*2*) are given in parentheses.

δ-value		Assignment
2.02		Aliphatic acetate
2.09	(2.10, 3H)	Cinnamyl acetate
2.26		Aromatic acetate
2.30		Aromatic acetate
3.07		H_β in β-β structures (*4*)
3.81		Protons in methoxyl groups
3.90	(3.89, 3H; 3.90, 3H)	Methoxyl protons in cinnamyl alcohol units
4.29		Hγ in several types of structures
4.40		Hγ in several types of structures
4.70	(4.71, 2H; J = 6.5 Hz)	Methylene groups in cinnamyl alcohol units, H_β in β-0-4 structures (*1*, R' = H) and H_α in β-β structures (*4*)
5.47		H_α in β-5 structures (*3*) and noncyclic benzyl aryl ethers (*1*, R' = Ar)
6.13	(6.16, 1H; J = 6.5 and 16 Hz)	H_β in cinnamyl alcohol units
6.57	(6.60, 1H; J = 16 Hz)	H_α in cinnamyl alcohol units
6.63		H_α in cinnamyl alcohol units
6.89	(≈ 6.9, 3H)	Aromatic protons
7.27		Chloroform (solvent)
9.65		Formyl protons in cinnamyl aldehyde units

Table 2. Peak positions in the difference spectrum (Fig. 3), obtained by subtraction of the spectrum in Fig. 2 from that in Fig. 1.

peak	maxima	minima
1		1.99
2	2.09	
3		2.29
4	3.06	
5	3.72	
6		3.81
7	3.91	
8		3.96
9	4.70	
10	5.47	
11		6.03
12	6.15	
13	6.57	
14	6.62	
15	6.89	
16		6.98
17	solvent	
18		7.41
19		7.53
20		9.63
21		9.84

cies of β-β, β-5 and β-0-4 structures and of cinnamyl alcohol end groups. However, the lower content of phenolic groups in DHP is not consistent with this hypothesis. The reasons for the structural differences between DHP and MWL require additional studies.

EXPERIMENTAL

Dehydrogenation polymerisates of coniferyl alcohol (DHP) were prepared according to the procedure desctibed in Ref. 1.

^{1}H NMR spectra were recorded with a 270 MHz instrument working in the pulse Fourier mode (Bruker WH 270). Solvents were chloroform-*d* (internal reference TMS) and dioxane-d_8—D_2O (5:1) (internal reference was the sodium salt of 3-(trimethylsilyl) propanesulphonic acid).

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