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A Structural Model of Softwood Lignin

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Summary. Various degradation products from soft- and hardwood lignins by hydrolysis with dioxanewater and catalytic hydrogenolysis are discussed. And a structural model for softwood lignin is proposed mainly based on these degradation products. The model has 28 units and indicates good agreement with the various analytical data obtained so far in the lignin chemistry.

Introduction

The elucidation of the structure of lignin is one of the most difficult problems in the chemistry of natural polymers. The reason for this resides in its mode of biogenesis. The theory of lignin biosynthesis now accepted is that p-hydroxycinnamyl alcohols are first enzymatically dehydrogenated, giving various radical mesomers. These couple subsequently automatically to give a lignin polymer with no participation of any enzyme. This assumption would reasonably explain why the degradation products of lignin have no optical activity in spite of the presence of many chiralities. Therefore, lignin has no simple structural units as those present in cellulose, starch, protein etc. Furthermore, the presence of many carbon-to-carbon linkages between the units makes it difficult to degrade the polymer to low molecular fragments. Moreover, it has not yet been possible to isolate all parts of lignin from plant tissues without change. The milled wood lignin (MWL) prepared according to the procedure of Björkman is thought to be "useful preparations for lignin chemists" because of a minimum of chemical change, but the yields are at most 50% of Klason lignins.

The biosynthesis of lignin in vitro, initiated by Freudenberg and co-workers in 1950, first threw a fresh light on this problem. The enzymatic dehydrogenation of coniferyl alcohol gave a polymer (DHP) which is very similar to spruce MWL, and the various di- and tri-lignols as intermediates suggest the linkage units involved in lignin molecule. These results made the lignin picture clear, and tempted Freudenberg to construct a lignin model which was subsequently modified several times (Freudenberg 1964; Freudenberg, Harkin 1964; Freudenberg 1965).

Various degradation products of lignins were later isolated, and their structures were elucidated, mainly in our laboratory and in that of Nimz. The results obtained by

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Nimz showed good agreement with ours, with the exception of some details. These degradation experiments added further information about the linkage units of lignin. Nimz (1974) proposed a constitutional scheme of beech lignin based on the degradation products from beech wood by thioacetic acid.

In the present paper, various degradation products obtained in our laboratory will be discussed, and a structural model of softwood lignin will be proposed, based mainly on the degradation products of protolignins obtained by catalytic hydrogenolysis and hydrolysis with dioxane and water.

Hydrolysis Products of Protolignins

Ezomatsu (*Picea jezoensis Carr.*), Yachidamo (*Fraxinus mandshurica*) and Mizunara (*Quercus mongolica*) woods were cooked at 180 °C for 20 min. in an autoclave, giving various lignols. The main hydrolysis products obtained so far are summarized in Figure 1 (Sakakibara 1977). They are very similar to the lignols isolated from the products of the enzymatically dehydrogenated coniferyl alcohol.

Some model experiments under the same conditions showed that arylglycerol-β-aryl ethers had undergone homolysis (Sano 1975; Sano, Sakakibara 1976; Sano et al. 1977). However, the hydrolysis products isolated from protolignins so far would not be those from homolysis for the following reasons: 1. Under these hydrolysis conditions, benzyl ethers were almost quantitatively cleaved to give various lignols. On the other hand, β-0-4 ethers, the predominant linkage unit in the lignin molecule, were not fissured (Sakakibara et al. 1966). Only a minor part of the β-0-4 linkage units with free phenolic hydroxyl would suffer homolysis, but the occurrence of these units in lignin may be rare. Practically, only benzylic ethers would be broken. 2. Only a part of the primary products first cleaved from benzyl aryl ether might suffer homolysis, but the amounts of the homolysis products would be too small to be detected, judging from the yield. Thus, pinoresinol and biphenyl (Sano 1975; Sano, Sakakibara 1976; Sano et al. 1977) which were obtained as homolysis products from model compounds could not be detected even in traces in the reaction mixture from protolignins.

Among the hydrolysis products, arylglycerol-β-aryl ether, diarylpropane, and resinol type compounds are found, but biphenyl type units were not obtained. Pinoresinol could not be detected among the products from softwood lignin, but from hardwood lignin a large quantity of syringaresinol was isolated. Trimers containing these linkages were also obtained (Compounds 16–19).

It should be noted that a glycerol side-chain was frequently observed in the products as seen in compounds 1 to 5. It is obvious that the glycerol side-chain is present originally in the lignin molecule, as indicated by the result of a model experiment (Sakakibara et al. 1966). Further, a small amount of arylglycerols was found among the enzymatic dehydrogenation products from p-hydroxycinnamyl alcohols by Higuchi and co-workers (1974).

Compound 10 was isolated recently (Aoyama, Sakakibara 1979). It has an ω-hydroxypropyl side-chain. Earlier, Klemola (1968) detected dihydrosinapyl alcohol in the

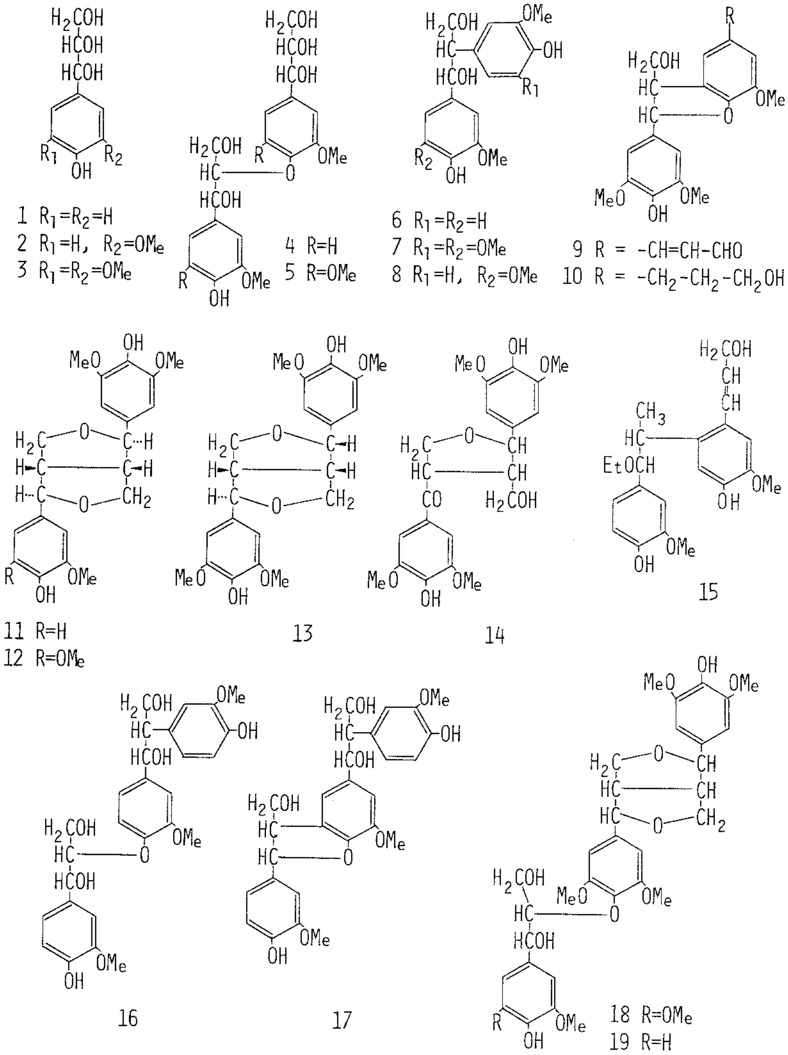


Fig. 1. Hydrolysis products of protolignins

steam hydrolysis products of birch wood. Compound 15 with a β-6 linkage is another example of units carrying reduced side-chains, and has a terminal methyl group (Sakakibara, Endo 1979). An ethoxyl group at the α-position may be artifact and introduced during the isolation procedure. From these results it seems very likely that some reductive mechanisms may operate during the formation of lignin.

Hydrogenolysis Products of Protolignins

Figures 2 a and b summarize the main hydrogenolysis products of lignin isolated in our laboratory (Sakakibara 1977). Under the conditions applied, almost all aryl-alkyl

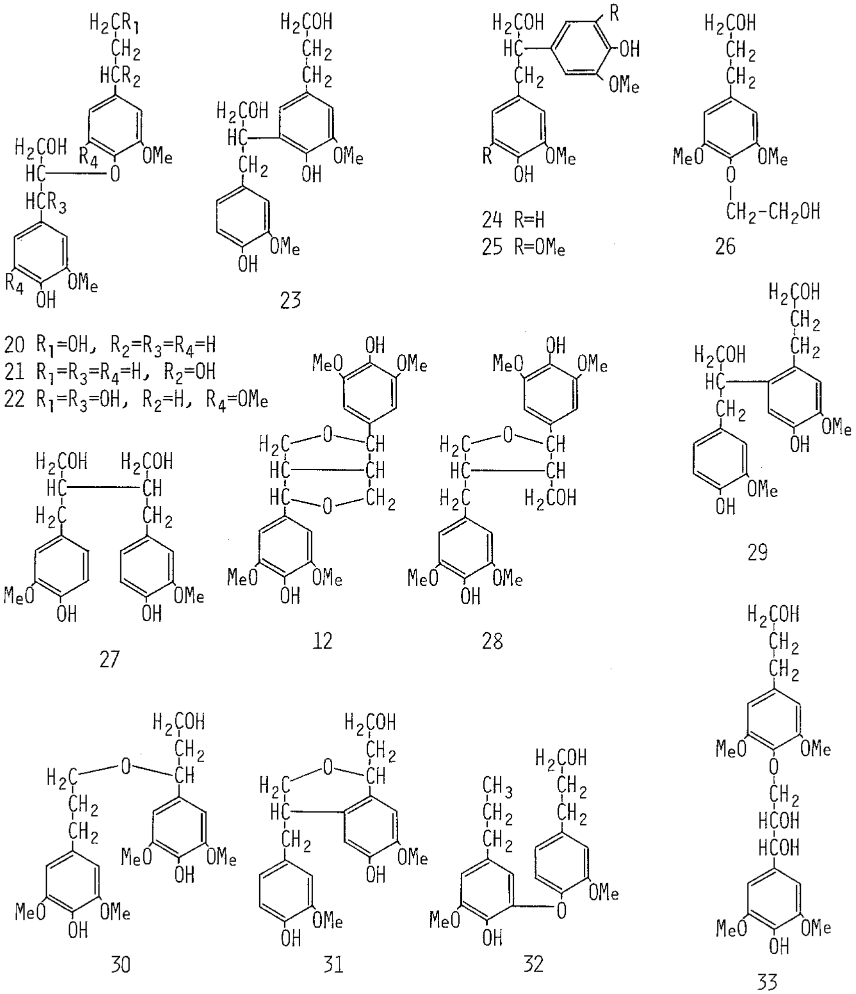


Fig. 2a and b. Hydrogenolysis products of protolignins

ethers were cleaved to give lower molecular products, although a small amount of the bonds survived, as seen in compounds 20–22, 26 and 33. On the other hand, alkyl-alkyl ether linkages are very stable under the hydrogenolysis conditions, as shown in model experiments (Matsukura, Sakakibara 1973). Thus, syringaresinol 12, compounds 28, 30 and 31 carrying α-0-γ-side-chain could be isolated without cleavage of the ether linkage. Compound 27 might not be formed after cleavage of dihydrofuran rings of pinoresinol but occurred as such in the lignin.

Compounds 29 and 31 have β-6 linkage which give metahemipinic acid on permanganate oxidation after methylation. Recently, we have isolated a dimeric compound 33 which has a γ-0-4 linkage (Hwang, Sakakibara 1979). The presence of a γ-0-4 linkage was first postulated by Freudenberg (1933), and then later by Brauns (1960) for the reason that this structural unit would yield acetovanillone and formaldehyde on hydrolysis and reversed aldol condensation.

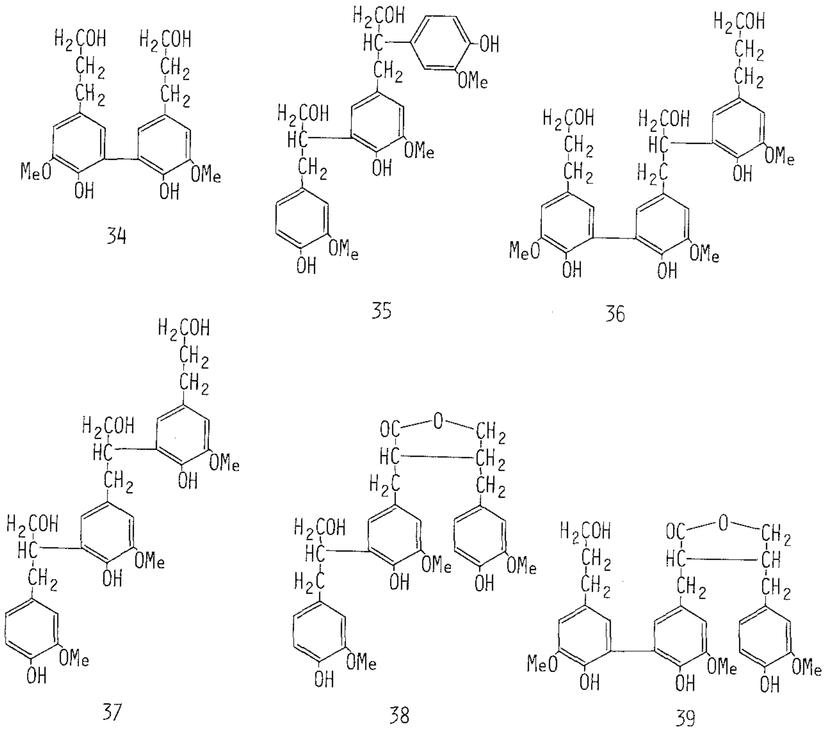


Fig. b.

We have also isolated two trilignols with lactone rings, 38 and 39 which arise from combination of dehydrogenation of ferulic acid and coniferyl alcohol (Yasuda, Sakakibara 1978). Dilignols with lactone rings (pinoresinolide and lignenolide) had been obtained from the dehydrogenated products of coniferyl alcohol (Freudenberg, Geiger 1963) (Later, the configuration of lignenolide was corrected by Nimz 1964). The absence of the optical activity in the two hydrogenolysis products indicates that they were not lignans. Recently, lignans optically active with similar configurations were isolated from the seeds of burdock (Ichihara et al. 1978). Compound 26 was isolated from hardwood lignin (Hwang, Sakakibara 1979a). It might indicate the existence of the ether of a displaced side-chain, but the possibility of an α-β cleavage of an arylglycerol-β-aryl ether unit on hydrogenolysis cannot be excluded. Compound 11, 18 and 19 were also obtained from hydrogenolysis (Hwang, Sakakibara 1979a). These results, together with those of Nimz give valuable information on the details of linkage type and of functional groups in the side-chain.

Proposal of a Structural Model of Softwood-Lignin

The most important linkages in lignin are β-0-4, and then 5-5 biphenyl, β-5, β-1 and α-0-4. β-β Resinol units may not be significant in softwood lignin, but are abundant in hardwood lignin. The frequency of α-0-γ and γ-0-4 units has not yet been established. 4-0-5 Diphenyl ether and β-6 units are found among degradation products of lignin. Other linkage units are not significant and correspond to minor units.

Figure 3 shows a structural model of softwood lignin consisting of 28 units. Some alternative units are indicated in parentheses. These units are mainly based on the results obtained on hydrolysis and hydrogenolysis. It is, of course, only a tentative structural outline and will probably be modified in the future, when new information is obtained. In constructing this scheme, uncertain units were omitted whenever possible. However, a part of the values of these linkages were arbitrarily selected

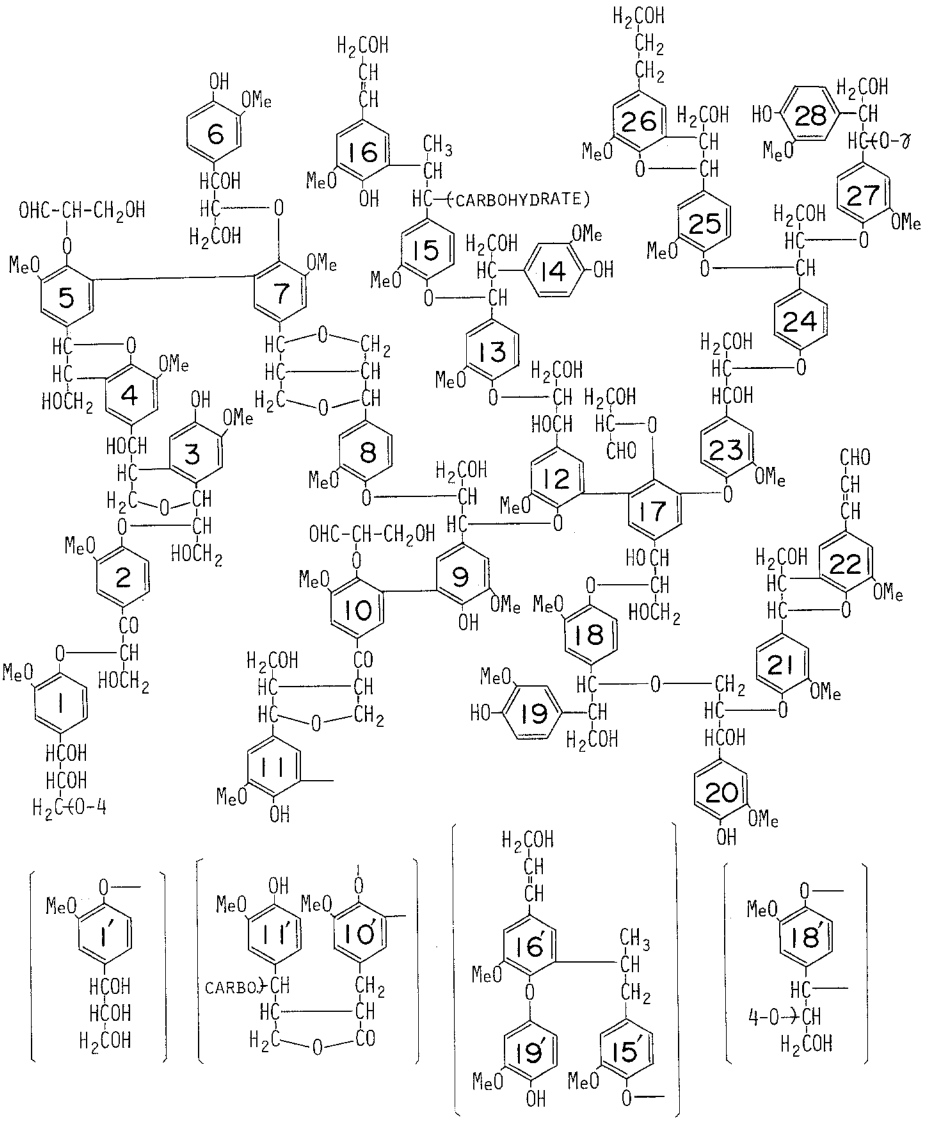


Fig. 3. A structural model for softwood lignin

Table 1. Analytical comparisons of spruce-MWLs and lignin structural models

Lignin and models	C_9-Formula	Methoxyl-free formula	Degree of dehydrogenation	Moles of added H_2O
Coniferyl alcohol	$C_9H_9O(OMe)$	$C_9H_{10}O_2$		
MWL (Björkman 1957)	$C_9H_{8.83}O_{2.37}(OMe)_{0.96}$	$C_9H_{9.05}O_2(H_2O)_{0.37}$	0.95	0.37
MWL (Freudenberg 1968)	$C_9H_{7.95}O_{2.40}(OMe)_{0.92}$	$C_9H_{8.07}O_2(H_2O)_{0.40}$	1.93	0.40
Model A	$C_9H_{7.93}O_{2.39}(OMe)_{0.93}$	$C_9H_{8.08}O_2(H_2O)_{0.39}$	1.92	0.39
Model B (alternative)	$C_9H_{7.96}O_{2.43}(OMe)_{0.93}$	$C_9H_{8.03}O_2(H_2O)_{0.43}$	1.97	0.43
Mean value of A and B	$C_9H_{7.95}O_{2.41}(OMe)_{0.93}$	$C_9H_{8.06}O_2(H_2O)_{0.41}$	1.94	0.41
Model A	$C_{252}H_{222}O_{67}(OMe)_{26}$	M. W. 5124		
Model B	$C_{252}H_{223}O_{68}(OMe)_{26}$	M. W. 5141		

because of a lack of adequate quantitative data. Of course, the small number of 28 units is not enough to cover all interunit linkage types and functional groups.

Characteristic units of the model are the phenylisochroman constructed from units 3 and 4 with β-6 and α-0-γ linkages, and the lariciresinol type with α-carbonyl (10, 11), non-cyclic α-0-γ (18, 20), γ-0-4 linkage units (1), and reduced side-chains in units 15 and 26. These units play an important role in this model. In spite of the small number units, this structural model agrees with the various analytical data obtained so far in lignin chemistry.

In Table 1, the compositions of the model structure (A) and an alternative one (B) are compared with those of spruce-MWL (Björkman, Person 1957; Freudenberg 1968). This presentation is shown according to Freudenberg (1968) and Sarkanen (1971). In these formulas, the methoxyl groups are replaced by a hydrogen atom. Two models have a composition very close to that of spruce MWL reported by Freudenberg (1968). The formula given by Björkman and Person (1957) has a much higher hydrogen content, indicating the presence of more reduced side-chains. A part of these protons may possibly be involved in the reduced side-chains, such as those of structural units 15 and 16.

In Table 2, the values of the structural units of the lignin models are compared with those of spruce MWL; they satisfy almost all analytical results. The value 0.43 for the total amount of β-0-4 units includes displaced side-chain-structures. The values in parentheses are only for those of arylglycerol-β-aryl ether units. The values are close to those obtained by Adler (1961) on acidolysis. The value for the total β-5 units is 0.14 and that in the parenthesis is the one for an open unit, which also agrees with that obtained by Adler (1961). The value of β-β units agrees well with that assumed by Sarkanen (1971). That obtained by Ogiyama (1968) is lower, but it was estimated by means of nitric acid oxidation which gives dilactones only from a dioxabicyclo-octane structure but may not be from a half-opened lariciresinol type unit (10, 11). The values for pinoresinol unit falls in the range of those given by Ogiyana and Kondo (1968). The unit β-1 type cannot be determined directly, but it seems to correspond to the amount of displaced side-chains which represent unconjugated carbonyl.

Table 2. Functional group and structural unit comparisons of spruce-MWL and lignin models (per C_6C_3)

Functional groups and structural units	Lignin models			Spruce-MWL	References
	A	B	Mean value		
Alcoholic OH	1.00	1.00	1.00	1.04 0.85	Lai, Sarkanen 1971 Björkman, Person 1957
Phenolic OH (free)	0.32	0.29	0.31	0.26 0.34	Adler et al. 1968 Freudenberg et al. 1964a
Total carbonyl	0.21	0.21	0.21	0.20	Adler, Marton 1959
α = CO	0.07	0.04	0.06	0.06–0.07	Adler, Marton 1959
Unconjugated carbonyl	0.11	0.11	0.11	0.10	Adler, Marton 1959
γ-Lactone	0	0.04	0.02	–	
Ar–CH=CH–CHO	0.04	0.04	0.04	0.03–0.04	Adler, Marton 1959
Ar–CH=CH–CH_2OH	0.04	0.04	0.04	0.03	Marton, Adler 1961
Ar–CHOH–CHOH–CH_2OH	0	0.04	0.02	–	
Ar–CH_2–CH_2–CH_2OH	0.04	0.04	0.04	–	
Ar–C–C–CH_3	0.04	0.04	0.04	0.04	Björkman, Person 1959
Benzyl ether (open) and alcohol	0.46	0.46	0.46	0.43	Marton, Adler 1961
α-0-4 (open)	0.11	0.11	0.11	0.10–0.13 0.06–0.08	Freudenberg et al. 1964a Erickson et al. 1973
p-Hydroxybenzyl aryl ether (open)	0.04	0.04	0.04	0.04	Adler et al. 1968
p-Alkoxy benzyl aryl ether (open)	0.07	0.07	0.07	0.05–0.09	Freudenberg et al. 1964a
p-Hydroxy benzyl alcohol	0.07	0.07	0.07	0.05–0.06	Adler, Marton 1959
p-Alkoxy benzyl alcohol	0.18	0.18	0.18	0.15	Adler, Marton 1959
α-0-γ (open)	0.07	0.07	0.07	0.06	Glasser et al. 1976
β-0-4	0.43 [a](0.32)	0.46 (0.36)	0.45 (0.34)	0.49–0.51 [a](0.25–0.30)	Erickson et al. 1973 Adler 1961
γ-0-4	0.04	0	0.02	–	
β-5	0.14 [b](0.04)	0.14 (0.04)	0.14 (0.04)	0.14 0.09–0.12 [b] (0.03)	Lai, Sarkanen 1971 Erickson et al. 1973 Adler 1961
β-6, (β-2)	0.04	0.04	0.04	0.025–0.03	Erickson et al. 1973
β-β	0.14 [c](0.07)	0.14 (0.07)	0.14 (0.07)	0.13 [c](0.05–1.0)	Lai, Sarkanen 1971 Ogiyama, Kondo 1968
β-1	0.11	0.07	0.09	0.15 0.02 0.07	Lai, Sarkanen 1971 Erickson et al. 1973 Adler 1977
5-5, 5-6	0.21	0.21	0.21	0.19–0.22	Erickson et al. 1973
4-0-5, 4-0-1	0.07	0.07	0.07	0.07–0.08	Erickson et al. 1973
Condensed units	0.46	0.43	0.45	0.45–0.50	Ludwig et al. 1964

[a] Except displaced side-chain units [b] Non-cyclic [c] Pinoresinol units

Glasser et al. (1976) claimed in their computer simulation studies that "the computation of model structures is not possible, which satisfy all experimental results, unless the concentration of linkages based on nondehydrogenative polymerization reaches levels of 22–24 % of the total number of linkages". They assumed that 0.06 per phenylpropane would be of the nature of dialkyl. However, it would be easy to construct the model structure without contradiction by introduction of the reduced side-chains as shown in units 15 and 26 in addition to the open type α-0-γ units such as unit 18.

Table 3 shows a comparison of protons per C_9 structural unit in acetylated spruce MWLs obtained in NMR spectra with those calculated from the models. The values are in close agreement with the figures obtained by Ludwig et al. (1964) and Lenz (1968). The NMR spectra obtained with a lower frequency (60 MHz) instrument reveal no carboxylic or aldehyde proton peak in Range 1, but with a higher frequency (270 MHz) instrument the amount of coniferyl aldehyde units was determined as 4 % (Lundquist, Olsson 1977), corresponding to a value of 0.14 per C_9 unit in acetylated MWLs. Range 2 includes aromatic and α-vinyl protons, and also β-vinyl protons of cinnamyl aldehyde side-chains. The values 2.71 and 2.75 in the models are probably too high.

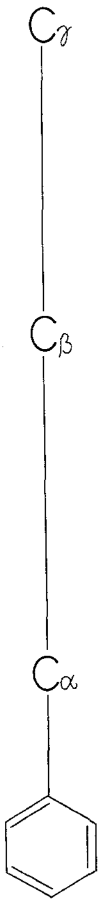
Table 3. Protons per C_9 structural unit in acetylated spruce MWLs and Lignin models as determined by the integrations of NMR spectra

Range δ-Values		Protons known to give signals within range	Spruce		Lignin models		
			MWL (Ludwig et al. 1964)	MWL (Lenz 1968)	A	B	Mean value
1	11.5–8.00	Carboxylic and aldehyde	–	–	0.14	0.14	0.14
2	8.00–6.28	Aromatic and α-vinyl, and β-vinyl of cinnamic aldehyde side-chain	2.56	2.57	2.71	2.75	2.73
3	6.28–5.74	Total β-vinyl and α-acetoxylated benzylic	0.39	0.32	0.29	0.29	0.29
4	5.74–5.18	α of phenylcoumaran, α of α-0-4 linkage, and β of acetylated glycerol side-chain	0.28	0.34	0.25	0.25	0.25
5	5.18–2.50	Total protons	6.37	5.81	5.83	5.86	5.84
		Methoxyl	2.82	2.55	2.79	2.79	2.79
		All other α, β, and γ protons	3.55	3.26	3.04	3.07	3.05
6	2.50–2.19	Aromatic acetoxyl except those of 5-5 linkage	0.83	0.83	0.86	0.75	0.81
7	2.19–1.58	Aliphatic acetoxyl and aromatic acetoxyl of 5-5 linkage	3.34	2.78	[a]3.14	3.14	3.14
8	1.58–0.38	High shielded aliphatic	0.24	0.06	0.14	0.14	0.14
		Total protons per C_9 structural unit	14.01	12.71	13.36	13.32	13.34

[a] The signal of two β-protons of unit 26 may stretch over both Ranges 7 and 8

Range 3 includes total β-vinyl and acetylated benzyl protons; the model structure has 0.29 and MWLs 0.39 and 0.32. In Range 4, MWLs have slightly higher values compared to those of the models. It should be noted, however, that less abundance of protons in Range 2 and over-abundant side-chain protons in Range 5 for spruce-MWLs may be due to the presence of small amounts of carbohydrates. Protons in Range 3, 4 and 7 may also be influenced by the admixture of carbohydrates in MWL preparations. Highly shielded aliphatic protons are those of methyl and β-methylene of the propyl group and a part of the β-methylene protons on the ω-hydroxypropyl side-chain. The peaks of the latter protons include both Range 7 and 8.

Lüdemann and Nimz (1974) observed some signals at upfield in carbon 13-NMR spectra of spruce and beech MWLs. The signals at δ 35.1 and 32.4 would likely be due



γ-OH	CONIFERYL ALCOHOL	0.04	1
γ-OH	DIHYDROCONIFERYL ALCOHOL	0.03	1
γ-OH	GUAIACYL GLYCEROL	0.02	0.5
γ-OH	OTHER PRIMARY ALCOHOL GROUPS	0.60	17
γ=O	CONIFERYL ALDEHYDE	0.03	1
γ-O-α	IN PINORESINOL, LARICIRESINOL, PHENYLISOCHROMAN AND OPEN UNITS	0.18	5
γ-O-4		0.02	0.5
γ-CH_3	METHYL GROUPS	0.04	1
γ-CH_2-	γ-LACTONE	0.02	0.5
γ-CO-	γ-LACTONE	0.02	0.5
	TOTAL	1.00	28
β-O-4	TOTAL	0.44	12.5
β-5	TOTAL	0.14	4
β-6	TOTAL	0.04	1
β-β	TOTAL	0.14	4
β-1	TOTAL	0.10	2.5
β-C_α	CONIFERYL ALCOHOL AND ALDEHYDE	0.07	2
β-H_2	DIHYDROCONIFERYL ALCOHOL UNITS	0.03	1
β-OH	GUAIACYL GLYCEROL	0.04	1
	TOTAL	1.00	28
α-OH	β-O-4 AND β-1 AND GUAIACYL GLYCEROL	0.25	7
α=O	α-O-KETO GROUPS	0.06	1.5
α=O	ALDEHYDES IN DISPLACED SIDE CHAINS	0.11	3
α-O-γ	IN PINORESINOL, LARICIRESNOL, PHENYLISOCHROMAN AND OPEN UNITS	0.20	5.5
α-O-4	IN β-5 UNITS	0.11	3
α=C_β	IN CONIFERYL ALCOHOL AND ALDEHYDE	0.07	2
α-H_2	IN DIHYDROCONIFERYL ALCOHOL AND IN OTHER UNITS	0.06	2
α-O-4	IN OPEN ETHERS	0.10	3
α-O-	CARBOHYDRATE OR OTHERS	0.04	1
	TOTAL	1.00	28

Fig. 4 Rydholm-diagram illustrating the distribution of functional groups in a lignin model

to α and β-carbons on the ω-hydroxypropyl side-chain, and the peaks at δ 30 and 20.8 may correspond to those of γ-methyl. In the structural models, highly 4 shielded protons are involved. They should be found at δ 0,98–1.90 in PMR spectrum. In Figure 4, the distribution of functional groups is illustrated in a Rydholm-diagram. It is very probable that the composition of protolignins from different sources may be different. This makes it difficult to describe the structure of lignin in one scheme. In the present paper, the average structure of A and B is probably a statistically representative lignin model.

As described above, this structural scheme agrees very well with the analytical data on lignin obtained so far despite its small number of units. It is, however, only tentative especially as a small part of its units was selected arbitrarily, and it would have to be modified when additional information becomes available. The most important problems now are to establish all linkage units existing in the lignin molecule, perhaps by further degradative experiments and to develop more reliable methods for a quantative determination of the functional groups and the interunit bonds in lignin.

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