

It is not easy to assess the isotope effect to be expected of eq. 20. It is not entirely clear, therefore, that eq. 16 and 17 would predict that the isotope effect at low conversions would be small, requirement e.

We have been able to place a number of restrictions upon the nature of the mechanisms which operate in these reactions and these establish that the mechanism previously advanced, eq. 1, is unsatisfactory for copper and probably for palladium and nickel. Mechanism 16 + 17 is a possible alternative, but further work will be necessary to elaborate and test it. It does, however, exemplify most of the features necessary in any mechanism for these reactions. It hardly seems worthwhile at this time to discuss the more complicated mechanisms which can be devised. One should mention, though, that a symmetric adsorbed species is not the only way in which racemization can be achieved. Thus, in eq. 15, one might imagine the interconversion of I to IV to involve two paths, one leading to retention and the other to inversion of configuration. This concept has been advanced by Rooney, Gault, and Kemball for similar stereochemical purposes.¹⁸ In attempting to apply this, we have seen no *simple* way to avoid the assumption that the rates of the two processes are accidentally identical at both 135 and 156°. While not impossible, this is not very attractive.

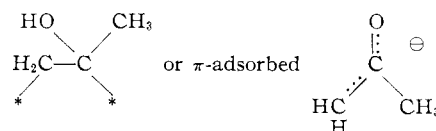
Exchange in Side Chains.—As shown in Table II, at low conversions the ratio

$$\frac{\text{fraction of reacted 2-butanol exchanged in side chains}}{\text{fraction of 2-butanone exchanged in side chains}} \simeq 1.5$$

(18) J. J. Rooney, F. G. Gault, and C. Kemball, *Proc. Chem. Soc.*, 407 (1960).

In computing the numerator of this expression, we sum d_2 , d_3 , and d_4 and divide by $1 - d_0$. Thus the reaction which leads to multiply exchanged species is more closely associated kinetically with adsorbed alcohol than with adsorbed ketone. The amount of multiply exchanged alcohol is too small to decide whether it is racemic or not. Further, the multiple exchange reaction might proceed by some side reaction on special sites. If, however, it proceeds by a branching from mechanism 16, the branch is not directly from species I of 15 because this would make the ratio much larger than 1.5, species I being essentially in equilibrium with vapor phase 2-butanol. Nor could the branching be direct from species II since, then, the ratio would be less than unity.

In any case the most likely species leading to multiple exchange are⁶



If one of these is to be associated with mechanism 16 it seems necessary to assume that IV is an intermediate in the interconversion of species I and II and that IV converts to I somewhat more rapidly than II; IV could readily convert to either of the two possible intermediates pictured above by conventional processes.

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[CONTRIBUTION FROM THE PULP MILLS RESEARCH, THE INSTITUTE OF FOREST PRODUCTS, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

Lignin. XII.¹ The High Resolution Nuclear Magnetic Resonance Spectroscopy of Protons in Compounds Related to Lignin

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The chemical shifts of n.m.r. signals from protons in a number of compounds related to gymnosperm lignins have been determined. Evidence has been found supporting the presence of stable hydrogen bonds between the α -hydroxyl and β -ether groups in arylglycerol β -aryl ether type model compounds. The n.m.r. of dehydrodiconiferyl alcohol indicates a *cis* configuration in its furan ring. The diequatorial configuration of pinosresinol is confirmed by n.m.r. characteristics. The potential utility of n.m.r. for studies on lignin structures is demonstrated.

Introduction

In spite of numerous investigations summarized in recent reviews²⁻⁴ the chemical structures of plant lignins have remained incompletely known. While it is generally agreed that lignins represent polymeric materials composed of various phenylpropane units bonded together by a complex system of ether and carbon-to-carbon linkages, the nature of this bonding system has remained a matter of more or less well-founded speculation.²⁻⁴

The phenylpropane, C_9 , units as they are visualized to exist in the lignin macromolecules (Fig. 1) contain protons connected with carbon and oxygen atoms that give signals with widely varying τ -values in the n.m.r. spectrum. In view of the potential usefulness of these signals for studies on the structure of lignins, the n.m.r. spectra of a number of small molecular weight lignin

model compounds were determined in order to obtain

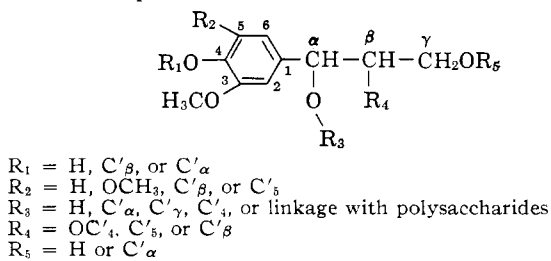


Fig. 1.—Some probable linkages in lignins.

information applicable to the more complex lignin spectra which are to be reported in a forthcoming publication.

The model compounds used are enumerated in Table I. Of these, the dimeric models VIId, VIIa, VIIId, and VIIc are particularly interesting, because they represent structures indicated to be present in the lignin macromolecules.^{2,3} Similarly, a linkage of the 5-5' type in IXa is thought to be a common occurrence in lignins.⁵

(1) J. Moacanin, H. Nelson, E. Back, V. F. Felicetta, and J. L. McCarthy, *J. Am. Chem. Soc.*, **81**, 2054 (1959).

(2) E. Adler, *Paperi Puu*, **43**, 634 (1961).

(3) K. Freudenberg, *Pure Appl. Chem.*, **5**, 9 (1962).

(4) F. E. Brauns, *Holzforchung*, **16**, 97 (1962).

Since changes in solvent markedly alter chemical shifts even when the same internal standards are used, it is important to select standard conditions for models that also may be used in the determination of lignin spectra. Lignin preparations possess limited solubility properties, but are, in general, readily soluble in

TABLE I
MODEL COMPOUNDS STUDIED

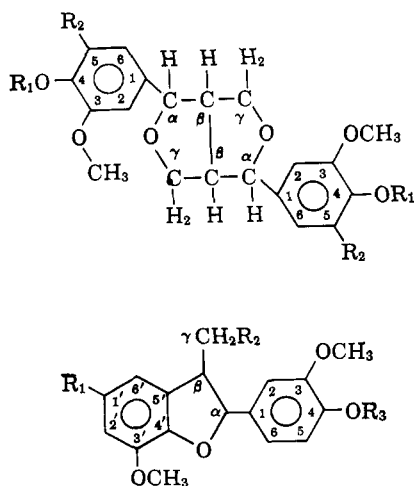
A. Monomeric models

Series I (α -Carbonyl compounds)		Series III (α -Hydroxy compounds and acetates)	
R ₁	R ₂	R ₁	R ₂
Ia -CHO	-H	IIIa -CH ₂ OH	-H
b -COCH ₃	-H	c -CHOHCH ₃	-H
c -COCHOHCH ₃	-H	b -CHOHCH ₂ CH ₃	-H
d -COCH ₂ CH ₂ OAc	-H	d -CHOAcCH ₃	-Ac
e -COOH	-Ac	e -CH ₂ OH	-Me
f -CHO	-CH ₃	f -CHOHCH ₃	-Me
		g -CHOAcCH ₃	-Me

Series II (α -Vinyl compounds)		Series IV (Miscellaneous)	
R ₁	R ₂	R ₁	R ₂
IIa -CHCHCH ₃	-H	IVa -H	-H
b -CHCHCOOPh	-H	b -CH ₂ CHCH ₂	-H
c -CHCHCOOPh	-Ac		
d -CHCHCH ₃ , <i>trans</i>	-Ac		
e -CHCHCH ₃ , <i>cis</i>	-Ac		

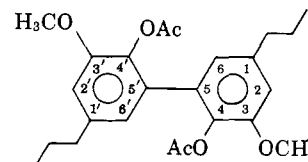
B. Dimeric models

Series V (α -Carbonyl- β -aryl ether compounds)		Series VI (α -Hydroxy- β -aryl ether compounds and acetates)		
R ₁	R ₂	R ₁	R ₂	R ₃
Va -H	-H	VIa -H	-H	-H
b -H	-CH ₂ OH	b -CH ₂ CH ₂ CH ₃	-H	-H
c -Ac	-H	c -CH ₂ CH ₂ CH ₃	-H	-Ac
d -CH ₂ CH ₂ CH ₃	-H	d -H	-CH ₂ OH	-H
		e -H	-CH ₂ OAc	-Ac



Series VII (Pinoresinol type compounds)		Series VIII (Phenyl coumaran type compounds)		
R ₁	R ₂	R ₁	R ₂	R ₃
VIIa -H	-H	VIIIa -CHCHCH ₃	-H	-H
b (epi) -H	-H	b -CHCHCH ₃	-H	-Ac
c -Ac	-H	c -CHCHCH ₂ OH	-OH	-H
d -H	-OMe	d -CHCHCH ₂ OAc	-OAc	-Ac

Series IX
(5,5'-Biphenyl type compound)



deuteriochloroform in the form of their acetylated derivatives. Consequently, we generally used 7 to 15% solutions of the compounds in deuteriochloroform with hexamethyldisiloxane, HMDS, as internal reference and τ -values were calculated by the formula $\tau = 9.948 - \delta$ int. HMDS. Exceptions to this rule are noted in Table II.

During the course of this study, chemical shifts for vanillin (Ia), acetovanillone (Ib), and veratraldehyde (If) were published.⁶ Except for hydroxyl and aldehydic protons signals which are notably temperature and concentration dependent, the published values for chemical shifts differ by less than 0.05 p.p.m. from values obtained in this study (Table II).

Results and Conclusions

The τ -values and coupling constants found for the compounds studied are compiled in Table II. By analyzing the data, certain generalizations may be made regarding n.m.r. signals from many of the types of protons present. Also it is apparent that certain of the more uniquely located protons in the dimeric model compounds give signals with τ -values peculiarly characteristic of the protons involved. Table III summarizes the τ -value ranges for protons of interest. Where possible these are compared with the values for similar type protons reported in reference 6. Since only acetylated lignin preparations are sufficiently soluble for n.m.r. studies, the τ -values which are uniquely associated with protons in nonacetylated compounds have not been included in Table III.

Beside the chemical shift data summarized above, other valuable information may be derived from a closer examination of the individual spectra, especially of the dimeric type compounds.

1. **Guaiacylglycerol β -Ether Dimers.**—The occurrence of the aryl glycerol β -aryl ether structure in lignin was predicted by Gustafsson⁷ and co-workers and Erdtman.⁸ Adler and co-workers⁹⁻¹¹ subsequently showed that model compounds of this type give the Hibbert type ketones on degradation by prolonged heating with alcoholic or aqueous acid, a reaction which is typical of lignin. Freudenbergs¹² has shown that guaiacylglycerol β -coniferyl ether is formed when coniferyl alcohol is dehydrogenated, lending support to its probable presence in lignin. Adler, *et al.*,¹¹ estimate that one fourth to one third of all the

(6) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalogue," Varian Associates, Palo Alto, Calif.

(7) C. Gustafsson, K. V. Sarkanen, S. Kahila, and E. Niskasaari, *Paperi Puu*, **33**, 74 (1951).

(8) H. Erdtman, *Research*, **3**, 83 (1950).

(9) E. Adler, B. O. Lindgren, and U. Saeden, *Svensk Papperstid.*, **55**, 245 (1952).

(10) E. Adler and E. Eriksoo, *Acta Chem. Scand.*, **1**, 34 (1955).

(11) E. Adler, J. M. Pepper, and E. Eriksoo, *Ind. Eng. Chem.*, **49**, 1391 (1957).

(12) K. Freudenbergs and H. Schluter, *Chem. Ber.*, **88**, 617 (1955).

(5) J. C. Pew, *J. Org. Chem.*, **28**, 1048 (1963).

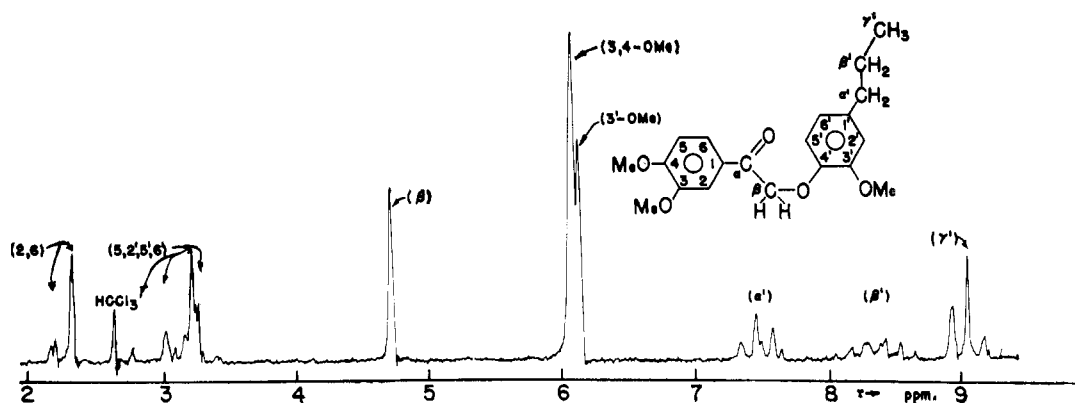
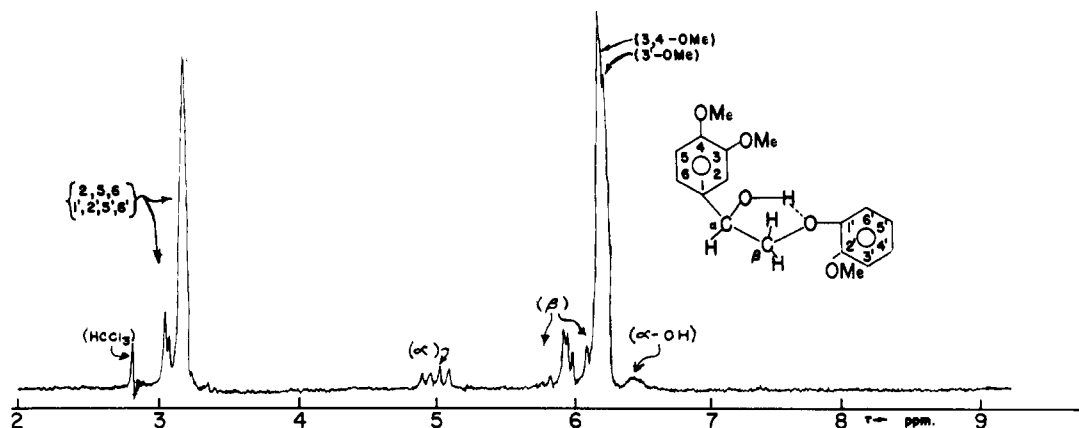
Fig. 2.— ω -(2-Methoxy-4-propylphenoxy)-3,4-acetoveratrone, Vd.

Fig. 3.—1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethanol, VIa.

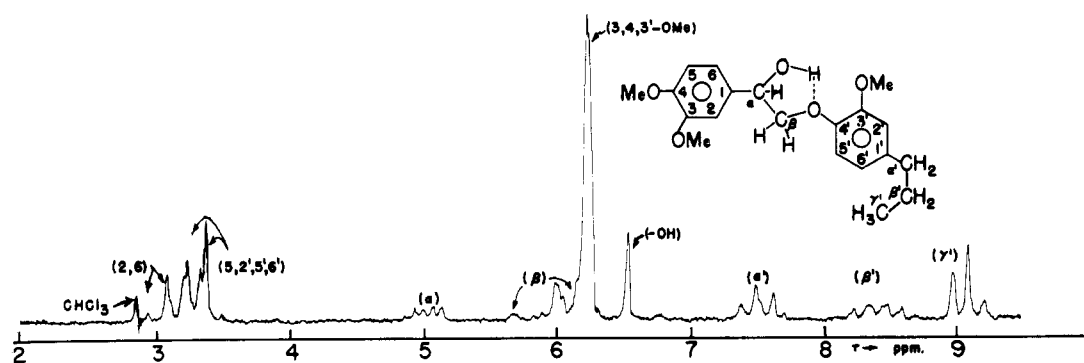


Fig. 4.—1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-propylphenoxy)-ethanol, VIb.

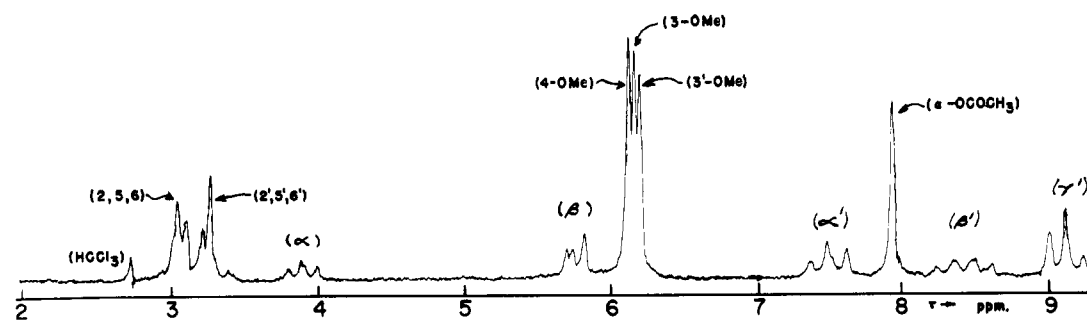


Fig. 5.—1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-propylphenoxy)-ethyl acetate, VIc.

C₉ units in lignin are connected by a β -aryl ether linkage to the next unit.

The n.m.r. spectra of compounds containing the β -aryl ether type linkages, Vb, VIa, VIc, VId, and VIe, are shown in Fig. 2 through 7, respectively; of these VIa, VIb, and VId have hydroxyl groups on their α -carbons. The signals given by the hydrogens

attached to these α -carbons range from 4.94 to 5.20. Acetoxy groups on α -carbons in compounds VIc and VIe lower the α -hydrogen signals to 3.91 and 4.00, respectively. The actual decrease for each of the two acetylated compounds was 1.03 p.p.m. compared with its parent compound. The position of the signals for these protons in the acetylated β -ether type compounds

TABLE II (Continued)

B. Dimeric compounds: Series V. α -Carbonyl- β -aryl ether compounds

The first row of numbers recorded after Va, Vb, etc., are from protons situated in that portion of the model compounds assigned numbers and letters without primes in Table I. Those following Va, Vb, etc., are from protons in that portion of the model compounds assigned numbers with primes in Table I.

Compound/H	2,6	1,5	α	β	γ	3-OMe	4-OMe	4-OH	Al-OH	4-OAc	Al-OAc	Other	$J_{\alpha\beta\gamma}$	$J_{\alpha\gamma}$
Va, ω -(2-methoxyphenoxy)-acetoveratrone	2.27-2.42 (m)	3.10-3.19 (m)	...	4.71 (s)	...	6.12 (s)	6.12 (s)
Va'	3.10 (m) to 3.19 (m)	6.17 (s)
Vb, α -(2-methoxyphenoxy)- β -hydroxypropioveratrone	2.16-2.36 (m)	3.10-3.29 (m)	...	4.46-4.62 (t)	5.88 (m)	6.08 (s)	6.08 (s)	...	5.8-6.2? (b)
Vb'	3.10 to 3.29 (m)	6.18
Vc, ω -(2-methoxy-4-acetylphenoxy)-acetoveratrone	2.30-2.68 (m)	3.07-3.32 (m)	...	4.61 (s)	...	6.14 (s)	6.11
Vc'	2.30-2.68 (m)	3.07-3.32 (m)	...	7.54 (s)	...	6.14 (s)
Vd, ω -(2-methoxy-4-propylphenoxy)-acetoveratrone	2.24-2.39 (m)	2.80-3.27 (m)	...	4.76 (s)	...	6.13 (s)
Vd'	2.80 (m) to 3.27 (m)	...	7.60 (t)	8.42 (m)	9.10 (t)	6.19 (s)
Series VI. α -Hydroxy- β -aryl ether compounds and acetates														
V1a, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethanol	2.91 (m) to 2.98 (m)	...	4.95 (q)	5.88-6.07 (m)	...	6.14 (s)	6.14 (s)	...	6.39 (s)	<i>cis</i>	7.9	...
V1a'	2.98 (m) to 3.11 (m)	6.18 (s)	<i>trans</i>	3.6	...
V1b, 1-(3,4-dimethoxyphenyl)-2-(2-methoxy-4-propylphenoxy)-ethanol	2.86-3.02 (m)	3.15-3.32 (m)	4.96 (q)	5.60-5.97 (m)	...	6.16 (s)	6.16 (s)	...	6.48 (s)
V1b'	3.15 (m) to 3.32 (m)	...	7.36-7.68 (t)	8.09-8.69 (m)	8.98-9.22 (t)	6.16 (s)
V1c, acetylated V11b	3.07 (m) to 3.13 (m)	...	3.91 (t)	5.71-5.82 (m)	...	6.17 (s)	6.14 (s)	7.92 (s)	...	5.7	...
V1c'	3.23 (m) to 3.29 (m)	...	7.49 (t)	8.41 (m)	9.09 (t)	6.19	7.2	7.2
V1d, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol	3.06 (m) to 3.17 (m)	...	5.03 (m)	5.93	6.44?	6.18	6.18 (s)	...	6.44 (s)
V1d'	3.06 (m) to 3.17 (m)	6.22 (s)
V1e, acetylated V1d	3.01 (m) to 3.33 (m)	...	4.00 (q)	5.27-5.51 (m)	5.82 (m)	6.18 (s)	6.18 (s)	7.95 (s)	8.01 (s)
V1e'	3.01 (m) to 3.33 (m)	6.23 (s)
Series VII. Pinosresinol type compounds														
V11a, pinosresinol	3.18 (m)	3.14 (m)	5.27 (d)	6.95 (m)	a-6.08 e-5.75 (m)	6.19 (s)	...	4.15 (s)
V11b, epipinosresinol (h)	3.07 (m) to 3.11 (m)	...	5.15 (d)	5.92 (m) to 7.28 (m)	...	6.15 (s)	...	4.52 (s)	5.0	?
V11b'	3.07 (m) to 3.11 (m)	...	5.56 (d)	5.92 (m) to 7.28 (m)	...	6.15 (s)	...	4.52 (s)	6.8	?
V11c, acetylated V11a	2.93 (m) to 3.24 (m)	...	5.22 (d)	6.91 (m)	a-6.11 e-5.72 (m)	6.19 (s)	7.72 (s)	4.2	...

Compound	Series VIII. Phenyl coumaran type compounds									
	3.42 (s)	...	5.27 (d)	6.91 (m)	5.50-6.06 (m)	6.16 (s)	4.40 (s)
VIIId, syringoresinol	3.42 (s)	...	5.27 (d)	6.91 (m)	5.50-6.06 (m)	6.16 (s)	4.40 (s)
VIIIa, dehydrodiisoeugenol	3.07 (m) to 3.25 (m)	4.94 (d)	6.58 (m)	8.68 (d)	6.18 (s)	4.49 (s)	8.9	6.9
VIIIa'	3.07 (m) to 3.25 (m)	3.65 (d)	4.04 (m)	8.17 (d)	6.23 (s)	15.4	5.3
VIIIb, acetylated VIIIa	2.95 (m) to 3.03 (m)	5.09 (d)	6.57 (m)	8.62 (d)	6.14 (s)	7.73 (s)	8.8	8.6
VIIIb'	3.25 (s)	3.65 (d)	4.04 (m)	8.19 (m)	6.22 (s)	15.2	5.3
VIIIc, dehydrodiconiferyl alcohol ^b	3.07 (m) to 3.21 (m)	4.46 ² (d)	5.81 ² (m)	6.97 ²	6.16 (s)	...	?	...	7.2	?
VIIIc'	3.07 (m) to 3.21 (m)	3.40 (d)	3.83 (m)	6.97 ²	6.21 (s)	16.2	?
VIIId, acetylated VIIIc	3.02 (m) to 3.11 (m)	4.49 (d)	6.21 (m)	5.66 (m)	6.10	...	7.71	7.91	7.2	?
VIIId'	3.02 (m) to 3.11 (m)	3.44 (d)	3.88 (m)	5.32 (d)	6.20 (s)	7.94 (s)	15.5	6.2
Series IX. 5,5'-Biphenyl compound										
IXa, acetylated tetrahydroeugenol	3.21 (d)	...	7.43 (t)	8.33 (m)	9.05 (t)	6.18 (s)	...	7.92 (s)	...	6.0
	3.31 (d)	7.0

The abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; m, partially resolved multiplet; b, broad; x, the hydroxyl proton band is concentration and temperature dependent; h, sample warmed. ^a 15-20% in CHCl₃ solvent containing 1% tetramethylsilane internal standard; chemical shifts in τ -values; $\tau = 10 - \delta$ TMS int. p.p.m. ^b 6% in CDCl₃ and acetone with hexamethyldisiloxane internal standard. All others are 7-15% in CDCl₃ containing 1% hexamethyldisiloxane internal standard; $\tau = 9.948$ — HMD int. p.p.m. ^c J -values are in c.p.s.

TABLE III
RANGES OF τ -VALUES FOR PROTONS IN COMPOUNDS RELATED TO LIGNIN^a

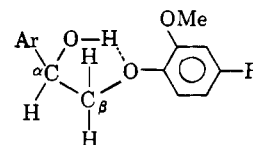
Type of proton	Numbers of models	—Ranges of chemical shifts— Found ^b	Reported ^c
Carboxylic			
vinyl		...	-1.73 to -3.21
aromatic	(1)	-1.50	-1.00
Aldehydic			
vinyl		...	0.43 to 0.52
aromatic	(1)	0.16 to 0.22	0.00 to 0.30
Aromatic			
<i>ortho</i> to α -carbonyl	(10)	2.30 to 2.68	2.03 to 2.60
all others	(48)	2.80 to 3.33	1.48 to 3.72
Vinyl			
α as in compd. VIIId	(1)	3.28 to 3.53	...
β as in compd. VIIId	(1)	3.68 to 4.13	...
Aliphatic			
α as in compd. VIe	(1)	3.95 to 4.06	...
α as in compd. VIIId	(1)	4.42 to 4.53	...
other α , β , and γ in compd. VIc, VIe, VIIa, VIIb, VIIc, and VIIId	(5)	5.10 to 7.28	...
Methoxyl			
aromatic, except series I and V	(38)	6.10 to 6.30	6.12 to 6.28
aromatic, series I and V	(10)	6.08 to 6.14	6.03 to 6.07
aliphatic		...	6.53 to 6.67
Acetoxyl			
aromatic, except <i>ortho</i> to bi-phenyl	(8)	7.71 to 7.73	7.70 to 7.75
aromatic, <i>ortho</i> to biphenyl	(1)	7.92	...
aliphatic	(7)	7.91 to 8.02	7.92 to 7.98
Aliphatic, highly shielded as in Vd', VIb', VIc', and IXa	(4)	8.09 to 9.22	8.33 to 9.12

^a Ranges include broadening due to coupling. ^b 7 to 15% in CDCl₃ or HCCl₃. ^c 7% in CDCl₃, ref. 4.

is significant because no other aliphatic protons in the compounds studied produced signals with τ -values in the range of 3.91 to 4.00.

For the monoalcohols VIa and VIb, the signals from the protons attached to α -carbons are quadruplets rather than triplets as would be expected if there were free rotation around the α - β carbon-carbon bond (Fig. 3 and 4).

These quadruplet signals may be accounted for by postulating the presence of a stable hydrogen bond between the α -hydroxyl hydrogen and the β -ether oxygen to form a five-membered ring in which the β -protons are nonequivalent, one being *cis* to the α -hydrogen, the other being *trans*. The *cis*-hydrogens having a dihedral angle close to 0° have a larger coupling constant than the *trans*-hydrogens which have a dihedral angle of close to 120°. ¹³ To test this hypothesis



H-bonded five-membered-ring in compounds VIa and VIb the alcohol VIb was acetylated to eliminate hydrogen bonding. The resulting acetate VIc showed a coupling pattern for the α -proton signal which was almost a normal triplet. A slight difference in the $J_{\alpha\beta}$'s is probably due to an inhibition of rotation by the bulky acetoxy group making the two β -protons nonequivalent (Fig. 5).

In the n.m.r. spectrum of the β -ether diol VIId the signal for the α -proton centered at 5.03 is composed of two superimposed doublets with slightly different chemical shifts and $J_{\alpha\beta}$'s of 7.5 and 5.9 sec.⁻¹. The presence of these two signals is ascribed to the existence of two diastereoisomers of this compound in about equal amounts. The γ -hydroxyl hydrogen which is

(13) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

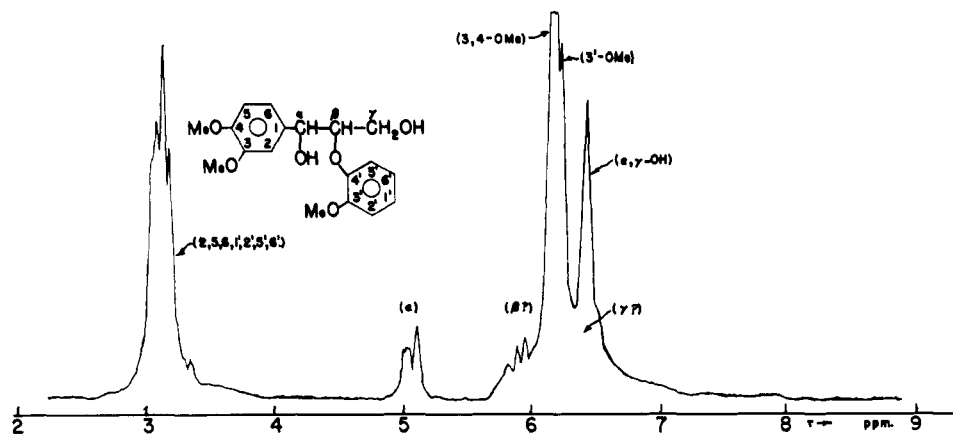


Fig. 6.—1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol, VIId.

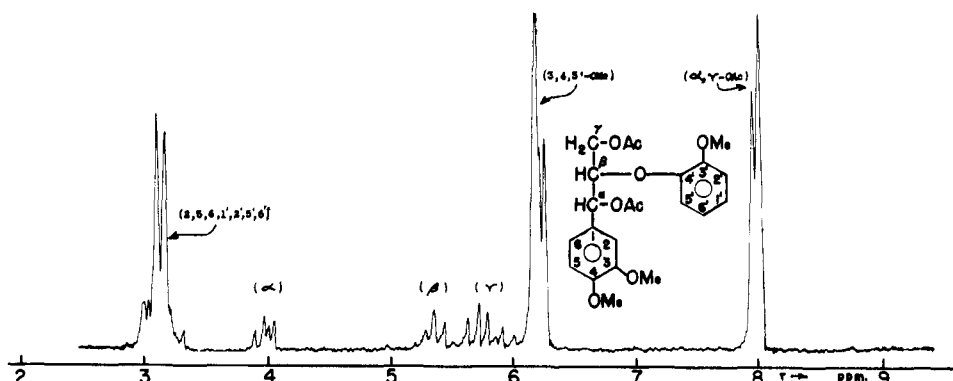


Fig. 7a.—1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol diacetate, VIe.

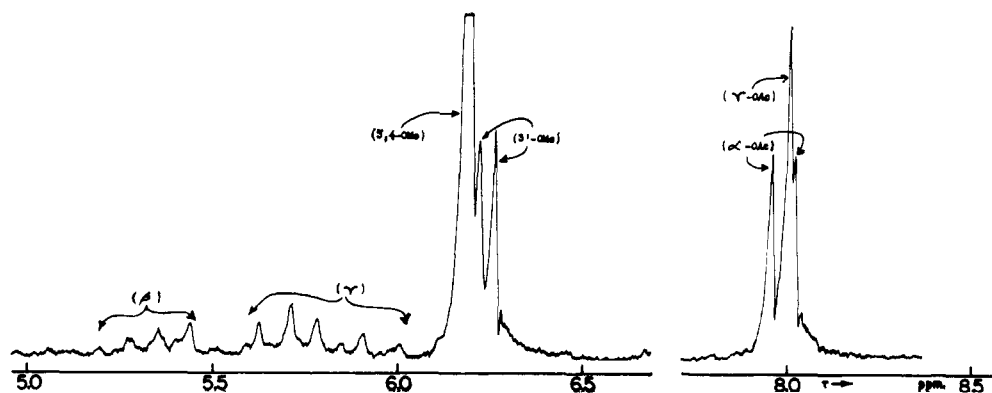


Fig. 7b.—Slow sweep of compound VIe.

present in this case but not in the previously discussed compounds VIa and VIb is apparently favored in hydrogen bonding with the β -ether group and thus inhibits the formation of a hydrogen bond with the α -hydroxyl hydrogen. An integration of this spectrum by cutting out peaks and weighing them indicated a ratio of aromatic to α to other hydrogens to be 7 : 1 : 14, thus confirming the presence of signals for the hydroxyl, β -, γ -, and methoxyl protons to be in the complex signal centered at 6.2.

The acetylated β -ether diol VIe gives the n.m.r. spectrum in Fig. 7a. Comparison with the n.m.r. spectra of other model compounds having α -acetoxy groups shows that the unsymmetrical quadruplet found at 3.90 to 4.06 comes from the α -protons and is a composite of the signals from the two diastereoisomers which are present in the sample, one giving a τ -value of 3.96 and a $J_{\alpha\beta}$ of 6.8 sec.⁻¹ and the other a τ -value of 4.02 and a $J_{\alpha\beta}$ of 5.3 sec.⁻¹. Gierer has recently succeeded in the separation of the *erythro* and *threo* diastereoisomers of this compound.¹⁴ The complex multiplet

in the region of 5.19 to 6.00 is a composite of the signals for the β - and γ -protons in both of the diastereoisomers. This region has not been completely analyzed because of its complexity. However, by comparison with other n.m.r. spectra it seems likely that the signals from 5.19 to 5.51 are from the β -protons and those from 5.63 to 6.00 are from the γ -protons.

The methoxyl and the acetoxy types of protons in compound VIe are shown by the spectrum taken at a slower sweep, Fig. 7b. Each produce three distinct signals rather than the two expected of a pure isomer. The smaller two at 6.21 and 6.25 for the methoxyl protons and at 7.96 and 8.02 for the acetoxy protons are assigned to the 3'-methoxyl and the α -acetoxy groups, respectively, because of their greater proximity to the optically active centers.

2. Pinoresinol Dimers.—The occurrence of the pinoresinol linkage in lignin has been postulated because of the apparent presence of α -alkyl ether linkages²

(14) J. Gierer, Swedish Wood Research Inst., Stockholm, Sweden, private communication.

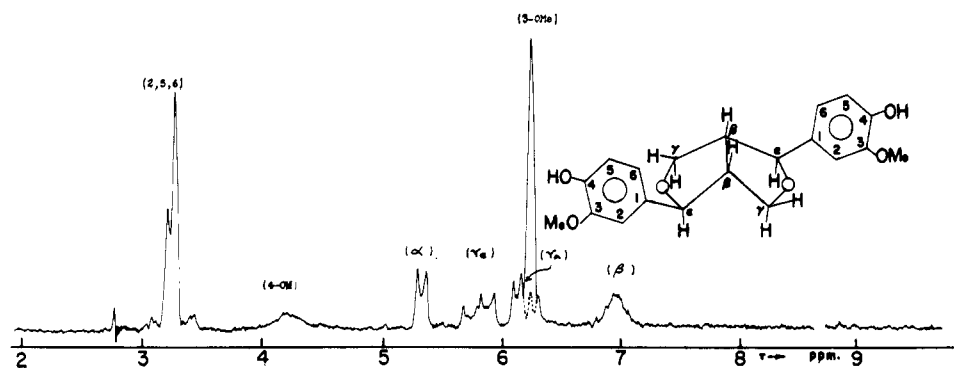


Fig. 8.—(+)-Pinoresinol, VIIa.

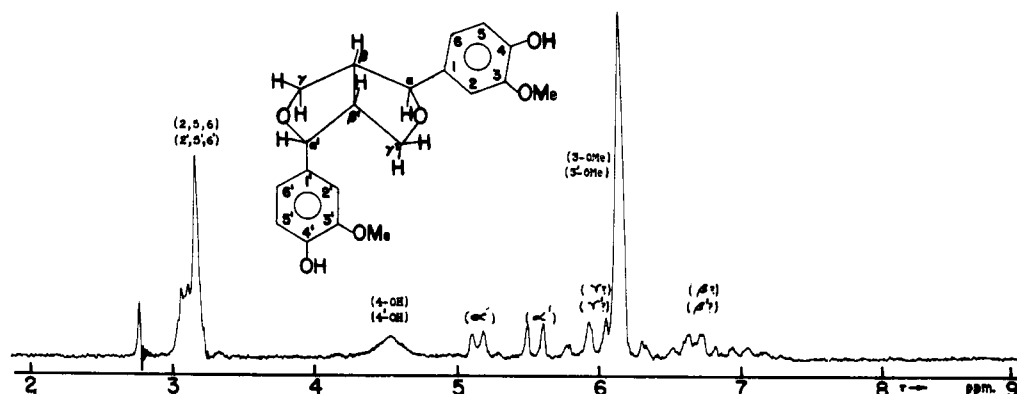


Fig. 9.—(+)-Epipinoresinol, VIIb.

and because of the isolation of pinoresinol from the reaction mixture resulting from the enzymatic dehydrogenation of coniferyl alcohol.^{3,12} However, no direct proof of its presence in lignin has yet been demonstrated.

In a recent study Freudenberg and Sidhu¹⁵ have conclusively demonstrated a diequatorial configuration for the aromatic groups in (+)-pinoresinol and equatorial-axial arrangement in (+)-epipinoresinol. While the n.m.r. spectra of these compounds have not been determined previously, Weinges¹⁶ and Jones, *et al.*,¹⁷ have reported spectra of the closely related compounds containing the perhydrofurofuran ring system.

The spectra of compounds VIIa and VIIb (Fig. 8 and 9) support the configurational assignment by Freudenberg and Sidhu.¹⁵ The signal for the α -protons in pinoresinol (VIIa), Fig. 8, is a doublet at 5.28 with a $J_{\alpha\beta}$ of 4.6 sec.⁻¹ as would be expected for protons *trans* to each other in a rigid five-membered ring and having a dihedral angle with respect to each other of about 125–130°. The α - and α' -protons in epipinoresinol (VIIb), Fig. 9, give separate signals, one at 5.14 with a $J_{\alpha\beta}$ of 5.0 sec.⁻¹ and another at 5.56 with a $J_{\alpha\beta}$ of 7.0 sec.⁻¹ because the former proton is *trans* to the adjacent β -proton and the latter proton is *cis* to its adjacent β' -proton.

The β -proton in pinoresinol is responsible for the broad complex signal centered at 6.91. The nonequivalent β - and β' -protons in epipinoresinol (VIIb) give a much less symmetrical and more complex signal at τ 5.92 to 7.28.

The signals assigned to the γ -protons in the pinoresinol spectrum show that the axial and equatorial protons are not equivalent. The equatorial proton

signals must be the quartet at 5.76 because of the $J_{\beta\gamma}$ of 7.0 sec.⁻¹. The quartet centered at 6.15 which is partially obscured by the methoxyl proton signal shows a $J_{\beta\gamma'}$ of 3.8 sec.⁻¹. These are values which are expected for signals of protons *cis* and *trans* to the β -hydrogens, respectively. The two nonidentical protons on each γ -carbon show a $J_{\gamma\gamma'}$ coupling constant of 9.23 c.p.s. These chemical shifts and splitting constants combine to give the pattern for α - and γ -proton signals in the pinoresinol spectrum. This type of signal is seen without the interfering methoxyl signal in the spectrum of sesamin.¹⁷ The γ -protons in epipinoresinol give the complex signal pattern in the methoxyl proton signal region which has not as yet been completely resolved. The n.m.r. spectrum of pinoresinol acetate (VIIC) shows very little difference from the pinoresinol spectrum except for the lack of the hydroxyl signal and the appearance of the acetoxyl signal at 7.72.

3. Phenylcoumaran Dimers.—Adler² presents evidence that the phenylcoumaran type linkage is present to the extent of about 0.08 per methoxyl group in Bjorkman spruce lignin. This linkage is present in acetylated dehydrodiconiferyl alcohol (VIIId). The n.m.r. spectrum of this compound is shown in Fig. 10.

The quadruplet at 5.61 must reflect nonequivalence of either the γ - or the γ' -protons. The fact that the γ' -protons in the spectrum of coniferyl benzoate (IIb) give a clean doublet, Table I, indicates that these γ' -protons should do so likewise. The possibility of the presence of a mixture of *cis* and *trans* isomers about the double bond is unlikely because of the typical pure *trans* type signal for the α' -proton with a splitting constant of 15.6 c.p.s. so the quartet has been assigned to the γ -protons and the doublet at 5.32 to the γ' -protons.

The quartet may be rationalized by assuming that the methyleneacetoxyl group is restricted in its rotation about the β - γ carbon-carbon bond and that the two γ -protons involved are consequently not identical so

(15) K. Freudenberg and G. S. Sidhu, *Tetrahedron Letters*, No. 20, 3 (1960).

(16) K. Weinges, *Ber.*, **94**, 2522 (1961).

(17) W. A. Jones, M. Beroza, and E. D. Becker, *J. Org. Chem.*, **27**, 3232 (1962).

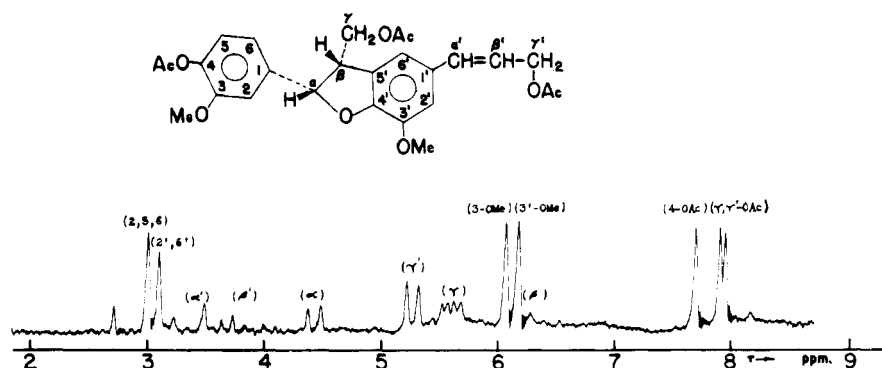


Fig. 10.—Dehydridiconiferyl alcohol triacetate, VIIIId.

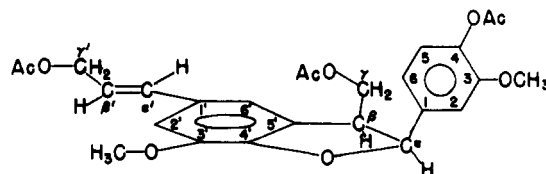
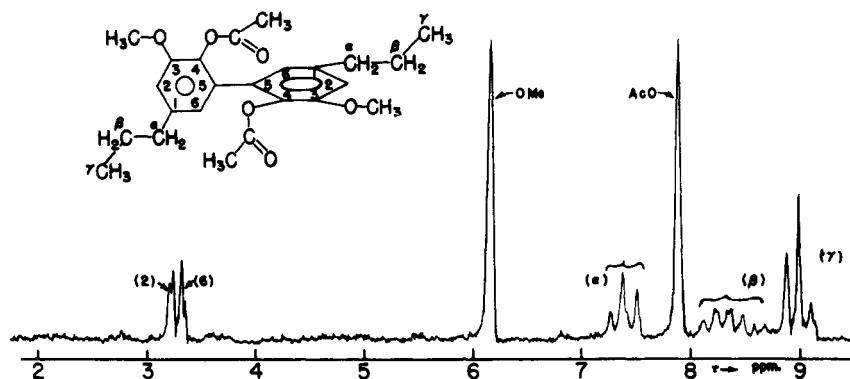
Fig. 11.—*cis* Configuration of acetylated dehydridiconiferyl alcohol.

Fig. 12.—Tetrahydrodehydrodieugenol diacetate, IXa.

that the quadruplet is actually two signals chemically shifted about 0.05 p.p.m. apart and split by the β -proton with two different coupling values of 6.0 and 6.6 c.p.s. This apparent restriction of rotation suggests that the methyleneacetoxy group attached to the β -carbon is *cis* to the aromatic ring on the α -carbon in the furan ring. Also the relatively large $J_{\alpha\beta}$ coupling constant of 7.2 sec.⁻¹ supports a *cis* relationship between protons attached to the α - and β -carbons. Thus we interpret the n.m.r. spectrum of compound VIIIId to support a *cis* configuration in the furan ring, Fig. 11. However, further chemical evidence is needed to demonstrate this conclusively, especially since Aulin-Erdtman and Tomita¹⁸ have recently reported conclusive chemical evidence to support the *trans* configuration in the furan ring of the related dehydridiisoeugenol (XIa).

4. 5-5' Linked Dimer.—Pew⁵ has recently conducted ultraviolet studies of lignins and model compounds and reports that coniferous lignin may well contain 25% or more of biphenyl linked units. The n.m.r. spectrum of a model of this linkage, compound IXa, is shown in Fig. 12. In compounds which contain the biphenyl linkage the *o*-hydrogens are deshielded by the diamagnetic π -electron circulations of the attached ring as well as their own ring. This generally lowers the values of such protons by about 0.36 p.p.m. As the rings are forced out of the plane by bulky *ortho* groups, the deshielding is reduced until at 90°, if ro-

tation out of the plane, the τ -values of *o*-hydrogens are actually higher by 0.05 p.p.m. than would otherwise be expected.¹⁹ In the n.m.r. spectrum of compound IXa the signals for the aromatic protons are found at 3.21 and 3.31 which are both in the upper part of the range found for aromatic protons in models studied, Table III. This shows that no deshielding occurs in this type of linkage. It is evident that the bulky acetoxy groups force the rings 60° or more out of the plane with each other. The nonplanarity also results in the positive shielding of the acetoxy hydrogens so that they produce signals at 7.87 in the range expected of aliphatic acetoxy protons rather than about 0.2 p.p.m. lower where the aromatic acetoxy protons usually produce signals.

The digest of chemical shift data in Table III provides a key for the understanding of n.m.r. spectra of lignin preparations. While it is true that considerable overlapping of signals has been found especially for protons attached to β - and γ -carbons of side chains involved in linkages thought to occur in lignin, there are many protons in these lignin models which have been shown to give signals suffering little interference from signals of other protons expected to occur in lignins.

Signals from the carboxylic and aldehydic type proton have values ranging, respectively, from -1.00 to -3.21 and 0.00 to 0.52. These types of protons

(18) G. Aulin-Erdtman and Y. Tomita, *Acta Chem. Scand.*, **17**, 535 (1963).

(19) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 128.

are predicted to occur in lignin only to a very limited extent; however, the knowledge of the chemical shifts expected of them may be of value in oxidation studies, in which such groups may be produced.

It is now well accepted that gymnosperm lignins contain predominately guaiacyl type aromatic nuclei. The chemical shifts for aromatic protons *ortho* to α -carbonyl groups are uniquely situated from about 2.30 to 2.68 so that appreciable amounts of this type of proton should be visible in spectra of lignins. All the other aromatic protons in model compounds give τ -values in the range 2.80 to 3.33. The α' -vinyl proton of compound VIIId produces a signal which slightly overlaps this. However, since very few vinyl groups are estimated to occur in lignins, this interference is not serious. An interesting possibility resulting from the unique location of the aromatic proton signals is that of determining the relative numbers of aromatic protons occurring in lignins. From such a determination the relative numbers of C₉ units condensed in the aromatic nucleus may be estimated.

Protons which are attached to the α -carbon in acetylated models of the benzylic type acetoxyls produce signals centered at about 4.00. The only signals from the models studied which interfere in this region are those produced by the β -vinyl protons as in compound VIIId'. These appear to be relatively rare in lignin. Consequently, signal intensity in this region should allow estimates to be made of the numbers of α -protons of the above type from n.m.r. spectra of lignin preparations.

The only proton found to give a signal in the range 4.42 to 4.53 is that attached to the α -carbon in the coumaran system of compound VIIId. Consequently, the intensity of the signal in this range should be an indication of the amount of this linkage in lignins.

Other protons attached to the α -, β -, and γ -carbons of side chains involved in linkages thought to occur in lignins appear in the range of 5.10 to 7.28 with much overlapping and with interference from the strong methoxyl proton signal, making it difficult to interpret this spectral region.

Aromatic methoxyl protons of the type found in lignins produce n.m.r. signals centered about 6.2. In models containing an α -carbonyl group on the side chain, the signal is lowered to a range of 6.08 to 6.14. The interference of the aliphatic protons mentioned above make it improbable that n.m.r. can be used successfully for quantitative determination of methoxyl protons. Aliphatic methoxyl protons are found to give signals in the range 6.53 to 6.67 which is of interest in studying methylated derivatives of lignins.

Protons of aromatic acetoxy groups, except those *ortho* to a 5,5'-linkage, give signals in the range of 7.70 to 7.75, and since there is no apparent interference from other protons in model compounds in this region this should provide a novel procedure for the determination of relative amounts of aromatic acetoxy groups in lignin preparations and, by inference, of the number of phenolic hydroxyls in the parent lignin preparations. Signals from the aliphatic acetoxy protons and the aromatic acetoxy protons *ortho* to a 5,5'-linkage are found in the range 7.91 to 8.02 with no known interference, providing a way for the estimation of relative numbers of these groups.

Any signal above the aliphatic acetoxy region would likely be produced by protons which have at least two carbons between them and any electron-withdrawing groups such as oxygens, aromatic systems, or carbonyl groups.

This compilation of chemical shift data has already proved to be of great assistance in the understanding

of the n.m.r. spectra of acetylated lignin preparations reported in the subsequent paper. Other future uses of the information may include: a study of low molecular weight fragments of lignins obtained either by degradation procedures or by fractionations, measurements of effects of reactions on the nature of lignins, differences between lignins from different kinds of plants, studies of Kraft lignins and other lignins isolated by many different ways, study of the nature of impurities which may be present in lignins, deuterium or tritium exchange studies, and comparison of synthetic and natural lignins. It appears that the proper use and understanding of n.m.r. may be of profound assistance to future workers in this field.

Experimental

All melting points are by capillary tube and are corrected. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium in Max-Planck-Institut, Mulheim (Ruhr), West Germany. Reagents used were analytical reagent grade unless otherwise specified.

Model compounds used which were available commercially, and those obtained from other workers were checked for purity by melting points or indices of refraction and purified by recrystallization or distillation when necessary.

α -Hydroxypropiovanillone was supplied by Karl Kratzl, University of Vienna, Austria; dehydrodisoeugenol, dehydrodiconiferyl alcohol, pinoselinol, epipinoselinol, and syringaresinol from Karl Freudenberg, Heidelberg, Germany; ω -(2-methoxy-4-propylphenoxy)-acetoveratrone and pinoselinol from Holger Erdtman, Stockholm, Sweden; β -acetoxypropiovanillone and p -hydroxybenzaldehyde from G. Merrill Andrus, formerly of University of Washington, Seattle, Wash.; veratral and 1-(3-methoxy-4-hydroxyphenyl)-propanol from S. W. Schubert, Seattle, Wash.; and tetrahydrodehydrodieugenol from J. C. Pew, Madison, Wis.

α -(2-Methoxyphenoxy)-acetoveratrone (Va) was prepared by the procedure of Adler, Lindgren, and Saeden²⁰ and was obtained in 94% yield, m.p. 93–94°, lit.²⁰ 90–92°.

Anal. Calcd. for C₁₇H₁₈O₅: C, 67.54; H, 6.00. Found: C, 67.57; H, 5.97.

α -(2-Methoxyphenoxy)- β -hydroxypropioveratrone (Vb) was prepared by the procedure Adler, *et al.*,²⁰ and was obtained in 94% yield, m.p. 117.5–118°, lit.¹¹ 114–116°.

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol (VId) was prepared by sodium borohydride reduction of Vb according to Adler, *et al.*²⁰ The ultraviolet spectrum of VId had a single maximum at 2800 Å, indicating that reduction was complete. The product was a glass obtained in quantitative yield.

Anal. Calcd. for C₁₂H₂₂O₆: C, 64.68; H, 6.63. Found: C, 64.40, 64.55; H, 6.60, 6.76.

The 3,5-dinitrobenzoyl diester of VIIId was prepared following the general procedure of McElvain²¹ to obtain a yellow oil which was crystallized from ethanol–acetone by cooling in a Dry Ice–acetone bath and scratching with a stirring rod. After being dried overnight at 78° and 5 mm. over P₂O₅ the yellow crystals melted at 97.5–98.5°.

Anal. Calcd. for C₃₂H₂₆N₄O₁₆: C, 53.17; H, 3.63; N, 7.79. Found: C, 53.36; H, 3.58; N, 7.79.

The Preparation of Benzylic Type Alcohols by Sodium Borohydride Reduction.—Apocynol (IIIb) was prepared following the general procedure of Adler and Hernstam²² by the reduction of acetovanillone (Ib) in aqueous sodium hydroxide solution using sodium borohydride. The crude yield was 51.3%. Purified product recrystallized from ethyl acetate and *n*-hexane melted at 100–102°, lit.²³ 101–102°.

Veratryl alcohol (IIIe) was prepared by the sodium borohydride of veratral (If) in 95% ethanol in 91% yield. This product was distilled and the fraction boiling at 132–133° representing 75% of the product was collected for use in n.m.r. studies, n_D^{25} 1.5518, lit.²⁴ n_D^{25} 1.555.

1-(3,4-Dimethoxyphenyl)-ethanol (IIIIf) was prepared by the sodium borohydride reduction of acetoveratrone in 95% ethanol in 90% yield, b.p. 140–143° (1.2 mm.), n_D^{25} 1.5372; lit.²⁵ b.p. 145–150° (4 mm.), n_D^{25} 1.5440.

(20) E. Adler, B. O. Lindgren, and V. Saeden, *Svensk. Papperstid.*, **55**, 252 (1952).

(21) S. M. McElvain, "The Characterization of Organic Compounds," Revised Ed., The Macmillan Co., New York, N. Y., 1953, p. 193.

(22) E. Adler and S. Hernstam, *Acta Chem. Scand.*, **9**, 314 (1955).

(23) H. Finnemore, *J. Chem. Soc.*, **93**, 1520 (1908).

(24) G. Vavon, *Compt. rend.*, **154**, 360 (1912).

(25) N. P. Zapevalova and M. M. Kotun, *Zh. Obshch. Kh. m.*, **27**, 2142 (1957).

TABLE IV
 ACETYLATION OF COMPOUNDS RELATED TO LIGNIN

Compound	Wt., g.	C ₆ H ₅ N	Ac ₂ O	Purification procedure	Product	Yield, g.
Vanillic acid (Ih)	1.00	7.5	4	Et ₂ O extract washed with dil. HCl, H ₂ O, NaHCO ₃ soln., H ₂ O, and dried	White crystals, m.p. 141–143° (Ie)	0.64
Apocynol (IIIb)	0.317	5	4	Same as Ih	Thick oil, <i>n</i> _D ²⁵ 1.5020 (IIIId)	0.301
1-(3,4-Dimethoxyphenyl)-ethanol (IIIc)	0.629	7.5	6	Same as Ib	Thin oil, <i>n</i> _D ²⁵ 1.5133 (IIIg)	0.263
Coniferyl benzoate (IIb)	1.0	15	12	Solvent evap. off and pptd. from Et ₂ O and pentane	Thick sirup. <i>Anal.</i> (IIc). Calcd.: C, 69.93; H, 5.56; OMe, 9.51 Found: C, 69.78; H, 5.48; OMe, 9.37	
1-(3,4-Dimethoxyphenyl)-2-(2-methoxy-4-propylphenoxy)-ethanol (VIIb)	0.3	4.5	3.6	Recrystd. from H ₂ O, EtOH dried, 0.1 mm., 65°, overnight	White solid, m.p. 87.4–88.0° (VIIc)	0.303
1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diol (VIIId)	0.336	5	4	Same as Ih	Thick oil. <i>Anal.</i> (VIIe). Calcd.: C, 63.14; H, 6.26; OMe, 22.25. Found: C, 63.08; H, 6.46; OMe, 22.22	0.19
Pinosresinol (VIIIa)	0.302	5	4	Recrystd. from AcOH and petr. ether, dried P ₂ O ₅ , 0.3 mm., 65°, overnight	White crystals, m.p. 165.4–166.9° (VIIIc)	0.195
Dehydrosisoeugenol (IXa)	0.313	5	4	Recrystd. from H ₂ O, EtOH, dried P ₂ O ₅ , 0.3 mm., 65°, overnight	White crystals, mp. 112.7–113.7° (IXb)	0.237
Dehydrodiconiferyl alcohol (IXc)	0.046	0.6	0.5	Same as Ih, dried 100°, 0.1 mm., overnight	Thick sirup, n.m.r. shows no unexpected signals (IXd)	0.035

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-ethanol (VIa) was prepared by the sodium borohydride reduction of ω -(2-methoxyphenoxy)-acetoveratrone (Va) in 87% crude yield; m.p. 131–131.5° after recrystallization from 95% ethanol and drying at 65° and 0.1 mm. for several hours.

Anal. Calcd. for C₁₇H₂₀O₅: C, 67.09; H, 6.62. Found: C, 67.07; H, 6.65.

Acetylations.—The compounds listed in Table IV were acetylated by mixing the amounts of reactants specified in an erlenmeyer flask equipped with a glass stopper, allowing the mixture to stand at room temperature 24 to 48 hr., hydrolyzing the products over cracked ice, and purifying them as described.

Nuclear Magnetic Resonance Spectra.—All n.m.r. spectra were obtained using a Varian Associates Model HR-60, equipped with a probe, V-4331-A. Calibrations were performed by the conventional side-band technique. For most of the work redrawn standard 5-mm. o.d. Pyrex glass tubing was used to make the sample tubes. Each tube was charged with about a 60-mg. sample dissolved in 540 mg. of CDCl₃ containing about 1%

hexamethyldisiloxane as internal standard. Some samples which were not easily soluble in the solvent at room temperature were placed in the tubes dry and then the proper amount of solvent was added. The tubes were degassed and sealed and examined at room temperature except when it was necessary to warm them gently to encourage solution.

Acknowledgment.—The authors express their appreciation to Professors Holger Erdtman, Karl Freudenberg, and Karl Kratzl, Mr. John C. Pew, Dr. S. W. Schubert, and Dr. G. Merrill Andrus for their gifts of model compounds used in this study; to Professor K. V. Sarkanen for his helpful suggestions regarding this manuscript; to Mr. Tharwat Saleh for the acetylation and n.m.r. work on compound IXa; and to the Northwest Pulp and Paper Association and Institute of Forest Products for financial assistance.

[CONTRIBUTION FROM PULP MILLS RESEARCH AND THE INSTITUTE OF FOREST PRODUCTS, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

Lignin. XIII.¹ The High Resolution Nuclear Magnetic Resonance Spectroscopy of Protons in Acetylated Lignins

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The n.m.r. spectra of protons in acetylated derivatives of dioxane acidolysis lignin, Bjorkman milled wood lignin, and Brauns native lignins from gymnosperm woods have been studied using a procedure for relating signals within certain ranges of chemical shifts to characteristic protons in lignin model compounds. Integration of the spectra allows semiquantitative estimates to be made on the number of condensed aromatic systems, free benzylic hydroxyls, aliphatic and aromatic hydroxyls, and total aliphatic hydrogens in the parent lignin preparations. The results essentially substantiate earlier analytical estimates and are unique in providing a reliable measure of condensed aromatic ring systems.

The n.m.r. spectra of model compounds related to lignins have been discussed in a previous publication.¹ This paper reports the application of the information gained in the model compound study to the interpretation of the more complex and diffuse lignin spectra.

(1) Lignin. XII: C. H. Ludwig, B. J. Nist, and J. L. McCarthy, *J. Am. Chem. Soc.*, **86**, 1186 (1964).

The gymnosperm lignin preparations, Table I, after acetylation were all found to be sufficiently soluble in deuteriochloroform for n.m.r. determinations. The same solvent and general conditions were used for these lignin studies as for the study of model compounds in order to justify direct comparisons between the chemi-