Table IV
Partial Methylation of Natural Dextran

	substd hydroxyl group, %			substd glucose unit, %		
DS	2-OH	3-OH	4-OH	unsubstd	monosubstd	disubstd
~1.0	55	25	20	~20	~60	~20

is present in the polymer sequence. The substitution pattern of partially methylated dextran is slightly different from that determined by paper and gas chromatography of its hydrolysate,[27] but follows the same pattern reported for partial O-acetylation of dextran.[29]

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Simulation of Reactions with Lignin by Computer (SIMREL). 6. Interpretation of Primary Experimental Analysis Data ("Analysis Program")†

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ABSTRACT: A computer program is described which converts primary lignin analysis data obtained from multiple experimental procedures into information pertaining to the composition of unifying phenylpropane (C_9) lignin substructures. Quantitative information on average phenylpropane units concerns interunit linkages and functionality. The input data converted by the "analysis program" include elemental composition, methoxy, total hydroxy, and carbonyl groups, impurities in the form of ash and hydrolyzable sugars, and gas and gel permeation chromatography data obtained with the permanganate oxidation product mixtures of unaltered and oxidatively depolymerized lignin preparations. Repeatability of all primary analysis data is assessed and evaluated in relation to the determination of specific structural features of the average C_9 unit, in terms of both functionality and interunit linkages.

Introduction

The analysis of polymeric lignin preparations is faced with the interpretation of a multitude of observations from analytical laboratory experiments in terms of a common structure of the statistical polyphenolic polymer. Such correlations between chemical structures and analytical behaviors are most suitably performed by computer techniques. Prior papers in this series have reported on the development of a linear computer program that simulates the formation of lignin on a structural level from a mixture of precursors.[1,2] In later papers, the predictive capabilities of this model were tested with regard to analytical features.[3,4] With this technique, several lignin model structures were obtained which satisfied the input parameters relating to polymerization mechanisms and which approximated closely prominent analytical data obtained experimentally.[5] In general, the distinction between "good models" and "bad models" must be made on the grounds that good models satisfactorily reflect primary analytical observations. Given the development of a computer program which permits the formulation of lignin's structure on the basis of several analytical features, the acquisition

† Part of the results have been presented in a paper given at the Spring Annual Meeting of the American Chemical Society, held in Honolulu, Hawaii, April 2–6, 1979. Previous paper: Glasser, W. G.; Glasser, H. R.; Nimz, H. H. H. *Macromolecules* **1976**, *9*, 866–7. The authors are Professor of Wood Chemistry, Computer Programmer, and Associate Professor of Wood Chemical Technology (on leave from Tokyo University of Agriculture and Technology, Fuchu, Japan), respectively.

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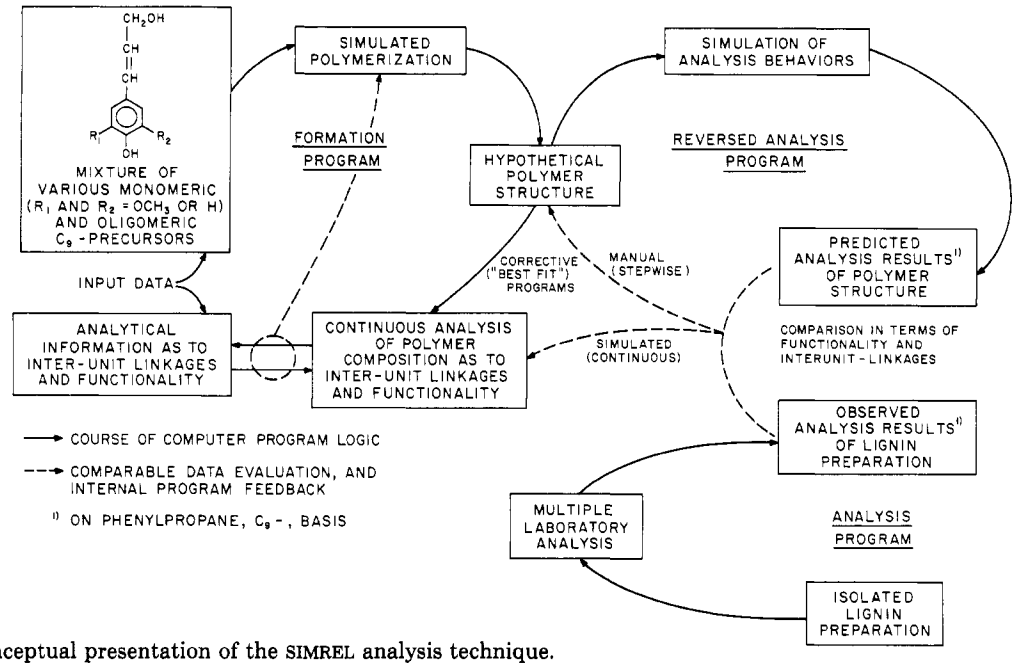

Figure 1. Conceptual presentation of the SIMREL analysis technique.

of primary analytical data, data reduction, and data interpretation in terms of the composition of average phenylpropane (C_9) units become a primary concern. The entire process of assigning a chemical structure to an isolated lignin preparation is illustrated in Figure 1. This scheme involves several distinct areas of computer and laboratory bench type experimental activities, and these are the following.

After an isolated lignin preparation has been subjected to several analytical tests—such as elemental analysis, functional group determinations, spectroscopic evaluations, and analytical degradations—all primary data are interpreted in terms of a unifying average phenylpropane structure by the "analysis program". Results from the analysis program are compared to data of the same type obtained from any hypothetical lignin model structure, such as one obtained by computer simulation[1,2] or one "manually conceived". The projecting of analytical results on the basis of a lignin model structure is also accomplished by means of a computer simulation program, the "reversed analysis program". The comparison of the experimental data (from the analysis program) with the projected analysis results (from the reversed analysis program) provides feedback via a manual (stepwise) or a simulated (continuous) computer program, a "best fit program" and eventually allows assignment of a structure to a particular isolated lignin sample.

The object of this paper is the analysis program, which interprets a variety of primary analytical data obtained by conventional laboratory techniques in terms of the structure of the average phenylpropane unit in a polymeric isolated lignin preparation.

Experimental Section

Data Acquisition. Analytical data routinely acquired for the purpose of structure evaluation involve the following techniques, and these are discussed in detail elsewhere:[6-12] elemental analysis; functional group analysis—OCH_3, total OH, total CO; impurities—ash, carbohydrates; ^1H NMR spectrum of lignin acetate; oxidative degradation by alkaline permanganate and H_2O_2, unchanged and oxidatively (CuO/OH^-) depolymerized preparation; gas and gel permeation chromatography, unchanged and depolymerized preparation.

Sample Preparation. The isolated lignin preparations discussed in this paper were prepared by the conventional ball-milling and solvent (dioxane–water)-extraction method.[13-15] Procedural details were discussed in an earlier paper.[16] Lignin preparations isolated by this method are termed "milled wood lignins" (MWL).

Table I
Analytical Data Corrections

analysis data	input data	corrected data
C, %	61.56	62.15
H, %	5.90	5.90
OCH_3, %	13.97	14.43
total OH, %	10.54	9.65
total CO, %	2.86	2.67
ash, %	0.10	
sugars, mg per hydrolysis		
arabinose (1.46)[a]	0.398	
xylose (1.38)[a]	0.504	
mannose (1.26)[a]	0.447	
galactose (1.14)[a]	0.824	
glucose (1.23)[a]	0.553	
lignin sample, hydrolyzed, mg	101.2	
total carbohydrates, %		3.05
hexosans, %		1.94
pentosans, %		1.11

[a] Hydrolysis factors in parentheses.

Data Reduction and Interpretation. The primary analytical data compiled in part in Table I provide the input into the SIMREL analysis program, which converts the data into structural information following the steps outlined in this paper.

Results and Discussion

Program. This study deals with the development of a method to derive detailed structural information on the composition of average phenylpropane (C_9) units. The conversion of elemental analysis results into the form of a C_9-based empirical formula is a generally accepted practice in lignin chemistry.[15,17-19] The C_9-based unit, the monomeric building block of lignin, presents a denominator which is commonly used for the correlation of hypothetical model structures with all types of analytical information. The presentation of this information in the form of an average phenylpropane monomeric unit has been termed Rydholm diagram,[1,2,15,17] in honor of S. A. Rydholm, who first employed this schematic representation.[19] Analytical information represented by this scheme concerns types and frequencies of functional groups and

Table II
Empirical Formulas of the Average Phenylpropane Unit

structural feature	simple version[a]	refined version
lignin		
C	9.0[b]	9.0
H total	8.52	8.52
aromatic H		2.46
hydroxy H, av		1.10
by NMR/by chem anal		1.11/1.09
side-chain H		4.96
O total	2.93	2.93
aromatic OH		0.35
aliphatic OH		0.75
aromatic OR		0.65
CO		0.18
unresolved		1.00
OCH_3	0.89	0.89
unit weight	191.1	
H/C_9 (unacetylated)	11.18	
impurities		
ash, as Na	0.002	
pentosan units	0.021	
hexosan units	0.037	
cumulative data		
unit weight	200.0	
H/C_9 (unacetylated)	11.7	
purity, %	96.85	

[a] Calculation as outlined by Lenz.[22] [b] Can be calculated to any predetermined C level.

interunit linkages on the basis of multiple experimental analysis.

Since lignin samples are rarely without contamination by ash, carbohydrates, or other impurities, the primary analysis data are in need of correction before they can suitably be converted to a C_9 basis. Quantitative determination and correction, rather than extensive purification, appear a more reasonable approach to achieving reliable analysis data on isolated lignin preparations. Hydrolyzable carbohydrates can be quantitatively determined as alditol acetates by gas chromatography following reduction with $NaBH_4$ and acetylation. With the assumption that carbohydrates are not attached to lignin as monosaccharides but rather as approximately trisaccharidic chains (average), lignin's elemental analysis data can be corrected as outlined in Table I. The corrected analysis data are subsequently employed for the computation of C_9 (or other C level)-based empirical formulas, as shown in Table II. The simple version of the empirical formula is based on elemental analysis and impurity data only. This can be "refined" by combination with functional group and ^1H NMR data, as shown in Table II.

^1H NMR spectra of acetylated lignins provide quantitative information on the overall hydrogen distribution in the sample. The spectra can be interpreted according to the recommendations made by Ludwig et al.,[20,21] Lenz,[22] and McCarthy et al.[23] This procedure involves subdividing ^1H NMR spectra into eight distinct regions and determining the amount of total hydrogen in each region. This method provides particularly useful information on the number of aromatic protons and hydroxyl groups, as depicted in Table II. These data take into account quantitative information about carbohydrate contents of the sample and make the necessary adjustments in terms of total hydrogen content and total and aliphatic hydroxyl contents.

Additional analytical information on lignin preparations is obtained by degradations to low molecular weight fragments such as the permanganate oxidation procedure.[24,25] The acquisition and interpretation of permanganate oxidation data obtained with unhydrolyzed and hydrolyzed lignin preparations have been the subject of two prior publications from this laboratory.[9,10] These articles outline the method by which lignin is depolymerized and separated into a series of mono- to oligomeric fragments. They also describe how yields of mono-, di-, and oligomeric degradation products from permanganate oxidation product mixtures may be adjusted and corrected for yield losses and how they can be converted into data reflecting theoretical yield levels. It is possible to assess the chemical structure of a polymeric lignin preparation in great detail by combining information on overall unit weights of average phenylpropane units with the results of permanganate oxidation experiments.

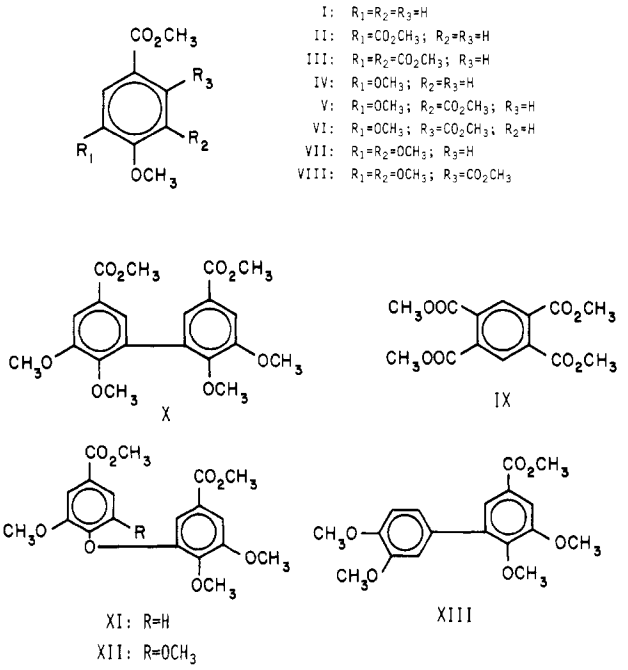

Figure 2. Monomeric and dimeric permanganate oxidation products.

A computer program, in Fortran IV, was written to perform this assessment by combining information from various analytical techniques. Input data for this program are summarized in Table III. Experimental results from the oxidative lignin degradation refer to data obtained with unaltered and hydrolyzed preparations involving both gas and gel permeation chromatographic data. The computer program (analysis program) is capable of identifying and quantifying mono- and dimeric degradation products separated by gas chromatography (GC) by (a) comparison with a known mixture of appropriate model compounds, (b) comparison of relative retention times with data reported by Larsson and Miksche,[26] (c) utilizing mass spectral data obtained by GC/MS, and (d) the use of an internal standard (tetramethyl pyromellitate (IX), Figure 2). In addition, the analysis program handles data from the separation of degradation product mixtures by gel permeation chromatography. These data provide quantitative information on the molecular weight distribution of the degradation product mixtures.[10]

Actual degradation product yields are subsequently corrected[10] to reflect theoretical yield data for mono- to hexamers (Table IV) and converted into figures representing the number of moles per C_9 according to the technique reported by Larsson and Miksche.[27] For the conversion of oligomeric fractions, it is assumed that the average unit weights are similar to those of typical guaiacyl-type degradation products. The subsequent calcula-

Table III
Data Input for SIMREL Analysis Program

analysis data	unmodified	depolymerized
elemental C and functional groups (after correction; cf. Table I)		
C, %	62.15	
H, %	5.90	
OCH_3, %	14.43	
total OH, %	9.65	
total CO, %	2.67	
carbohydrates		
hexosans, %	1.94	
pentosans, %	1.11	
H NMR spectrum (acetate in $CDCl_3$)		
range 1, %	1.0	
range 2, %	17.3	
range 3, %	3.5	
range 4, %	3.5	
range 5, %	47.0	
range 6, %	7.4	
range 7, %	18.9	
range 8, %	1.5	
permanganate oxidation		
starting material		
total, mg	100.0	46.00
impurity free, mg	96.85	44.55
internal standard, mg	3.45	5.97
retention times (cf. Figure 2)[a]		
I	410/362-81596	359/338-50547
IV	743/661-1142307	642/621-1216314
VII	943/846-26599	828/793-15271
II	1039/945-6803	898/900-9944
V[b]	1187/1096-145259	1046/1040-92124
VI	1239/1147-58364	1101/1098-17262
III	1382/1294-5361	1282/1228-2793
IX	1553/1456-321488	1393/1382-451655
XIII[c]	1800/- - - -17299	1697/- - - -55577
XI	2294/2195-75190	2097/2107-58333
X[b]	2340/2225-118374	2131/2128-179605
XII[c]	- - - -/- - -	2179/- - - -23706
gel permeation chromatogram[d]		
1- and 2-mers	157.2	347.9
3-mers	16.5	70.6
4-mers	7.1	38.8
5-mers	2.8	17.0
6-mers and higher	1.7	7.0

[a] First number = retention time of lignin-derived mixture (arbitrary time units); second number = retention time of model mixture (arbitrary time units); third number = integrated area (arbitrary integration units); partial listing only. [b] Identified visually. [c] Not available as model; identified by GC/MS. [d] In milligrams of paper clipped from the GPC recorder tracing of each section.

tion of "percent moles" and "balance" (hydrolyzed minus unhydrolyzed data) is carried out in analogy to Larsson and Miksche's procedure.[27] For the computation of linkage distributions and frequencies, the assumption is made that oligomeric fractions are connected exclusively by linkages between aromatic rings, such as 4–0–5, 5–5, and 1–5 interunit bonds. The overall frequency of 4–0–5, 5–5, and 1–5 linkages in the dimeric fraction are taken to be representative for the oligomeric fractions. The method of computing linkage distribution data on the basis of results obtained from the permanganate oxidation of unhydrolyzed and hydrolyzed lignin preparations is illustrated in Table IV.

The combination of analytical data from multiple analysis procedures in the form of a Rydholm diagram is illustrated in Table V. It is obvious that this kind of data interpretation may result in certain differences, deviations, and even contradictions between results obtained from different experimental sources. However, the overall agreement of figures for the loblolly pine MWL preparation illustrated in Table VI serves as an excellent indication of the power of this combined data interpretation technique.

This systems approach to the interpretation of lignin analysis data represents a new technique of unifying primary experimental observations with lignin. However, it is far from presenting a flawless picture of lignin's chemical structure. Additional and more reliable analytical techniques must be explored and their value for structure evaluation assessed.

Program Appraisal. The computer program described in the first section of this paper digests analytical information and interprets it in terms of the structure of an average phenylpropane building unit of lignin. The quality and dependability of this interpreted information depend solely on the quality of the primary analytical data obtained. Thus, it becomes important to understand the quantitative relationship between primary analytical data and interpreted structural information. In the following section, this relationship is assessed (a) by determining the repeatability and dependability of primary data used in this program and (b) by evaluating the dependence of structural features on primary data in a quantitative and semiquantitative fashion.

A. Repeatability of Primary Analytical Data. An important source of structural information of isolated

Table IV
Computation of Linkage Distributions

analysis data	yield, mg/100 mg of lignin: original UH	original H	corrected[a] UH	corrected[a] H	moles/C_9 UH	moles/C_9 H	% of moles UH	% of moles H	balance of moles	no. of linkages per 100 C_9 units: β-5	SC-2/6	4-0-5	5-5	1-5	α/β-0-4	condensed units
I	0.71	1.17	1.04	1.74	0.63	1.05	1.20	2.01	0.81						0.81	
IV	10.24	29.20	15.14	43.53	7.72	22.21	14.81	42.59	27.78						27.78	
VII	0.23	0.35	0.33	0.52	0.15	0.23	0.28	0.44	0.16						0.16	
II	0.06	0.25	0.14	0.55	0.06	0.25	0.12	0.47	0.35	0.47						0.47
V	1.54	2.61	3.36	5.81	1.32	2.29	2.54	4.39	1.85	4.39						4.39
VI	0.58	0.46	1.27	1.02	0.50	0.40	0.96	0.77	−0.19		0.77				0.00	0.77
VIII	0.03	0.36	0.07	0.80	0.03	0.28	0.05	0.54	0.49		0.54				0.49	0.54
III	0.06	0.09	0.20	0.29	0.07	0.10	0.14	0.20	0.06	0.20	0.20					0.39
XIII	0.17	1.48	0.25	2.21	0.04	0.33	0.07	0.64	0.56					0.32	0.56	0.32
XI	0.86	1.78	1.87	3.95	1.00	2.10	1.91	4.03	2.13			2.02			1.06	2.02
X	1.08	4.39	2.36	9.75	1.21	5.00	2.32	9.59	7.27				4.79		7.27	9.59
XII	0.01	0.63	0.02	1.41	0.01	0.69	0.02	1.34	1.32			0.67			0.66	0.67
subtotal	15.57	42.76	26.06	71.57	12.73	34.93	24.42	67.01	42.60	5.05	1.51	2.68	4.79	0.32	38.79	19.15
3-mers			2.73	17.94	1.38	9.10	2.66	17.46	14.81	1.72	0.51					
4-mers			1.17	9.85	0.59	5.00	1.14	9.59	8.46	0.94	0.28					
5-mers			0.45	4.33	0.23	2.20	0.44	4.21	3.77	0.41	0.12	8.14	14.55	0.97	16.04	
6+-mers			0.28	1.79	0.14	0.91	0.27	1.74	1.47	0.17	0.05					42.41
subtotal			4.62	33.90	2.35	17.21	4.50	33.01	28.50	3.24	0.97	8.14	14.55	0.97	16.04	42.41
grand total			30.69	105.47	15.09	52.14	28.93	100.01	71.10	8.30	2.48	10.82	19.34	1.29	54.83	61.56

[a] For correction technique, see Morohoshi and Glasser.[10]

Table V
Experimental Data Sources of Rydholm Diagram Figures

position	substituent	data base[a]
side chain	total H	EA, NMR
	SH, SO_3H, SCH_2CO_2H, etc.	EA
	OH	EA, NMR, FGA
	OAr	EA and NMR (by diff), PO-GPC
	CO	FGA
	CAr	PO-GPC
1	1-5	PO-GPC
2,6	condensed	PO-GPC
	H	EA, NMR
3,5	OCH_3	FGA (PO)
	Gua:Syr:POH ratio	PO-GPC
	condensed	NMR, PO-GPC
	OAr, 5-5, β-5	PO-GPC
	H	EA, NMR
4	OH	FGA, NMR, PO-GPC
	OR	NMR (diff), PO-GPC
	α- and β-0-4, β-5, 4-0-5	PO-GPC

[a] EA = elemental analysis, NMR = ^{1}H NMR spectrum of lignin acetate, FGA = functional group analysis (chemical techniques), PO = permanganate oxidation (unhydrolyzed and hydrolyzed with CuO/OH^-), GPC = gel permeation chromatography (in DMF on Sephadex LH20).

Table VI
Composition of the Average Phenylpropane Unit of Loblolly Pine MWL

positions in C_9 unit	frequency
C-α,β,γ	
H total	4.96
OH	0.75
OAr	0.62
CO	0.18
CAr	0.11
C-1	
C,H,O	1.0
C-2,6	
H	1.98
condensed units	0.02
C-3,5	
OCH_3	0.89
Gua	0.86
Syr	0.02
POH	0.13
condensed units by NMR	0.65
condensed units by PO	0.62
4-0-5	0.10
5-5	0.39
1-5	0.01
β-5	0.08
H	0.49
total no. of positions in C-2,3,5,6	3.99
C-4	
OH by NMR	0.35
OH by PO	0.29
OR by PO	0.73
α/β-0-4	0.55
β-5	0.08
4-0-5	0.10

lignins involves ^{1}H NMR spectra of their acetylated derivatives. The repeatability of NMR spectra has been studied with various isolated lignin preparations (MWL; cf. Experimental Section) from three wood species, and repetition concerns either isolation or purification. The results are summarized in Table VII in terms of the distribution of hydrogen in eight ranges, with their respective standard deviations. Repeatability is generally good, with standard deviations of less than 2.0, except in the case of

Table VII
Distribution of Hydrogen in Lignins by ^{1}H NMR Spectroscopy (%)—Averages, Standard Deviations, and 95% Confidence Intervals

samples	^{1}H NMR ranges (according to Ludwig, Nist, and McCarthy[20])								
	1	2	3	4	5	6	7	6 + 7	8
Douglas fir									
av[a] (10)	0.9	16.2	3.6	3.5	47.7	6.7	19.6	26.3	1.8
SD	0.48	1.44	0.58	0.75	3.03	0.44	3.40	3.21	0.93
95% CI,[b] low	0.52	15.20	3.19	2.98	45.52	6.39	17.20	24.04	1.09
95% CI,[b] high	1.20	17.26	4.03	4.06	49.86	7.01	22.06	28.62	2.42
loblolly									
av[a] (6)	0.8	17.8	3.6	3.3	46.7	6.0	20.7	26.7	1.2
SD	0.40	1.04	0.33	0.26	0.79	0.78	1.48	1.39	0.25
95% CI,[b] low	0.34	16.74	3.20	3.01	45.84	5.17	19.18	25.28	0.92
95% CI,[b] high	1.18	18.92	3.90	3.57	47.50	6.81	22.30	28.20	1.44
red alder									
av[a] (16)	0.6	13.2	3.5	2.7	50.8	6.5	20.6	27.1	1.9
SD	0.59	1.48	0.50	0.80	2.97	1.66	3.93	2.97	1.35
95% CI,[b] low	0.00	12.45	3.26	2.30	49.25	5.58	18.53	25.51	1.22
95% CI,[b] high	1.41	14.03	3.80	3.16	52.42	7.35	22.71	28.63	2.66
$\overline{SD}$	0.49	1.32	0.47	0.60	2.26	0.96	2.94	2.52	0.84

[a] Number in parentheses gives the number of lignin samples averaged. [b] 95% confidence interval, low and high boundaries.

Table VIII
Distribution of Predominant Monomeric and Dimeric Permanganate Oxidation Products (in Percent of Total Yield of Compounds I-XIII, Figure 2)

samples	total yield of six compd, mg	IV[b]	V	VI[c]	XIII	XI[d]	X
loblolly pine, unhydrolyzed							
av[a] (4)	11.8	64.6	9.5	3.9	1.7	5.5	7.0
SD	1.96	1.92	1.06	0.49	0.63	0.61	0.39
loblolly pine, hydrolyzed							
av[a] (2)	33.4	65.7	6.3	2.2	1.9	4.7	11.3
SD	8.35	5.06	0.14	1.56	0.07	0.63	1.27
loblolly pine, "assorted"							
av[a] (7)	11.5	68.4	10.8	2.1	0.8	4.0	8.4
SD	3.96	3.79	1.99	1.31	0.17	1.28	2.09
spruce, hydrolyzed							
av[a] (2)	57.8	80.2	3.9	0.6	1.8	5.4	4.2
SD	1.36	2.25	0.66	0.19	0.49	0.30	0.24
kraft lignin							
av[a] (5)	15.5	65.0	8.6	1.6	1.9	2.9	8.3
SD	5.52	4.05	1.78	1.23	1.72	0.92	0.79

[a] Number in parentheses gives the number of lignin samples averaged. [b] Including compound VII for red alder sample. [c] Including compound VIII for red alder sample. [d] Including compound XII for red alder sample.

range 5 (methoxyl and side-chain H) and range 6 + 7 (acetoxy H). Repeatability of the combined ranges 6 (aromatic acetoxy H) and 7 is in every case better than those of range 7 (aliphatic acetoxy H) alone. This implies that the determination of total acetoxy group contents by NMR is always better than the distinction between phenolic and aliphatic acetoxy groups.

A similar appraisal of the repeatability of permanganate oxidation results was attempted in Tables VIII and IX for GC and GPC data, respectively. The results from four permanganate oxidations of loblolly pine MWL samples show good repeatability with regard to the six major monomeric and dimeric compounds in the mixture (Table VIII). The CuO–prehydrolyzed MWL samples show greater standard deviations; however, only two data sets were available for comparison. A series of "assorted" oxidation experiments with loblolly pine MWL, performed with different hydrolysis conditions, showed similar repeatabilities with all six compounds. For the purpose of comparison, results with spruce lignin, kraft lignin (pine), and Douglas fir and red alder MWL are listed also. In summary, the data suggest that the repeatability of the separation of product mixtures is always somewhat better than the repeatability of total product yield (degradation).

Table IX
Repeatability of GPC Data Obtained with Permanganate Oxidation Product Mixtures

mol wt distribution[a]	spruce MWL, hydrolyzed		Organosolv lignin, unhydrolyzed	
	av of 2	SD	av of 2	SD
1- and 2-mers	65.4	2.66	45.9	5.34
3-mers	13.3	1.02	21.4	0.96
4-mers	9.3	0.45	14.7	0.08
5-mers	7.3	1.15	10.0	1.90
6+-mers	4.8	2.08	8.0	2.40
GPC ratio[b]	3.8	0.82	2.1	0.41

[a] Primary data, in percent of total degradation product mixture, by GPC (assuming constant absorptivities). [b] Σ(1- to 3-mers)/Σ(4- to 6+-mers).

The repeatability of molecular weight distributions of permanganate oxidation product mixtures was tested in two cases in which entire degradations were replicated. The results summarized in Table IX indicate good repeatability of the two preparations. The "GPC ratio" weighing the amount of 1- to 3-mers to higher oligomers

Table X
Yields and Molecular Weight Distributions of Permanganate Oxidation Product Mixtures

analysis data	Douglas fir		loblolly pine		red alder		Organosolv lignin (red alder)		kraft lignin (indulin-AT)	
	UH	H	UH	H	UH	H	UH	H	UH	H
total yield of six major monomers and dimers[a]	8.9	37.9	9.8	27.5	6.3	28.5	19.6	22.6	19.4	21.8
yield of										
1- and 2-mers[b]	56.3	74.4	47.2	70.9	73.5	76.2	49.6	46.3	43.3	40.8
3-mers[b]	19.5	11.3	18.2	15.4	15.0	12.3	20.8	18.2	20.3	15.7
4-mers[b]	13.6	5.2	14.8	8.5	6.5	6.4	14.6	14.7	13.6	13.1
5-mers[b]	10.5	5.0	10.8	3.7	2.6	3.3	8.7	11.0	11.6	13.6
6+-mers[b]	10.2	4.1	9.0	1.5	2.5	1.8	6.3	9.8	11.2	16.9
GPC ratio[c]	1.9	6.0	1.9	6.3	7.7	7.7	2.4	1.8	1.7	1.3

[a] In milligrams of methyl ester/100 mg of lignin (gas chromatography); includes compounds IV, V, VI, XI, XII, and XIII, plus the three syringly analogues VII, VIII, and XII in the case of hardwood samples. [b] In percent of total degradation product mixture (gel permeation chromatography); assuming constant absorptivities. [c] Σ(1- to 3-mers)/Σ(4- to 6+-mers).

Table XI
Variability of Prominent Structural Features of Average C_9 Units in Relation to Variability of Primary Analysis Results (in Percent/Percent;[b] Three Wood Species)

analysis data	structural features of refined empirical formula									
	H	O	OCH_3	aromatic H	aliphatic H	OH (by NMR)	OH (by chem)	aromatic OH	aliphatic OH	unresolved O
carbon										
DFS	−1.08	−3.19	−1.09	−1.02	−1.08	−1.08	−1.24	−0.698	−1.20	−6.60
RAS	−1.16	−3.28	−1.18	−1.16	−1.15	−1.07	−1.07	−1.39	−1.27	−5.66
LOB	−1.08	−3.31	−1.10	−1.19	−1.06	−1.05	−1.07	−1.11	−1.04	−7.47
hydrogen										
DFS	+1.55	−0.17	0	+1.31	+2.13	+0.84	0	+0.84	+0.25	−0.55
RAS	+1.88	−0.20	0	+1.21	+2.66	+0.97	0	+0.68	+0.42	−0.53
LOB	+1.46	−0.20	0	+1.17	+1.92	+0.85	0	+0.68	+0.30	−0.74
OCH_3										
DFS	−0.19	−0.14	+1.11	+0.08	−0.39	+0.09	+0.05	+0.10	+0.09	−0.41
RAS	−0.30	−0.22	+2.21	+0.13	−0.55	+0.11	+0.12	+0.11	+0.17	−0.48
LOB	−0.18	−0.17	+1.12	+0.09	−0.36	+0.08	+0.08	+0.08	+0.08	−0.52
ash										
DFS	0	−1.20	0	0.14	−0.04	−0.15	−0.25	+0.22	−0.16	−2.90
RAS	0	−1.71	0	0	−0.01	−0.04	−0.04	+0.11	−0.06	−3.45
LOB	0	−0.42	0	0	0	0	−0.01	0	0	−1.23
sugar										
DFS	−0.04	−0.06	+0.05	+0.07	+0.07	+0.12	−0.15	+0.03	−0.18	−0.02
RAS	−0.07	−0.10	+0.09	+0.08	−0.10	−0.17	−0.26	+0	−0.34	−0.07
LOB	−0.02	−0.05	+0.03	+0.04	−0.04	−0.08	−0.10	+0.01	−0.14	−0.02
NMR zone 2										
DFS	NA[a]	NA	NA	+0.93	−0.29	−0.26	NA	0	−0.14	+0.02
RAS	NA	NA	NA	+0.96	−0.26	−0.16	NA	−0.05	−0.09	+0.05
LOB	NA	NA	NA	+1.02	−0.45	−0.19	NA	0	−0.07	−0.12
NMR zone 5										
DFS	NA	NA	NA	−0.19	+0.57	−0.99	NA	−0.48	−0.50	+0.34
RAS	NA	NA	NA	−1.22	+0.76	−1.47	NA	−0.37	−1.02	+0.55
LOB	NA	NA	NA	−1.10	+0.78	−0.71	NA	−0.72	−0.31	+0.31
NMR zone 6 + 7										
DFS	NA	NA	NA	−0.04	−0.10	+1.10	NA	+0.71	+0.39	−0.23
RAS	NA	NA	NA	−0.06	−0.13	+1.36	NA	+0.68	+0.56	−0.29
LOB	NA	NA	NA	+0.03	−0.13	+0.98	NA	+0.99	+0.33	−0.34

[a] NA stands for not applicable. [b] Example: If H content of loblolly pine lignin varies by 5% (from 5.9 to 6.20), aromatic H/C_9 varies by (5 × 1.17) = 5.85%; this is equivalent to a range of 2.32-2.60 for the sample listed in Table II.

becomes a useful figure for expressing the degree of internal condensation in a lignin: A high figure indicates ready depolymerizability of a lignin to mono- and dimers; a low figure expresses a lignin's resistance to depolymerization.

Table X summarizes the results of several "native" lignin preparations (MWL) as compared to those of several degraded lignins. Total yields of six major monomeric and dimeric degradation products, determined by gas chromatography, are compared to molecular weight distribution data, obtained by gel permeation chromatography, and GPC ratios. The similarity of data for Douglas fir and loblolly pine is noteworthy. In contrast to the prehydrolyzed native lignins, which all have mono- and dimer fractions in excess of 70% of total, Organosolv and kraft lignins have considerably smaller low molecular weight fractions. Softwood MWL preparations oxidized ($KMnO_4$) without prior preoxidation with CuO have significantly less mono- and dimers, suggesting that many of its free phenolic units are of the condensed type. Similar indications were reported previously.[9]

B. Dependence of Structural Information on Primary Analysis Data. The following section is an attempt to correlate variability of primary analytical type data with variability of structural information as it is obtained from the SIMREL analysis program. This relation-

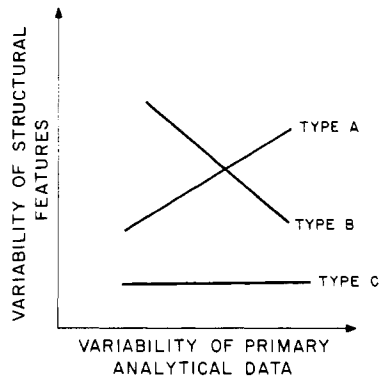

Figure 3. Conceptual relationship between variability of analytical data and variability of structural features.

ship between analytical data variability and its influence on variability of structural features is illustrated in Figure 3. Three types of correlations are discerned: type A illustrates positive correlation, type B illustrates negative correlation, and type C shows no dependence of structural features on primary analytical information. The following parameters were assessed in an attempt to evaluate this dependence quantitatively (Table XI): contents of carbon, hydrogen, methoxyl, ash, and carbohydrates and ranges 2, 5 and 6 + 7 of the NMR spectra. Variability in these data is correlated with variability in the information listed in the refined empirical formula (Table II) of an average phenylpropane unit. The information is listed in terms of percent variability on either side. Thus, for example, if the hydrogen content of loblolly pine varies by 5%, say, for example, from 5.9% to 6.2%, the aromatic hydrogen content of the average C_9 unit would be variable by $5 \times 1.17 = 5.85\%$, or ± 0.14 H per C_9. The results in Table XI illustrate quantitatively the dependence of each structural feature of the revised empirical formula on primary analytical data. Thus, the total oxygen content of the average phenylpropane unit depends most greatly on the precision of the carbon and ash determinations, and the total OH contents depend on the precision of the NMR spectra and integration in the range 6 + 7. Ash determinations significantly influence the total oxygen content and the unresolved oxygen content of C_9 units. If this dependence of the structural features of empirical formulas is combined with the repeatability data of Table VII, significance levels can be estimated for prominent features of the empirical formula (Table XII). The results listed in this table suggest that most structural features can be determined with accuracy exceeding 10% error, except for the content of unresolved oxygen, which greatly depends on ash determination. Total hydroxyl contents and aromatic hydroxyl contents can be determined with slightly less than average reliability.

The value of the permanganate oxidation procedure for lignin analysis lies in its ability to determine quantitatively the interunit linkage distribution in lignin samples. This is accomplished by a combination of the following three measurements: (a) the monomeric and dimeric oxidation products are quantitatively determined by gas chromatography; (b) the degradation product yields from an authentic and a predepolymerized lignin preparation (with CuO/OH^-) are determined and compared; and (c) the degradation product mixtures are separated according to their molecular weights by gel permeation chromatography. A quantitative assessment of the information concerning interunit linkages on these three types of analytical data is more difficult than in the case of other analysis data because it is complicated by an interdependency of all

Table XII
Variability of Prominent Structural Features of Average C_9 Units in Relation to Standard Deviations of Most Influential Analysis Results (Three Wood Species)

structural features	most influential analysis	Douglas fir				loblolly pine				red alder			
		SD of MA[c]	av C_9 composition	range	error, %	SD of MA[c]	av C_9 composition	range	error, %	SD of MA[c]	av C_9 composition	range	error, %	av error, %
C			9				9				9			
H														
total	EA (H)	0.3[b]	7.89	7.22–8.56	8.5	0.3[b]	8.52	7.89–9.15	7.4	0.3[b]	8.24	7.44–9.04	9.7	8.5
aromatic	NMR (2)	1.44	2.42	2.22–2.62	8.2	1.04	2.46	2.31–2.61	6.1	1.48	2.15	1.92–2.38	10.7	8.3
OH (NMR)	NMR (6–7)	3.21	1.43	1.07–1.39	13.4	1.39	1.11	1.05–1.17	5.1	2.97	1.17	1.00–1.34	14.9	11.1
side chain	NMR (5)	3.03	4.42	4.26–4.58	3.6	0.79	4.96	4.89–5.02	1.3	2.97	4.99	4.77–5.21	4.4	3.1
O														
total	EA (C)	0.3[b]	3.22	3.17–3.27	1.6	0.3[b]	2.93	2.88–2.98	1.6	0.3[b]	3.39	3.33–3.45	1.7	1.6
aromatic OH[a]	NMR (6)	0.44	0.28	0.27–0.29	4.7	0.78	0.35	0.30–0.40	12.9	1.66	0.39	0.32–0.46	17.5	11.7
aliphatic OH[a]	NMR (7)	3.40	0.95	0.89–1.01	6.7	1.48	0.75	0.73–0.77	2.4	3.93	0.71	0.63–0.79	10.7	6.6
unresolved	ash	0.05[b]	1.26	0.65–1.87	48.3	0.05[b]	1.00	0.39–1.61	61.5	0.05[b]	1.68	0.96–2.40	43.1	51.0
OCH_3	FGA (OCH_3)	0.3[b]	0.87	0.85–0.89	2.3	0.3[b]	0.89	0.87–0.91	2.4	0.3[b]	1.36	1.31–1.41	3.6	2.8

[a] Based on average figures of total OH by NMR and by chemical analysis. [b] Estimated variability. [c] MA stands for most influential analysis.

Table XIII
Variability of Prominent Interunit Linkages of Average C_9 Units in Relation to Variability of Primary Analysis Results (in Percent/Percent)

analytical data	linkages				
	α/β-0-4	β-5	5-5	4-0-5	phenolic OH
1. individual compound variability					
V	0.04	0.54	−0.03	0.0	−0.06
XI	<−0.01	−0.04	0.07	0.03	<−0.01
X	<−0.01	−0.03	0.05	0.02	<−0.01
2. UH/H ratio variability[a]					
loblolly pine	−0.62	0.06	0.04	0.0	+0.93
Douglas fir	−0.90	0.32	0.11	0.0	+0.80
red alder	−0.82	0.0	0.0	0.04	+0.81
av	−0.74	+0.11	+0.05	+0.01	+0.87
3. GPC ratio variability[b]					
loblolly pine			−0.80	−0.72	
Douglas fir			−1.57	−1.10[c]	
red alder		0.52	−1.13	−0.98	
av			−1.17	−0.93	

[a] Σ(1- and 2-mers in authentic (unhydrolyzed) product mixture)/Σ(1- and 2-mers in prehydrolyzed degradation product mixture). [b] Σ(1- to 3-mers)/Σ(4- to 6+-mers) (at constant UH/H ratio); identical GPC data for both the UH and the H samples. [c] Estimated.

three data types. However, an attempt at this evaluation is presented in Table XIII.

The first group of data evaluates the effect of variability in compounds V, XI, and X on linkage distribution and phenolic OH groups. It is apparent that variations in isohemipinic acid (V) concentration have a marked effect on β–5 linkages and that concentration variations of compounds XI and X affect the 5–5 and 4–0–5 linkages, respectively. However, within the precision of the degradation and quantitative determination technique, only insignificant differences on the order of ±5% can be detected with regard to the concentration of interunit linkages. Thus, it is found that the variability of individual compound concentrations in degradation product mixtures has only a slight effect on structure evaluations.

By contrast, the ratio of the amount of degradation products from the authentic vs. the preoxidized sample seems to be of greater significance to the overall evaluation of interunit linkages of lignin. From Table XIII it appears that the concentration of α/β–0–4 linkages is inversely related to variations in the UH/H ratio and that phenolic OH contents are proportionately related to that figure. Other interunit linkages seem to be relatively unaffected by this ratio.

Variability of GPC data may be expressed in terms of the ratio of the percentage of mono-, di-, and trimers to that of tetra-, penta-, and hexamers. A lignin with a high content of linkages between aromatic rings, of types 4–0–5 and 5–5, would be typified by a low GPC ratio, as opposed to a primarily aryl alkyl ether linked lignin, which would be represented by a high GPC ratio figure. Such differences are illustrated in Tables IX and X. Table XIII assesses the effect of variability in this ratio on overall linkage distributions of lignins. It is obvious that a significant inverse relationship exists, meaning that when monomeric and dimeric degradation products become more abundant in the total product mixture, the reflected concentration of 5–5 and 4–0–5 linkages declines noticeably.

It can be concluded that the distribution of interunit linkages in lignin may be determined on the basis of permanganate oxidation results and that this determination is most sensitive to variations in the ratio of mono- and dimeric products from the authentic and predepolymerized lignin preparations and to the ratio of high vs. low molecular weight degradation products in the product mixture. Variations of this type have a primary effect on the α/β–0–4 and the 5–5 and 4–0–5 linkages, respectively.

Conclusions

1. Analytical results from multiple experimental procedures can be interpreted in terms of the composition of a unifying average phenylpropane structure representing the monomeric lignin building unit.

2. Elemental and functional group analyses (including ^1H NMR spectroscopy) render information on the overall makeup of the C_9 skeleton, and analytical degradation experiments with alkaline permanganate solutions and H_2O_2 help reveal the distribution of major interunit linkages involving the aromatic ring of the phenolic oxygen.

3. Correction and adjustment of primary analytical data for identified and quantitatively determined impurities seem an acceptable practice and yield meaningful structural information that does not contradict any particular analysis result.

4. Repeatabilities of several experimental analysis techniques were studied, and it was concluded that all structural features of the refined empirical formula could be determined with better than ±10% average error with the exception of the total OH and the phenolic OH contents by NMR and the total oxygen content which were more variable.

5. The analysis of interunit linkages in lignin was more dependent on the ratio of degradation products from the authentic vs. the predepolymerized sample (UH/H ratio) and the ratio of low vs. high oligomeric degradation products (GPC ratio) than the yield of individual degradation products.

6. The systems approach to the interpretation of lignin analysis data was found to strengthen the value of individual analytical procedures by permitting the correlation and comparison of structural features with various primary experimental observations.

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Photoresponsive Polymers. 2.[1] Reversible Solution Viscosity Change of Polyamides Having Azobenzene Residues in the Main Chain

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ABSTRACT: Polyamides having a photoisomerizable unsaturated linkage in the backbone of the polymer chain were synthesized in an attempt to construct photoresponsive polymer systems. Solution viscosity of polyamides composed of azobenzene and phenylenediamide residues under ultraviolet irradiation ($410 > \lambda > 350$ nm) was 60% lower than the viscosity in the dark in *N,N*-dimethylacetamide. The viscosity that was reduced by the irradiation returned to the initial value in 30 h at 20 °C after removing the light. The slow recovery of the viscosity in the dark was accelerated by visible light irradiation ($\lambda > 470$ nm). On alternate irradiation with ultraviolet and visible light, the solution viscosity was reversibly controlled by as much as 60%. Spectroscopic study and the effect of rigidity of chain segment on the photoviscosity behavior indicate that the photodecrease arises from the trans–cis photoisomerization of the azobenzene residues in the backbone of the semiflexible chain. Photocontrols of conductivity and pH value were also achieved by using photoresponsive polyamides having terephthalic acid groups.

Introduction

The photoinduced cis–trans isomerization of organic molecules about an unsaturated linkage is a well-known photochromic phenomenon that has been extensively studied. The isomerization process can be symbolized by

$$\text{trans} \underset{h\nu',\,\Delta}{\overset{h\nu}{\rightleftharpoons}} \text{cis}$$

A photosensitive chromophore in the trans form is converted under irradiation into the cis form, which returns to the initial state either thermally or photochemically. The isomerization is always accompanied by significant changes of physical properties such as dipole moment, melting and boiling points, and refractive index. In other words, we can photocontrol the physical properties of materials by using photoisomerizable molecules.

When we incorporate the photoisomerizable chromophores into the backbone of polymer chain, photoinduced isomerization of the chromophores is expected to induce a conformational change of the polymer chain. The photoinduced conformational change reversibly converts physical and chemical properties of the polymers and the polymer solutions.

In a previous paper[1] we reported the reversible photodecrease of solution viscosity of poly(methyl methacrylate) having spirobenzopyran side groups. The viscosity change is caused by intramolecular solvation by the ester side groups of the photogenerated polar merocyanines. This paper describes another type of photoresponsive polymers having a photoisomerizable unsaturated linkage in the backbone of the polymer chain. We adopted azobenzene as a photosensitive chromophore and synthesized polyamides having the azobenzene residues in the backbone of the polymer chain.[2,3] Azobenzene is a well-known photochromic molecule, which undergoes isomerization from the trans to the cis form under ultraviolet irradiation; the cis form can return thermally or photochemically to the trans form as follows:

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