

HIGH-PRESSURE HYDROGENATION OF MAPLE WOCD

by

James Morley Pepper

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CLAIMS TO ORIGINAL RESEARCH

- 1. An investigation of various hydrogenation catalysts has been made with relation to their effectiveness in bringing about degradation of a maple lignin, isolated from maple wood in a neutral aqueous ethanol medium, by a combined high-pressure hydrogenolysis-hydrogenation treatment. Raney nickel and copper chromium oxide were found the most suitable.
- 2. The important factors involved in the extraction of lignin from maple wood by high pressure hydrogenation have been studied. These involved consideration of (a) nature of catalyst and solvent; (b) time; (c) temperature and (d) pH of the reaction medium with the object of isolating, in maximum yield, the native lignin in the form of alkylphenol entities, molecular or dimolecular in type.
- 3. The complete solubilization of maple wood was effected by high pressure hydrogenation at 165° in an acidic aqueous ethanol medium using Raney nickel as catalyst. It was shown that the solubilized lignin still retained its essentially aromatic character and was soluble to

a high degree in petroleumether.

- 4. Hydrogenation of maple wood meal in alkaline aqueous dioxane, using Raney nickel as catalyst, removed the entire lignin. From this hydrogenated lignin mix-ture three new lignin aromatic degradation products were isolated: 4-hydroxy-3-methoxyphenyl ethane, 4-hydroxy-3,5-dimethoxyphenyl ethane and 2-(4-hydroxy-3,5-dimethoxyphenyl) ethanol in yields of 2.2, 15.4 and 6.2% respectively based on the Klason lignin content.
- 5. The isolation of these products supplies additional confirmatory evidence of the essentially aromatic (alkyl phenolic) nature of lignin.

TABLE OF CONTENTS

I.	HISTO	ICAL INTRODUCTION
	A.	General Review of Lignin Chemistry
		1. First Phase of Lignin Research
		2. Second Phase of Lignin Research
		3. Third Phase of Lignin Research
		(a) Alkaline Oxidation
		(b) High Pressure Hydrogenation 5
		(c) Ultraviolet Absorption
		4. Fourth Phase of Lignin Research
	B.	Studies on Protolignin Formation
		1. Biochemical Aspects 9
		(a) Plant Synthesis of Simple Phenols 9
		(b) Flant Synthesis of Propylphenol Derivatives 11
		2. Protolignin Formation from Propylphenol Units
		(a) General Theories of Polymerization 15
		(b) Polymerization of Guaiacyl Type Compounds 16
		(c) Polymerization of Syringyl Type Compounds
	C.	Lignin Progenitors as Possible Respiratory Catalysts
II.	CATAL ORGAN	TIC HYDROGENATION AND HYDROGENOLYSIS IN C CHEMISTRY
	A.	General Discussion of Hydrogenation and Hy- drogenolysis

	B.	Catalysts for Hydrogenation		
		1. Factors Affecting Hydrogenation Catalysts 2'		
		(a) Surface 2'		
		(b) Promoter Catalysts 27		
		2. Types of Hydrogenation Catalysts 28		
		(a) Very Reactive		
		(b) Less Reactive 28		
	C.	Classification of Reactions with Hydrogen 28		
		1. Hydrogenation (Reduction) 28		
		(a) Ethylenic Linkage 28		
		(b) Carbonyl Linkage 29		
		(c) Benzenoid and Furanoid Linkages 30		
		2. Hydrogenolysis (Cleavage)		
		3. Hydrogenation Accompanied by Hydrogenolysis 3]		
		4. Selective Hydrogenation		
III.	HYDRO	GENATION OF LIGNIN		
IV.	HYDRO	GENATION OF WOOD AND RELATED MATERIALS 43		
v.	REVIE	V OF EXPERIMENTAL RESULTS		
	A.	Introduction		
	B.	Preliminary Experiments on Hydrogenation of Maple Wood Meal in Aqueous Ethanol (1:1) fol- lowed by Rehydrogenation		
		1. Preparation of "Maple Lignin (A)" 50		
		2. Object Sought in the Investigation of "Maple Lignin (A)"		
		3. Choice of Catalysts 53		
		4. Conclusions		
		 (a) Effect of Catalyst Type on Nature and Yields of Hydrogenation Products from Maple Lignin (A) "		

		(b) Effect of Solvent Type on Nature and Yields of Hydrogenation Products from "Maple Lignin (A)"	56
		(c) Variation in Yield of Propylcyclohex- ane Derivatives	56
C.	Inv Yie gena	estigation of Factorsinfluencing Type and ld of Products from a Single-Stage Hydro- ation of Maple Wood Meal	57
	1.	Investigation of Variables Involved in Hy- drogenation of Maple Wood Meal	57
		(a), (b), (c) Effect of Temperature, Time and Catalyst	57
		(d) Nature of the Reaction Medium	57
		(e) pH of the Reaction Medium	59
	2.	Action of Aqueous Ethanol (1:1) on Maple Wood in Absence of a Catalyst	60
	3.	Effect of Structure of Acid Addendum	60
	4.	Selection of Most Suitable Hydrogenating Conditions for a Single-Stage Hydrogena- tion	60
D.	Pre: in 1	liminary Hydrogenations of Maple Wood Meal Alkaline Aqueous Ethanol (1:1)	62
E.	Cho	ice of Solvent for Hydrogenation	64
F.	Pren gena ous lys	paration of Experimental Material by Hydro- ation of Maple Wood Meal in Alkaline Aque- Dioxane (1:1) using Raney-Nickel as Cata- t	65
	1.	Distillability of Products	65
	2.	Group Separation of the Crude "Maple Lig- nin (C)" by a Combined Process of Distil- lation and Chemical Separation	66
	3.	Identification of Products by Fractiona- tion and Chemical Identification ••••••	67
G∙	Rest tion (1:1	ume of Yields Obtained in the Hydrogena- n of Maple Wood Meal in Aqueous Dioxane 1) using Raney-Nickel as Catalyst	ר7
	-		

		1.	Identification of Distillable Products 72	2
		2.	Identity of Constant-Boiling Fractions 73	3
	H.	Rela Str	ation of the Experimental Results to the ucture of Native Lignin	5
		1.	Non-identity of Spruce and Maple Native Lignins	y .
		2.	Structure of the Isolated Products 77	7
		3.	Relation of the Isolated Hydrogenation Products to the Higher Lignin Polymers 79)
VI.	EXI	PERIN	MENTAL RESULTS)
	A.	Pre] Map] lowe	liminary Experiments on Hydrogenation of le Wood Meal in Aqueous Ethanol (1:1) fol- ed by Re-hydrogenation)
		1.	Hydrogenation Apparatus and Technique 80	1
			(a) Apparatus 80	ſ
			(b) Technique	1
		2.	Preparation of Hydrogenated "Maple Lignin (A)"	1
			(a) Solvent Extraction of Maple Wood Meal 82	•
			(b) Hydrogenation of Solvent-extracted Maple Wood Meal	, t
		3.	Investigation of Hydrogenation Catalysts 85)
			(a) Preparation of Catalysts 85	`
			(b) Activation of the Catalysts by Reduction	۲
			(c) Testing of Catalytic Activity 87	۶
			(d) Re-hydrogenation of Hydrogenated "Maple Lignin (A)" (Section A2) 88	3
			(e) Claisen Distillation of Re-hydrogena- Products of Hydrogenated "Maple Lig- nin (A)"	3
		4.	Fractional Distillation Apparatus and Tech- nique	l

	((a)	High-vacuum Apparatus	91
	((b)	Fractionating Columns and Receivers	91
	((c)	Electrical Heating Apparatus	94
5	• I	Re- hy	drogenation of "Maple Lignin (A)"	94
		(a)	Re-hydrogenation over CuCrO at 250 ⁰ for 8 hours	97
	ł	(b)	Re-hydrogenation over CuCrO at 2250 for 2 1/2 hours	98
		(c)	Re-hydrogenation over RaNi at 225 ⁰ for 2 1/4 hours	9 8
B. I Y t	nve iel ion	stiga d of of N	ation of Factors Influencing Type and Products from Single-stage Hydrogena- Taple Wood Meal	100
1	•	Effec Wo o d	et of pH on the Hydrogenation of Maple Meal	100
2	•	Effec Maple	et of Time on the Hydrogenation of	105
3	•	Misce tion	ellaneous Experiments on the Hydrogena- of Maple Wood Meal	105
C. S i	mal n A	1-sca queou	ale Hydrogenation of "Maple Wood Meal" as Ethanol	110
l	• •	P repa (B)"	aration of Hydrogenated "Maple Lignin	110
2	• 1]	Solve ment (Flow	ent Fractionation and Subsequent Treat- of the Hydrogenated "Maple Lignin (B)" Sheet III)	111
	ł	(a)	Solvent Fractionation of "Maple Lig- nin (B)"	111
		(Ъ)	Distillation of Combined "Phenolic Fractions" (0)	112
	ļ	(c)	Distillation of "Phenolic Fraction" (M) and "Acidic Fraction" (R)	115
	-	(a)	Re-hydrogenation of "Non-distillable" Fractions from Experiments 80 and 71 (Flow Sheet III)	116

D.	Choi	ice of	f Hydrogenation Solvent	118
E.	Larg in A	ge-sca Aqueor	ale Hydrogenation of "Maple Wood Meal" us Dioxane	120
	1.	Prepa (B)"	aration of Hydrogenated "Maple Lignin	120
		(a)	Seriès A (Experiments 84 - 90)	120
		(b)	Series B (Experiments 93 - 95, 97 - 99)	120
	2.	Inves nin	stigation of Hydrogenated "Maple Lig- (C)" (Series A.)	123
		(a)	Claisen Distillation	123
		(b)	Solvent Fractionation of Distillate	123
		(c)	Fractional Distillation of Water- Insoluble Portion (c) of Distillate Al	124
		(d)	Identification of 4-hydroxy-3- methoxyphenyl ethane	128
		(e)	Identification of 4-hydroxy-3,5-di- methoxyphenyl ethane	128
	3.	Inves (Ser:	stigation of "Maple Lignin (C)" ies B.)	129
		(a)	Claisen Distillation	129
		(b)	Solvent Fractionation of Combined Dis- tillates B2, B3, and B5 (Section 3a)	129
		(c)	Fractional Distillation of the Water- soluble portion (x) of Distillates B2, B3 and B5 (Section 3b)	130
		(d)	Fractional Distillation of the Water- insoluble Portion (\tilde{y}) of Distillates B2, B3 and B5 (Section 3b)	130

		(e)	Ident dimet	ification of 4-hydroxy-3,5- hoxyphenyl ethane	134
		(f)	Isola hydro	tion and Identification of 2-4- xy-3,5-dimethoxyphenyl) ethanol	135
			(i)	Isolation	135
			(ii)	Identification	135
		(g)	Re-hy Clais of "M	drogenation of Resins from en and Fractional Distillations aple Lignin (C)" (Series B.)	137
			(i)	Re-hydrogenation Procedure	137
			(ii)	Treatment of Re-hydrogenation Products	138
			(iii)	Analysis of Products from the Fractionation Treatment (Sec- tion ii)	14 1
		(h)	Re-hy Boili tilla (Seri	drogenation of Non-constant ng Portions from Fractional Dis- ations of "Maple Lignin (C)" es A and B.)	142
			(i)	Re-hydrogenation Procedure	142
			(ii)	Identification of 4-ethylcyclo- hexanol	145
			(iii)	Identification of 4-n-propyl- cyclohexanol	145
			(iv)	Identification of 3-cyclohexyl- l-propanol	145
F.	Synt	theses	s of R	eference Compounds	146
	1.	Synth ethar	nesis ne	of 4-hydroxy-3-methoxyphenyl	146
	2.	Synth ethar	nesis ne	of 4-hydroxy-3,5-dimethoxyphenyl	147
		(a)	Prepa pyrog	aration of 1-acety1-2,6-dimethy1	147

	(b)	Preparation of 4-hydroxy-3,5- dimethoxy acetophenone	148
	(c)	Reduction of 4-hydroxy-3,5-dimethoxy- acetophenone	148
3.	Syntl etha	hesis of 2-(3,4,5-trimethoxyphenyl nol	149
	(a)	Preparation of trimethyl gallic acid	150
	(b)	Preparation of 3, 4, 5-trimethoxy- benzoyl Chloride	150
	(c)	Preparation of 3, 4, 5-trimethoxy- phenyl diazomethyl ketone	150
	(d)	Hydrolysis of 3, 4, 5-trimethoxy- phenyl diazomethyl ketone	151
G. Mis	(e) scella	Reduction of 3, 4, 5-trimethoxyphenyl hydroxymethyl ketone neous Experiment	151 1 53
1.	Hydr Aque	ogenation of Maple Wood Meal in ous Dioxane (Run 91)	153
SUMMARY	• • • • •		154
BIBLIOGRA	PHY		156

INDEX OF FIGURES

I.	Effect of pH on the Hydrogenation of Maple Wood	59 a
II.	Effect of Time on the Hydrogenation of Maple Wood	59a
III.	Fractionating Column, Condenser and Receiver	92
IV.	Semi-micro Fractionating Column	93 .
V.	Spiral Screen Column Packing	95
VI.	Heating Circuits	96
VII.	Hydrogen Absorption Curve of Hydrogenation Run 88	121
VIII.	Fractional Distillation of Bicarbonate-insoluble Hydrogenation Products from Series A.	127
IX.	Fractional Distillation of Water-insoluble Hydro- genation Products from Series B, Distillate B2, B3 and B5	133
X.	Fractional Distillation of Re-hydrogenated Resins from Series B.	140
XI.	Fractional Distillation of the Re-hydrogenated non-constant-boiling Fractions from the Fractiona- tion of Al, B2, B3 and B5	144

INDEX OF TABLES

I.	Yields of Water-Soluble Ethanolysis Products	8
II.	Effect of Pressure on Extent of Hydrogenation	26
III.	Examples of Hydrogenation of Ethylenic Bond	29
IV.	Examples of Hydrogenation of Carbonyl Bond	29
v.	Examples of Hydrogenation of Benzenoid Nucleus	30
VI.	The Hydrogenation of Various Lignins over Copper- Chromium Oxice (26)	37
VII.	Summary of Yields from Small-scale Hydrogenation Runs 80 and 81	63
VIII.	Yields of Lignin Products from Hydrogenation of Maple Wood Meal after Distillation through a 21 or 28-plate column	72
IX.	Summary of the Distillable Lignin Products from the Hydrogenation of Maple Wood (500 g.) exist- ing as Flats	74
X.	Summary of Yields of Identified Lignin Products from the Hydrogenation of Maple Wood (500 g.) \dots	75
XI.	Preparation of Hydrogenated "Maple Lignin (A)" (Section A2.)	84
XII.	Re-hydrogenation of Hydrogenated "Haple Lignin (A)" (Section A2.)	8 9
XIII.	Claisen Distillation of Hydrogenated "Haple Lig- nin (A)" Hydrogenation Products	90
XIV.	Effect of Varying the pH on the Hydrogenation of Maple Wood Meal	108
XV.	Effect of Time on the Hydrogenation of Maple Wood Meal	102
XVI.	Miscellaneous Experiments on the Hydrogenation of Maple Wood Meal	106
XVII.	Analysis of Distillates from combined "Phenolic Fractions" (0)(Flow Sheet III)	115
XVIII.	Analyses of Fractions from the Re-hydrogenation of Resins (Series B)	141

INDEX OF FLOW SHEETS

I.	Scheme for Separation and Identification of Products from Hydrogenation of Maple Wood	
	Series A and B.)	68
II.	Treatment of Products from Single-stage Hydro- genation of Maple Wood	101
III.	Summary of Small-scale Hydrogenation of Maple Wood Meal in Aqueous Ethanol (Experiments 80 and 81)	113
IV.	Solvent Separation of Hydrogenation Products (Run 82)	119
v.	Treatment of Products from Hydrogenation Run 84 (Series A.)	12 2

I. HISTORICAL INTRODUCTION

A. General Review of Lignin Chemistry

(1) First Phase of Lignin Research

Klason's original "coniferyl-oxyconiferyl alcohol hypotheses" developed in 1897 (1) postulated that lignin was related to coniferyl alcohol and was therefore an aromatic substance. This theory, which may be regarded as constituting the <u>first phase</u> of lignin research, was based (i) on the universal occurrence of coniferyl alcohol in young plant tissue (2), (ii) on the data derived from the analysis of the spruce lignin sulphonic acids and from solvent-extracted spruce wood, (iii) on the data obtained from lignin alkali-fusion reaction mixtures, which contained such products as catechol, guaiacol and protocatechuic acid.

(2) Second Phase of Lignin Research

During this period (1926 - 1932) new methods were developed for the isolation of lignin from wood, with subsequent identification of the methoxyl, hydroxyl and carbonyl groups and of the aromatic nucleus in the extracted lignins. The methods employed in this connection involved the use of concentrated sulphuric acid (3) hydrochloric acid (4), mixtures of hydrochloric and phosphoric acids (5), as well as the alcoholysis procedure (6) using alcohols, glycols, glycerol and glycerol chlorhydrin. Freudenberg's earlier theory on the structure of lignin (7) was based on the analytical results obtained from a study of spruce hydrochloric acid lignin. These results indicated (a) aromatic character and absence of free phenol groups; (b) attachment of the methoxyl groups to aromatic nuclei; and (c) presence of aliphatic hydroxyl groups in the side chains. Freudenberg modified Klason's original view of lignin as a propylphenol derivative by assuming that the building units were joined through ether linkages to give a linear-type condensation polymer (7, p. 134) (I).



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The presence of the dioxymethylene group was assumed to be indicated by the isolation of a small amount of formaldehyde (up to 1.2 per cent) (8, 9, 10). Freudenberg suggested that possible side chains included R-CHOH-CHOH- CH_2OH , R-CH₂-CHOH-CH₂OH, R-CHOH-CH₂-CHO and R-CHOH-CHOH₃ (7 page 135) and defined this series of compounds to be "biochemically identical". This expression has, scientifically, no biochemical significance and can only be assumed to imply they are in equilibrium with each other, at least in vivo.

More recent work by Freudenberg on the alkali degradation of spruce lignin, followed by methylation and oxidation (11, 12, 13) has led him to substitute the ether-type linear linkage by a carbon-to-carbon type involving oxygenring formation between side chains and aromatic nuclei (14, p. 95) (II).



II

III



The similarity of this structure (II) to the dimer resin-type polymer (e.g. dehydrodiisoeugenol, (III)) suggested by Erdtman (15) is very marked.

Several objections to this new Freudenberg concept have been noted. The assumed presence of the dioxymethylene group on centrally disposed (14, pages 95, 109) aromatic nu-

clei has been criticized from the point of view of the nonisolation of piperonyl units. Also in such a dehydrodiisoeugenol type of polymer the inclusion of such centrallylocated nuclei implies a new and unusual form of condensation. Important too is that such a polymer (II) could not be formed from syringyl derivatives in which the position ortho to the phenol group is blocked by a methoxyl group.

(3) Third Phase of Lignin Research

Several more recent developments which have contributed greatly to the understanding of the structure and origin of protolignin may be said to constitute the <u>third</u> <u>phase of lignin research</u>. These include (a) alkaline oxidation of wood, lignin and lignin sulphonic acids; (b) high pressure hydrogenation of wood and lignin; and (c) ultra violet absorption spectra of various lignins and related compounds.

(a) <u>Alkaline Oxidation</u>. - The action of alkali on spruce lignin sulphonic acid yielded 6 - 7 per cent of vanillin (16) and smaller amounts of 4-hydroxy-3-methoxyacetophenone (17) and guaiacol (18). If oak lignin sulphonic acid is used, syringal-dehyde (19), 4-hydroxy-3, 5-dimethoxyacetophenone (20) and 1,3-dimethoxypyrogallol (19) are obtained.

More recently Freudenberg and co-workers (21) have developed an alkali-nitro benzene oxidation technique by which yields of 20-25% of vanillin from spruce wood (softwood) and spruce lignin sulphonic acid are obtained. An extension of this method to maple and aspen woods (hardwoods) yielded a mixture of vanillin and syringaldehyde amounting in certain

cases to 46 - 48%, calculated on the weight of the lignin. It is of interest in this connection to note that a ratio of 1 of vanillin to 3 of syringaldehyde was found to be nearly true for all species of hard woods investigated (62). Since high yields of aldehydes are obtained from the nitro-benzene oxidation of wood, and no aldehydes are obtained from similar oxidations of holocellulose, the validity of Klason's assumption that lignin has a fundamentally aromatic structure is established.

(b) <u>High Pressure Hydrogenation of Wood and</u> <u>Lignin.</u> - A more detailed account of the hydrogenation of lignin and wood is given in later sections. Using the high pressure hydrogenation technique, complete liquefaction of maple wood (22) has been accomplished. Identified products obtained from the hydrogenated protolignin include 4-n-propylcyclohexanol (IV) and 3-(4-hydroxycyclohexyl)-l-propanol (V) in yields of 19.5 and 5.8 per cent respectively (based on the Klason lignin content of the wood).





Using greatly improved distillation techniques (23) workers in these laboratories have isolated a new lignin product, 3-cyclohexyl-l-propanol (VI). Using the carbon content of these isolated units and of the "methoxyl-free protolignin" in the wood as a basis for calculation, the combined yield of propylcyclohexane derivatives represents a recovery of 39.8% (23). The catalytic hydrogenation of lignin has shown, in addition to contributing valuable evidence for the presence of the propylphenol unit in lignin, that a high percentage of the propylcyclohexane derivatives obtained from wood (22) and certain lignins (24, 25, 26) contain oxygen atoms attached to the terminal carbon atom in the propyl chain. This result provides the only experimental proof of the presence of oxygen in that position in protolignin.

Furthermore, application of the hydrogenation technique to lignin chemistry has resulted in a classification of lignins according to their relative complexities (based on the yield and nature of hydrogenation resins). Adkins and coworkers (26, 27) have shown that sulphuric, soda and alkali lignins are more complex than either protolignin (22) or alcoholysis lignins (24, 25).

c. <u>Ultraviolet Absorption Spectra of Lignin</u>. -The ultraviolet absorption curves of various lignins (amorphous spruce and maple ethanol lignins) have been investigated and compared with similar curves obtained from model compounds of the coniferyl alcohol type including the propylphenol units isolated from the ethanolysis oils (6). A satisfactory inter-

pretation of the spectra of the amorphous ethanol lignins (28) is now possible if these lignins are assumed to be formed from lignin precursors of the series exemplified by hydroxypropiovanillones and hydroxypropiosyringones. Such studies have confirmed the essentially aromatic character of lignin and a quantitative estimation of the lignin components indicates a high percentage of propylphenol units on the lignin molecule (50 to 100% (28).

(4) Fourth Phase of Lignin Research

The <u>fourth phase</u> of lignin research may be regarded as that associated with the more recent contributions of Hibbert and co-workers on the action of ethanolic hydrogen chloride on various plant materials. This method provides a much milder extraction process for the removal of lignin from the wood than heretofore used.

While experimenting with various alcohols to determine their suitability for lignin extraction, (during which it was shown that ethanol was the most suitable) it was observed that the sum of the weights of the amorphous waterinsoluble extracted lignin and of the Klason lignin remaining in the wood residue was almost always less than the weight of the Klason lignin in the untreated wood. Experiments by Cramer, Hunter and Hibbert (29) showed that in the case of the ethanolysis of spruce and maple woods this weight discrepancy was due to the water solubility of a large proportion (12 per cent for spruce; 30 per cent for maple) of the Klason lignin. Extensive investigations of the <u>water-soluble</u>

products by Hibbert and co-workers have led to the isolation. of several new compounds, summarized in Table I.

TABLE I

Yields of Water-Soluble Ethanolysis Products (Values in % Klason Lignin in Wood.)

		Compound	Spruce	Maple
R	(or	R')-CO-CHOH-CH ₃ (OEt)	R 2.0 R'	4.0 4.0
R	(or	R')-CHOH-CO-CH ₃ OEt	R 0.6 R' ••	0.6 * 1.8 *
R	(or	R')-CO-CO-CH ₃	R 0.2 R' ••	0.6 1.9
R	(or	R ⁺)-CH ₂ -CO-CH ₃	R 0.02 R'	0.06 0.23
R	(or	R*)-CHO	R 0.11 R' ••	0.11 0.64
R	(or	R')-COOH	R trace R'	••
		TOTALS	2.93	13.94

- * estimated yields of compounds at present in the course of isolation and synthesis.
 - R = 4-hydroxy-3-methoxyphenyl
 - R' = 4-hydroxy-3, 5-dimethoxyphenyl.

B. Studies on Protolignin Formation.

(1) <u>Biochemical Aspects</u>

(a) <u>Synthesis of Simple Phenols</u>. - Early theories which have been advanced concerning the synthesis of phenolic compounds in plants were based on assumed transformation of hexoses (30, 31). More recent views consider these phenolic substances as being formed from intermediate photosynthetic and plant respiratory products. These views include (i) a free radical theory (32) and (ii) a methyl glyoxal theory of phenol formation (33).

(i) <u>Free Radical Theory.</u> - According to this theory an equilibrium exists, in the active stages of plant growth, between certain chemical types (formic acid (VII), glycollic aldehyde (VIII) and acetaldehyde (IX)) and the corresponding enolradicals:

HCOOH (VII) CH₂OH.CHO (VIII) (VIII)

CH3.CHO

(\underline{IX})

Union of the free radicals may give rise to hydroaromatic compounds which, by loss of water could yield phenols, as for example in the synthesis of phloroglucinol from glycollic aldehyde:



(ii) Methyl Glyoxal Theory of Phenol Formation. - Methyl glyoxal known to be an intermediate in animal cell respiratory processes (34, p. 244), presumably occupies a somewhat analogous position in plant carbohydrate metabolism (35, p. 264). It has, in fact, actually been isolated from higher plants (36). Hibbert has suggested the following possibility for the plant synthesis of phenols and propylphenol derivatives.



Two molecules of methyl glyoxal may condense to yield a cyclic dihydroxydiketone (XIII) capable of undergoing the indicated reactions to give quinone (XIV) and 1,2dihydroxy-4-ketocyclohexadiene (XV). This latter compound (XV) on reduction could give rise to a hydroxy-enediol (IVI), which, upon the loss of a mole of water, could yield catechol (XVII). Pyrogallol, the precursor of the syringyl nucleus, could be formed by enzymatic oxidation of catechol just as the latter is formed from phenol (37).

(b) <u>Syntheses of Propylphenol Derivatives</u>. -The above mentioned series of reactions after methoxylation, may be continued further to yield propylphenol derivatives as follows:





The only questionable reaction of this series is concerned with the intramolecular change involving an allyl shift in (XIX) to give the primary dismutation isomer (XXI) (38). Apparently there are no analogous reactions described in the literature, although, if it is assumed that (XIX) is in equilibrium with its aldehyde form (R-CH₂-CO-CH₂OH \longrightarrow R-CH₂-CHOH-CHO), then the reaction undergone by its analog, benzyl glycollic aldehyde, (XXVI), in the presence of ethanol and sulphuric acid is highly significant (39) in view of its conversion, by this means, into a mixture of phenyl acetyl carbinol (XXVII) and benzoyl acetone, (XXVIII) $2 C_{6H_5}$ -CH₂-CHOH-CHO \longrightarrow C_{6H_5} -CHOH-CO-CH₃ + C_{6H_5} -CO-CO-CH₃

(XXVI) (XXVII) (XXVIII)

Several previously reported reactions support the postulated equilibrium between the primary dismutation isomer (XXI) through the ene-diol intermediate (XXIII) and the benzoin derivative (XXIV). The best known examples of such dismutation reactions are to be found in carbohydrate chemistry, as for example, the Lobry de Bruyn equilibrium transformation of glucose and of glyceric aldehyde and dihydroxyacetone (40). Studies on the equilibrium system

R-CHOH-CO-CH₃ \rightleftharpoons R-C(OH) = C(OH)-CH₃ \rightleftharpoons R-CO-CHOH-CH₃ where R is a para substituted benzene radical, have shown (41, p. 42) that R-CO-CHOH-CH₃ is more stable than R-CHOH-CO-CH₃. Support for this is seen in the nature of the isolated products from the ethanolysis of wood, these being the ethyl ethers of (XXIX) and (XXX) the stabilized form R(R')-CO-CHOH-CH₃.

R-CO-CH-CH₃ I OEt (XXIX) R'-CO-CH-CH₃ I OEt (XXX)

R = 4-hydroxy-3-methoxyphenyl

R' = 4-hyd roxy-3, 5-dimethoxyphenyl.

(XXIX) and (XXX) are possibly only stabilized end products of the assumed lignin progenitors, $R-CH_2-CO-CH_2OH$ and $R'-CH_2-CO$ CH_2OH which are the first members of the proposed new aromatic system of plant respiratory catalysts (6) (see p. 23).

It is of interest too to consider how other ethanolysis products, namely vanilloyl- (XXV) and syringoylmethyl ketones (XXXI), may also represent stabilized end products of more reactive lignin progenitors.

$$R^{-C} - C^{-C} - CH_{3}$$

$$R^{*} - C^{-C} - CH_{3}$$

$$(XXV)$$

$$(XXXI)$$

A consideration of a series of products, coniferyl alcohol (XXXII) (R-CH = CH-CH₂OH); oxyconiferyl alcohol (XXXIII) $(R-CH_2-CO-CH_2OH \rightleftharpoons R-CH = C(OH) - CH_2OH)$ and dioxyconiferyl alcohol (XXXIV) (R-CO-CHOH-CH_2OH ਵ R-C(OH)=C(OH)-CH_2OH) indicates the possibility of a similar dismutation equilibrium involving the dioxy-ketone (XXXIV) as one constituent: $R-CO-CHOH-CH_2OH \rightleftharpoons R-C(OH) = C(OH)-CH_2OH \rightleftharpoons R-CHOH-CC-CH_2OH$.

Examination of enediol (XXXIV) shows that it differs only from that present in the system R-CO-CHOH-CH₃ \longrightarrow R-C(OH) = C(OH)-CH₃ \longrightarrow R-CHOH-CO-CH₃ in that the methyl group is replaced by a terminal -CH₂OH, and by analogy this dioxyconiferyl alcohol type of compound might be expected to yield vanilloyl methyl ketone in the presence of dilute acids:

$$R-C(OH) = C(OH) - CH_2OH \implies R-C(OH)_2-C(OH) = CH_2 \implies R-CO-CO-CH_3$$

The plant origin of these dioxyconiferyl alcohol derivatives is, as yet, unknown. However their plant synthesis may be visualized as follows:



in which a primary condensation of two moles of methyl glyoxal is followed by the loss of a mole of water and a further condensation with a molecule of hydroxymethyl glyoxal.

2. <u>Protolignin Formation from</u> Propylphenol Units

(a) General Theories of Polymerization.

The synthesis of the simple phenols and the propylphenol derivatives has been discussed in preceding pages and attention can now be centered on the mechanism of polymerization and the structure of the complex polymers. Carothers (42) has classified polymeric materials, according to the mechanism of their formation, as "addition" or "condensation" polymers, the former giving rise to the true high molecular weight, long chain polymers, and the latter to the lower molecular weight materials.

The addition polymers are characterized by their formation from unsaturated building units, molecules containing double or triple bonds or strained ring structures, through a mechanism involving the preliminary formation of activated nuclei. Polymerization changes in a few types comparable to the lignin propyl phenol units have been reported. Thus \prec - and \mathscr{G} -methyl styrenes have been shown to be much more difficult to polymerize than the parent compound (43, 44, 45 and 46), and to give relatively low molecular weight polymers. If treated with stannic chloride at 25 - 45° (47), styrene forms a low molecular weight (1200 - 2700) polymer, and eugenol, isoeugenol, safrole and isosafrole. behave similarly (48). The extracted amorphous lignins show a degree of polymerization of about twenty propylphenol units. which agrees well with the low molecular weights of polymers from these "normal type" products.

The propylphenol derivatives which have been isolated and identified in the ethanolysis products of wood (6) do not fulfill the requirements of building units for "addition polymers" since they contain neither ethylenic, acetylenic nor strained ring structures. The enolic forms of $-CH_2-CO-$ where the -CO- is present either as $\prec -$ or *G*-carbonyl in the -C-C-C side chain would, however, contain the styrene configuration, $C_{6}H_5-C=C-$, and might undergo "addition" polymerization.

(b) Polymerization of Guaiacyl Type Compounds.

Several workers including more especially Freudenberg, Erdtman and Hibbert have advanced theories of lignin formation involving the propylphenol type of building units which have been described in a previous section. Although lacking experimental proof of the presence of propyl phenol units in lignin, Freudenberg has postulated several theoretical lignin polymer structures. The earliest of such structures (I)



was later discarded for two main reasons: (1) ether cleavage agents did not produce high yields of the expected propylphenol type cleavage products; (2) furthermore, polymerization to secondary, more complex entities involving this di-

CH₃O Η CH₃O H Ŭ C − CH₃ **Г**(ОН) CH3 HO HO ŌН (XXI) CH30. II C - CH₃ CHOH CH38 CH₃O C(OH)-CH3 CH CH3 + HO HO n 0 оснон – С CH3 снон --CH₃ CH₃O-CH30 (XXXV) CH 30 CH₃0 CH_3O CHOH CH-CHOH HO HCOH нсон HCOH CH2OH CHZ ĊH20H

meric polymer is impossible. Later, Freudenberg considered a carbon-carbon type of polymer linkage as shown below (XXXV and XXXVI)

17.

He also suggested the building units may contain the groupings

(XXXVI)

-CHOH-CHOH-CH₂OH, -CH₂-CHOH-CHO, -CHOH-CH₂-CHO and CHOH-CO-CH₃ (7) in the side chain. This type of condensation would lead to a polymer type as shown (XXXVII)



yielding a benzofurane type of dimer upon elimination of water, while further condensation with a third mole of (XXI) would yield a trimer and so on.

Hibbert (52) has applied the principle of isoeugenol polymerization to oxyconiferyl alcohol and suggests possible lignin dimers as shown, (XXXVIII) and (XXXIX),



Erdtman has recently pointed out the presence of a propylphenol type of building unit in a wide variety of plant resins, e.g. olivil, lariciresinol and conidendrin. The similarity between these naturally-occurring products and dehydrodiisoeugenol (III)



(III)

with respect to the dimer formation involving the *β* - carbon atom of the side chain, led Erdtman to believe that such dehydrogenative coupling is very important in the biogenesis of plant products.

Hibbert (6) points out that the tendency for polymerization of lignin building units is greatly enhanced by the presence of a phenol group together with a carbonyl or an unsaturated linkage.

However, this type allows of further polymerization, and since dehydrodiisoeugenol does not polymerize beyond the dimer stage, and analytical data indicate the presence of only part of the postulated primary hydroxy groups, this theory was replaced by another derived from oxyconiferyl alcohol. For this new polymer Hibbert has postulated loss of water between the terminal primary hydroxyl group and the phenolic
hydroxyl and subsequent ring formation through the β - carbinol group and the active ortho nuclear hydrogen





Such polymers (XL) and (XLI) agree well with known properties of spruce lignin including, (1) presence of primary (although only in small amounts), secondary and tertiary hydroxyl groups; (2) formation of labile and stable sulphonic acids; (3) oxidation to vanillin and (4) presence of terminal methyl groups. (b) Polymerization of the Syringyl Type Compounds

Since in the syringyl type building units the nuclear position ortho to the phenolic hydroxyl group is blocked, a similar type of dehydrogenative coupling is impossible. Hibbert (6) has pointed out that since the proposed lignin building units may undergo enolization to give derivatives of styrene, a styrene type of polymerization is therefore possible. Furthermore, in view of the ease with which cinnamyl derivatives undergo the ally shift and form dicinnamyl ethers (50) it is possible that the syringyl units may exist as ethers in the plant, this accounting for their readier extraction by the ethanolysis and hydrogenolysis techniques.

Experiments carried out by Holmberg (51), Freudenberg (12) Hagglund (52) and Ruhtzenhain (53) on the reaction of lignin and related compounds with thioglycollic acid lend support to the above theories of lignin structure.

However, to summarize, no single type of lignin polymer yet suggested is in agreement with all of the experimental data.

(c) Lignin Progenitors as Possible

Respiratory Catalysts

The continuous supply of energy necessary for living animal cells is obtained largely from the stepwise oxidation of sugars to carbon dioxide and water. Respiration entails both decarboxylation and dehydrogenation reactions with the greater part of the energy being liberated during the reaction of hydrogen with oxygen. The energy is, however, liberated in only small amounts and this is accomplished by transferring the hydrogen, under the influence of dehydrogenase enzymes, to a carrier system. Here, the hydrogen is transported from one substance to another in a series of stepwise oxidationreduction systems until finally the union with oxygen is attained.

Szent-Györgyi has demonstrated the presence, in various plants, of an enediol oxidation-reduction system functioning by transfer of hydrogen by the catalytic action of dehydrogenase enzymes. Such a system has been shown to function with catechol (XLII) (54), ascorbic acid (XLIII) (55) and dioxymaleic acid (XLIV) (56).



(XLII) (XLIV)

22.

Hibbert has suggested that the principal watersoluble ethanolysis products, representing possible enediol-1, 2-diketone oxidation-reduction systems, are stabilized endproducts, and their forerunners, being lignin progenitors, are present in the plant cell as hydrogen-transporting catalysts. These later are converted into more complex condensation polymeric products. The oxidation-reduction system of plant respiratory catalysts, proposed by Hibbert (6) is analogous to the C_4 -dicarboxylic acid system of Szent-Györgyi (57) for animals, in that one of the -COOH groups is replaced by the syringyl or guaiacyl radical, the other by the carbinol $(-CH_0OH)$ group.

	Szent-Györgyi System
A	HOOC-CH2-CO-COOH
	- 2H + 2H
В	HOOC-CH2-CHOH-COOH
	- H ₂ 0
C	HOOC-CH = CH-COOH (fumaric acid)
	+ 2H - 2H
D	HOOC-CH2-CH2-COOH (succinic acid

**

Hibbert System

A' $R-CH_2-CO-CH_2OH$ + 2H - 2HB' $R-CH_2-CHOH-CH_2OH$ $\int - H_2O$ C' $R-CH = CH-CH_2OH$ (coniferyl alcohol) + 2H - 2H

R Syringyl or guaiacyl radical

(A') R-CH -CO-CH OH is the keto-alcohol believed to

be obtained from the condensation of three moles of methyl glyoxal (page10.). The passage from this new system to the enedicl-1, 2-diketone system can take place by an allylic rearrangement of the oxyconiferyl alcohol isomer as already shown by experimental work in these laboratories, with formation of the ethyl ethers of R-CO-CHOH-CH₃ and R-CHOH-CO-CH₃ these being found among the ethanolysis products of spruce wood (38). As described later, hydrogenation of spruce and maple woods has led to the isolation of compounds with a terminal (-CH₂O-) grouping, and this provides added support for this suggested allylic rearrangement.

Further information on the topics discussed in this section may be found in references 58 to 85 inclusive.

II. CATALYTIC HYDROGENATION AND HYDROGENOLYSIS OF ORGANIC CHEMISTRY

A. <u>General Discussion of Hydrogenation</u> and Hydrogenolysis

Unless otherwise stated the term hydrogenation will be used to include the reactions more strictly defined by hydrogenolysis. Correctly defined, the term hydrogenation means reduction by means of molecular hydrogen, but more commonly it now includes reduction by means of molecular hydrogen in the presence of a catalyst. The brief outline presented here is limited to those variables, catalysts and types of reaction adaptable to laboratory investigations, and does not include commercial processes.

It is very important to realize that nearly all hydrogenation reactions are reversible, (86) and hence in order to being about a desired result, all variables must be carefully controlled. The more important of these include temperature, pressure, time, solvent, concentration and quantity of catalyst.

It is usually desirable to work at as low a temperature as possible since practically every hydrogenation reaction can be reversed if the temperature is raised sufficiently (86, page 411). On the other hand, increased temperature tends to increase the speed of the reaction. Increased rate with a rise in pressure is generally observed as a concentration effect; increased concentration of reactants if in the gas phase, and increased solubility of hydrogen in the liquid phase. The pressure effect is illustrated in Table II (87).

TABLE II

Extent of Reaction (%) in Specified Time

(Catalyst: Ni(k))

Pressure (atm.)	Benzene (0.5 hr.)	Aniline <u>(6 hrs</u>).	Acetoacetic ester (0.5 hr.)
30	40	29	40
200	68	65	72
350	75	75	100

The time necessary for a hydrogenation is dependent on the nature of the material being hydrogenated.

The choice of solvent for any given hydrogenation is important since it must be stable to the conditions selected and be used below its critical temperature. Adkins has shown that the solvent does affect the rate of hydrogenation (88). Changes in concentration appear to affect the hydrogenation only if the material is complex and side reactions are possible.

The ratio of catalyst to acceptor must not be overlooked in hydrogenation studies since catalysis in general is based upon surface activation and is therefore dependent upon the amount of surface.

B. Catalysts for Hydrogenation

An excellent review of the subject of hydrogenation catalysis is presented on the "Twelfth Catalysis Report" (90).

(1) Factors affecting Hydrogenation Catalysts.

(a) <u>Surface</u>. - A highly extended surface is essential to obtain an active hydrogenation catalyst, and this surface is more effective when obtained by chemical and not mechanical means. A nickel catalyst prepared according to the method of Raney (91) as a good example. In this process equal parts of aluminum and nickel are alloyed and the aluminum is then dissolved out with sodium hydroxide leaving the atomic nickel lattice work. The actual crystallographic structure of the catalyst surface has been indicated as exerting a specific role in hydrogenation (91 a).

(b) <u>Promoted Catalysts</u>. - It has been found that the activity of some catalysts is greatly enhanced, or promoted, by the addition of minute traces of other elements. The use of these mixed metal catalysts has greatly increased, and include well-known types as Ni-Cu (92), NiAl₂C₃ (93), Cu-ZnO (94), Cu-CrO (95) and ZnO-CrO (96).

27.

(2) Types of Hydrogenation Catalysts

(a) <u>Very Reactive Types</u>. - To this classification belong those catalysts which permit of maximum addition of hydrogen to compound, in some cases causing cracking and degradation to methane. Common catalysts belonging to this type consist of iron, cobalt and nickel, molybdenum and tungsten sulphides and oxides (90).

(b) <u>Less Reactive Catalysts</u>. - These catalysts will effect hydrogenations just as rapidly as the more active hydrogenation types but they function stepwise in hydrogenations, or at least they do not permit the reaction to proceed to the hydrocarbon stage. Such catalysts include Cu, ZnO, CrO, MnO, and the noble metals Pt and Pd and their oxides. (97)

C. Classification of Reactions with Hydrogen

(1) Hydrogenation

In this and succeeding sections, either nickel or copper chromium oxide catalysts has been used in the examples quoted.

(a) Ethylenic Linkage: (C=C). - In general, the alkene linkage is saturated at so low a temperature and so rapidly that other groups such as benzenoid and furanoid are not reduced (98). A comparable study of the two most widely used catalysts is given in Table III.

TABLE III

Substance	Press. atm.	Temp. °C.	Time <u>min.</u>	Catalyst	Product
Styrene	3	20	75	Ni(K)	Ethylbenzene (99)
Styrene	34	20	25	Ni(K)	Ethylbenzene (99)
Styrene	34	125	7	CuCrO	Ethylbenzene (99)
Cinnamyl Ethyl Ester	200	250	180	CuCrO	3-Phenyl-propanol-1 (100)

(b) <u>Carbonyl Linkage: (C=0)</u>. - This group can be reduced either partially, to give an alcohol, or entirely to give a hydrocarbon. If a phenyl or pyrryl group is adjacent to the carbonyl group then the hydroxyl group first formed may be reduced further to the methylene group.

TABLE IV

Substance	Press. atm.	Temp. °C.	Time mins.	Catalyst	Product
Acetophe- none	100	110	10	RaNi	91% Ø *-Me-carbinol (101)
Acetophe- none	100	150	30	CuCrO	95% Ø -Me-carbinol (101)
Heptalde- hyde	• • •	150	240	RaNi	92% heptanol-1 (101)
Glucose	• • •	160	240	CuCrO	97% sorbitol (92)
Benzalacet	one	175	12	CuCrO	97% 4-ø-butanol-2 (102)

(c) <u>Benzenoid and Furanoid Nuclei</u>. - The reduction of the benzenoid or furanoid nuclei requires more drastic conditions than does that of the alkene or carbonyl groups. The phenols are more rapidly hydrogenated than other derivatives of benzene.

TABLE V

Substance	Temp. OC.	Time hrs.	Catalyst	Product
Benzene	150	1.0	RaNi	100% Cyclohexane (103)
Toluene	175	0.12	RaNi	100% Me-cyclohexane (103)
Benzene	125	0.25	Ni(K)	100% Cyclohexane (103)
Di- Ø - methane	150	7.0	Ni(K)	100% Dicyclohexylmethane (99)
Phenol	150	3.0	Ni(K)	- Cyclohexanol (104)
Anisol	200	4.4	RaNi	66% Methylcyclohexyl ether (105)
Aniline	175	9.0	Ni(K)	80% Cyclohexylamine (104)
Meth yl salicylate	200	9.0	Ni(K)	96% Methylhexahydrosalicylate (106)

Over RaNi, the furyl derivatives are reduced in yields of 80 - 97% to the corresponding tetrahydro compound (107).

(2) <u>Hydrogenolysis</u> (Cleavage)

Hydrocarbon (C-C) cleavage occurs most commonly at very high temperatures over the "very reactive type " catalyst (RaNi) although with certain groupings C-C cleavage may occur over CuCrO, (108, 109, 110, 111).

Hydrogenolysis of the C-O bond especially in alcohols is extremely difficult below 250° C. except where the hydroxyl group is in the β -position with respect to an ethylenic or carbonyl group (112).

Most of the reported work on C - O - C cleavage in ethers has been done using RaNi and very little using CuCrO catalyst. It appears that the benzyl ethers undergo hydrogenolysis at lower temperatures than do others (effect of $C = C - C \dots O \dots$) and benzyl-aryl ethers cleave at lower temperatures than do benzyl alkyl ethers. The arylalkyl ethers are most stable towards hydrogenolysis while the di-aryl ethers are somewhat more stable than benzylalkyl ethers. Some work on the comparative use of RaNi and CuCrO is given by De Benneville and Connor (113).

(3) Hydrogenation Accompanied by Hydrogenolysis

This type of reaction is becoming more and more important in the laboratory as a means of preparing alcohols from acids (or their esters) (109, 114). The yields decrease as the ideal situations for C - O hydrogenolysis are approached (e.g. proximity of phenyl carbonyl, furyl or hydroxyl groups) (114).

31.

(4) <u>Selective Hydrogenation</u>

By selective hydrogenation is meant the hydrogenation of hydrogenolysis of one functional group in the presence of another which remains unreduced. The important variables in selective hydrogenation are (a) selection of catalyst, (b) temperature and duration of reaction and (c) nature of reaction medium. For example, using CuCrO, aldehydes, ketones and esters containing an aryl group may be hydrogenated to the corresponding hydroxylated aliphatic benzene derivatives, while, if RaNi is used, esters containing cyclohexyl groups may be obtained from the parent aryl compound. Other examples of such selective hydrogenations are given in the Discussion.

The careful control of temperature and time is probably the most common method of attaining selective hydrogenation. In general, there is a pronounced tendency for one group to be completely hydrogenated before reaction with another commences, and this along with the fact that usually the most reactive group will hydrogenate at a lower temperature, allows of selective hydrogenation by interrupting (quenching in cold water) the reaction.

It must be remembered, however, that the relative rates of reaction of two compounds with different functional groups taken separately cannot be used safely to predict the relative rates of hydrogenation of the two compounds in a mixture, or of the two groups when both are in the same molecule (115) in as much as the nature of the compounds to be hydrogenated is very important.

32.

III. Hydrogenation of Lignin

The first truly successful hydrogenation of an <u>isolated</u> lignin was reported by Harris, D'Ianni and Adkins (25) in 1938. Although lignin had been treated with hydrogen under various conditions prior to this time, no detailed analyses of the products had been made. These earlier investigations are described briefly in the following paragraphs.

The earliest reference to the hydrogenation of lignin is that of Fischer and Schrader (116) in 1921. These investigators obtained a "thin brown oil of ethereal odor" by reduction of lignin with sodium formate at 400° C, but the product was not examined further. In the following year Willstätter and Kalb (117) studied the reduction of lignin and of carbohydrates by a mixture of hydriodic acid and phosphorus and since similar compounds were isolated in both cases concluded that a close chemical relationship existed between the two.

In 1925 Fierz-David (118) and Fierz-David and Hannig (119) described experiments in which lignin was subjected to a temperature of 400[°] in the presence of a nickel catalyst and an atmosphere of hydrogen. Almost quantitative conversion into gaseous and aqueous distillates was claimed and some alkyl furanes and phenols were isolated. The amounts of the identified substances were not given.

Bowen and Nash (120) (1926) hydrogenated Willstätter lignin (121) over an Al_2O_3 -NiO catalyst at 350-450°C in the absence of solvent and obtained a thick black tar which was

- 33 -

reported to contain an insoluble organic residue (6.2%), an aqueous distillate (19.8%), a chloroform soluble oil (37.3%), an ether insoluble solid (2.9%), an ether soluble neutral oil (21.7%), phenols (4.8%), and phenol soluble material (3.7%). 3.4% of the phenols distilled below 210°C and 54% between 210° and 244°C. No further investigations were reported by these authors.

Ipatiev and Petrov (122) described the pyrolytic decomposition of the constituents of wood tar in the presence of excess hydrogen and catalysts (Al_2O_3 , Fe_2O_3) and showed that the maximum yield of liquid products was obtained at a temperature of 440-460°C. The hydrogenated material contained considerable amounts of benzene and other aromatic hydrocarbons as the result partly of cracking and partly of the reduction of unsaturated and oxygen-containing compounds.

Von Wacek (123) employed palladium absorbed on barium sulphate as a catalyst for the hydrogenation of acetic acid, acetone, and cyclohexanol solutions of methylated lignins. Under similar hydrogenation conditions, using a methylated lignin, (2 g. lignin, 4 g. catalyst, 140-150°C, 25-30 atm. of hydrogen for 2 hours) the methoxyl value of the reduction product obtained from the acetic acid medium was markedly lower (by 5.25%) than that of the reduction product using cyclohexanol. Because of this great methoxyl loss the work was discontinued.

- 34 -

Lindblad (124) hydrogenated alkali lignin using cobalt sulphide as catalyst and obtained about 70% of the lignin as a chloroform soluble tar containing a considerable quantity of phenols and alcohol-soluble substances. The tar was found to be capable of partial distillation without decomposition, but was not investigated further.

By distilling lignin at 400°C over zine dust in an atmosphere of hydrogen, Fhillips (125) recovered 16% of the weight of starting material as an oil of which 55% was phenolic. Guaiacol and n-propylguaiacol were identified in very low yields.

Trefil'ev and Filaretov (126) have described a two stage hydrogenation of wood tar using MoS_3 and also $MoS_3 + ZnCl_2$ as catalysts. The hydrogenation fractions obtained at $180-300^{\circ}C$ contained benzene, toluene, xylene and naphthalene.

In 1935 Moldavskii and Vainstein (127) hydrogenated sulphuric acid lignin at high pressures and temperatures of 400-500°C. Five catalysts, viz. $Sn(OH)_2$, $(NH_4)_2MoO_4$, FeS₂, MoS₂ and CoS, were tested and the last two found to be the most efficient. In a second series of experiments in which a ligneous tar was used as the solvent and MoS₂ as the catalyst, liquid products amounting to 44% of the lignin were obtained, while the gaseous reaction products (56% of the lignin) contained 50% methane and 2-3% carbon dioxide plus carbon monoxide. Benzoic and 1,3-terephthalic acids were obtained by oxidation of the tars with alkaline potassium permanganate.

- 35 -

Freudenberg (128) investigated the use of phosphorusiodine mixtures and also nickel as hydrogenation catalysts and found that using hydrogen at pressures of 230-250 atmospheres for 9 hours, lignin sulphonic acids yielded two liquid fractions. a light coloured portion acidic in nature, and a neutral dark brown aqueous solution.

Hibbert and Moore (129) hydrogenated methylated methanol lignin at relatively low temperatures and pressures in the presence of both Adams platinum catalyst and Raney nickel. The starting material remained unchanged indicating the complete absence of the ethylenic double bonds which these procedures were designed to reduce.

Harris, D'Ianni and Adkins (25) hydrogenated methanol lignin (aspen) over CuCrO at 255° (5000 lb./sq.in. pressure). The hydrogenation products isolated and identified were methanol (28%); 4-n-propyloyclohexanol, \underline{I}^{\times} (11.5%); 4-n-propyloyclohexanediol-1,2, \underline{II}^{\times} (3.8%); 3-(4-hydroxycyclohexyl)-propanol-1, III $\overset{\times}{}$ (25%); and a high boiling resinous residue (32%).

This process has been extended to other ligning by Harris and Adking (26). The results obtained by these investigators are shown in Table VI. At a later date Harris (127) reported 9 to 11% water as an additional product from these hydrogenations.

Apparently the yields reported by Harris and Adkins (37) for 3-(4-hydroxycyclohexyl)-propanol-1 are decidedly open to

The underlined numerals refer to Table VI, page 64.

- 36 -

TABLE VI

THE HYDROGENATION OF VARIOUS LIGNING OVER COPPER-CHRONIUM

]	Propor	rtion of	Methoxyl		Products Isolated				
Lignin	Total Lignin in Wood %	Content of Lignin	MeOH %	I Ģ	II %	III %	Residue %	Total Return % (a)	
Sethanol (aspen)		60	27.0	26.5	11.0	3.2	24.0	22.0	56.7
Clason (spruce)		- 30	20.6	19.0	6.0	2.0	15.0	45.0	90.0
Alkali (aspen)		60	11.6	10.5	4.0	1.4	9.0	66.0	90 .9
Methanol (spruce)	25	23.0	15.0	7.0	2.0	12.0	52.0	55.0
Alkali (black gu	m'y	60	11.8	11.0	5.0	1.0	14.0	60.0	91 .1
The following re	sults	were re	ported by Ha	rris,	D'Ian	n i an	d Adkine	(36))	
Methanol (aspen)		90		28.0	11.5	3.8	25.0	32.0	100.3

%(a) = Percentage of original weight of lignin

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question. This is particularly true with regard to those reported in the case of soda lignin (aspen and black gum); namely 9 and 14% respectively. Adkins has found recently (27) that soda lignins from hardwoods yield only traces of this glycol, and this investigator emphasizes the fact that Harris "has given no substantial evidence that he has isolated or characterized the glycol among the products of their hydrogenation of soda lignin", in referring to a previous paper by Harris (128) and co-workers.

The resins obtained in the hydrogenation of lignin have been studied by Harris, D'Ianni and Adkins (25) who found that the resinces residue obtained in the hydrogenation of methanol lignin (aspen) contained 73% carbon and 10.8% hydrogen. This residue was dehydrated with alumina and the unsaturated hydrocarbons thus obtained were rehydrogenated over Raney nickel yielding saturated hydrocarbons containing 86.6% carbon and 12.5% hydrogen. From the physical properties of these hydrocarbons (particularly boiling-point) Adkins concluded that, since the minimum number of carbon atoms present in the simplest hydrocarbon was fifteen, the original lignin was composed, at least in part, of units containing more than fifteen carbon atoms.

A more detailed investigation of the resins was made by Adkins, Frank and Bloom (27). The high-boiling residue obtained in the hydrogenation of alkali lignin (hardwoods), which contained 79.9% carbon and 11.4% hydrogen, was dehydrated with oxalic acid

- 38 -

and then re-hydrogenated. The hydrocarbons thus obtained were carefully fractionated and analyzed. The results indicated that: (a) The soda lignin was converted to alcohols and glycols related to polycyclic hydrocarbons having 20 to 70 (or more) carbon atoms in the molecule: (b) although high molecular weight compounds were also obtained from methanol lignin (25), they were present in smaller amounts and were more highly oxygenated than the products of similar physical properties obtained from soda lignin; (c) the products from methanol lignin contained one oxygen atom per six carbon atoms, while the products from soda lignin had one oxygen atom per average of 13.5 carbon atoms.

Harris, Saeman, and Sherrard (128) have hydrogenated methanol lignin, alkali lignin, sulfuric acid (Klason) lignin and cellosolve lignin in an aqueous medium in the presence of Raney nickel. The reaction products are stated to include methanol, propylcyclohexane, hydroxy derivatives of propylcyclohexane and resins, but no yields or properties of these products have been reported.

Cooke, McCarthy and Hibbert (24) subjected maple ethanol lignin to hydrogenation (250°, 3400 lb./sq.in. initial pressure, 18 hours) over CuCrO and obtained water, methanol, ethanol, 4-n-propylcyclohexanol, 4-n-propylcyclohexanediol-1,2, 3-(4-hydroxycyclohexyl)-propanol-1, an apparently new, unidentified substance and high boiling resins in yields of 13.6, 5.0, 8.7, 8.1, 1.9, 3.2, 2.1 and 29.5% respectively. The variations in yield, especially of 3-(4-hydroxycyclohexyl)-propanol-1 as

- 39 -

compared with the results of Harris, D'Ianni and Adkins (25) using aspen methanol lignin suggest that a difference may exist in the chemical structure of the two types of lignin. Similar products (24) were obtained for various ethanolysis lignin products.

Recently Freudenberg (66) and co-workers have hydrogenated (at 250-340° and 80-140 atmospheres pressure) Willstätter and cuproxam lignins in alkaline media (up to 5% NaOH) with the purpose of cracking the side chain while hindering the saturation of the nucleus. With a Cu-Ni-Al₂O₃ catalyst (low activity) 45 to 50% (lignin basis) of phenolic components were obtained together with small amounts of cyclohexyl lignin degradation products. Monocyclic phenolics (15% of lignin) included guaiacol, creosol and pyrocatechol. Ni catalysts precipitated on the lignin as the hydroxide or the carbonate gave similar results. With a highly-active catalyst (Ni-Al₂O₃, Raney Ni) under the same conditions (.66), cyclohexyl derivatives (36-40%) were obtained, 15% (lignin basis) being monocyclic cyclohexanols.

In another paper Freudenberg and Adam (6g) describe an experiment in which the lignin, impregnated with a Ni catalyst, is heated (in a revolving tube) while a stream of hydrogen is passed over it. At 220° a yellowish-brown oil begins to distill over and the distillation continues as the temperature is raised to 350°. Up to 50% of the weight of the lignin (spruce HCl lignin) is obtained as an ether-soluble oil of which 65 to 70% consists of distillable phenols. The overall

- 40 -

yields (average) are given as: phenols up to 35% (lignin basis); neutral up to 7%; acids, 0.2 to 0.3%. In these fractions the identified substances, all of which may be readily related to the phenylpropane structure for lignin, include the following (with the quoted percentage): phenol (5.5); p-Et phenol (1.1); guaiacol (5.9); p-cresol (7.1); p-Et guaiacol (1.6); o-Et guaiacol (0.5); isoeugenol (1.3); pryocatechol (2.9); p-Pr pyrocatechol (0.1); homopyrocatechol (1.1); toluene (0.7); o-Et-anisole (0.5); p-homoveratrole (2.0); methanol and ethanol (0.5); methylcyclopentanol (0.5) and higher boiling components (12).

Hatihama et al. (132) hydrogenated hydrochloric acid lignin (16.32% OMe) and methylated lignin (30.91% OMe) at 260-270°C under a pressure of 230 atmospheres of hydrogen. Of the catalysts used (nickel oxide, reduced nickel, copper chromium oxide, ammonium molybdate and cobalt sulphide) nickel oxide gave the best results. The effect of several different solvents (dioxane, decalin, methanol and ethylene glycol) was also studied and it was concluded that dioxane was the most suitable. The ether soluble portion (46.7% of the lignin) of the reduction products contained 4-propylguaiacol, protocatechuic acid, pyrocatechol and p-hydroxybenzoic acid.

Two recent patents by Sherrard, Harris and Saeman (133, 134) and by Kato and Sugino (135) describe processes for the hydrogenation of extracted lignins. The former workers obtained methanol, n-propyloyclohexane and water-soluble resins from alkaline or neutral aqueous media at temperatures not exceeding 300° in the presence of nickel, palladium, platinum or molybdenum catalysts, while the Japanese investigators reported the formation of oily products by the hydrogenation of a solution of lignin from pulp waste (presumably lignin sulphonic acids) in a reduced naphthalene solvent.

In 1941 Lautsch (136) studied the hydrogenation and degradation of spruce lignin. With dilute alkalis at 200-260°C, and in the presence of a catalyst, mainly phenols and ringhydrogenated products were obtained, while at 540-350° with, or without, a catalyst, a pronounced cracking of the side chains and ring-hydrogenation occurred. HCl-lignin and similar products gave a higher yield of low molecular weight compounds than the lignin sulphonates. Black liquor from alkali cooks of pine wood gave no useful results on hydrogenation at 260°, but at 340-350° about 60% of hydro-aromatic substances was obtained.

The most recent work on the production of lignin hydrogenation products has been done by Bower and is described in the following section (see p.44)

IV. Hydrogenation of Wood and Related Materials

Most of the earlier experiments on wood hydrogenation were associated either with attempted production of liquid fuels or with the destructive distillation of wood in the presence of hydrogen and no attempt was made to separate and identify individual reaction products. The work done prior to 1935 will not be reviewed here beyond making reference to the admirable survey of this phase of the development by Boomer and co-workers (137).

The only wood hydrogenation investigations furnishing information as to the structure of lignin are those of Godard, McCarthy and Hibbert (22), Harris (130) and Bower, Cooke and Hibbert (138). The first-mentioned workers (22) treated maple wood meal with hydrogen at 400 atmospheres pressure in the presence of CuCrO at 280° for 19 hours and isolated 4-n-propylcyclohexanol (19.5%) and 3-(4-hydroxycyclohexyl)-1-propanol (5.8%) from among the hydrogenation products. (The yields are based upon the Klason lignin content of the wood.)

Harris (150) claimed to have isolated and identified a high percentage of the products obtained by hydrogenation of maple, aspen and spruce woods over Raney nickel catalyst in an aqueous alkaline medium. In one experiment 30 g. of aspen wood suspended in 300 cc. of 1% aqueous sodium hydroxide were treated with hydrogen (300 atmospheres pressure) at 175° for 4 hours. The yieldsof products (percentage of original wood)

- 43 -

- 44 -

claimed were: julp, 40%; methanol, 5.1%; propanol, 16%; propylcyclohexane derivatives, 20%; resin, 14%; unidentified residue, 2%; total recovery, 97%. Since aspen wood contains 20-22% lignin (139), it would appear that the quantity of propylcyclohexane derivatives isolated by Harris accounts for nearly 100% of the Klason lignin content of the wood. According to the results obtained by Zartman and Adkins (110), carbohydrate materials yield considerable quantities of water upon hydrogenation so that it is difficult to conceive of a 97% recovery of wood hydrogenation products exclusive of water. No evidence was given to indicate that the propylcyclohexane derivatives were identified through the formation of derivatives. Brewer. Cooke and Hibbert (142) have been unable to duplicate the work of Harris, and the latter has disclaimed authorship of the work in question.

Recent work by Bower, Cooke and Hibbert (138) on the hydrogenation of maple wood meal and maple holocellulose has shown that the propylcyclohexyl derivatives isolated from the former are of <u>lignin</u> and not of carbohydrate origin. Two new compounds, 3-cyclohexyl-l-propanol (LXI) and n-pentanol (LXII), have been isolated,

$$\begin{array}{c} \text{S} \\ \text{(LXI)} \end{array} \begin{array}{c} \text{CH}_2 - \text{CH}$$

the former from maple and spruce woods and various maple lignin fractions and the latter from maple wood alone. In the early investigations of Hibbert and co-workers (22) on the hydrogenation of spruce and maple woods, the water-insoluble hydrogenation products were fractionally distilled and it was assumed that the fraction of refractive index range 1.4600-1.4700 at 25° consisted of 4-n-propylcyclohexanol (IV). The reinvestigation of this material by Bower (138) using a column of greatly increased efficiency (140) has shown that the product is really a mixture of 4-n-propylcyclohexanol (IV) and 3-cyclohexyl-1-Thus the percentage of lignin (based on the propanol (LXI). carbon content of the methoxyl-free lignin) isolated as cyclohexyl hydrogenation products having a terminal carbinol group is increased from 7.5% to 25.7% and supporting evidence furnished for Hibbert's recent hypothesis in which the important role played by hydroxy and dihydroxyconiferyl alcohols as lignin building units is emphasized. Whether the entire "native" lignin is composed of units containing end carbinol groups is Recent investigations by McGregor and still uncertain. Hibbert (141) have shown that the chromic acid oxidation of both spruce and maple woods yields no acetic acid. Inasmuch as this oxidation technique is a specific, almost quantitative, test for terminal methyl groups, this work is in excellent accord with the above-mentioned theory.

V. REVIEW OF EXPERIMENTAL RESULTS

L. Introduction

It was pointed out in the historical review that native spruce lignin, as present in spruce wood meal, can be oxidized to vanillin with a yield of around 25%, and that this is also true of a variety of gymnosperms. With angiosperms (silver maple, ash, birch ...) maximum yields (48-51%) of a mixture of syringaldehyde and vanillin in an approximate ratio of 3:1 were obtained. Assuming, on the basis of the substantial experimental evidence outlined previously (β . 4-11) that with angiosperms each of the aldehydes represents a degradation product derived from a C₆-C₃ propyl phenol lignin entity of one of the types:

(R = 4-hydroxy-3-methoxyphenyl or 4-hydroxy-3,5-dimethoxy phenyl)

the calculated yield amounts to about 62-65%. In the case of spruce and other gymnosperms the value would be 30-32%.

The oxidation data thus indicate that a very large proportion of the lignin structure, especially in angiosperms, is aromatic in character, but provide no information as to the nature of the three-carbon side chain.

- 46 -

On the other hand, while the yield of identifiable lignin products isolated in the ethanolysis of wood is very low, in the case of spruce (2-3%), and much higher with maple wood (around 13-14%), the products isolated possess a very marked significance with respect to the structure of lignin inasmuch as they probably represent stabilized end products of the more reactive true lignin progenitors.

The ethanolysis products, already identified, have the following structures:

- (a) <u>Benzoin types</u> R-CHOH-CO-CH₃ and R-CO-CHOH-CH₃ (as their ethyl ethers)
- (b) 1,2 Diketones R-CO-CO-CH3
- (c) Desoxybenzoins R-CH2-CO-CH3
- (d) Aldehydes R-CHO

with R having the same significance as outlined above.

Each of these types has been isolated from both spruce and maple wood ethanolysis products, thus pointing to their origin from lignin progenitors of similar structure in all higher plants.

Hibbert has pointed out that experimental evidence has now been obtained indicating that each of these ethanolysis products actually could be formed, during the extraction procedure, from a single type of lignin progenitor, namely, oxyconiferyl (or oxysyringyl) alcohol, as illustrated in the following chart and supporting evidence for all these changes, has, in fact, been material the product (R=CH₂COCH₂Cl) R = 3,4-dimethoxy phenyl.

Chart typifying intramolecular reactions of oxyconiferyl



Due to the extraordinary reactivity of oxyconiferyl alcohol, the it undergoes, in/presence of the ethanolysis reagent, not only the above series of intramolecular changes, but also simultaneous conversion, to a large extent, into amorphous lignin condensation products not reconvertible into monomolecular units of the C_{6} -C-C type.

In order to remove from wood the native lignin structure intact, or as nearly so as possible, a much less drastic procedure than that of ethanolysis is necessary, since only then will it be possible to prove

(a) the totally aromatic character of native lignin as represented by a skeletal propylphenol nucleus, either 4-hydroxy-

3-methoxyphenyl or 4-hydroxy-3,5-dimethoxyphenyl in type,

(b) the attachment, in the position para to the phenol hydroxyl group of a three-carbon oxygenated side chain,
and (c) the nature of the side chains and their mode of linkage in the polymeric form or forms of which native lignin is composed.

The problem assigned to the writer was two-fold;

(a) to study the catalytic hydrogenation of a new type of isolated lignin ("Maple Lignin (A)")^X, developed in these laboratories, with the object of determining the most useful catalyst for such a hydrogenation and, if possible, to increase the yield of propyl cyclohexane products.

(b) to investigate the possibility of extracting native lignin from maple wood by hydrogenolysis and hydrogenation under such conditions that:

(i) degradation to simple aromatic units could be effected in maximum yields,

(ii) the nature of the side chain of the lignin building would unit/be left unchanged in so far as possible intramolecular changes are concerned, the reduction thus being characterized only by reduction of unsaturated groups or fission of oxygen linkages,

(iii) the isolation in large yield of identifiable dimers of the (C₆-C-C-C) type on the assumption that these units

^{* &}quot;Maple Lignin (A)" is the designation used for the chloroform soluble fraction of the products obtained by catalytic hydrogenation of maple wood meal in an initially neutral aqueousethanol (1:1) medium using Raney nickel as the catalyst. It is distillable to the extent of 35-40% and represents 50-90% of the original native lignin.

probably represent the hypothetical dimers of which (in the light of our present knowledge) native lignin is, to a large degree, composed.

B. Preliminary Experiments on Hydrogenation of Maple Wood Meal in Aqueous Ethanol (1:1) followed by Rehydrogenation

1. Preparation of "Maple Lignin (A)"

Preliminary investigations by Brewer (142) on "Maple Lignin (A)" obtained from maple wood meal under initially neutral conditions of hydrogenation, using Raney nickel in aqueous ethanol, (1:1) indicated this product as a valuable new material for use in determining the structure of lignin. He found that:

(a) the product was obtained in high yield (80-90% of Klason lignin) and contained free phenol groups. The original methoxyl groups were still intact, indicating its essentially aromatic structure,

(b) carbonyl groups and ethylenic linkages were absent so that both the composite product and its individual constituents were much more stable than the propylphenol (C_6-C_3) units isolated by the ethanolysis of wood,

(c) when refluxed with ethanol-HCl (2%) for 48 hours apparently little or no degradation had occurred as indicated by its solubility in petroleum-ether (30-50°). (d) the marked ease of solubility in chloroform and, to a large extent in petroleum ether, indicated a simpler state of aggregation than that found in other extracted lignins such as cuproxam lignin, ethanol lignin etc.

(e) the conditions for extraction were very mild. Hydrelysis of the lignin-hemicellulose complex evidently precedes lignin extraction, and the milder the conditions under which this can be effected, the greater the probability of isolating undegraded lignin. The originally neutral extraction medium became slightly acidic during the extraction process (pH 7.5 to pH 5.5), owing to the formation of small amounts of acetic and formic acids (143). The slight acidity thus imparted is sufficient, at the temperature used, to bring about an effective hydrolysis of the carbehydrates from the lignin.

2. Object Sought in the Investigation of "Maple Lignin (A)"

The high pressure catalytic hydrogenation of isolated ligning over a copper chromium catalyst has been studied thoroughly (25, 26, 24). Previous results on the hydrogenation of methanol-(aspen), Klason- (spruce), alkali- (aspen), methanol- (spruce), alkali- (black gum) ligning are given in Table VI, p. 37. Cooke and Hibbert's (24) hydrogenation results on methanol and ethanol lignin obtained from hard woods indicate a difference in structure, in that while 3-(4-hydroxycyclohexyl)-l-propanol (V)

- 51 -

was present in large yield (25%) in the hydrogenation products from the former, in those from the latter it amounted to only 2-3%. These workers have also applied a similar hydrogenation technique to several ethanolysis lignin fractions from maple wood meal (24)and conclude from their results that the rate of hydrogenation to propyleyelohexyl units increases with the solubility of the lignin fractions in organic solvents, this solubility having a very direct relationship to the degree of polymer-condensation; regarded as much less complex with a C-O-C type of polymer union than with a C-C-C type in the lignin fractions.

Adkins, Frank and Bloom (27) hydrogenated another type of commercial alkali lignin (Meade, "soda" lignin) at 250-300° over copper chromium oxide. Although the hydrogen absorption was similar to that obtained with methanol aspen lignin there was no predominance of C_6-C_3 compounds in the reduction products, cyclic compounds containing from six to at least seventy carbon atoms being indicated. The higher boiling products from methanol lignin have been shown by these authors to contain one oxygen atom for each 6 carbon atoms, while in the products from soda lignin there was present one oxygen to 13.5 carbon atoms.

In view of the known complexity of the alcoholysis and soda lignins it appeared that "Maple Lignin (\blacktriangle)", isolated as it is, under relatively mild conditions of extraction (see p. 49) of and showing a remarkably high degree/solubility in organic solvents, would provide an excellent experimental material for

- 52 -

comparison with the other isolated lignins.

From the results obtained by the above-mentioned workers on the catalytic hydrogenation of isolated lignins as well as those of Godard (22) and Bower (138) on the direct hydrogenation of wood, it appeared that the hydrogenating conditions used by these authors with copper chromium oxide as catalyst were those corresponding to the maximum yield of identifiable products. For this reason other catalysts were investigated by the author with the object of,

(a) increasing the yield of propyloyclohexyl products;

(b) obtaining new lignin degradation products arising from a different mode of cleavage of the lignin entity.

. 3. Choice of Catalysts

The catalysts chosen for this investigation included (a) nickel chromium oxide; (b) zinc chromium oxide; and (c) copper aluminum oxide (mixed oxide catalysts similar in structure to copper chromium oxide); (d) copper chromium oxide; (e) Raney nickel (an effective catalyst for ether cleavage (9g)); (f) Raney nickel promoted with platinic chloride and (g) palladiumized charcoal. Frazer and Jackson (145) have described the preparation of active nickel chromium oxide catalyst for hydrogenation of ethylenic (C=C) bonds. Zinc chromium oxide has been reported by several workers (146, 147, 103, 148, 96), but in general it is less active than copper chromium oxide and tends

- 53 -

to catalyze condensation reactions. It has been used as a selective catalyst (148) for hydrogenations of the type -

and $CH_3CH=CHCHO + H_2 \longrightarrow CH_3CH=CHCH_2OH$ $CH_3CH_2CH_2CHO + H_2 \longrightarrow CH_3CH_2CH_2CH_2OH$

while Sauer and Adkins (96) reported the selective reduction of unsaturated fatty esters to unsaturated alcohols using this catalyst.

Ipatieff and Hoensel (149) prepared an active (pyrophoric in air) copper aluminum oxide catalyst for the selective hydrogenation of allylphenylketones to the secondary alcohols. Several members of the platinum family have been shown to have a strong promoter action when deposited on Raney nickel (150). Luber and Smith (151) noted a pronounced enhancing effect of platinic chloride on the hydrogenation of many organic compounds. For example the rate of hydrogenation of benzaldehyde was increased five to six times by the addition of 0.075 g. of platinic chloride to 2.6 g. Raney nickel.

4. Conclusions

a. Effect of Catalyst Type on Nature and Yields of Hydrogenation Products from "Maple Lignin (1)"

From a consideration of the yields of distillable products obtained by the catalytic hydrogenation of "Maple Lignin (Δ)"

- 54 -

(Tables XII and XIII) the catalysts may be arranged in decreasing order of effectiveness: (1) copper chromium oxide (92.3%); Raney nickel (89%); (3) palladiumized charcoal (57.4%); (2) (4) Raney nickel and platinic chloride (55.8%) and (5) nickel ohromium oxide (30.4%). Attempts to prepare an active copper alumina catalyst were unsuccessful. Only the first two (copper chromium oxide and Raney nickel) were considered of sufficient importance for the present investigation since by the use of these catalysts the "Maple Lignin (A)", (initially 35-40% distillable) on treatment for ninety minutes at 225° in dioxane medium was converted into a material containing 80-90% distillable The yield obtained with copper chromium oxide was pröduots. higher than with Raney nickel, but in both cases not more than 50% could be distilled through the 21-plate column. If the temperature of hydrogenation of the "Maple Lignin (A)" were increased to 250° and the time to 8 hours (Run 29, Table XIII), the actual distillability through the same column was increased to 95% and the distillate exhibited marked "flats" .

The results from these experiments indicate: (1) the <u>types</u> of lignin degradation arising from the rehydrogenation and the number of same are dependent on the temperature, using a specified catalyst, and (ii) the <u>extent</u> of any specified type of degradation increases with time.

x Regions in which the fractions have nearly identical refractive indices.
b. Effect of Solvent Type on Nature and Yields of Hydrogenation Products from "Maple Lignin (A)"

The yields and distillabilities of the products obtained by hydrogenation of "Maple Lignin (A)" found in Experiments 37, 37A, 41, 42, 42A, 43 and 44 (Table XII) indicate that a variation in the reaction medium (dioxane, methylcyclohexane and ethanol) exerts only a negligible effect.

c. Variation in Yield of Propylcyclohexane Derivatives

No increase in yield of propylcyclohexane units was found in the hydrogenation of "Maple Lignin (A)" over that obtained previously by a <u>one-step</u> hydrogenation treatment of maple wood using the same medium, dioxane, and catalyst, copper chromium oxide (138).

In view of these results considerable experimentation was devoted to the isolation in high yield from maple wood meal, by a one-stage hydrogenation process, of the entire native lignin in the form of readily soluble and (if possible) completely distillable identifiable hydrogenated propyl-phenol derivatives.

It was found that the total native lignin could be readily extracted as a chloroform soluble product by carrying out the hydrogenation in aqueous ethanol in presence of either acid or alkali at 165°C. for 4 hours using Raney nickel as catalyst (Expt. 73, Table XIV). Wider variations were found, however, in the actual amounts of distillable products present in the completely chloroform-soluble reaction products and this necessitated carrying out an extensive series of investigations to determine the conditions for giving both maximum chloroform (or other solvent) solubility and maximum distillability.

C. <u>Investigation of Factors Influencing Type and Yield of</u> <u>Products from a Single-Stage Hydrogenation of Maple Wood Meal</u>

1. <u>Investigation of Variablesinvolved in Hydrogenation</u> of Maple Wood Meal

The variables calling for consideration were (a) temperature; (b) time; (c) type of catalyst; (d) solvent medium and (e) pH of reaction medium.

(a) (b) (c) Effect of Temperature, Time and Catalyst

A large number of similar experiments carried out by Brewer (142) in these laboratories indicated the best operating temperature as 165°, the length of time as 4 hours, with Raney nickel as a very efficient catalyst and employing an initially neutral reaction medium. These findings were confirmed by the author.

(d) Nature of the Reaction Medium

Solution of the author's problem, it was believed,

involved the following considerations: (i) Use of a hydrogenating medium capable of bringing about a primary hydrolysis of the lignin-carbohydrate complex; (ii) rapid and effective solubilisation of the wood constituents; and (iii) rapid saturation of unsaturated linkages (carbonyl, ethylene) and avoidance of concurrent intramolecular transformations of the lignin with resulting formation of polymer condensation products. Water, alone, has only a slight solubilising effect on the total wood content (152) while with aqueous aliphatic alcohols (ethanol, propanol, butanol) this is very marked, especially at higher temperatures (160-180°) and such solvents serve as very efficient lignin extractants (153, 154, 155). The initially neutral medium becomes slightly acidic during the treatment due to the formation of small amounts of acetic and formic acids.

Hewson has shown earlier (153) that small amounts of both acid and alkali exert a marked catalytic effect on the rate and extent of lignin removal by ethanolysis, while more recently Brewer (142) has found that use of initially neutral aqueous ethanol (1:1) as a hydrogenating medium results in the formation of hydrogenated ligning characterised by high chloroform and petroleum ether solubility.

These latter results were also confirmed by the writer and indicated the use of aqueous ethanol (1:1) as the most suitable medium.

- 58 -

(e) pH of the Reaction Medium

- 59 -

The effect of pH on lignin removal, solubility and distillability of the extracted hydrogenated lignin was investigated in a series of seven hydrogenations carried out in aqueous ethanol (1:1) for 4 hours at 160-165° using Raney nickel as catalyst, and varying the pH as indicated in Table XIV.

These show (1) maximum petroleum ether solubility is associated with maximum solubilisation of the wood (Expt. 77). Table XIV and Fig.1); (2) This increased solubility is coincident with increasing acidity to an optimum value (Expts. 57, 58, 59, Table XIV and Fig.1) above which the solubility decreases, this in turn denoting an increase in extent of polymerisation. These results indicate that a hydrolytic agent is necessary for lignin (3) The maximum yield (78.8% based on Klason lignin removal. in wood) of petroleum ether soluble product is obtained using 0.86 cc. of 12 N HCl per 100 cc. solvent (Expt. 77, Table XIV). This yield is on a weight basis and it is possible this product contained some hydrogenated carbohydrate material. (4) With an acid content of 0.716 cc. of 12 N HCl per 100 cc. of hydrogenating solvent the lignin extraction is very rapid and practically complete after 2 hours (Expts. 68, 69, 71, 79, Table XV and The amount of polymerisation (judged by constancy of Fig. II). petroleum ether solubility over a period of 15 hours)was not very (5) Complete solubilisation of the wood is effected in aquehigh. ous ethanol (containing 0.8 cc. 12 N HCl per 100 cc. solvent medium) at 165° for 4 hours using Raney nickel (Expt.73, Table XIV).



59a -

2. Action of Aqueous Ethanol (1 : 1) on Maple Wood in Absence of a Catalyst.

In Experiments 66 and 70 (Table XVI) use of aqueousethanol (l : l) alone under pressure, in an inert atmosphere (CO_2) at 165-170° for four and eight hours respectively was shown to be effective in removing practically the whole of the native lignin.

The total chloroform soluble amounted to 105 and 109% of the Klason lignin respectively, the loss of methoxyl during the lignin extraction being respectively 31% and 15%. Under these non-reducing conditions, the unsaturated groupings, presumably remain more or less intact and the extracted lignin is, in consequence, much more reactive as shown in the almost complete resinification taking place on fractionation of the ethyl ether soluble portion (Exp. 70).

3. Effect of Structure of Acid Addendum.

p-Toluene sulphonic acid acts as efficiently as hydrochloric acid in facilitating the lignin removal during the hydrogenolysis-hydrogenation treatment (Exps. 75, 76, Table XVI).

4. Selection of most suitable Hydrogenating Conditions for a Single-Stage Hydrogenation.

Chief consideration was given to two factors; (a) maximum yield of petroleum-ether soluble material and (b) maximum identifiable C₆-C-C-C units in the total chloroform-soluble fraction of the extracted hydrogenated lignin.

Examination of the experimental data (Tables XIV, XV, XVI and Figs. I and II) indicated the probable suitability, (using aqueous ethanol (1 : 1) as reaction medium and Raney Nickel as catalyst) of three types of reaction media containing (a) HCl; (b) NaOH (3-5%) and (c) p-toluene sulphonic acid (1%). With the last-named, it would be necessary, in order to obtain the desired results, to subject the total crude hydrogenated product to a subsequent rehydrogenation in presence of alkali (3%).

The results obtained under these conditions (Exps. 73, 74, 75 and 76, Tables XIV and XVI) are shown below:

No. of Experiment	Addendum	Chloroform soluble as % K.L.	% of Original methoxyl left in the Chloroform- soluble fraction *	*
(a) 73 (b) 74	HCl NaOH	110 12 3	87 .4 77 . 5	
(c) (75 +(76	p-toluen e sulphonic a	acid ¹³⁹	84.3	

The methoxyl values are calculated as total alkoxyl.

The petroleum ether soluble fraction from Exp. 73 contained 43.8% of the Klason lignin as alkali soluble phenols. On the other hand, the ethyl ether soluble portion, from Exp. 74 and combined Exps. 75 and 76 contained distillable oils amounting to 82.8 and 85.0% respectively. The disadvantages using an acid medium are: (a) poisoning of the catalyst which does not take place in presence of alkali; in fact, in the alkaline medium the catalyst was still found to be active (pyrophoric) after removal from the bomb; (b) the tendency towards increased polymerization: which is minimized in alkali due to the blocking of the phenolic hydroxyl groups and (c) the increased tendency towards formation of hydroaromatic derivatives at a lower temperature (156). The disadvantage associated with the use of p-toluene sulphonic acid was that it could only be used effectively in a two-stage hydrogenation process.

To overcome these marked disadvantages it appeared desirable to operate in an alkaline medium under the following conditions: (a) solvent medium, aqueous ethanol (1:1) containing NaOH (3%); (b) catalyst, Raney nickel; (c) temperature, 165° C. and (d) time, four hours. Two experiments (Nos. 80 and 81, Flow Sheet III) were carried out under these conditions.

D. Preliminary Hydrogenations of Maple Wood Meal in Alkaline Aqueous-ethanol (1:1) (Exps. 80, 81, Flow Sheet III).

In each case the quantities and conditions of hydrogenation were identical (60 g. wood meal, ethanol-water (873 cc.), sodium hydroxide (27 g.), Raney nickel, (48 g.), temperature 175°, time 8 hours). The time increase was necessitated by the change from the smaller to the larger bomb.

The crude hydrogenated products were separated into solvent-soluble groups by the methods shown (Flow Sheet 111)

- 62 -

and a summary of the yields is given below (Table VII).

TABLE VII

Summary of Yields from Small-scale Hydrogenation. Exps. 80 and 81 and Flow Sheet III.

Nature of Material	% of Klason Lignin	% of Methoxyl in Wood
Total CHCl ₃ soluble fraction (F.)	104	67.9
Ethyl ether-soluble fraction (G.)	91.2	59.3
fractions (0,J)	47.6	
Total Recovery (a) Lignin Products Obtained (b) Cassing-off during re-	75.1	
hydrogenation of (P,0,J)	N) 19.1	

The alkali-soluble fraction (0) (Flow Sheet III) was fractionally distilled (p.114). Analyses of the resulting three constant-boiling portions (flats) unfortunately did not yield data in agreement with known anticipated structures. This apparent non-homogeneity of the products received further confirmation in the non-isolatability of their phenyl urethanes, and was evidently due to the presence of partially ethoxylated derivatives presumably originating from the ethanol used. If this were the case it would increase, to a marked degree, the difficulty of identification of the hydrogenated products. It was therefore considered advisable to select a more suitable hydrogenating medium.

E. Choice of Solvent for Hydrogenation

In view of the apparent partial ethoxylation occurring in the aqueous alcoholic medium during hydrogenation, (Exps. 80, 81, p.110), and the fact that aqueous dioxane (1:1) was found to be equally as efficient as a solvent (Exps. 61, 62, Table XV) a further hydrogenation (Exp. 82, p.11g) was carried out in the latter medium. Analyses for alkoxyl and methoxyl made on the solvent-soluble hydrogenated lignin are summarized below.

No. of Exp.	Solvent	Product Analysed	Ana	alyses	
		· · ·	Total Alkoxyl Calc. as (OCH3) %	(OCH3)3%	(OEt) %
80, 81 (page 110)	Ethanol- water (1:1)	Fraction #255 from Phenol frac- tion (C) Flow Sheet III	[34.0	30.2	5 .6
82 (page 1 1 8	Dioxane- water (1:1)	Petroleum ether-soluble fraction Flow Sheet IV	23.6	23.4	0.29

Apparently, ethoxylation had occurred in the aqueous ethanol medium but not in the aqueous-dioxane and the latter solvent was therefore used in all subsequent hydrogenations. F. Preparation of Experimental Material by Hydrogenation of Maple Wood Meal in Alkaline Aqueous Dioxane (1:1) using Raney Nickel as Catalyst.

The factors concerned in the development of a suitable process for the extraction of the native lignin from maple wood meal by a combined process of hydrogenolysis and hydrogenation have been reviewed above. The best conditions, in the light of these results, for obtaining a maximum yield of extracted hydrogenated lignin in the form of solvent-soluble, monomeric, identifiable aromatic type derivatives are outlined in the Experimental Section p.120. These embrace the use of maple wood meal; aqueous dioxane (1:1) as hydrogenating medium; Raney nickel as catalyst; temperature 175° and time 6 hours in the large (2500 cc. capacity) Aminco bomb.

A considerable number of duplicate runs was made to provide the necessary experimental material designated as "Maple Lignin (C)". The analysis of this material necessitated a series of investigations involving the following factors: (1) distillability of products, (2) group separation by distillation and chemical separation and (3) identification of products.

1. Distillability of Products.

Simple removal of the solvent (aqueous dio ane) left a reddish viscous oil, "Maple Lignin (C)" which was vacuum distillable from a Claisen flask to the extent of 59.9% or 68.1%. by weight, of the original Klason lignin. This large fraction could be distilled repeatedly under the same conditions without decomposition or resinification. Rehydrogenation of the residuel resin (40.2% or 45.6% of the original Klason lignin) in pure dioxane, using copper chromium oxide as catalyst and a higher temperature (280° instead of 175°) yielded around 17.7% of readily distillable identifiable propylcyclohexane derivatives (p.137). The total readily distillable hydrogenated lignin thus obtained amounted to 85.8% of the original native lignin.

2. Group Separation of the Crude "Maple Lignin (C)" by a Combined Process of Distillation and Chemical Separation

The <u>first stage</u> involved simple fractionation from a Claisen flask to give (a) a distillate boiling below 150° (or 180°)/1mm.; (b) a second distillate boiling below 250°/1mm. and (c) a non-distillable resin (p.123). The <u>second stage</u> consisted, on the one hand, of a simple extraction treatment of the <u>first</u> distillate with aqueous bicarbonate solution to remove acidic substances, followed by a highly efficient fractionation and, on the other hand, an extraction with water of the <u>second</u> distillate also followed by fractionation of both the watersoluble and -insoluble fractions. (Flow Sheet I.).

In order to obtain additional amounts of distillable and identifiable products two other procedures were adopted: (i) the <u>third</u> non-distillable resin fraction (c) Flow Sheet I. was rehydrogenated at a "higher" temperature (280° as compared with 175°) and the resulting hydrogenated products fractionally distilled and (ii) the total non-constant-boiling material isolated from the fractionations of the above materials was also

- 66 -

rehydrogenated under the conditions specified under (i).

<u>3. Identification of Products by Fractionation</u> and Chemical Identification.

This was accomplished in a series of four stages (Flow Sheet I.). The first stage, namely a Claisen distillation, has been reviewed in the case of crude "Maple Lignin (A)" section 1, p.65 . The resulting three Claisen distillates, (a) the distillate boiling below 150° (or 160°)/1mm. and bicarbonate extracted; (b) the distillate boiling below 250°/1mm., water-soluble fraction; and (c) the distillate boiling below 250°/1mm. water-insoluble fraction, were now separated by fractional distillation through the highly efficient (21 or 25-plate) columns, each distillation involving upwards of three to four days continuous operation.

The third Claisen non-distillable resin fraction was subjected to a rehydrogenation at a higher temperature (250° as compared with 175°) in order to degrade it into simpler distillable products suitable for chemical identification. In addition the total non-constant-boiling fractions, isolated in the various fractionations, were also rehydrogenated and then again submitted to a careful refractionation followed by chemical identification.

These initial treatments are summarized in Flow Sheet

I.



STAGE I. Description of Flow Sheet I.

This consisted of a simple Claisen distillation of the "Maple Lignin (C)" (p.123) and has been described in section 1, (p.65).

STATE II. (a, b, c,) This involved careful fractionation of the three products, isolated as shown in Flow Sheet I. STACE IIa.

The complete fractionation of the pale yellow mobile oil (24.6 g.) from 500 g. maple wood meal, is shown in Fig.VIII, p.)27. Regions of constant-boiling material (flats) were indicated by the constant refractive index values within the ranges :

(1) 1.5230 - 1.5251 (A)

(2) 1.5323 - 1.5344 (B)

Products (A) and (B) were identified as 4-hydroxy-3-methoxyphenyl ethane and 4-hydroxy-3,5-dimethoxyphenyl ethane respectively by the preparation of their p-nitrobenzoate derivatives and comparison with the corresponding derivatives obtained from authentic samples of 4-hydroxy-3-methoxyphenyl ethane and 4-hydroxy-3,5-dimethoxyphenyl ethane.

STAGE IIb.

Fractional distillation of this material (5.0 g.) gave no regions of constant refractive index.

STAGE IIC.

The complete fractionation of the pale yellow oil (33.3 g.) is shown in Fig. IX., p.133. A "Flat" was indicated

by the constant refractive index values within the range; 1.5320 - 1.5339, and this distillable material was identified as 4-hydroxy-3,5-dimethoxyphenyl ethane, (See Stage IIa.). From the non-distillable portion boiling below 250°/1mm. a crystalline material separated. After removal of the occluded oils by washing with ether it was identified as 2-(4-hydroxy-3,5-dimethoxyphenyl) ethanol. This was accomplished by methylating with diazomethane, preparing an Q-maphthyl urethane of the methylated product, and determining the mixed melting point with the urethane prepared from an authentic sample of 2-(3,4,5trimethoxyphenyl) ethanol.

STAGE III.

Details of the rehydrogenation of the run are given on p.137. Refractionation of the recovered rehydrogenation products is Shown in Fig. X. "Flats" corresponding to refractive index ranges of 1.4882 - 1.4900, 1.4909 - 1.4910 and 1.4992 -1.5007 were obtained. Ultimate analyses of these flats are given on p.141, but the compounds were not identified. STAGE IV.

Details of the origin and rehydrogenation of the combined non-constant boiling portions isolated in the various fractionations are given on p. 142, and Fig. XI. "Flats" were indicated by the constant refractive index values within the ranges:

(1) 1.4582 - 1.4611 (C)
(2) 1.4616 - 1.4629 (D)
(3) 1.4650 - 1.4664 (E)

Products (C), (D) and (E) were identified as 4-ethylcyclohexanol, 4-n-propylcyclohexanol and 3-cyclohexyl-1-propanol respectively by preparation of their urethane derivatives and comparison with the corresponding product from authentic samples of these compounds.

G. Resume of Yields Obtained in the Hydrogenation of Maple Wood Meal in Aqueous Dioxane (1:1) using Raney Nickel as Catalyst.

Two series of experiments (A) and (B) were performed using in each case 500 g. maple wood meal; the material in each case being hydrogenated in a series of seven runs as outlined in Flow Sheet V. The crude hydrogenated product left in each case after removal of the solvent was then subjected to a straight distillation, under reduced pressure, from a Claisen flask. The experimental data of <u>Series A</u> are concerned entirely with the Claisen distillate boiling below $150^{\circ}/1$ mm. obtained from 500 g. wood meal. Those of <u>Series B</u> relate to (1) the total Claisen distillate boiling in the range $180 - 250^{\circ}/1$ mm. and (2) the non-distillable resin boiling above $250^{\circ}/1$ mm. obtained similarly from a further 500 g. of maple wood meal.

The yields of hydrogenated extracted lignin from 500 g. of maple wood isolated either as fractionally distillable products through either the 21 or 28-plate columns, or obtained as a crystalline material boiling above 180°/1mm. are shown in Table VIII.

- 71 -

TABLE VIII.

Yields of Lignin Products from

Hydrogenation of Maple Wood Meal,

After Distillation through a 21,28-plate Column.

Nature	of	Material	Weight of distillate g.	Distillate as % of Klason Lignin
Series	Α,	bicarbonate-insoluble fraction boiling belo 150°/lmm.	₩ 24.51	23.0
Series	Β,	fraction boiling above 150°/1mm.	18.54	17.4
Series	Β,	crystalline material from fraction boiling above 180°	ç 6.6	6.2
Series	В,	product from rehydro- genation of resins	20.6	19.4
		Total Recovery	70.25	66.0

1. Identification of Distillable Products.

The results obtained by the careful final fractionations of Series A, Series B and Series (A. + B.) were graphed by plotting refractive index against weight of distillate. The results obtained from Series A. are shown in Fig. VIII, those from Series B in Fig. IX. and X. and from Series A. and B. in Fig. XI. An examination of these curves showed the presence of a number of constant-boiling fractions (flats) as judged by constancy of refractive index. The flats associated with each Series are indicated clearly by the numberings shown for the individual fractions in Table IX. Also included, in this table, are the corresponding weights of these fractions, the percentages of each, calculated on a weight basis and on the weight of original Klason lignin in the wood, and the data on their refractive indices.

<u>2. Identity of Constant-boiling Fractions.</u> (Flats) (Table IX.).

These fractions could represent either pure compounds or constant-boiling mixtures and were therefore subjected in each case to a rigorous chemical investigation as described in the Experimental Section. Six pure products were definitely identified, namely, 4-hydroxy-3-methoxyphenyl ethene (LXIII), 4-hydroxy-3,5-dimethoxyphenyl ethane (LXIV), and 2-(4-hydroxy-3,5-dimethoxyphenyl)-ethanol (LXV),



TABLE IX.

SUMMARY OF THE DISTILLABLE LIGNIN PRODUCTS FROM THE HYDROGENATION OF MAPLE WOOD (500g.) EXISTING AS FLATS

Nature of	f Material	Inclusive Fraction Numbers	Weight of Flat g.	Flat as % of Klason Lignin	Range of Refractive Indices 25°	Most Common Refractive Index
Series A:	Bicarbonate - in- soluble fraction of distillate boiling below 150°/1mm.	41 3-42 5 44 2-48 6	2.3 9.4	2.16 8.82	1.5230-1.5251 1.5323-1.5344	1.5240 1.5340
Series B:	Water-insoluble fraction of dis- tillate boiling above 180°/1mm.	518-549 511-517 561-563	7.05 1.62 0.74	6.62 1.52 0.69	1.5320-1.5339 1.5304-1.5319 1.5364-1.5370	1.5330 1.5308 1.5370
	Crystalline Material Product from re- hydrogenation of resins(Flow SheetI	- 663-639 670-673) 683-694	6.6 3.27≠ 2.83≠ 7.28≠	6.20 3.07 2.67 6.83	- 1.4882-1.4900 1.4909-1.4910 1.4992-1.5007	- 1.4898 1.4910 1.4998
Series A Total Rec	and B Product from re- hydrogenation of a fraction not inclu ed in above flats	692-702 11704-715 117716-720 a-722-726	0.54 1.99 0.92 0.87 45.43	1.87 0.86 0.82 42.7	1.4470-1.4488 1.4582-1.4611 1.4616-1.4629 1.4650-1.4664	1.4470 1.4584 1.4620 1.4656

f Calculated from Fig.X on basis of 500g.Maple Wood.

.74 -

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Table X

Summary of Yields of Identified Lignin Products from the Hydrogenation of Maple Wood Meal (500 g.)

	Compound	Fraction Numbers	Page no. Expt. Pt.	n ²⁵ D	Weight g.	% Klason Lignin	M.P. of Derivatives
•							p-Nitrobenzoates
⊥.	4-Hydroxy-3-methoxy- phenylethane	413-425	128	1.5240	2.3	2.16	9 5 -99 *
2.	4-Hydroxy-3,5-di- methoxyphenyl- ethane	442 -486 518-549	128	1.5340 1.5330	9.4 7.05	8.82	153.5-154.5 153.5-154.5
							<u>a-Naphthyl urethane</u> of methylated product
3.	2-(4-Hydroxy-3,5-di- methoxyphenyl)- ethanol	crystal- line	135	-	6.6	6.2	132 - 133
							Phenyl urethane
4.	4-Ethylcyclohexanol	704-715	145	1.4484	1.99	1.87	113.5 - 114.5
5.	4-n-Propylcyclo- hexanol	716-720	145	1.4620	0.92	0.86	123.5-124.5
6.	3-Cyclohexyl-l- propanol	722-726	145	1.4656	0.87	0.82	- 83 -84
				Recovery	29.13	27.35	

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* Reported by Reichstein (157) as 100°.



Their origin, identification, weight obtained and percentage on a Klason lignin basis and other physical properties are summarized in Table X.

The yield of identified ethylphenol (C_6 -C-C) products was 23.8% and that of cyclohexane derivatives 3.55%, or a total combined yield of 27.35% based on the original weight of Klason lignin present in the wood (500 g.). Three of them, namely, (LXIII), (LXIV) and (LXV) have been isolated for the first time as lignin degradation products.

H. Relation of the Experimental Results to the Structure of Native Lignin

The bearing of earlier work and notably those results from ethanolysis and oxidation of wood and its hydrogenation in a neutral dioxane medium over copper chromium oxide were discussed in the historical review and the general conclusion drawn that native lignin is derived from one of several propyl phenol building stones, the most important of which appears to be oxy-coniferyl or oxy-syringyl alcohol and/or their equivalent keto forms

 $(R-CH_2-CO-CH_2OH \xrightarrow{} R-CH = C(OH)-CH_2OH)$ (R = 4-hydroxy-3-methoxyphenyl or 4-hydroxy-3,5-dimethoxyphenyl)

The conclusion also seemed permissible that these units are present largely as dimers and to a lesser extent as higher polymers (trimers and tetramers) and certain tentative suggestions made by Hibbert regarding their structure were given and it is of interest to enquire as to the extent to which such views find support in the present experimental results.

(1) Non-identity of Spruce and Maple Native Lignins.

The previously observed readier extractability (by ethanolysis and oxidation) of the syringyl components of the native lignin from maple wood, as compared with those of the guaiacyl type, finds confirmation in the author's results on the hydrogenation of maple wood in an <u>alkaline</u> medium. They show the presence of guaiacyl and syringyl components in a ratio of 1 to 10.

(2) Structure of the isolated products.

The aromatic character of three of the author's identified hydrogenated products (4-hydroxy-3-methoxyphenyl ethane, 4-hydroxy-3,5-dimethoxyphenyl ethane and 2-(4-hydroxy-3,5-dimethoxyphenyl) ethanol) as well as those (3-(4-hydroxy-3,5,-dimethoxyphenyl)-1-propanol, 3(4-hydroxy-3,5-dimethoxyphenyl)-1-propane, dihydroconiferyl alcohol) isolated by Brewer in a concurrent investigation in these laboratories by hydrogenation of maple wood in an initially <u>neutral</u> medium (ethanolwater 1:1) would seem to have an important bearing on the problem of lignin structure since this is the first time that <u>aromatic</u>, as contrasted with <u>hydroaromatic</u> products have been isolated as hydrogenated derivatives of degradation products from native lignin. The Brewer derivatives are of the C6-C-C-C type, principally syringyl in character (9.63% as compared with guaiacyl 0.84%, calculated on the original Klason lignin) thus again illustrating the easier breakdown, and lesser complexity of the syringyl lignin components. The high proportion of terminal carbinol-containing units present in his products would seem to support the theory of Hibbert as to their presence, in the syringyl derivatives either as such or as a relatively simple type of oxygen linked dimer R-C-C-CH2-O-C-. The presence, among the writer's hydrogenation products, in relatively high yield, of aromatic C_6 -C-C units is difficult to interpret and is an indication of the more drastic degradation arising from the presence of the alkali.

The isolation of the syringyl derivatives 4-hydroxy-3,5-dimethoxyphenyl ethane (LXIV) and 2-(4-hydroxy-3,5-dimethoxyphenyl) ethanol (LXV) would seem to indicate their derivation from a polymeric (probably dimeric) form in which the side chains of the two building units are united through an oxygen linkage in the β position. The presence of this type of linkage in all plant resins (lignans) has been emphasized by Erdtman and Haworth. Such a dimer could also contain terminal ethanol groups which would be removable under the drastic hydrogenating conditions employed, while being retained under the less drastic conditions used by Brewer (neutral medium).

- 78 -

(3) Relation of the Isolated Hydrogenation Products to the Higher Lignin Folymers (Resins)

The assumptions previously made as to the greater complexity of the guaiacyl lignin components find confirmation in the similar character of the hydrogenation products isolated, by the writer, from the <u>hydrogenated resins</u> obtained from maple wood and those recently isolated by Mead, in these laboratories, by a rehydrogenation of the analogous hydrogenated lignin resins isolated from spruce wood.

In the former case the resins on rehydrogenation yielded products, essentially dimeric (not monomeric) in type as shown by ultimate analyses. These dimeric products were found to have the same general characteristics (empirical analyses, refractive indices, boiling points, and molecular weights) as those obtained from the analogous spruce resins, which of necessity were guaiacyl derivatives.

VI. EXPERIMENTAL RESULTS

A. <u>Preliminary Experiments on Hydrogenation of Maple</u> <u>Wood Meal in Aqueous Ethanol (1:1) followed</u> by Re-hydrogenation

1. Hydrogenation Apparatus and Technique

(a) Apparatus

The equipment used in all hydrogenation experiments consisted of: (1) a 500 cc. capacity high-pressure reduction apparatus manufactured by the Parr Instrument Company and described in their bulletin E-44; (2) a 2500 cc. capacity highpressure hydrogenator (No. 406-Ola, catalogue #406; American Instrument Company); (b) a type 100 Variac manufactured by the General Radio Company which was used to control the temperature; (4) a hydrogen pressure "booster" pump (#406-135, American Instrument Company) which made it possible to increase the pressure to any desired value above cylinder pressure; (5) a slide-wire potentiometer calibrated to read temperatures directly, was used to measure voltages from a copper-constantin thermocouple, the hot junction of which was inserted in a well in the bomb.

The arrangement of the hydrogenation equipment is shown in Plate 1.

PLATE I.

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- 81 -

HYDROGENATION APPARATUS.



- A. Parr Apparatus.
- B. Aminco Apparatus.
- C. Booster Pump.
- D. Slide-wire Bridge.

(b) Technique

The charge, consisting of the material to be hydrogenated plus solvent and catalyst, was placed in the bomb and the latter flushed out three times with low pressure (500-800#) hydrogen. The required pressure was then obtained with the booster pump and the bomb allowed to rock for 10-15 minutes before heating was begun. Pressure and temperature readings were taken at frequent intervals during the course of the hydrogenation and the hydrogen concentration calculated from the gas law PV = nRT. In the small bomb the absorption of hydrogen could be interrupted at any desired time by quenching the bomb in cold water.

2. Preparation of Hydrogenated "Maple Lignin (A)"

(a) Solvent Extraction of Maple Wood Meal

Maple wood meal (40 mesh) was extracted continuously with a mixture of ethanol and benzene (4:1) for 48 hours, then with ethanol for 24 hours, washed overnight with hot water, air-dried for 2-3 days and finally dried in a vacuum oven at $50-55^{\circ}/15$ mm. for 36 hours.

Analyses of the dried wood meal used in all experiments (except where otherwise noted) gave the following results: moisture, 3.5%; OCH₃, 5.95% (159); Klason lignin, 20.6% (160).

(b) Hydrogenation of Solvent-extracted Maple Wood Meal

A sufficient supply of hydrogenated lignin for the rehydrogenation experiments was obtained from eleven runs, described in detail in Table XI. In each case the total hydrogenated mixture was filtered to remove residual pulp and catalyst and the filtrate extracted three times with chloroform (200 cc., 175 cc. and 175 cc. portions) in which the degradation and hydrogenation products from the carbohydrate constituents of the wood are insoluble. The chloroform solution was dried over anhydrous sodium sulphate and concentrated to dryness under reduced pressure ($50^{\circ}/10-15$ cm.). The hydrogenated "Maple Lignin (A)" thus obtained was a viscous dark red oil.

Preliminary investigations of this material by Brewer (142) showed:

(i) the product, obtained in high yield (80-90% of the Klason lignin), contained free phenol groups. The original methoxyl groups were also still intact, indicating the essentially aromatic composition.

(ii) carbonyl groups and ethylenic linkages were absent.

(iii) when refluxed with ethanol-HCl (2%) for 48 hours apparently little or no degradation occurred as indicated by the solubility in petroleum-ether $(30-50^{\circ})$.

(iv) the marked ease of solubility in chloroform and, to a large extent in petroleum ether indicated a simpler state of

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PREPARATION OF HYDROGENATION "MAPLE LIGNIN (A)" (SECTION A2)

Ba	d	ŭ	harge		Moles Ho	1001 1001	E	1	•
N	EN	ple Wood≠ g. (wet)	E tOH-H20 1:1 cc	RaN1 g. (wet)	absorbed /100g.wood	time brs.		HYArogena g.	%Klason Lignin
HHHONNON TON	manon-ana voro	666 666 666 666 666 666 666 666 666 66	1000 900 900 900 900 900 900 900 900 900	2 c z z z z z z z z z z z z z z z z z z	0.64 0.66 0.07 0.63 0.63 0.63 0.63 0.63 0.63 0.63 0.63	6.7 6.7 6.7 7 8.2 7 7 7 7 7 7 7 7 7 7	187 185 185 185 185 185 185 185 185 185 185	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	78 78 79 70 70 70 70 70 70 70 70 70 70 70 70 70
1 16	Initi The w	al pressur(ood meal u(H20, 2	e (cold) = 295 sed in runs 27 2.83%; 00H ₃ ,	50 ± 50 to 39 6.25%;) lb/sq.in. had the follc Klason ligni	wing analy n; 21.3%	Si 8		

84

aggregation than that found in other extracted lignins such as cuproxam lignin, ethanol lignin etc.

The necessity for rehydrogenation of this lignin was apparent if greater yields of monomolecular units, aromatic or hydroaromatic in type, of use in elucidating the structure of native lignin, were to be obtained. This hydrogenated "Maple Lignin (A)" was used to determine the suitability of various catalysts to be employed in its rehydrogenation.

3. Investigation of Hydrogenation Catalysts

(a) Preparation of Catalysts

(i) Raney Nickel (RaNi)

The method of preparation followed was that described by Mozingo (161).

(ii) Copper chromium oxide (CuCrO)

This catalyst was prepared according to the procedure given by Connor, Folkers and Adkins (162) except that double quantities were used.

(iii) Nickel chromium oxide (NiCrO)

The method employed was that of Frazer and Jackson (145) (iv) Zinc chromium oxide (ZnCrO) The procedure of Sauer and Adkins (96) was used.

(v) Copper aluminum oxide (CuAlO)

The preparation of this catalyst has been reported by Ipatieff and Haensel (149) but no quantities were given in their published paper and the following procedure was developed in analogy with similar preparations. Copper nitrate (235.6 g.) and aluminum nitrate (43.0 g.) were dissolved in 1 litre of water and a 10% ammonium carbonate solution (680 cc.) added with continuous stirring. The resulting suspension was heated slowly to 80°, then allowed to cool and filtered. Ammonium carbonate solution was added to the filtrate until no further precipitation occurred. The combined precipitates were dried in an air bath by heating at 220-230° for 7-1/2 hours and yielded a finely divided black powder (74 g.).

(vi) Palladiumized Charcoal

Preparation of Purified Charcoal - Animal charcoal was heated for 2-3 days with a mixture of 20% hydrochloric acid and a few cos. of concentrated nitric acid until the filtrate gave no test for iron. The charcoal was filtered, washed with hot water until free from chloride and dried at 100° . The purified material was heated with a luminous flame for 15 minutes under reduced pressure (15 mm.) and then allowed to cool slowly.

Preparation of the Catalyst - Formaldehyde (10 cc. of 40% solution) and the purified charcoal (3 g.) were added to a cold (0°) solution of palladium chloride (0.5 g.) in a mixture of water (25 cc.) and concentrated hydrochloric acid (0.5 cc.). A 50% solution of potassium hydroxide (10 cc.) was added dropwise with stirring to the <u>cold</u> suspension. The temperature was

- 86 -

then raised to 60° for a few hours. The catalyst was filtered, then washed with water, dilute acetic acid and hot water and finally dried in a vacuum desiccator.

(b) Activation of the Catalysts by Reduction

The apparatus used consisted of a large, electrically heated, "Hevi-Duty" furnace containing a combustion tube 3-1/2 feet long and 1.7 cm.I.D. The powder to be reduced was spread along the length of the combustion tube and held in place at each end by asbestos stoppers containing inlet and outlet tubes for the reducing gas mixture. Reduction was accomplished by a regulated mixture of nitrogen and hydrogen. The combustion tube was rotated slowly by means of an electric motor.

Nickel chromium oxide and zinc chromium oxide were successfully reduced in this manner according to directions given in the literature (145, 96) but nine attempts to reduce a copper aluminum catalyst failed to yield a highly pyrophoric product. The reduced catalyst was extremely active, (pyrophoric) while hot but lost its activity upon cooling under a solvent such as benzene or methylcyclohexane.

(c) Testing of Catalytic Activity

The activity of the Raney nickel catalyst was tested with benzene (93, p. 50 and 57) and the copper chromium oxide with acetone (93, p. 50). Both were found satisfactory under the conditions recommended by Adkins (93). The nickel chromium oxide catalyst was tested on benzene and on cinnamyl alcohol. Benzene (44 cc.) was completely reduced in 7-1/3 hours at 210-220°. using 4 g. of catalyst and an initial hydrogen pressure of 3040 lbs/sq.in. Freshly distilled cinnamyl alcohol (16.35 g.) was hydrogenated over nickel chromium oxide (3.0 g.) in dioxane (150 cc.) at an initial hydrogen pressure of 2960 lbs/sq.in. Between 65-107° 1 mole of hydrogen was absorbed per mole of cinnamyl alcohol and

The activity of the zine chromium oxide catalyst was shown to be satisfactory by the reduction of acetone (96). Activity tests on each of the copper aluminum oxide preparations were made on solutions of acetophenone in cyclohexane (149). The failure of these solutions to absorb hydrogen indicated the oatalysts to be inactive.

at 150-160° a further 2.3 moles over a period of 1-1/2 hours.

(d) <u>Rehydrogenation of Hydrogenated "Maple</u> Lignin (A)" (Section A2)

A series of runs was made to determine which of the above catalysts was most satisfactory for the rehydrogenation and complete details are given in Table XII.

(e) <u>Claisen Distillation of Rehydrogenation Products</u> of Hydrogenated "Maple Lignin (A)"

The reduction products were centrifuged to remove the catalyst and the clear supernatant liquor concentrated under

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Tab	

Rehydrogenation of Hydrogenated "Maple Lignin (A)" (Section A2)

un o	Lignin used g.	y Lignin Distillable (Spath)	vol. Solvent cc.	t Catalyst	Cata- Lyst g.	Temp.	Time hrs.	H absorp- tion moles per 100 g. lignin	b.p. 101°C. g.
1050	10 6.08	32.2	240 150	ZnCrO ZnCrO	10	210-215 260	8 7-1/2	0.98 0.98	9.59 6.34
180	10	34.1	250	RaNi Ptcl ₄	0.15	200-210	6-1/2	1.1	۰ ۳ ۱
0 0	ရိုက	36.6 36.4	150 150	CuCrO Nicro	6 0	250 200-214	8 9-1/2	0.0 4.0,	بة 20 بالم
	ω <mark>ί</mark>		50 20 20	ZnGrO CuGrO	ഗവ	225-228	1-1/3	0.4 0.0	
A A L	9	I	200 150	CuCrO	مە	225-230 225	1-1/4	0.8 5.08	- 65 - 7
ຸ	Ъ	42.3	100	GuGrO	3.0	thermo cou working,re	Iple not ached hed	13	
28 28	Ś	,	175 180	CuCrO CuCrO	~~ 00	225-235 225-235 225-235	1,10 1,10 0,110	0.26	3.48 1 39
- 4	ſ	36.0	100	Rani	# 60	225-228	1-1/2	12.2	1.26
~~~	ς Γ	36.5	100	RaNi	₩. 160	(175)	1.1 1-1/4	1.06	1.86
الأربغ	ഗഗ	34.6	100 155	ZnCr0 CuCr0	3.0	29 to 297 223-230	2-1/2 1-1/2	80. 50	3.06 0.06
	ι Γυ	0.04	100	NIGrO	ot	<pre>&lt; 115 &lt; 200-250 &lt;250-293</pre>	1/2 1-3/4 2-1/4	04.4 0.4.4	1.37
22 23 23	3.0	t	100 118	Pd charcoal Pd charcoal		55-60 100-115	2-1/2 1-1/3	0.9 1.66	2.75

Run No.	Lignin _used g.	Spath Bulb Distillability of Lignin (A) used %	Distillation Pressure (microns)	Wt. prior to distil- lation g.	Wt. Resin g.	Wt. Distil- late g.	Recov- ery %	Disti] labili
25	10		200	9.59	5.842	3.479	98.2	36.6
25B1		-	400	3.512	0.270	2.00	96.5	89.0
26	6.08	32.2	200	7.96	4.15	2.197	80.0	34.6
25	10	34.1	90	11.5	4.212	5.326	96.6	55.8
20	10	36.6	80	8.5	0.266	6.202	96.5	92.3
29	5	36.4	100	5.5	2.358	2.768	95.0	54.0
30 31	5	40.8	200	5.63	2.470	1.810	94.5	42.3
374	10	34.6	300	6.778	1.002	4.559	95.4	84.5
<b>H</b> 2V	5	42.3	100	3.402	0.423	2.451	102	87.5
117	5	-	500	2.71	0.269	1.48	?	85.0
<b>モラ</b> 海九	5	36.0	500	1.773	0.115	1.125	94.5	90.5
<del>тт</del> ЦС	5	34.6	80	1.662	0.218	1.22	89.5 [·]	86.0
中0 117	5	36.5	70	2.225	0.094	1.53	77.5	89.0
	ノ 5	40.0	100	1.35	0.83	0.38	92.0	30.4
51 52B	3.0	-	100	3.32	1.13	1.53	96.7	57.4

TADLE ALLI.

Claisen Distillation of Hydrogenated "Maple Lignin (A)" Hydrogenation Products

Note: The temperature of distillation was 250?

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t
reduced pressure  $(50-60^{\circ}/5-15 \text{ om.})$ . The rehydrogenation product was distilled from a small Claisen flask. The details of these distillations are given in Table XIII.

# 4. Fractional Distillation Apparatus and Technique

The crude rehydrogenated "Maple Lignin ( $\blacktriangle$ )" was a mixture of closely related aromatic and hydroaromatic derivatives, the separation of which necessitated the employment of a highly efficient fractionation column. The electrically-heated high plate efficiency fractionating units designed in these laboratories by Cooke and Bower (140) (Fig.III, IV) proved very satisfactory for the purpose.

## (a) <u>High-vacuum Apparatus</u>

A Cenco "Hi-Vac" oil pump, backing a mercury diffusion pump, was used to obtain the vacuum and a McLeod gauge served for pressure determinations in the range 0.05-2.0 mm.

#### (b) Fractionating Columns and Receivers

Two 23-inch vacuum-jacketed columns (illustrated in Fig. III) were used, one built by Bower (28 plates), the other by the author (21 plates). A small vacuum-jacketed micro column (circa 7 plates) (Fig. IV) was used for the fractionation of smaller samples (0.5-2.0 g.).

The column packing was made of Monel metal gause (60 mesh) formed in the following manner: a narrow strip of the gauge with the edges smoothed down and fitting easily into the





inner tube of the column, was twisted in order to obtain the maximum number of "platelets", at right angles to each other, along the entire length of the strip (Fig. V). This packing was then adjusted to fit snugly into the column tubing. The column efficiency was determined by the method of Morton (163) on a mixture of n-heptane and methylcyclohexane. The analytical data of Bromily and Quiggle (164) were used to evaluate the results.

The column was wound with 7 feet of nichrome ribbon (6 ohms/ft.) for effecting adiabatic control. The still-pot was heated by immersion in either a Wood's metal bath or a wax bath wound with 33 feet of nichrome wire (1.5 ohms/ft.).

The distillation receiver was so designed that a number of fractions could be obtained without breaking the vacuum by simply turning the external handle of the receiver holder (Fig.III).

#### (c) Electrical Heating Apparatus

The electrical circuit shown in Fig. VI made it possible to vary the column voltage from 0 to 66 volts and the bath voltage from 23 to 71 volts, ranges which permitted of all temperature variations required in this work.

## 5. Rehydrogenation of "Maple Lignin (A)"

The following rehydrogenations were all carried out with hydrogenated "Maple Lignin (A)".



SPIRAL SCREEN COLUMN PACKING.

- 95 -FIGURE V.







- Notes. 1. With switch at position A the voltage across the column may be varied from 0 to 29 volts.
  - 2. With switch at position B the voltage across the column may be varied from 22 to 66 volts.

## (a) Rehydrogenation over CuCrO at 250° for 8 Hours

A portion of the rehydrogenated product (5.23 g.) of Run 29 (Tables XII and XIII) was first submitted to a Claisen distillation and then fractionally distilled through the 28-plate column. The results are listed below.

Fraction	Weight	n ²⁵ D
210	0.035	1.4583
211	0.125	1.4625
212	0.247	1.4640
213	0.182	1.4639
214	0.199	1.4660
215	0.124	1.4666
216	0.360	1.4659
217	0.206	1.4665
<b>918</b>	0.140	1.4679
219	0.320	1.4800
220	0.190	1.4806
230	0.416	1.4846
200 271	0.116	1.4859
070	0.343	crystalline
<b>606</b> 977	0.108	1.4909
200 074	0.274	1.4930
204	0 190	1.4970
200	0.150	1,4955
200	0.100	2 . 2

# Distillation Weight Balance

Weight Weight Weight	of of of	material fractionated distillate resin	5.23 3.71 0.19 0.53	g•
Weight Weight	of in	cold-trap	0.21	
-		Recovery -	4.64	(88.7%)

(b) Rehydrogenation over CuCrO at 225° for 2-1/2 Hours

"Maple Lignin ( $\lambda$ )" was hydrogenated for 1-1/2 hours at 225° over CuCrO (Run 37, Table XII) and the filtrate rehydrogenated for 1 hour under the same conditions (Run 37A, Table XII). The final product was distilled in a Claisen flask and the distillate (4.56 g.) fractionated, through the 28-plate column previously described, with the following results.

Fraction	Weight	n25 D
200	0.180	1.4641
201	0.145	1.4653
202	0.097	1.4722
203	0.819	1.4797
204	0.180	1.4810
205	0.350	1.4830
206	0.230	1.4889

(c) Rehydrogenation over RaNi at 2250 for 2-1/4 Hours.

The product (1.43 g.) obtained by the hydrogenation (Run 47, Table XII) and subsequent Claisen distillation (Table XIII) of "Maple Lignin (A)" (5 g.) in methylcyclohexane (100 cc.) over RaNi (8 g.) was fractionally distilled through the micro column with the following results.

Fraction	220	221	222	223	224	225	226	227	228	229
Weight	0.088	0.148	0.132	0.200	0.140	0.148	0.133	0.149	0.018	0.033
P25	1.4565	1.4569	1.4618	1.4728	1.4765	1.4872	1.4962	1.4955	1.4938	I

# B. Investigation of Factors Influencing Type and Yield of Products from Single-stage Hydrogenation of Maple Wood Meal

#### 1. Effect of pH on the Hydrogenation of Maple Wood Meal

A series of nine hydrogenation runs was made in order to study the effect of pH on the nature of the hydrogenation products from maple wood meal. The wood meal, catalysts (RaNi and CuCrO) and the hydrogenation apparatus and procedure have been described in a previous section (Section  $\Delta$ ). The RaNi catalyst was stored under an organic solvent (ethanol or dioxane) and in all cases was weighed while still wet (1.5 g. of "wet" catalyst is equivalent to approximately 1.0 g. of "dry" catalyst). Complete details of these experiments are given in Table XIV.

The contents of the bomb were filtered, the residual pulp and catalyst dried at 105° and weighed and the weight of pulp obtained by subtracting the weight of "dry" catalyst.

The filtrate (neutralized with hydrochloric acid in the case of the alkali runs) was extracted with 5 or 4 portions of chloroform and the combined chloroform solutions dried over anhydrous sodium sulphate, concentrated to an approximately 10% solution and then precipitated, in a fine stream, into twenty times the volume of petroleum ether (30-50°) (see Flow Sheet II). Small aliquots were removed from the total chloroform soluble, the petroleum ether-soluble and petroleum ether-insoluble fractions. These were dried and weighed, the yields calculated and the samples used for alkoxyl analyses. The results are given in Table XIV. Explanatory notes containing data pertinent to the individual hydrogenations and solvent separations are appended.

#### Flow Sheet II

#### Treatment of Products from Single-stage Hydrogenation of Maple Wood



-101 -

C h r 8 g е Run Maple Moles H absorbed² Moles Wt. EtOH-CC. HCI No. Catalyst Final Temp. Time wood Catagas Wt. water / 100 cc. hrs. meal /100 g. °C. pH "emitted" Pulp lyst cc. solvent / 100 g. g. wood g g. wood 58 10.0 RaNi 8.3 100 1.02 2.66 166-170 4 0.6 0.3 2.5 57 10.0 RaNi 8.3 100 1.00 3.21 160-170 4 0.4 0.9 3.2 59 10.0 RaNi 8.3 100 0.92 160-170 2.55 4 0.7 0.3 2.5 77 10.0 RaNi 8.3 100 0.86 3.03 160-170 4 0.7 0.4 1.2 73 10.0 8.3 RaNi 100 0.80 2.98 165 4 0 0.7 79 2.39 8 10.0 RaNi 16.5 0.716 200 165-170 -4 1.3 55 20.0 RaNi 16.5 200 buffered at pH 7.0 8.81 155-165 4 -18.0 -56 (155-165 (2.75 (170-175 (1.8 20.0 16.5 RaNi 200 (0 (a)(0) 10.5 (0.55 74 20.0 RaNi 16.5 200 (b) 160-170 4 0.15 0.15 3.0 (a) NaOH (6 g.) used in this run (b) NaOH (10 g.) used in this run (continued) Effect of Time of the Hydrogenation of Maple Wood Meel Table XV. 71 10.0 RaNi 8.3 100 0.716 3.57 160-170 2 2.9 79 10.0 RaNi 8.3 100 0.716 165-170 -----4 1.3 68 10.0 RaNi 8.3 100 0.716 160-170 5-1/2 3.36 0.6 0.2 0 69 10.0 RaNi 8.3 100 0.716 3.68 165 15 0

Table XIV. Effect of Varying the pH on the Hydrogenation of Maple Wood Meal

(continued)

Table XIV continued

Run		Total Ch	loroform	Soluble	To	Total Petroleum Ether Soluble				Total Petroleum Ether			
No.	Wt. g.	% of K.L.	% О <u>М</u> е*	% of OMe	Wt. g.	% of K.L.	% OMe	% of OMe	Wt. g.	% of K.L.	<b>%</b> OMe	% 0 OMe	
58	2.63	123	23.6	99.4	1.04	48.8	24.9	41.5	1.11	52.1	22.9	40.	
57	2.7	127	23.1	<b>9</b> 9.7	1.03	48.4	26.1 .	43.0	1.35	63.5	30.5	66.	
5 <b>9</b>	1.9	\$9.3	24.8	75.4	1.5	70.5	25.5	61.2	0.69	32.5	21.6	23.	
77	2.35	110	23.2	87.4	1.68	78.8	25.2	<b>6</b> 2.7	0.83	39.0	-		
73	3.07	144	20.4	100	1.43	67.2	21.9	50.2	1.57	73.7	19.8	49.7	
79	2.39	112	25.0	95.5	0.98	46	27.3	44.5	1.40	65.6	23.5	27.2	
55	2.31	54.0	20.2	37.4	0.13	3.6	5.7	0.59	1.62	38.0	21.5	27.9	
56	(2.3)	105	(16.5)	(30.4	0.85	20.0	23.5	16	3.83	90.0	15.9	48.7	
74	5.18	123	18.7	77.5	1.28	30.0	23.6	24.2	4.24	5.6	-	-	
	* Cal	culated a	as OR (R	= alkyl)								<b></b>	
					Tab]	Le XV co	ontinued					·	
71	2,18	102			0.91	42	25.2	37.1	1.27	60	23.8	48.4	

- 103

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71	2.18	102	-	-	0.914	42	25.2	37.1	1.27	60	23.8	4 <b>8.4</b>
79	2.39	112	25.0	<b>95.</b> 5	0.98	46	27.3	44.5	1.40	65.6	23.8	27.2
68	3.24	152	18.9	98.0	0.48	45.5	20.1	31.0	1.04	98.0	18.6	61.8
69	2.86	134	21.0	96.2	0.89	41.7	<b>22</b> .5	32.5	1.9	89.2	18.5	56.2

#### Notes Supplementing Tables XIVa and XIVb.

#### (1) Run 55

The mixture prior to hydrogenation was buffered to the neutral point with barium carbonate by adding to a suspension of maple wood meal (20.0 g.) in water a barium nitrate (6.0 g.) solution while the mixture was being stirred. Sodium carbonate (2.4 g.) solution was then added slowly, the mixture filtered and the residue thoroughly washed with water.

_ 104 ·

#### (2) Runs 56 and 74

In these hydrogenations in an alkaline medium the separation procedure was modified slightly. The filtrate from Run 56 was extracted, directly, twice with chloroform (100 cc. and 50 cc.) and the remaining aqueous ethanol solution then neutralized with 12 N hydrochloric acid (Congo red) and again extracted with chloroform. Separate weight aliquote were taken from each chloroform extract and the remainder of the solutions combined. In Run 74 the total petroleum ether insoluble fraction (4.24 g.) was divided into ethyl ether-soluble (3.50 g.) and -insoluble (0.23 g.) fractions. The petroleum ether and <u>ethyl</u> ether soluble fractions were combined and Claisen-distilled (240°, 0.6 mm.). The distillate represented 82.8% of the Klason lignin.

#### (3) Run 77

The petroleum ether-soluble fraction (1.68 g.) was separated into sodium bicarbonate soluble (1.28% of the Klason lignin), sodium hydroxide soluble (43.8% of the Klason lignin) and sodium hydroxide insoluble (11.2% of the Klason lignin) fractions.

## 2. Effect of Time on the Hydrogenation of Maple Wood Meal

These experiments embraced a series of four runs. The technique used being similar to that described in Section Bl. Details of hydrogenation and separation of products are given in Table XV.

# 3. Miscellaneous Experiments on the Hydrogenation of Maple Wood Meal

Several additional hydrogenation experiments similar to those described above were made using various catalysts and solvents in an attempt to determine the conditions which would give the maximum amount of hydrogenated "native" lignin as "identifiable" products. Complete details of the hydrogenation conditions and separation of the products are shown in Table XVI. The appended notes contain data pertinent to individual runs.

	······	C h a	rg	e					<u> </u>	Moles H	Moles	
Run No.	Maple Wood Meal g.	Catalyst	Wt. cata- lyst g.	Solvent	Vol. Sol- vent cc.	Other Com- ponent	Final pH	Temp. °C.	Time hrs.	absorbed ² /100 g. wood	gas emitted /100 g. wood	We
60	20.0	CuCrO	9.0	EtOH-water	200		-	165-170	4	0.25	0.25	1
64	10.0	CuCrO	6.0	<b>11</b> 11	100	0.92 cc.	3.61	160-170	4	0.1	0.4	
65	1	/2 filtra CuCrO	te from	No.64			8.72	160-170	4	-	-	-
61	20.0	RaNi	16.5	dioxane- water	200		5.54	165-175	4	0.10	-	13.3
62	10.0	RaNi	8.3	11 11	100	0.92 cc. conc. HCl	2.79	165-175	3.75	0.5	0.5	4.0
66*	20.0	0		EtOH-water	200	0	5.43	165	4	-	-	13.4
67	1	/2 filtra RaNi	te and 8.3	pulp of No	. 66	0	5.70	165	4	0.4	0.2	4.5
70 <b>*</b>	75.0	0		EtOH-water	900	0	4.80	165 <b>-170</b>	రో	-	-	40.5
75	20.0	RaNi	16.5	11 11	<b>20</b> 0	1% p-tolu- ene sul- phonic aci	- 2.98 1d	160-170	4	0.85	-	6.6
76	נ	./2 filtra RaNi	te and 8.3	pulp of No	. 75	3.5 g. NaOH	-	165-170	4	0.6	0.3	1.2

Table XVI. Miscellaneous Experiments on the Hydrogenation of Maple Wood Meal

* These experiments were carried out in an atmosphere of CO₂, not hydrogen.

(continued on next page)

Table XVI, continued

Run	Tota	.1 Chlor	oform s	Boluble	То	tal Peti	oleum E	ther Soluble	Tot	al Pet	roleum	Ether
No.	Wt. g.	% of K.L.	% OMe	% of OMe	`₩t. g.	% of K.L.	% OMe	% of OMe	Wt. g.	% of K.L.	% OMe	% of OMe
60	4.5	105.8	25.8	92.8	0.46	10.9	23.7	<b>8</b> .7	2.1	49.4	25.5	42.4
64	2.28	107	-	-	1.28	60.0	17.5	35.8	1.0	47.0	19.7	31.5
65	0.224	21.1	16.7	12.0	0.107	10.0	16.2	5.56	0.127	11.9	16.4	6.67
61	3.42	80.3	23.8	65.1	1.17	27.5	22.6	21.2	2.0	47.0	21.7	34.7
62	2. <b>2</b> 6	106.0	22.8	82.4	1.15	54	23.6	43.4	1.16	54.4	20.6	38.2
66	2.24	105	19.2	68.8	0.95	44.5	17.6 ·	26.8	1.44	67.5	18.8	43.3
67	2.12	100	19.3	65.6	0.512	24.0	17.0	13.9	1.98	93.0	19.7	62.4
70	17.4	109	22.9	85	10.68 [‡]	68.1	23.9	44.7	6.91**	43.3	-	
75	4.2	98.5	22.4	<b>7</b> 5.4	2.38	55 <u>9</u>	21.6	41.1	1.84	43.1		
76	2.98	139	17.7	84.3	1.54	72	19.9	49.0	0.15	6.9		

* Ethyl ether soluble
** Ethyl ether insoluble

#### Notes Supplementing Table XVI

#### (1) Run 60

The weight of the petroleum ether soluble fraction is uncertain due to experimental losses. A more correct value is obtainable by determining the difference between the total chloroform soluble and the petroleum ether insoluble fractions.

#### (2) Run 64

The filtrate, following hydrogenation was divided into two parts, 64A and 64B. 64A was treated in the usual manner (Flow Sheet II). 64B was neutralized (pH 7.0), the dark brown flocculent precipitate (1.1 g.) removed by filtration and the filtrate rehydrogenated (Run 65).

#### (3) Run 66

The filtrate from this run was divided into two portions 66A and 66B. The former (66A) was separated into petroleum ether-soluble and -insoluble fractions in the usual manner. (Flow Sheet II), while the latter (66B) was combined with half of the residual pulp from Run 66 and the mixture rehydrogenated (Run 67).

#### (4) Run 70

An attempt to fractionally distill at 295°/0.008 mm., one-half (5.5 g.) of the diethyl ether-soluble fraction from this run yielded only two small fractions, the remainder of the material being converted to a black resin.

Fraction	I	0.178	g•	$n_{D}^{25}$	1.5109
Fraction	II	0.221	g.	n ² 5	1.5319

109

Fraction I gave a positive test with 2,4-dinitrophenylhydrazine showing the presence of free carbonyl groups.

#### (5) Run 75

The filtrate from this run was divided into two portions, the first being rehydrogenated (Run 76) and the second treated as follows: The dioxane was removed from the solution by evaporation under reduced pressure and the residue (2.1 g.) then dissolved in ca. 5 cc. of acetone. 30-35 cc. of 5% NaOH solution were added (sufficient to saponify the esters of the acid and leave a large excess (30%)) and the solution heated on a steam bath for 5 hours. The product was acidified with 5 cc. of 6 N hydrochloric woid and then extracted with chloroform. The extract was dried over sodium sulphate and precipitated into petroleum ether (30-50°).

#### (6) Run 76

The petroleum ether-insoluble fraction (1.0 g.) was divided into an ethyl ether-soluble fraction (0.86 g.) and an ethyl ether-insoluble fraction (0.14 g.). The petroleum ethersoluble and the ethyl ether-soluble fractions were combined and distilled from a Claisen flask ( $270^{\circ}/0.8$  mm.). The distillate represented 85.0% of the Klason lignin in the wood.

# C. <u>Small-scale Hydrogenation of Maple Wood Meal</u> in Aqueous Ethanol

# 1. Preparation of Hydrogenated "Maple Lignin (B)"

Using the conditions employed in Experiment 56, Table XIV, for obtaining the maximum yield of petroleum ether-soluble hydrogenation products, duplicate runs were made (Flow Sheet III) in the small bomb to obtain sufficient material for further investigation. In each run dried maple wood meal  $(\mathbf{A}^{\mathbf{X}})$  (60 g., moisture, 1.43%; methoxyl, 7.25%; Klason lignin, 21.3%) was hydrogenated at 175° for 8 hours in 873 cc. of ethanol-water (1:1) containing 27 g. of sodium hydroxide (3%) and 48 g. (wet) The bomb contents were filtered, washed with Raney nickel. ethanol-water (1:1) and the residual pulp and catalyst (B) dried at 105°. The pulp residue was heated with 2 N hydrochloric acid for 1 hour on the steam bath to remove the nickel, and the pulp filtered off, washed, dried and weighed. The aqueous ethanol filtrate (D) was acidified (Congo red) with concentrated hydrochloric acid (61 cc.) and the resultant pale yellow solution extracted four times with chloroform (150, 100, 75 and 50 cc. portions), concentrated to a volume of 75 cc. (E) and again extracted with chloroform (25, 25 and 20 cc. portions).

X

Capital letters refer to the fractions thus designated in Flow Sheet III.

## 2. Solvent Fractionation and Subsequent Treatment of the Hydrogenated "Maple Lignin (B)"

#### (a) Solvent Fractionation of "Maple Lignin (B)"

The first four chloroform extracts, containing the "Maple Lignin (B)", were combined (F) and concentrated (50°, 5-10 cm, CO2 atmosphere) to a volume of 150 cc. and the solution precipitated into 3 litres of ethyl ether. The combined ethyl ethersoluble portions from the two runs (G) (22.8 g.) were dissolved in 120 cc. of chloroform, the solution extracted five times with 25 cc. portions of 8% sodium carbonate solution (N) and back extracted once with chloroform (25 cc.). The combined chloroform solutions (H) were extracted once with 5% sodium hydroxide The extracted material was designated as "phenolic (25 cc.). When a second alkaline extraction was (L). fraction" attempted a flocculent precipitate (M) appeared. The mixture was centrifuged, the upper alkaline layer, "phenolic fraction" (L!) separated and combined with (L) while the precipitate (M) was filtered from the residuol chloroform solution (I). The excess solvent was removed from (I) leaving the "neutral" Fractions (N), (L+L') and (M) were acidified fraction (N). separately with hydrochloric acid, extracted with chloroform and the chloroform extracts (R), (0) and (S) respectively, concentrated to remove the solvent. All aqueous residues from this solvent fractionation were combined, concentrated

to a small volume (75 cc.) and extracted continuously with benzene for 10 days.

A complete weight balance for this small-scale hydrogenation experiment is given in Flow Sheet III.

## (b) <u>Distillation of Combined "Phenolic Fractions" (0)</u> (Flow Sheet III)

This combined product (0) (10.4 g.) was fractionally distilled through the 21-plate column with the following results.

Fraction	Weight	n ²⁵ D
250	0.052	1.5257
251	0.167	1.5272
9 <b>5</b> 9	0,202	1.5276
0 53	0.205	1.5270
051	0.166	1.5302
055	0.278	1.5363
200	0.309	1.5363
200 057	0.219	1.5351
201	0 250	1,5353
2,00	0.266	1,5351
209	0.264	1,5349
260	0 1 96	1,5349
261	0.170	1,5476
262	0.200	1,5399 3
263	0.196	<b>T</b> •0066 - <b>F</b>
264	0.195	1.0044
265	0.279	1.0411
266	0.229	-
267	0.794	1.5431
268	0.186	1.5409
269	0.195	1.5374
070	0.346	1.5500
6 I V	<b></b>	

**E** Refractive indices of  $263 \Rightarrow 270$  taken at  $50^{\circ}$ .

Fractions 263-268 were crystalline.

#### FLOW SHEET III

## SUMMARY OF SMALL-SCALE HYDROGENATION OF MAPLE WOOD MEAL IN AQUEOUS ETHANOL (EXPERIMENTS SO AND S1)



(continued on next page)

- 113

U I



Weight of (0) 10.4 g. Weight of distillates 5.28 g. Weight of resin 3.94 g. Weight of column hold-up 0.41 g. Weight in cold trap 0.12 g. Recovery - 9.75 g.

The following analyses (Table XVII) were made on representative samples chosen from the "flat" portions of the distillation curve obtained for the combined "phenolic fractions" (0).

## Table XVII

Analyses of	<u>D</u> :	<u>isti]</u>	llates	from	Combined	"Phenolic
Fraction	.s "	(0)	(Flow	Sheet	; III)	

Fraction	ø	Ana]	ysis	m.p. of	% alkoxyl of
No.	Alkoxyl	с 	H	a-napthyl urethane	a-napthyl urethane
2 52	19.7	71.3	8.8	102.5-104	10.1
255	34.0		۳.	134-136	16.6
259	34.5	66.8	8.3		-

(c) <u>Distillation of "Phenolic Fraction" (M)</u> and "Acidic Fraction" (R)

The "phenolic fraction" (M) was fractionally distilled through the micro column with the following results:

- 115_

Fraction	Weight	$n_{D}^{25}$
242 243	0.097 0.132	1.5162 1.5296
2 <b>44</b> 2 <b>45</b> 246	0.148 0.205	1.5338 1.5348
247 248	0.052	1.5347 1.5330
249	0.083	1.5218 ¥ 1.5369 ¥

Semi-crystalline fractions, refractive indices taken at 50°

		Recove	ry			1.57	g.
Weight	of	resin		0.57	g•		
Weight	of	distillates		0.99	g.		
Weight	of	material (M	)			1.77	g.

The bicarbonate-soluble "acidic fraction" (R) was Claisen distilled  $(280^{\circ}/0.15 \text{ mm}_{\circ})$  to give a very viscous yellow oil  $(0.23 \text{ g}_{\circ})$  which was not characterized further.

(d) <u>Rehydrogenation of "Non-distillable" Fractions</u> from Experiments 80 and 81, Flow Sheet III

These fractions were combined and rehydrogenated.

ChargeXEthyl ether-insoluble fraction (P)3.26 g.Resin from fractionation of (O)3.94 g.Resin from fractionation of (S)0.57 g.Resin from fractionation of bicarbonate-<br/>soluble fraction (R)0.66 g.Dioxane<br/>CuCrO catalyst250 cc.6.0 g.

The capital letters refer to those used in Flow Sheet III.

This charge was hydrogenated in the Parr bomb for 10 hours at 225° during which time 0.03 moles of hydrogen were absorbed. Since the catalyst appeared to have been poisoned (red colour) in this run a fresh 6 g. of CuCrO was added and the mixture rehydrogenated for 8 hours at 250°. A further 0.22 moles of hydrogen were absorbed. The light yellow coloured product (4.4 g.) was distilled at 270°/0.8 mm.

Weight of distillate	2.1	g.
Weight of resin	1.7	g.
Recovery (loss due to gassing off)	87%	

# D. Choice of Solvent for the Hydrogenation of Maple Wood Meal

In order to determine whether or not hydrogenation in an aqueous ethanol medium was effecting partial ethoxylation of the propylphenol units, a single run (No. 82) was made in aqueous dioxane and the methoxyl and ethoxyl contents of the products determined.

Charge:	Maple wood meal	20.0 g.
	Raney nickel catalyst (wet)	16.5 g.
	Soalum nyaroxiae (5%)	10.0 8.
	Dioxane-water (1:1)	200 cc.

Hydrogenation Conditions

Time	4 Hours
Temperature	165 ⁰
Hydrogen absorption	0.65 moles
Final pH	10.9

Complete details of the treatment of the hydrogenated products are given in Flow Sheet IV. Total alkoxyl, methoxyl and ethoxyl contents of the petroleum ether-soluble lignin obtained in this run (No. 82) are compared in the following table with similar determinations made on Fraction No. 255 of the previously described "Phenolic Fraction" (0) (Flow Sheet III), from the small-scale ethanol-water hydrogenation.

Sample	% Alkoxyl	% Methoxyl	% Ethoxyl
255	34.0	30.2	5.6
Pet. ether-sol. fraction, Run 82	23.6	23.4	0.29

#### Flow Sheet IV

#### Solvent Separation of Hydrogenation Products (Run 82)



# **B.** Large-scale Hydrogenation of Maple Wood <u>Meal in Aqueous Dioxane</u>

## 1. Preparation of "Maple Lignin (C)"

#### (a) Series A (Runs 84-90)

A series of seven hydrogenations of maple wood meal (total weight 500 g.) was made in aqueous dioxane in order to obtain a large supply of this type of hydrogenated lignin for further experimentation. The first six runs were identical. the charge consisting of 75.5 g. of wood meal, 55 g. (wet) of Raney nickel catalyst, 900 cc. of dioxane-water (1:1) and 27 g. of sodium hydroxide. An initial hydrogen pressure of 3000 lbs/sq.in. was used and the bomb maintained at 173° for six hours. In Run 90, 49.5 g. of wood meal were hydrogenated under the same conditions and with the same ratio of solvent, catalyst and sodium The rate of hydrogen absorption for one run (No. 88) hydroxide. is shown in Fig. VII. The hydrogenated product from each run was treated in the manner outlined in detail for one run (Run 84) in Flow Sheet V.

#### (b) Series B (Runs 93-95 and 97-99)

A further series of six runs was made under conditions identical with those of Series A and the hydrogenated product submitted to the same treatment as shown in Flow Sheet V.



121 -

1

#### FLOW SHEET V

TREATMENT OF PRODUCTS FROM HYDROGENATION RUN 84 (SERIES A)



- 122

I

## 2. Investigation of "Maple Lignin (C)" (Series A)

#### (a) Claisen Distillation

The chloroform soluble fractions from runs 84, 85 and 86 (Series A)(Flow Sheet V) were distilled from a Claisen flask at  $250^{\circ}/1$  mm. to yield a distillate (26.8 g.) and a non-distillable resin (19.0 g.). Those from runs 87, 88 and 90 were combined, the Claisen distillate from runs 84 to 86 added and the resulting mixture also Claisen-distilled. The second Claisen distillate was collected as three fractions:

	(1)	distilling below 150° (bath temperature) and 1 mm. pressure (A1)	36 <b>.7</b> g.
	(2)	distilling above 1500/1 mm. (A2)	25.62 g.
an <b>d</b>	(3)	non-distillable resin (A-resin)	26.0 g.

(b) <u>Solvent Fractionation of Distillate Al (Section 2a)</u> Distillate Al (36.7 g.) was solvent fractionated according to the following scheme:



# (c) Fractional Distillation of Water-insoluble Portion (c) of Distillate Al (Section 2b)

The greater part of this water-insoluble fraction (c) (24.6 g.) was fractionally distilled through the 21-plate column. The distillation curve (refractive indices vs cumulative weight) is given in Fig. VIII and details of the fractions are shown below:

Fraction	Weight	n ²⁵ D	% och3
401	0.008		
402	0.041	1.4478	
403	0.068	1.4453	
404	0.089	1.4476	
405	0.108	1.4838	
406	0.286	1.5018	
407	0.304	1.5108	
408	0.255	1.5128	
409	0.456	1.5158	
410	0.361	1.5203	
411	0.406	1.5203	18.7
412	0.413	1.5222	
413	0.315	1.5230	
414	0.249	1.5238	
415	0.198	1.5239	20.1
416	0.249	1.5238	
417	0.225	1.5242	
418	0.216	1.5240	20.4
419	0.173	1.5239	
421	0.188	1.5250	
422	0.188	1.5251	19.6
423	0.195	1.5243	
424	0.244	1.5244	
425	0.278	1.5225	
126	0.204	1.5150	
40 <b>7</b>	0.130	1.5092	
198	0.133	1.5078	
429	0.241	1.5021	15.4

- 125 -

Fraction	Weight	n ²⁵ D	% OCH3
430	0.245	1.5146	
431	0.227	1.5241	
432	0.291	1.5329	
433	0.329	1.5296	
434	0.335	1.5303	32.3
435	0.439	1.5312	
436	0.280	1.5318	
437	0.334	1.5303	
438	0.222	1.5313	32.8
439	0.235	1.5313	
440	0.269	1.5321	
441	0.218	1.5320	
442	0.200	1.5001	
443	0.271	1.53020	
444	0.210	1 5% 90	<b>33 Q</b>
440	$0 \cdot 202$	1 5329	00.0
440	$0 \cdot 209$	1 5%28	
447 A A Q	0.242	1.5339	
440	0.225	1.5324	
447	0.220	1.000.1	
450	0.262	1.5338	33 <b>.3</b>
451	0.242	1.5338	
452	0.229	1.5323	
<b>4</b> <i>5</i> 3	0.287	1.5331	33.4
454	0.282	1.5344	
455	0.257	1.5337	
456	0.257		
457	0.269	1.0009	
458	0.004	1.5470	33 O
459	0.228	1.0002	00.0
460	0.199	1.5340	
461	0.189	1.5340	33•4
462	0.216	1.5338	
<b>463</b>	0.233	1.5342	
<b>464</b>	0.248	1.5040	
465	0.223	L•0041 7 5740	
466	0.260	1 004V 7 5744	
467	0.200	<b>エ・ひじ 44</b> コ ニペメペ	
468	U•217	1 5340 1 5340	
469	0.200	I ● 00%4	

Fraction	Weight	n ²⁵ D	% OCH ₃
470	0.214	1.5339	
471	0.200	1.5342	
472	0.239	1.5341	
473	0.206	1.5341	33.5
474	0.200	1.5339	
475	0.235	1.5342	
476	0.202	1.5341	
477	0.211	1.5339	
478	0.187	1.5340	
479	0.242	1.5339	
480	0.220	1.5337	
481	0.235	1.5340	3 <b>3.4</b>
482	0.256	1.5344	
483	0.207	1.5334	
484	0.282	1.5340	
485	0.217	1.5333	
486	0.232	1.5339	33.4
<b>487</b>	0.210	1.5321	
488	0.185	1.5313	
489	0.205	1.5274	
490	0.202.	1.5257	
491	0.181	1.5230	
492	0.190	1.5200	
493 <b>A</b>	0.252	1.4668	
<b>494</b>	0.203	1.4748	
495	0.255	1.4725	
496	0.195	1.4740	
497	0.233	1.4728	
498	0.507	1.4730	
	23.025		

* Fractions 493-498 existed in two layers. Refractive indices are given for top layer only.

Weight of material to be fractionated24.6 g.Weight of distillates23.03 g.Weight of resin0.09 g.Weight of column hold-up0.23 g.Weight in cold trap1.25 g.Recovery -24.6 g.

- 126 -


(d) Identification of 4-hydroxy-3-methoxyphenyl Ethane

A fraction No. 418 (p.124, was selected as typical of the "flat" represented by fractions 413-425 inclusive (Fig. VIII). Analyses of this material gave the following results.

<u>Anal.</u> Calc'd. for  $C_9H_{12}O_2$ : C, 71.0; H, 7.9; OCH₃, 20.4. <u>Found</u> (C, 70.4; H, 7.8; OCH₃, 20.5.

A crystalline p-nitrobenzoate prepared from Fraction 418 according to the method of Shriner and Fuson (165) melted at 98-99⁰:a mixed melting point with an authentic sample of the p-nitrobenzoate of synthetic 4-hydroxy-3-methoxyphenyl-ethane showed no depression.

(e) Identification of 4-hydroxy-3,5-dimethoxyphenyl Ethane

A representative sample (No. 472, 7.126 has chosen for investigation of the flat composed of fractions 442-486 inclusive. Analyses of this material gave the following results. <u>Anal</u>. Calc'd. for  $C_{10}H_{14}O_3$ : C, 65.9; H, 7.8;  $OCH_6$ , 34.1.

Found C, 65.2; H, 7.7; OCH₃, 33.6.

The orystalline p-nitrobenzoate prepared from Fraction 472 melted at 153.5-154.5° and a mixed melting point with an authentic sample of the p-nitrobenzoate of 4-hydroxy-3,5-dimethoxyphenyl) ethane showed no depression.

# 3. Investigation of "Maple Lignin (C)" (Series B)

# (a) Claisen Distillation

The total chloroform soluble fraction (123.1 g.) (see Section 1 (B) and Flow Sheet V) was distilled from a Claisen flask with the following results.

x Bath Temperature.	Total Recovery -	121.1 g.
Weight of resin (B4)		52.0 g.
Weight of distillate (215-260°/1 mm.)	(B3)	11.86 g.
Weight of distillate (180-215°/1 mm.)	(B2)	23.44 g.
Weight of distillate (below 1800/1.2 mm.)	(Bl) ) <del>x</del>	33.82 g.

The resin (52.0 g.) was transferred to a smaller pot and

distilled through a goose-neck at 280°/0.1 mm. Weight of distillate (B5) 3.39 g. Weight of resin (B6) 48.61 g.

> (b) Solvent Fractionation of Combined Distillates B2, B3 and B5 (Section 3a)

The higher boiling distillates B2, B3 and B5 (Section 3a) were combined (38.7 g.), dissolved in chloroform (150 cc.) and extracted with water (four 30 cc. portions). The aqueous solution was back extracted with chloroform (20 cc.). The resulting aqueous and chloroform solutions were concentrated separately under reduced pressure and yielded a water-soluble fraction ( $\mathbf{x}$ ) (5.0 g.) and a water-insoluble fraction ( $\mathbf{y}$ ) (33.3 g.) (c) Fractional Distillation of the Water-soluble Portion (x) of Distillates B2, B3 and B5 (Section 3b)

The above water-soluble fraction (x) (5.0 g.) was fractionally distilled through the 21-plate column with the following results.

Fraction	Weight	n ²⁵ D
572	0.219	1.4572
573	0.340	1.4650
574	0.338	1.4672
5 <b>75</b>	0.416	1.4760
576	0.221	1.4760
577	0.171	1.4788
578	0.342	1.5064
579	0.307	1.5324
580	0.357	1.5376

Distillation Weight Balance

Weight	of	material fractionated	l	5.0 g.
Weight	of	distillate	2.71 z.	
Weight	of	resin	0.76 g.	
Weight	of	column hold-up (crystalline)	1.15 g.	
Weight	in	cold-trap	0.20 g.	
		Total Recovery	-	4.83 g.

Distillation was discontinued when a crystalline material accumulated in the condenser.

(d)	Fractional	Dis	tillation	of	the	Wat	er-i	nsc	luble	
	Portion (y	) of	Distilla	tes	B2,	B3	and	B5	(Section	<u>3b)</u>

The water-insoluble portion (y) (33.3 g.) was fractionally distilled through the 28-plate column. The distillation curve

# is given in Figure-IX and details of the individual fractions

follow.

55555555555555555555555555555555555555	55555555555555555555555555555555555555	51 51 51 51 51 51 51 51 51 51 51 51 51 5	502 503 503 503 503 503 503 503 503 503 503	Fraction
0.173 0.215 0.228 0.228 0.213 0.213 0.2213	0.184 0.184 0.212 0.212 0.200 0.162 0.199 0.224 0.224 0.284	0.225 0.225 0.225 0.255 0.255 0.213 0.213	0.027 0.175 0.217 0.217 0.217 0.217 0.217 0.217 0.213	Weight
1.5323 1.5328 1.5328 1.5328 1.5323 1.5323 1.5323 1.5323 7	1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.5328 1.	1.5319 1.5317 1.5304 1.5308 1.5310 1.5310 1.5323	1.5172 1.5200 1.5200 1.5160 1.5160 1.5158 1.5253 1.5253	р 25

Fraction	Weight	<b>В</b> В В В В В В В В В В В В В В В В В В
540	0.190	1.5326
541	0.202	1.5339
542	0.219	1.5329
543	0.202	1.5339
544	0.634	1.5339
545	0.189	1.5339
546	0.190	1.5328
547	0.256	1.5338
548	0.186	1.5322
549	0.214	1.5329
550	0.227	1.5339
5 <b>51</b>	0.225	1.5330
552	0.272	1.5274
553	0.209	1.5289
554	0.221	1.5296
555	0.255	1.5280
556	0.270	1.5247
557	0.259	1.6238
558	0.227	<b>1.6255</b>
509	0.256	1.5200
<b>560</b>	0.351	1.5323
561 562	0.105	1.5370
202 202	0.200	1.5364
568	0.382	1.5370
D04	0.238	<b>1 - 5280</b>
<b>DGD</b>	8 <b>7</b> 0.0	1.5260
000 100 100 100	0.450	
<b>567</b>	0.009	1.5438
568 569	0.430 0.255	1.5410 1.5390
570	0.280	1.5368
571	0.258	1.5390
	17.116	



# Distillation Weight Balance

Weight of material to be fractionated 33.3 g. Weight of distillates 17.12 g. Weight of non-distillable resin 14.26 g. Weight of column hold-up (orystalline) 0.94 g. Weight in cold trap 0.47 g. Recovery - 32.79 g.

Distillation was discontinued when on attempting to remove a fraction, a crystalline material accumulated in the condenser.

The residual product (14.3 g.) was separated into three fractions by distillation through a goose-neck, and gave distillate I, 11.66 g.; distillate II, 1.36 g. and a non-distillable portion 1.14 g.

### (e) Identification of 4-hydroxy-3,5-dimethoxyphenyl Ethane

Analysis of a representative sample, (Fraction 536 (p.131)), chosen from the flat containing fractions 521 to 549 inclusive gave the following results:

<u>Anal</u>: Calc'd. for  $C_{10}H_{14}O_3$ : C, 65.9; H, 7.8; OCH₃, 34.1. Found C, 65.3; H, 7.8; OCH₃, 33.8.

The crystalline p-nitrobenzoate of Fraction 536 melted at 153.5-154.5° and a mixed melting point with an suthentic sample of the p-nitrobenzoate of 4-hydroxy-3,5-dimethoxyphenyl ethane gave no depression.

# (f) <u>Isolation and Identification of 2-(4-hydroxy-3,5-</u> dimethoxylphenyl) Ethanol

(i) Isolation - Distillate I (11.66 g.) obtained from the resin remaining after fractionation of the water-insoluble portion (y) of distillates B2, B3 and B5, (Section 3d) became partially orystalline on standing. The occluded oils were removed by washing the mixture with ether and a white crystalline material (3.9 g.) remained. A further 0.96 g. were obtained by concentration of the ether mother liquors. Weight of unidentified oil, 6.8 g.

An additional yield of the crystalline material was obtained from the following sources:

1 • 9	Column hold-up (Section 30, p.130)	0.74 g.	
<b>с.</b> З.	Fraction 571 (Section 3d, p.132)	0.08 g.	
	Total weight of crystalline material -		6.6 g.

(ii) Identification - The crystalline compound was recrystallized to constant melting point (116-117°) from etherpetroleum ether and from ethanol-petroleum ether mixtures.

Determination of Nuclear Structure - The crystalline material (0.6 g.) was methylated three times with diazomethane at intervals of 12 hours. The ether solution containing the methylated product was extracted with 5% sodium hydroxide, washed with dilute sulphuric acid and sodium bicarbonate and dried. Removal of the solvent and distillation of the oily residue ( $180^{\circ}/0.2 \text{ mm.}$ ) yielded 0.51 g. of the methylated product; alkoxyl as OCH₃: 42.0%; Calc'd. for C₁₁H₁₆O₄,43.8%.

The methylated product (0.25 g.) was dissolved in acetone (10 cc.), water (10 cc.) added and the solution heated on the A 3% solution of potassium permanganate (40 cc.) steam bath. was added drogwise with vigorous stirring over a period of 1 hour and the precipitated manganese dioxide was then filtered and washed. The filtrate was extracted with ether to remove the by-products and unchanged material, the aqueous solution then acidified and again extracted with ether. After drying with sodium sulphate and removing the solvent from the second ether extract a solid residue (0.12 g.) remained. This, after recrystallizations from ether-petroleum ether and petroleum ether-ether mixtures melted at 167-168°. A mixed melting point with 3, 4, 5-trimethoxybenzoic acid showed no depression thus establishing the presence of the syringyl nucleus.

Chromic Acid Oxidation: - An examination of the product for the presence of a terminal methyl group using the Kuhn and L'Orsa method (166) involving oxidation with chromic acid, gave a negative result.

# Ultimate Analysis -

<u>Anal.</u> Calc'd. for  $C_{10}H_{14}O_4$ : C, 60.6; H, 7.1; OCH₃, 31.3. Found C, 60.7; H, 6.9; OCH₃, 31.3.

Comparison of the Methylated Derivative with a Synthetic Product - The crystalline compound (1 g.) was methylated four times with diazomethane (400% excess). The resulting yellow oil was distilled at 220-2350/0.02 mm. to yield a product (0.44 g.) analysing for % OCH₂, 43.6.

Calc'd. for  $C_{11}H_{16}O_4$ , % OCH₃, 43.8.

An anapthyl urethane of this methylated product, prepared according to the method of Tarbell, Mallatt and Wilson (167) melted at 132-133°. A mixed melting point with the A-napthyl urethane of an authentic sample of 2-(3,4,5-trimethoxyphenyl) ethanol showed no depression.

> (g) Rehydrogenation of Resins from Claisen and Fractional Distillations of "Maple Lignin (C)" Series B.

# (i) Rehydrogenation Procedure

The non-distillable resins obtained during the fractionation of "Maple Lignin (C)" (Series B) were combined (50.5 g.) and rehydrogenated. These included:

- The resin left after the Claisen distillation (a) of the "Maple Lignin (C)" (Series B) (Section 3a, p.129)
- (b) The resin from the distillation of the watersoluble portion (x) of the distillate B2 (Section 3a, p.130) 0.76 g.

48.6 g.

(c) The resin from the distillation of the water-insoluble portion (y) of the distillate B2 (Section 3a, p.134)
 1.14 3.

Three 14.0 g. samples of these combined resins were rehydrogenated over copper chromium oxide (6 g.) in 215 cc. of dioxane for 6 hours at  $255^{\circ}$ . In average of 3.4 moles of hydrogen was absorbed per 100 g. of resin.

### (ii) Treatment of Rehydrogenated Products

The combined rehydrogenated products, from the 42.0 g. of resins, weighed 29.8 g. and contained 4.2% methoxyl. One half of this product (14.9 g.) was again rehydrogenated in dioxane (200 cc.) over copper chromium oxide (6 g.) for 6 hours at  $280^{\circ}$ . 1.81 moles of hydrogen were absorbed per 100 g. of resin. The resulting colourless methoxyl-free product (12.5 g.) was fractionally distilled through the 28-plate column with the results shown in the distillation curve (Fig. X) and the following table.

Fraction	∛eight	n ²⁵ D
6.50	0.094	1,4538
651	0.148	1.4618
6 52	0.187	1.4648
6 53	0.151	1.4668
6 <b>54</b>	0.241	1.4670
655	0.109	1.4732
656	0.178	1.4702
657	0.145	1.4700
658	0.163	1 42790
659	0.108	T • 4000

	1	
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139 1	Weight 0.209 0.255 0.104 0.158 0.159 0.159 0.229 0.229	0 	0.063 0.202 0.192 0.170 0.170 0.170 0.125 0.068 8.174
	Fraction 662 662 665 665 668 668 668	6 6 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	00000000000000000000000000000000000000



# Distillation Weight Balance

Weight	of	material to be fractionated		12.5 g.
Weight	of	distillates	8.17 g.	
Weight	of	regin	2.42 g.	
Weight	of	column hold-up	0.39 g.	
Weight	in	cold trap	1.22 g.	

Recovery -

12.1 g.

# (111) Analyses of Products from the Fractionation Treatment (Section 11)

Fractions 663-669, 670-673 and 682-692 (p.139) represented flats (portions of constant refractive index).

Ultimate analyses of representative samples of these flats are given in Table XVIII.

# Table XVIII

	Analyses	of Fractions	from the Re	hyd <b>r</b> ogena	ation o	f the
		Resins	(Series B)			
Fracti	on	Weight g•	% Meth <b>oxyl</b>	с.	H.	Molecular Weight (Rast.)
6 <b>67</b>		1.09	0.5	-79.9	<del>1</del> 1.9	235
6 <b>73</b>		0.98	0.4	81.3	12.7	215
685		2.23	1.0	82 <b>•5</b>	12.6	288

# (h) <u>Rehydrogenation of Non-constant-boiling Portions</u> <u>from Fractional Distillations of "Maple Lignin</u> (C)" - Series <u>A</u> and <u>B</u>

# (i) Rehydrogenation Procedure

All the non-constant-boiling portions representing 7.57 g. from Series A and 16.43 g. from Series B were combined (24.0 g.) and rehydrogenated in dioxane (200 cc.) over copper chromium oxide (9.2 g.) for 18 hours at  $280-290^{\circ}$ . The resulting pale yellow solution was filtered and concentrated under reduced pressure ( $50^{\circ}/5-10$  cm.), to a fluid oil (10.1 g.) which was fractionally distilled through the 28-plate column (distillation curve, Fig. XI) with the following results:

Fraction	Weight	n ²⁵ D
697	0.063	1.4233
698	0.117	1.4360
699	0.107	1.4470
700	0.201	1.4488
701	0.134	1.4480
702	0.093	1.4470
703	0.194	1.4573
704	0.211	1.4582
705	0.146	1.4582
706	0.163	1.4582
707	0.192	1.4584
701	0.164	1.4584
709	0.122	1.4584
710	0.178	1.4585
710	0.164	1.4586
/ L L 171 0	0.153	1.4600
714 773	0.165	1.4610
7 L O M 7 A	0.174	1.4611
715	0.179	1.4610

Fraction	Weight	n ²⁵ D
716	0.220	1.4620
717	0.206	1.4620
718	0.169	1.4616
719	0.186	1.4620
720	0.142	1.4629
721	0.129	1.4639
722	0.194	1.4650
723	0.250	1.4657
724	0.137	1.4656
725	0.110	1.4655
726	0.183	1.4664
727	0.198	1.4682
728	0.184	1.4700
729	0.171	1.4715
730	0.129	1.4734
731	0.169	1.4752
732	0.094	1.4750
733	0.205	1.4790
734	0.253	1.4830
735	0.322	1.4852
736	0.307	1.4853
737	0.238	1.4830
738	0.139	1.4830
739	0.279	1.4870
Total Weight -	7.628	

# Distillation Weight Balance

Weight	of	material to be	fractionated			10.1	g.
Weight	of	distillates		7.63	g.		
Weight	of	resin		2.19	g.		
Weight	of	oolumn hold-up		0.18	g•		

Recovery -

•

10.0 g.



# (ii). Identification of 4-ethyloyclohexanol

Fraction 709 (p.142) was chosen as representative of the flat embracing fractions 704 to 712 inclusive.

A phenyl urethane prepared from this fraction according to the method described by Tarbell, Mallatt, Wilson (167) melted at 113.5-114.5[°] and a mixed melting point with an authentic sample of the phenyl urethane of 4-ethylcyclohexanol showed no depression.

# (iii) Identification of 4-n-propyloyclohexanol

Fraction 717 (p.143) was selected as a typical sample of the flat represented by Fractions 716 to 721 inclusive.

A phenyl urethane of this fraction melted at 123.5-124.5⁰ and a mixed melting point with an authentic sample of the phenyl urethane of 4-n-propylcyclohexanol gave no depression.

## (iv) Identification of 3-cyclohexyl-lepropanol

Fraction 724, (p. 143) representative of the flat containing fractions 722 to 726 inclusive, was used in the identification.

A phenyl urethane of this fraction melted at 83-84⁰ and a mixed melting point with an authentic sample of the phenyl urethane of 3-cyclohexyl-l-propanol showed no depression.

# F. Syntheses of Reference Compounds

# 1. Synthesis of 4-hydroxy-3-methoxyphenyl Ethane

This substance was obtained by the catalytic hydrogenation of acetovanillone in ethanol using Raney nickel as the catalyst.

Charge:	Acetovanillone	10.0 g.
	Raney nickel (wet)	<b>4</b> .0 g.
	Ethanol	100 cc.

# Hydrogenation Conditions

Temperature	180-190 ⁰
Time at 180-190 ⁰	35 min.
Hydrogen absorbed	0.21 moles.

The resulting product (7.8 g.) was extracted with sodium hydroxide, the alkaline solution acidified and extracted with ether. The dried ether extract was concentrated, the residual oil distilled and collected in two fractions.

	Weight	²⁵ D	Vapour Temp. OC.	Pressure mm.
I	0.540	1.5281	91-100	15
II	0.414	1.5242	100-103	15

**A** sample of Fraction II was acylated with p-nitrobenzoyl chloride and the p-nitrobenzoate recrystallized from ethanolwater. Melting point  $98-99^{\circ}$ . Reported for  $C_{9}H_{12}O_{2}$ : p-nitrobenzoate, m.p.  $100^{\circ}$  (157).

# 2. Synthesis of 4-hydroxy-3,5-dimethoxyphenyl Ethane

The synthesis was carried out according to the following reactions.



# (a) Preparation of 1-acety1-2,6-dimethylpyrogallol (LXVIII)

2,6-Dimethylpyrogallol (LXVII) (5.0 g.) was dissolved in anhydrous benzene (5 cc.) containing anhydrous pyridine (3.3 g.) and acetyl chloride (3.0 g.) added dropwise to the vigorouslystirred solution. The mixture was then heated at  $60^{\circ}$  for 2 hours, cooled and the pyridinium chloride removed by filtration. Removal of the solvent from the filtrate and distillation of the residual oil (120-130°/0.01 mm.) gave the required product (5.7 g.) (90%) (OCH₃, 31.0%). Calc'd. for  $C_{10}H_{12}O_3$ ; OCH₃, 31.6%.

(b) <u>Preparation of 4-hydroxy-3,5-dimethoxy</u> <u>Acetophenone (LXIX)</u>

1-Acety1-2,6-dimethylpyrogallol (LXVIII) (5.7 g.) and powdered anhydrous aluminum chloride (7.7 g.) were added to nitrobenzene (35 cc.) in a 3-necked flask fitted with a mercurysealed stirrer and a reflux condenser. The solution was stirred for two hours at 2 to 5°. allowed to stand at room temperature for 22 hours and then poured into a mixture of ice (250 g.) and concentrated hydrochloric acid (25 cc.). This mixture was extracted with chloroform (125 cc.) and the chloroform solution shaken with sodium hydroxide (25 cc. of 5% solution). The alkaline solution was acidified, extracted with chloroform (125 cc.), the chloroform solution dried and the solvent removed under reduced pressure. The residual oil on distillation at 160-1750/0.01 mm. yielded a crystalline product 0.80 g. (14%). Recrystallized from ether, m.p. 121-122°. A mixed melting point with an authentic sample of (LXIX) showed no depression.

> (c) <u>Reduction of 4-hydroxy-3,5-dimethoxy Acetophenone</u> (LXIX)

4-Hydroxy-3,5-dimethoxy acetophenone (LXIX) (0.4 g.), zinc, amalgamated prior to use, (20 g.) and a 50% solution of hydrochloric acid (100 cc.) were refluxed for 6 hours. The hot solution was filtered and the cooled filtrate extracted with ether. The ether extract was dried, the solvent removed and the residual oil distilled at  $160-170^{\circ}/0.02$  mm. giving an oily distillate. Yield 0.17 g. (46%), OCH₃, 33.8%. Calc'd. for  $C_{10}H_{14}O_3$ : OCH₃, 34.1%.

A p-nitrobenzoate derivative of this oil, after several recrystallizations from ethanol-water and ether-petroleum ether melted at 151-152°.

# 3. Synthesis of 2-(3,4,5-trimethoxyphenyl) Ethanol

The synthesis was carried out according to the following reactions.







## (a) Preparation of Trimethyl Gallic Acid (LXXII)

Trimethyl methyl gallate (LXXI) (25.0 g.) was heated under reflux for 10 minutes with 20% sodium hydroxide solution (200 cc.) and then added to 10% hydrochloric acid (600 cc.). The mixture was cooled (5°), filtered and the filter washed with three portions of water (60 cc.). The resulting product was dissolved in chloroform (500 cc.) and the solution dried over sodium sulphate. Petroleum ether ( $o0-50^{\circ}$ ) was added to the filtered chloroform solution and a thick crop of microcrystals separated immediately. Yield 22.5 g. (96%); m.p. 168-169°.

<u>Anal.</u> Calc'd. for  $C_{10}H_{12}O_5$ : OCH₃, 43.8. <u>Found</u> OCH₃, 43.7.

### (b) Preparation of 3,4,5-trimethoxybenzoyl Chloride (LXXIII)

Trimethyl gallic acid (LXXII) (2.0 g.) and purified thionyl chloride (7 cc.) were heated under reflux in an all-glass apparatus for one hour. The reaction mixture was then transferred to a small Claisen flask and the excess  $SOCl_2$  removed by co-distillation with anhydrous benzene. The resulting product was used directly in the next step.

# (c) <u>Preparation of 3,4,5-trimethoxyphenyl Diazomethyl</u> Ketone (LXXIV)

The acyl chloride (LXXIII) prepared in section (b) was dissolved in benzene and the solution added slowly to an ethereal solution of diazomethane prepared from nitrosomethylurea (7.0 g.) and allowed to stand at 0° for 16 hours. The solvent together with the excess diazomethane were removed under reduced pressure. The crude product (2.1 g.) (95%) was used directly in the following step.

# (d) <u>Hydrolysis of 3,4,5-trimethoxyphenyl Diazomethyl</u> <u>Ketone (LXXIV)</u>

The diazomethyl ketone (LXXIV) prepared in section (c) was hydrolyzed by heating at 70° for three hours with aqueous 2%sulphuric acid (100 cc.). The solution, after cooling, was extracted with chloroform, the chloroform solution dried over anhydrous sodium sulphate and concentrated to remove the solvent. The resulting product was recrystallized from ether. Yield, 1.5 g.; m.p. 77-78°.

<u>Anal</u>. Calc'd. for  $C_{11}H_{14}O_5$ : OCH₃, 41.1. <u>Found</u> OCH₃, 40.85.

> (e) <u>Reduction of 3,4,5-trimethoxyphenyl Hydroxymethyl</u> Ketone (LXXV)

3,4,5-Trimethoxyphenyl hydroxymethyl ketone (LXXV) (1 g.) was catalytically reduced over copper chromium oxide catalyst at 150-160° for 1 hour.

Charge	Compound (LXXV)	1.0 g.
	CuCrO catalyst	0.5 g.
	Ethanol	100 oc.

Hydrogenation Conditions

Tempera ture	150-160 ⁰
Time	l hour

The bomb contents were filtered to remove the catalyst. The filtrate was concentrated under reduced pressure  $(60^{\circ}/15 \text{ cm} \cdot)$ . The resulting yellow oil was distilled at 220-240°/0.02 mm. to yield the desired product (0.8 g.). <u>Anal</u>. Calc'd. for  $C_{11}H_{16}O_4$ : OCH₃, 43.8. <u>Found</u> OCH₃, 43.5.

An *A*-naphthyl urethane of this product (LXXVI) was prepared according to the method of Tarbell, Mallatt and Wilson (167), m.p. 131-133⁰.

### G. Miscellaneous Experiment

# 1. Hydrogenation of Maple Wood Meal in Aqueous Dioxane (Run 91)

This run was made in a similar manner to those on the preparation of "Maple Lignin (C)" (Series A and B, section El, p.120) but for 1-1/4 hours only, instead of 6 hours.

Charge	Maple wood meal	75.5 g.
	Raney nickel (wet)	55.0 g.
	Dioxane-water (1:1)	900 cc.
	Sodium hydroxide	27.0 g.

### Hydrogenation Conditions

Temperature	173 ⁰
Time at 1730	1-1/4 hours
Hydrogen absorbed	0.32 moles.

The bomb contents mere filtered, neutralized and extracted with chloroform. The chloroform extract (15.1 g.) was dried, the solvent removed under reduced pressure, and the product distilled from a Claisen flask at  $250^{\circ}/0.4$  mm. A distillate (7.8 g.) and a resin (6.9 g.) were obtained.

The hydrogen absorption (0.32 moles) indicated completion of the reduction after a 1-1/4 hour period instead of the six hour interval previously used (Fig. V) in which 0.34 moles of hydrogen were absorbed for a similar amount of wood meal.

### SUMMARY

An investigation of various hydrogenation catalysts has been made with relation to their effectiveness in bringing about degradation of a maple lignin, isolated from maple wood in a neutral aqueous ethanol medium, by a combined high-pressure hydrogenolysis-hydrogenation treatment. Raney nickel and copper chromium oxide were found the most suitable

The important factors involved in the extraction of lignin from maple wood by high-pressure hydrogenation have been studied. These involved consideration of (a) nature of catalyst and solvent; (b) time; (c) temperature and (d) pH of the reaction medium with the object of isolating, in maximum yield, the native lignin in the form of alkylphenol entities, molecular or dimolecular in type.

The complete solubilization of maple wood was effected by high pressure hydrogenation at 165° in an acidic aqueous ethanol medium using Raney nickel as catalyst. It was shown that the solubilized lignin still retained its essentially aromatic character and was soluble to a high degree in petroleum ether.

Hydrogenation of maple wood meal in alkaline aqueous

dioxane, using Raney nickel as catalyst, removed the entire lignin. From this hydrogenated lignin mixture three new lignin aromatic degradation products were isolated: 4hydroxy-3-methoxyphenyl ethane, 4-hydroxy-3,5-dimethoxyphenyl ethane and 2-(4-hydroxy-3,5-dimethoxyphenyl) ethanol in yields of 2.2, 15.4 and 6.2% respectively, based on the Klason lignin content.

The isolation of these products supplies additional confirmatory evidence of the essentially aromatic (alkyl phenolic) nature of lignin.

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