

in this report is not to be explained by any dissociation of zein at temperature 50°. The two sets of data illustrate the necessity of conducting the experiments over a very wide frequency range.

By using recent theoretical developments of Onsager and Wyman, the measurements are interpreted to indicate a dipole moment for the zein molecule of approximately 400D. Of course there is a considerable uncertainty in this calculation but it is believed to be a better evaluation than the much lower value, approximately 50D, obtained by the direct application of the classical Debye theory.

**Acknowledgment.**—Grateful acknowledgment is made to the Wisconsin Alumni Research Foundation and to the University Research Committee for financial assistance which has made this work possible.

### Summary

1. A combination of the Debye dipole theory and the Perrin study of the hydrodynamics of an ellipsoid of revolution is applied to experimental data involving the protein zein in aqueous alcoholic solution.

2. A resonance apparatus for making precision dielectric constant measurements with conducting solutions in the frequency range of 1.5 to 40 megacycles is described briefly. The principal feature of the method is the high accuracy of relative values at different frequencies.

3. The experimental dispersion of dielectric constant data with dilute zein solutions in the frequency range 25,000 to 30,000,000 cycles is accounted for quantitatively by theoretical equations if the molecules are treated as ellipsoids of revolution. The values 38,000 for the molecular weight and  $1/7$  for the ratio of minor to major axis of the zein molecule are obtained directly from these data.

4. It has been possible to analyze the dispersion of dielectric constant curve for zein in solution by considering the molecule to have the form of an ellipsoid of revolution to give relaxation times characteristic of rotation about its different axes.

5. There is no dielectric constant evidence of a temperature dissociation of zein molecules in solution between 0 and 50°.

MADISON, WISCONSIN

RECEIVED JANUARY 11, 1939

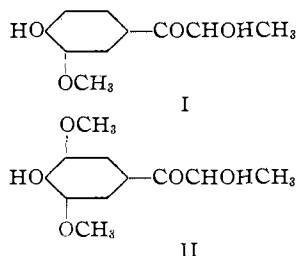
[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

## Studies on Lignin and Related Compounds. XXXVII. The Structure of Lignin and the Nature of Plant Synthesis

BY HAROLD HIBBERT

The isolation, in considerable yield, of  $\alpha$ -ethoxypropiovanillone by "ethanolysis" from spruce and of this, together with  $\alpha$ -ethoxypropiosyringone, from maple wood<sup>1</sup> would seem to be of marked importance not only in regard to the elucidation of the structure of lignin, but also with respect to the mechanism of plant synthesis.

The evidence indicates that these products are formed either from the corresponding free hydroxy compounds I and II



(1) (a) Cramer, Hunter and Hibbert, *THIS JOURNAL*, **61**, 509 (1939); (b) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

or from relatively simple building units, and that "extracted" lignins are, at least in very large part, condensation polymers of I and II or their dismutation forms XV, XVI and XVII, XVIII of these. This view is in harmony with the ease<sup>2</sup> with which an "extracted" lignin, isolated from oak wood, under very mild conditions, may readily be converted into simpler building units similar to those already described.<sup>1</sup>

In the case of maple wood,<sup>1b</sup> the total amount of I and II isolated in the form of their  $\alpha$ -ethoxy derivatives was 12.4 g., based on a weight of 100 g. of lignin (Klason) in the original wood. The "ethanolysis" products of maple contain, in addition to the distillable phenolic substances, also aldehydic, acidic and neutral substances, to the extent of 5.4, 1.6, 2.1 g., respectively. In other words, some 21.5 g. of distillable derivatives was obtained from maple wood containing 100 g. of lignin (Klason).

(2) Peniston, McCarthy and Hibbert, *ibid.*, **61**, 530 (1939).

TABLE I  
APPROXIMATE (KLASON) LIGNIN BALANCE OF MAPLE WOOD LIGNIN PRODUCTS OBTAINED BY "ETHANOLYSIS" AND HYDROGENATION

	Total products		Distillable products		Non-distillable products	
	Wt. <sup>a</sup> g.	% <sup>b</sup>	Wt. <sup>a</sup> g.	% <sup>b</sup>	Wt. <sup>a</sup> g.	% <sup>b</sup>
I "Crude" water soluble oils:	52	42	..	..	..	..
(a) Distillable products						
1. Phenolic			13.5			
2. Aldehydic			7.2			
3. Neutral			4.4			
4. Acidic			nil			
Total of (1) to (4)			25.1	20		
(b) Non-distillable products					27	22
II Water-insoluble "ethanol lignin"	37	29				
Distillable products after hydrogenation			37	29		
III Ethoxylated "lignin" left in wood residue	37	29			37	29
Total	126	100	62.1	49	64	51

<sup>a</sup> Weights based on products obtained from 467 g. of dry extracted maple wood (contains 100 g. (Klason) lignin).

<sup>b</sup> Percentages roughly corrected for ethoxyl and based on the original 100 g. of (Klason) lignin. For example: % "crude" water-soluble oils =  $(52/126) \times 100 = 42$ .

In addition it has now been found possible to convert the water-insoluble "ethanol lignin," formed simultaneously in the "ethanolysis" reaction, into readily distillable liquids containing principally cyclohexanol derivatives and aliphatic alcohols, in practically quantitative yields, by catalytic hydrogenation at 2000–5000 pounds per square inch (133–267 atm.) pressure,<sup>3</sup> as recently applied to methanol lignin<sup>4</sup> by Harris, D'Ianni and Adkins.<sup>5</sup>

More recently, by improvements in the methods of extraction<sup>6</sup> it has now been possible to increase the total yield of "crude oils" in the ethanolysis process<sup>1</sup> (based on a weight of 100 g. of original lignin (Klason) present in maple wood) to around 52 g., with corresponding increases in the weight of the phenolic, aldehydic and neutral substances to 13.5, 7.2 and 4.4 g., respectively, or a total weight of 25.1 g. Under these new conditions, the amount of acids formed is practically nil.

Using this improved technique, the yields of the various products of ethanolysis and hydrogenation are as listed in Table I.

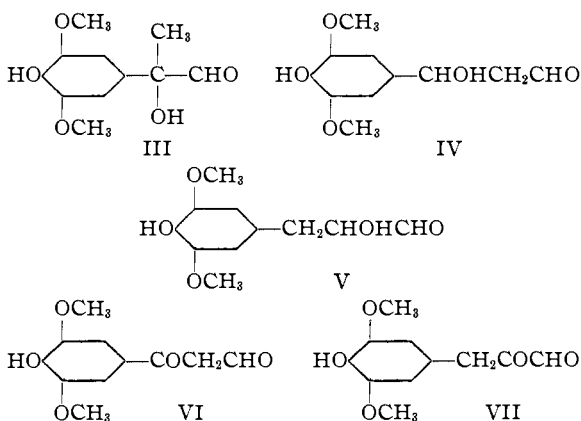
Preliminary investigation<sup>3</sup> of the "non-distillable liquids" from the "crude water-soluble oils" has shown that these substances can be converted by hydrogenation, in practically quantitative yields, into distillable products.

(3) Cooke, McCarthy and Hibbert, unpublished results.  
(4) Hibbert and co-workers, *Can. J. Research*, **B13**, 28 (1935); **B14**, 12, 55, 115, 404 (1936); **B15**, 38 (1937).  
(5) (a) Harris, D'Ianni and Adkins, *THIS JOURNAL*, **60**, 1467 (1938); (b) Harris and Adkins, *Paper Trade J.*, **57**, 38 (1938).

(6) Brickman, Pyle, McCarthy and Hibbert, unpublished results.

It is thus apparent that approximately 50% of the lignin (Klason) in maple wood can be converted readily into distillable products while an additional yield of these, in amount of approximately 22%, can be obtained by a subsequent hydrogenation of the non-distillable products from the crude water-soluble oils, or a total of 72%.

In a previous note<sup>7</sup> it is shown that the principal constituent of the aldehydic fraction is an aldehyde with the empirical formula  $C_{11}H_{14}O_4$  or  $C_{11}H_{12}O_4$ , corresponding to the aldehyde structures III, IV, V, VI and VII.

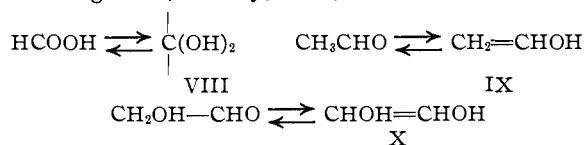


and the question arises, "What is the relationship of these different ethanolysis products to the structure of lignin and the nature of plant synthesis?"

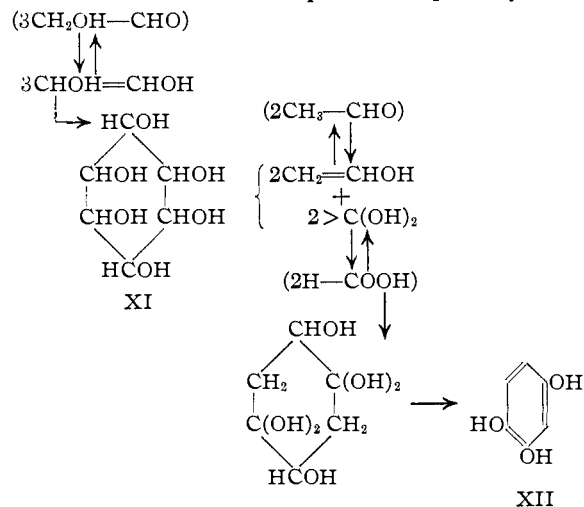
As a result of the intensive work carried out in this field with a large number of co-workers, the writer feels justified in proposing the following new theory.

(7) Brickman, Pyle and Hibbert, *THIS JOURNAL*, **61**, 523 (1939).

In a recent, and as yet unpublished, address<sup>8</sup> on this subject by the author, it was suggested that perhaps, in view of the continued lack of experimental evidence in their support, the older view of formaldehyde<sup>9</sup> as the primary product of plant synthesis and the theory that hexoses<sup>10</sup> are the precursors of the phenolic substances present in tannins, lignins and plant pigments, do not provide a satisfactory solution of the problem of plant synthesis. A new conception was then presented, in the above address, incorporating the ideas of earlier workers<sup>11</sup> according to whom the first product of plant metabolism is formic acid, which undergoes transformation to glycolic aldehyde and this into hexoses. It was suggested on that occasion that the possible role of certain intermediate products such as acetaldehyde, formed in plant respiration, had been to a large degree overlooked, and that phenolic substances might very well originate in the plant as the result of condensation reactions between three types of building units, namely, VIII, IX and X

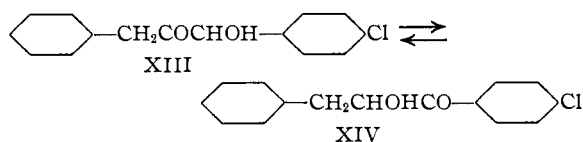


as shown below, for example, in the plant synthe-



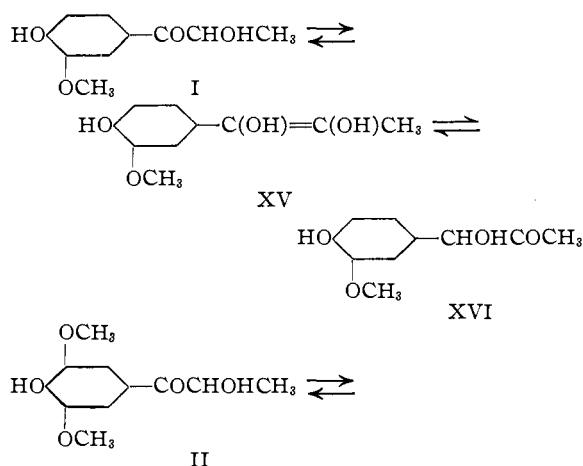
sis (theoretical) of inositol (XI) and 1,3,4-trioxybenzene (XII) from 3 moles of glycolic aldehyde and from two moles of formic acid with two moles of vinyl alcohol, respectively.

The recent identification of the two derivatives  $\alpha$ -hydroxypropiovanillone (I) and  $\alpha$ -hydroxypropiosyringone (II), as probable building units of "extracted" lignin permits of an extension of this point of view, especially when their structure and properties are compared with those of analogous products such as glyceric aldehyde and dihydroxyacetone,<sup>12</sup> benzoin and methyl hydroxybenzyl ketone,<sup>13</sup> glucose, fructose, mannose,<sup>14</sup>  $\alpha$ -phenyl- $\beta$ -oxo- $\gamma$ -hydroxy- $\gamma$ -(*p*-chlorophenyl)-propane and  $\alpha$ -phenyl- $\beta$ -hydroxy- $\gamma$ -oxo- $\gamma$ -(*p*-chlorophenyl)-propane,<sup>15</sup>  $\alpha$ -phenyl- $\beta$ -benzoyl propiolactone and



$\alpha$ -phenyl- $\beta$ -hydroxy- $\gamma$ -oxo- $\gamma$ -(*p*-methoxyphenyl)-propane.<sup>16</sup>

It is to be anticipated that such products as I and II will most probably be in equilibrium with, or at least readily interchangeable into, their "dismutation" isomers (XV, XVI and XVII, XVIII). If this is true, it is possible to draw certain far-reaching conclusions regarding the nature of "extracted" lignins and plant synthesis.



(8) Spring Meeting, American Chemical Society (Cellulose Division), April, 1937.

(9) Baeyer, *Ber.*, **3**, 63 (1870).

(10) Robinson, "The Molecular Architecture of Some Plant Products," International Congress of Pure and Applied Chemistry, Madrid, 1934, in which the author states (p. 6), "The author considers that the benzene nuclei, in most cases, represent original C<sub>6</sub> sugar units, but it is unlikely that this is invariably the case."

(11) Rochleder, "Phytochemie," 1854, p. 321; Erlenmeyer, *Ber.*, **10**, 634 (1877); Ballo, *ibid.*, **17**, 10 (1884); Michael, *J. prakt. Chem.*, **N. F.** **60**, 483 (1899); Euler, *Z. physiol. Chem.*, **59**, 122 (1909); Baur, *Naturwissenschaften*, **1**, 474 (1913); Parnas, *ibid.*, **1**, 819 (1913).

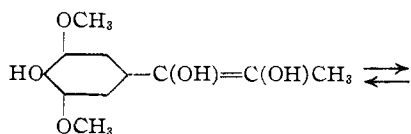
(12) Wohl, *Ber.*, **38**, 3095 (1900); Fischer, *ibid.*, **60**, 479 (1927); Evans, *THIS JOURNAL*, **47**, 3085 (1925); **48**, 2703 (1926).

(13) Favorsky, *Bull. soc. chim.*, **39**, 215 (1925).

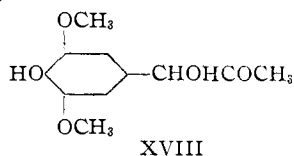
(14) Lobry de Bruyn, *Ber.*, **28**, 3078 (1895).

(15) Philip G. Stevens, Ph.D., Dissertation, Harvard University, 1929. This work is of especial interest in that the author establishes the existence of an identical equilibrium commencing with either product.

(16) (a) Kohler and Kimball, *THIS JOURNAL*, **56**, 729 (1934); (b) Kohler and Leers, *ibid.*, **56**, 981 (1934).



XVII



XVIII

In the writer's opinion the general mechanisms of carbohydrate metabolism in higher plants, and of alcoholic fermentation by bacteria (the latter representing the lowest form of plant life), are closely related. The mechanism of both respiration in the higher plants and of alcoholic fermentation involves the conversion of carbohydrates into the end-products, carbon dioxide and water, whereas plant synthesis is essentially the reverse of this process. Although the mechanisms of the different phases of carbohydrate metabolism in various forms of plant life have not been definitely established, many theories have been suggested to account for these transformations.

Earlier workers<sup>17</sup> believed that methyl glyoxal was the principal intermediate in alcoholic fermentation, and Onslow<sup>18</sup> has even suggested that this derivative may be an intermediate in the formation of carbon dioxide during respiration in the higher plants. Recent work by Meyerhoff and Lohmann,<sup>19</sup> however, has shown the existence of an equilibrium between hexose diphosphate and phosphodihydroxyacetone, and Robinson<sup>20</sup> has based his most recent views on alcoholic and lactic acid fermentations on this dihydroxyacetone as the principal intermediate in both processes. Nevertheless, the frequent occurrence of methyl glyoxal in fermentation reactions and the isolation of enzymes capable of bringing about its dismutation, which are present not only in bacteria, but also in the higher plants,<sup>21</sup> indicate that methyl glyoxal presumably could occur as an intermediate constituent in one or other phase of carbohydrate metabolism.

The dismutation form of I, namely, XVI, on

(17) Wohl, *Ber.*, **34**, 1139 (1901); Neuberger and Kerb, *Biochem. Z.*, **31**, 173 (1911); **36**, 68 (1911); **58**, 158 (1913).

(18) Onslow, "Principles of Plant Biochemistry," Cambridge University Press, 1931.

(19) Meyerhoff and Lohmann, *Naturwissenschaften*, **22**, 134 (1934); *Biochem. Z.*, **271**, 89 (1934); **237**, 413 (1934); **275**, 430 (1935).

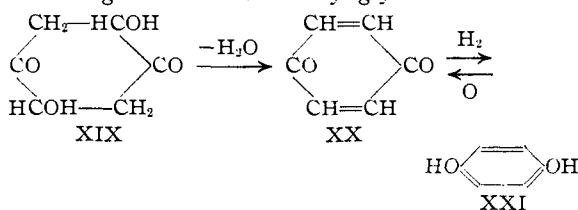
(20) Robinson, *Biochem. Rev.*, **5**, 187 (1936).

(21) Neuberger and Gorr, *Biochem. Z.*, **171**, 475 (1926); Neuberger and Kobel, *ibid.*, **179**, 459 (1926).

examination, is seen to be an aldol derived from condensation of guaiacol and methyl glyoxal, while XVIII is the corresponding analog from pyrogallol 1,3-dimethyl ether. It was pointed out some forty years ago by Michael<sup>22</sup> that this type of condensation occurs readily at room temperature in presence of a small amount of acid, and it is significant that he should have written at that time (22a, p. 349): "The above results make it extremely probable that the formation of at least some of the resins in the vegetable world is due to aldehydes and phenols coming into contact with the contents of the cells, as both of these classes of compounds are undoubtedly among the products formed in plant life."

These condensation products, as already shown<sup>1,2</sup> are very unstable substances and readily undergo conversion, under the influence of mild chemical reagents, into derivatives closely resembling "extracted" lignins.

Methyl glyoxal is an extraordinarily reactive substance, the properties of which have been little investigated. It is known to form a dimer<sup>23</sup> the structure of which has not been established. It is possible that this dimer is a cyclic diketone (XIX) formed by an intermolecular aldol condensation, involving two moles of methyl glyoxal



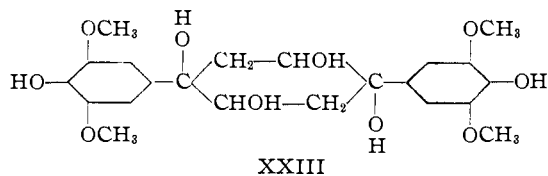
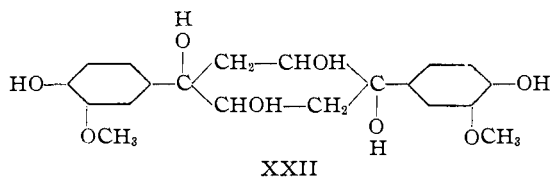
which on loss of water would yield benzoquinone (XX). The presence of the latter substance as one component of an oxidation-reduction system (XX-XXI) would provide a mechanism through which numerous processes of plant synthesis could be effected.

It is therefore of interest that Cross and Bevan<sup>24</sup> some sixty years ago reported the presence of chloroquinones in the reaction products obtained by the action of chlorine on lignin. The cyclic diketone XIX could condense with *two* moles of guaiacol or 1,3-pyrogallol dimethyl ether, respectively, to give XXII and XXIII, and these products may be the parent substances from which

22) Michael, *Am. Chem. J.*, (a) **5**, 338, 349 (1884); (b) **9**, 130 (1887).

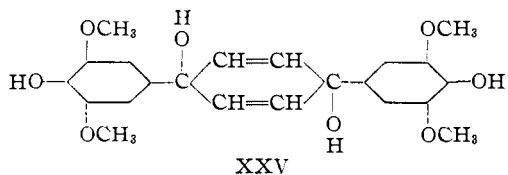
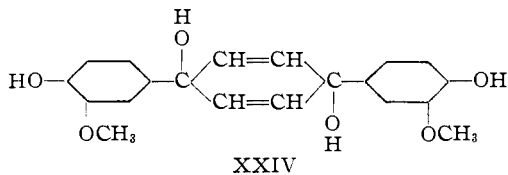
(23) Moulds and Riley, *J. Chem. Soc.*, 621 (1938).

(24) Cross and Bevan, *ibid.*, **38**, 666 (1880); *ibid.*, **41**, 109 (1882); "Cellulose," Longmans, Green and Company, London, 1895, pp. 134-137.



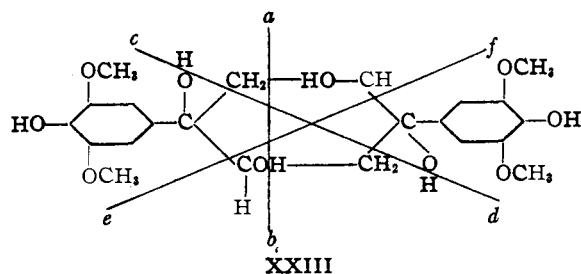
the ethoxy derivatives corresponding to I and II are derived, the latter formed by simultaneous cleavage and ethoxylation, as indicated below.

It is, of course, also possible that they could be formed from the analogous condensation products XXIV and XXV



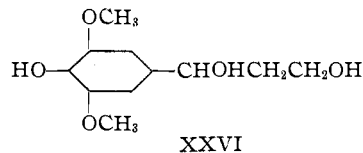
which represent condensation products, formed by loss of water from XXII and XXIII, or by direct condensation of benzoquinone with the two phenols.

In the case of XXIV and XXV, ring fission would give the vinyl derivatives and such products are known to add on water and alcohol very readily. The manifold reactivity of the above postulated condensation products formed from XXII, XXIII, XXIV and XXV may be illustrated by the varied manner in which cleavage could occur, for example with XXIII



Along (ab) two moles of the aldehyde (III) would

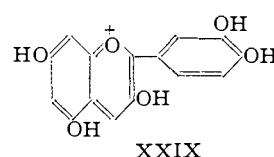
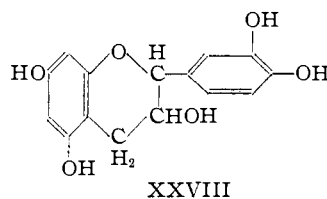
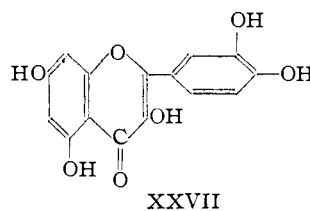
be formed; along (cd) two moles of  $\alpha$ -hydroxypropiosyringone (II); along (ef) two moles of  $\beta$ -syringyl- $\beta'$ -hydroxypropionaldehyde (IV) and one mole each of syringoyl acetaldehyde (VI) and 1-syringyl-1-hydroxypropanol-3 (XXVI).



It is significant that an aldehyde isolated from the soluble ethanolysis products from maple wood,<sup>6</sup> and now identified as having the structure IV, should appear as a (theoretical) cleavage product of the above unit (XXIII).

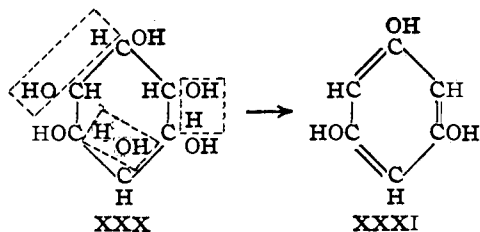
The important role played by such dimeric substances (XXIII) in the biogenetic synthesis of plant phenol resins has been shown quite recently by H. Erdtman<sup>25</sup> in a comprehensive review of this field.

**Synthesis of Plant Pigments.**—These are characterized by the presence of the skeletal forms XXVII, XXVIII and XXIX (quercetins, catechins, cyanidins, respectively)

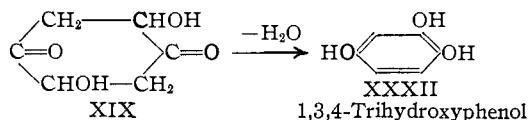


which can be visualized as formed by a process of condensation between phloroglucinol and a  $C_6-C_3$  derivative, the latter being related possibly to the recently isolated lignin building units I and II. Phloroglucinol XXXI may be postulated as arising from inositol XXX by loss of three moles of water

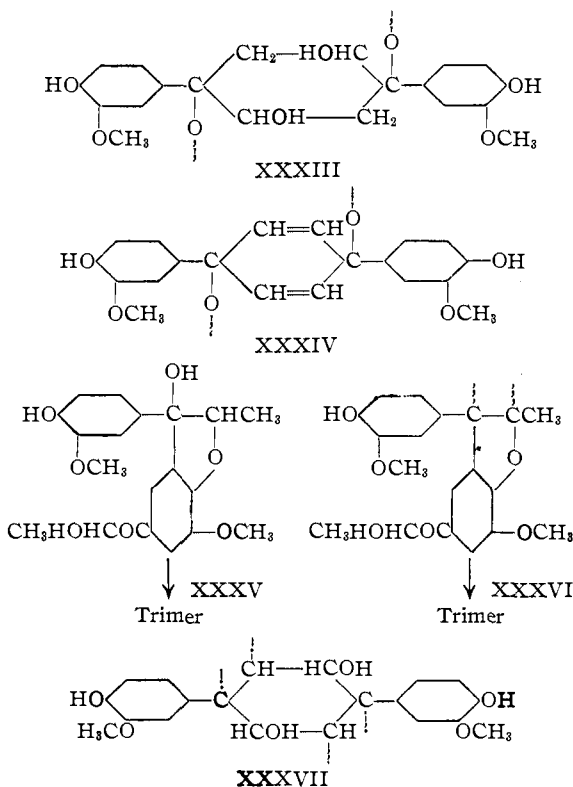
(25) Erdtman, *Svensk. Kem. Tid.*, **48**, 250 (1936).



A plant synthesis of phenolic derivatives from the methyl glyoxal dimer also may be formulated as taking place along the following lines



With such reactive substances present in wood as those indicated by XXII, XXIII, XXIV and XXV, as well as their fission products, namely, I, II, it is evident that a wide variety of polymerization and condensation reactions are possible under the influence of the reagent used as the extraction medium to give "extracted" lignins, a few types of which are shown below



The type of condensation shown by XXXV is of interest in that it is not possible for two moles of the corresponding syringyl derivative to undergo polymerization in this manner. It might thus

account for the well-known marked differences shown by spruce and maple in their behavior toward extractants.

The nature of these condensation polymers represented by the insoluble "ethanolysis" and other "extracted" lignins is under intensive investigation and experiments on hydrogenation are expected to throw much light on this subject.

An investigation on the structure of synthetic lignins such as methanol, etc., from the building units I and II is under way as is also one on the nature of the methyl glyoxal dimer and of the products obtained in the condensation of methyl glyoxal with guaiacol and other phenols.

In forthcoming papers experimental evidence will be given in support of the theory presented here, from new data acquired in studies on the action of acids (sulfuric acid, sulfurous acid, etc.), alkalis, methylating, acetylating, and chlorinating agents, etc., on the newly isolated lignin building units I and II.

#### Possible Biogenetic Synthesis of the Lignin Building-Unit from Vanillin and Acetaldehyde.—

While in the foregoing, the plant biogenetic synthesis, from guaiacol and methyl glyoxal, of the lignin building-unit has been emphasized, the possibility must not be overlooked that this could take place also through a "carbolygase enzyme synthesis"<sup>26</sup> from vanillin and acetaldehyde (the latter a well-recognized intermediate product of fermentation and also of plant respiration) in a manner similar to the classical synthesis of  $\alpha$ -hydroxypropiophenone by Neuberg and coworkers<sup>26</sup> by the addition of benzaldehyde to a solution of glucose undergoing vigorous yeast fermentation. Experiments are in progress on such a synthesis, using vanillin in place of benzaldehyde. The resulting product on dismutation would yield I and this on dimerization could give XXII.

#### Summary

1. A new theory of plant synthesis is proposed in which methyl glyoxal, or its dismutation isomers, formed during plant metabolism is postulated as the key substance concerned in the formation of lignins, tannins and pigments.

2. It is considered that methyl glyoxal readily can undergo transformation to a dimeric cyclic ketone, the result of an intermolecular aldol condensation reaction. Both monomer and dimer

(26) Neuberg and Hirsch, *Biochem. Z.*, **115**, 282 (1921); Neuberg and Liebermann, *ibid.*, **121**, 311 (1921); Neuberg and Ohle, *ibid.*, **127**, 327 (1922); **128**, 610 (1922).

can then further react with guaiacol, for example, to give  $C_6-C_3$  and  $C_6-C_6-C_6$  systems.

The probable existence of two types of  $C_6-C_6-C_6$  systems is postulated, namely, one from the cyclic diketone and one from benzoquinone. It is regarded as more probable that the  $C_6-C_6-C_6$  systems form the true basic lignin building units present in wood. Action of acids results in cleavage of these to give very reactive  $C_6-C_3$  types which then undergo, to a greater or lesser extent, polymerization-condensation reactions under the influence of the extractant to yield water-insoluble "extracted" lignins.

3. On the basis of the new experimental evidence it seems likely that there are present four types of "lignin" in wood, corresponding to: (a) the simple  $C_6-C_3$  unit; (b) the simple  $C_6-C_6-C_6$  unit; (c) reversible polymers of (a) and (b); (d) irreversible polymers of (a) and (b).

4. "Extracted" lignins correspond to Types (c) and (d).

5. The marked difference existing between spruce and maple woods in regard to the amounts of extractable, water-soluble, "ethanolysis" products points to a fundamental difference between the lignin constituents of soft and hard woods, and is explainable on the assumption of the inability of the syringyl building units present only in hard woods to undergo condensation to *irreversible* condensation polymers.

6. The suggestion is put forward that tannins and pigments originate in the plant as a result of a series of related condensation reactions between phenols and a  $C_6-C_3$  unit, the latter arising from condensation reactions between methyl glyoxal and a phenol.

7. The possibility that the lignin building-unit may be formed in the plant through the agency of a "carboligase enzyme" reaction from vanillin and acetaldehyde is pointed out.

MONTREAL, CANADA

RECEIVED NOVEMBER 14, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Relative Reactivities of Organometallic Compounds. XXI. Organolead Radicals and Derivatives

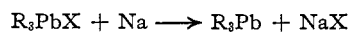
BY HENRY GILMAN AND JAMES C. BAILIE

### Introduction

The general procedures for the preparation<sup>1</sup> of organolead radicals may be classified roughly as reductions and direct alkylations. The best illustrations of reduction are the preparation of triethyllead by electrolysis of triethyllead hydroxide, and by the recently reported<sup>2</sup> reaction of sodium in liquid ammonia on triethyllead bromide. Direct alkylations have been effected by interaction of sodium-lead alloys and alkyl halides, and by reaction of lead chloride with the Grignard reagent or organolithium compounds. The Grignard method has been the best procedure used hitherto for the synthesis of triaryllead compounds.<sup>3</sup> It is quite probable that  $R_3Pb$  compounds are formed as intermediates<sup>4</sup> in the prepa-

ration of  $R_4Pb$  compounds by the Grignard reaction. However, tricyclohexyllead and no tetracyclohexyllead is formed from cyclohexylmagnesium bromide and lead chloride.<sup>5</sup>

In connection with studies on relative reactivities, organolead hydrides and dissociable triaryl-triarylmethyllead compounds, we have prepared seven additional triaryllead compounds, each substituted in the nucleus with so-called positive groups. These compounds were prepared by the conventional Grignard procedure. In addition, some of them were synthesized by the sodium in liquid ammonia reduction method which is so effective with triethyllead.<sup>2</sup>



Although this method of preparation involves more steps than the Grignard procedure, it is a method of choice for some thermally unstable  $R_3Pb$  types and offers access to unsymmetrical organolead radicals:  $R_2R'PbX + Na \longrightarrow R_2R'Pb + NaX$ . The general sodium-liquid ammonia

(1) For excellent accounts of organolead compounds, see (a) Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937; (b) Calingaert, *Chem. Rev.*, **2**, 43 (1925).

(2) Calingaert and Soroos, *J. Org. Chem.*, **2**, 535 (1938).

(3) Krause and co-workers, *Ber.*, **52**, 2165 (1919); **54**, 2060 (1921); **55**, 888 (1922); Goddard, *J. Chem. Soc.*, **123**, 1161 (1923); Austin, *This Journal*, **53**, 1548 (1931).

(4) See p. 409 of Ref. 1a.

(5) Krause, *Ber.*, **54**, 2060 (1921).