SOME FISSION PRODUCTS
OF
FURANS AND LIGNIN

SOME FISSION PRODUCTS OF FURANS AND LIGNIN

A Thesis

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for the Degree of Doctor of Philosophy

by

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PART ONE.

SOME FISSION PRODUCTS OF FURANS

PART ONE. CLAIM TO ORIGINAL RESEARCH

1. The mechanism of conversion of furfuryl alcohol to methyl levulinate, has been studied, and a more satisfactory mechanism suggested than the one proposed by Pummerer.

2. The use of 2,4-dinitrophenylhydrazine hydrochloride, as a reagent, for the study of ring opening in the furan series, has been developed.

3. Some older methods for the recovery of carbonyl compounds from their derivatives, namely distillation with aqueous sodium hydroxide (10%), or sodium carbonate (saturated), chromic acid oxidation and ozonolysis, have been applied to 2,4-dinitrophenylhydrazones.

4. A method has been proposed for the synthesis of derivatives of δ-methoxy-levulinaldehyde-dimethylal.

5. The assumption that δ-methoxy-levulinaldehyde-dimethylal is an intermediate in the conversion of furfuryl alcohol into methyl levulinate, as proposed by Pummerer, has been shown to be incorrect.

HISTORICAL REVIEW

PART ONE A. GENERAL INTRODUCTION

(a) History of Furan Chemistry

The discovery of Furoic acid as a pyrolysis product of mucic acid by Scheele 1) in 1780, opened up a complex and extremely interesting field of chemistry. In spite of the early discovery of furans, knowledge of this particular branch of organic chemistry is still very limited.

Most attempts at determination of structure by substitution and addition reactions have failed, since furan and substituted furans are highly sensitive to the action of mineral acids. In most cases, these bring about the formation of tars, resins and heavy oils of such complex structures that it has been impossible as yet, to determine their nature.

The sensitivity of the furan compounds depends upon the nature of substituent groups, and as one consequence, considerable work has been carried out on the more stable furoic acid.

Furan derivatives can be converted into more or less simple aliphatic compounds, and it is the ease of this conversion which has enabled investigators to clarify many of the structures and reactions of furan.

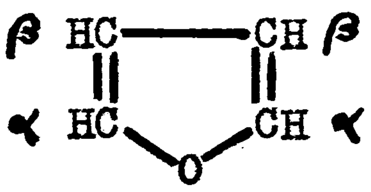
At the present time, there is available a large supply of furan raw material. However, in spite of this, no extended commercial use has been developed for same.

The principal source of furans is to be found in the carbohydrate present in waste products (oat hulls, etc.) and the fact that they or their decomposition products may represent an essential part of the lignin structure 2)3), makes a study of their properties of considerable interest.

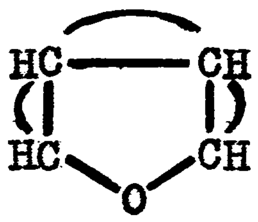
(b) The Constitution of Furan

Furan is a heterocycle consisting of four carbon atoms, and one oxygen atom. Little proof has been offered as yet, of the structure of furan outside of the fact that there is a heterocyclic ring present.

Numerous formulae have been offered for the heterocyclic viz:



1.



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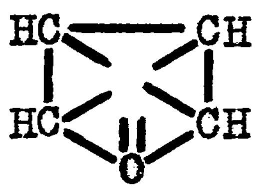

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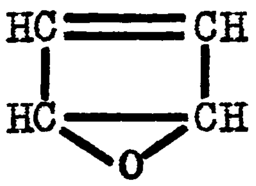

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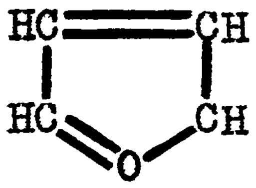


5.

and each one explains some of the facts of furan chemistry. However, formula 1. above is the one in common usage, since it can be used to explain the greatest number of experimental facts. Structure 4. shown above, cannot be entirely discarded since it may be applied to certain phenomena which cannot be properly explained on the basis of formula 1.

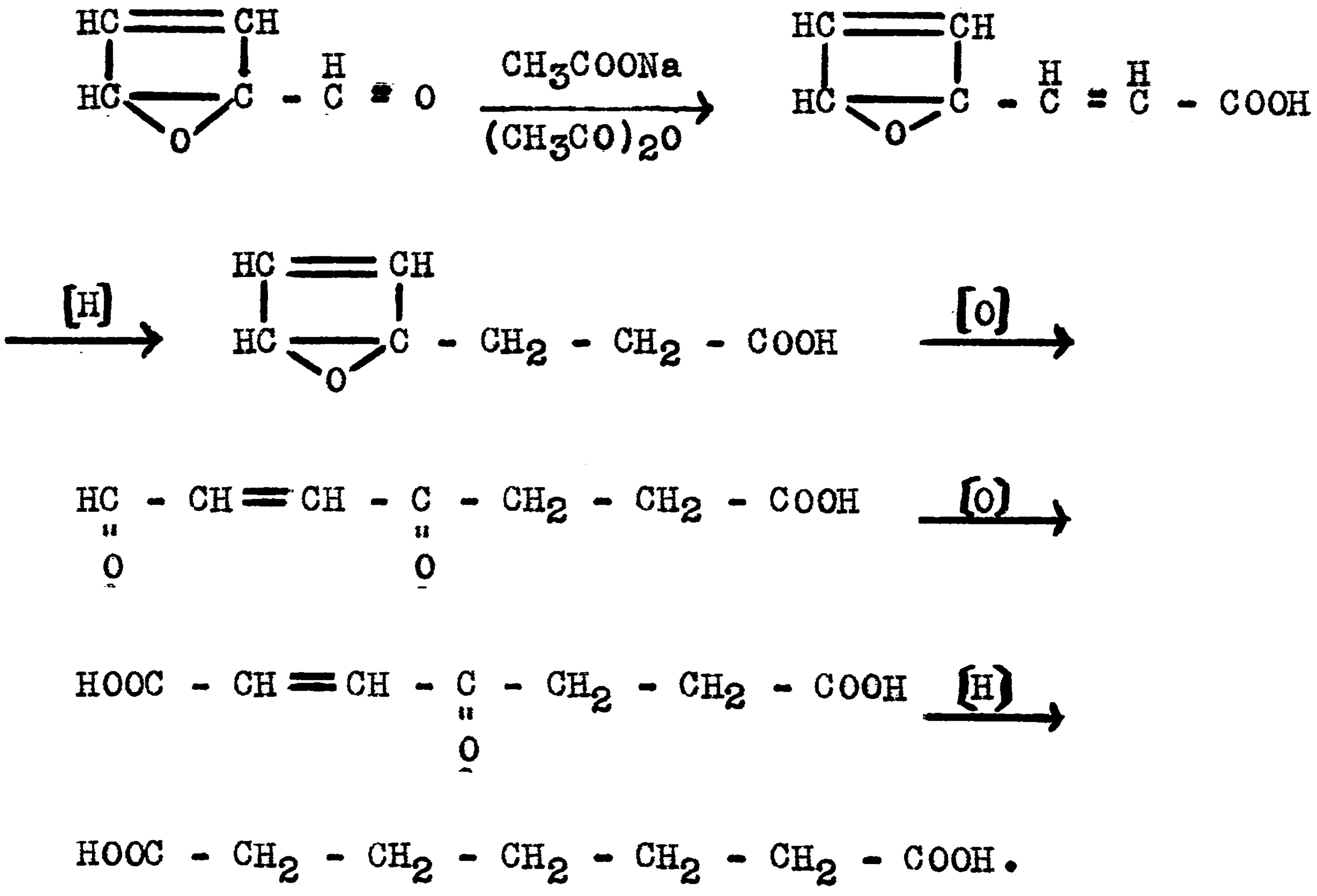
It will be noticed that the generally accepted formula 1. contains a conjugated system of double bonds, a necessary postulation since several cases of 1,4-addition 4) 5) 6) 7) have been reported in the literature. Furthermore, furans undergo condensation with maleic anhydride 6) to give typical condensation products of a conjugated system with one, which contains a double bond.

On the basis then, of 1,4-addition and the occurrence of the Diels-Alder reaction, it is proposed to use in this thesis the modern accepted formula for furans, but at the same time, the fact must not be overlooked that this is accepted with reservations by various workers in the furan field. Others assume that furan is not merely one compound but an equilibrium mixture of two or more of these forms.

B. STRUCTURE OF FURFURAL AND OTHER α-SUBSTITUTED FURANS

Furfural, which is an aldehyde substituted furan, is available in large quantities. Because it can be formed in relatively high yields from pentosan waste materials, it has been the subject of numerous investigations. Furthermore, its constitution has been definitely established, and it may be converted by reliable reactions into other important α-substituted furans.

The structure of furfuraldehyde as an α-substituted aldehyde was established by von Baeyer [8] in 1877 by the following reactions;



$$\xrightarrow{[H]} \text{C}_4\text{H}_3\text{O}-CH_2-CH_2-COOH \xrightarrow{[O]}$$

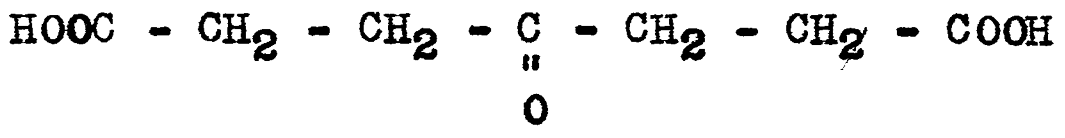
$$\overset{}{\underset{O}{\underset{\|}{HC}}} - CH{=}CH - \underset{O}{\underset{\|}{C}} - CH_2 - CH_2 - COOH \xrightarrow{[O]}$$

$$HOOC - CH{=}CH - \underset{O}{\underset{\|}{C}} - CH_2 - CH_2 - COOH \xrightarrow{[H]}$$

$$HOOC - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - COOH.$$

von Baeyer used this series of reactions to prove the ethylene oxide structure for the furan nucleus. The Perkin synthesis necessarily gave rise to an unsaturated acid, and the succession of reactions, ending with the formation of pimelic acid, established the presence of the acrylic acid group on the α-carbon atom, as otherwise a branched chain compound would have been formed.

Curiously enough von Baeyer used the above series of reactions to prove the ethylene oxide structure for the furan nucleus, whereas Marckwald 9) considered the same series of reactions proved the diolefin formula for the nucleus. The latter started with furyl acrylic acid, obtained from furfuraldehyde and on ring opening with alcoholic-HCl isolated the following acid:



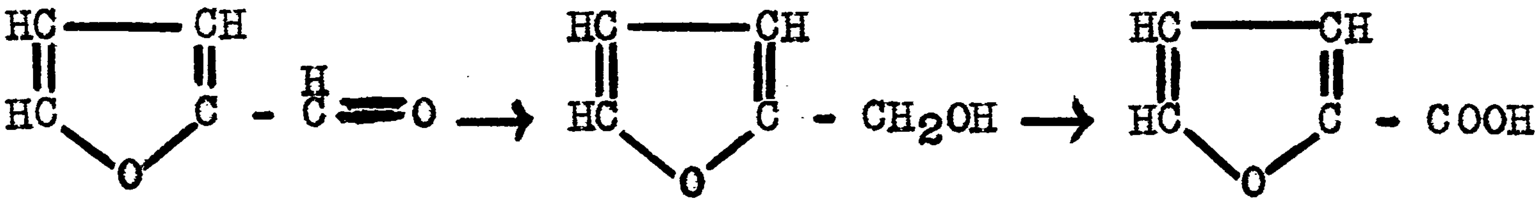
$$HOOC - CH_2 - CH_2 - \underset{\overset{\|}{O}}{C} - CH_2 - CH_2 - COOH$$

which on reduction gave pimelic acid;

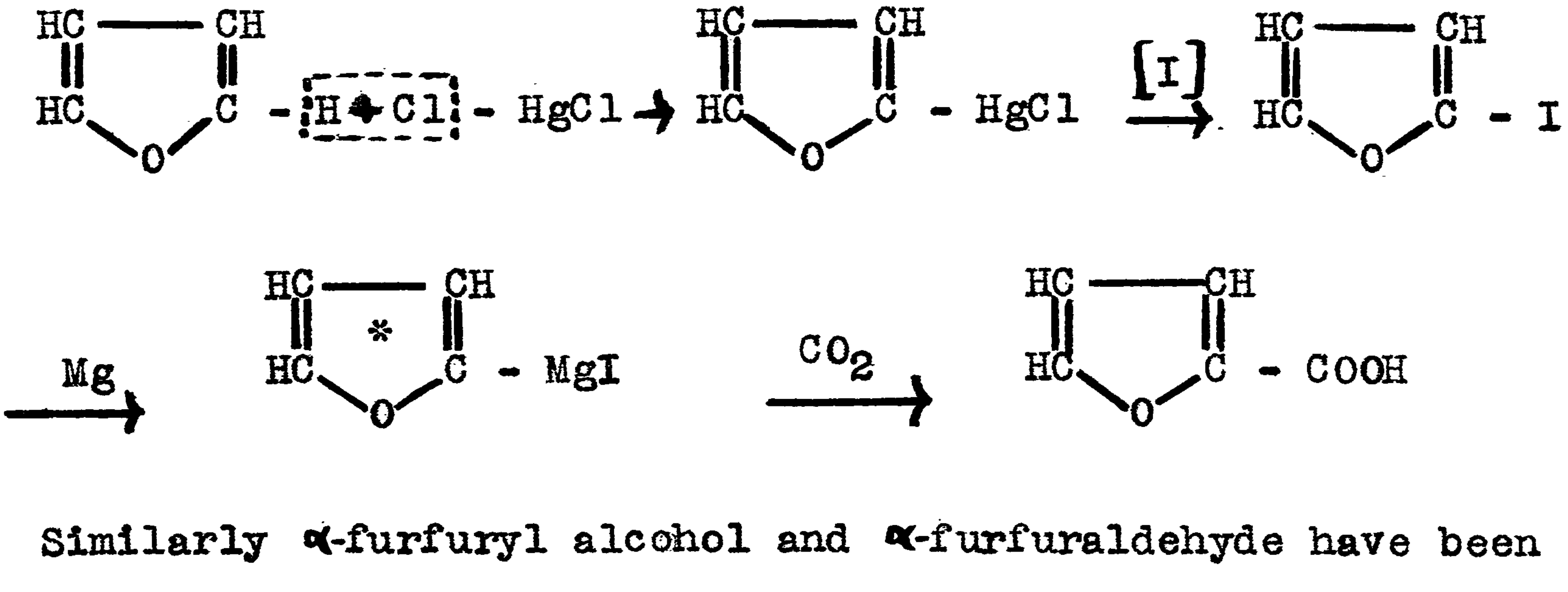
$$HOOC - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - COOH$$

Since both investigators thus proved the presence of the aldehyde as an α-substituent in the furan ring, it necessarily followed that many of the furan types which had been derived from it, were also of the α-type.

Sylvan, prepared from furfural by the use of hydrazine hydrate and solid sodium hydroxide is thus an α-methyl furan. Furfuryl alcohol and furoic acid obtained from furfural by a Cannizzaro reaction are consequently α-substituted furans as shown below:



By a comparison of these compounds with others secured by direct nuclear substitution of furan, the structure of the latter could be easily proven. For example, furan can be mercurated with mercuric chloride and converted into furoic acid, identical with that secured from a Cannizzaro reaction with α-furfuraldehyde:

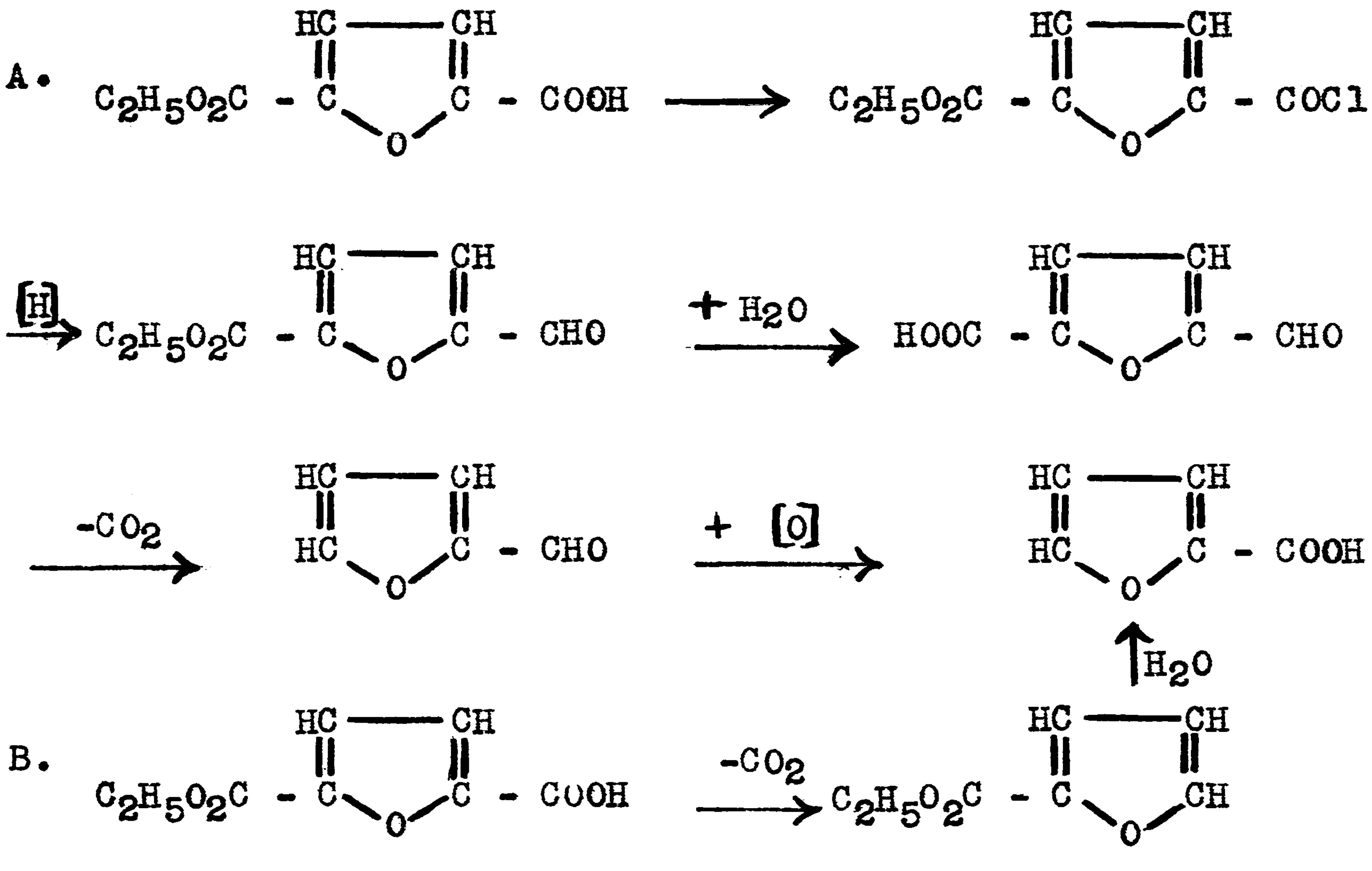


Similarly α-furfuryl alcohol and α-furfuraldehyde have been formed from the above Grignard reagent * 10) 11).

Other nuclear substitution reactions, viz. the Friedel-Crafts reaction, the Gatterman-Koch modification, and replacement of nuclear hydrogen by alkali metals, lead to substituents which, by relation to the foregoing reactions, are necessarily α-substituents. It would appear that direct nuclear substitution takes place in the α-position since up to the present time it has been impossible to isolate any β-monosubstituted product from such a substitution reaction.

C. IDENTITY OF THE TWO α-POSITIONS IN FURAN

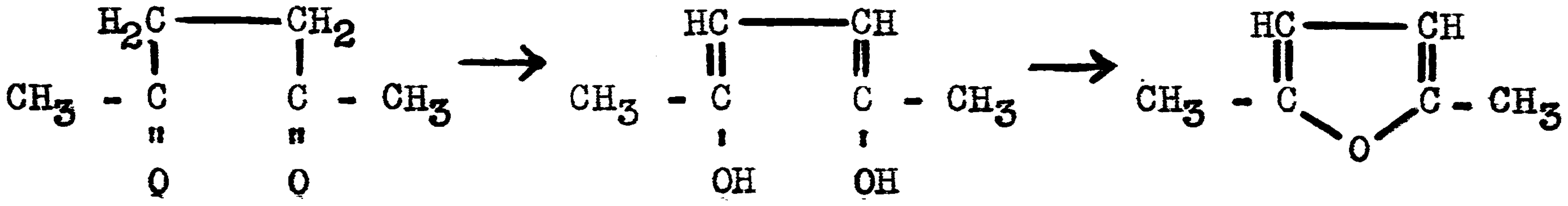
Since it is possible to isolate only one monosubstituted furan from a reaction mixture it might be concluded that the two α-positions are similar. For direct proof however, Plyler 12) carried out the following series of reactions:



In each case the identical 2-furoic acid was obtained. Of course one assumption was necessary in this series of reactions, viz., the stability of the carbon to carbon linkage which would make a 2,5-rearrangement of the substituent impossible.

Nuclear substitution of an α-substituted furan usually takes place in the free α-position, no matter what the nature of the previous substituent. This has been shown in a number of ways.

Primarily, disubstituted compounds have been compared with disubstituted compounds of known structure. Secondly, disubstituted compounds have been made from disubstituted compounds with concurrent removal of one of the original substituents. And finally, disubstituted compounds have been secured through ring closure of known compounds, e.g.:



and the synthesis of 2,5-dimethyl furan supplies a reference compound for other disubstituted compounds.

In this thesis it has been decided to omit any reference to tri- or tetra-substituted furans as it is believed that there is no relationship between them and the work investigated.

D. SUPER AROMATIC PROPERTIES OF FURAN

Furan derivatives are believed by Gilman and co-workers to have "super-aromatic" properties, that is, in those reactions which demonstrate a difference between the so-called aromatic and aliphatic series, furan reacts as if it possessed a more aromatic nature than does benzene.

With the ethyl ester of 2-furylacrylic acid, bromine shows a greater tendency to replace the nuclear hydrogen than it does to form an addition product with the unsaturated aliphatic side chain. Further, nitration of furyl phenyl ketone leads to formation of a nitrofuryl phenyl ketone rather than to formation of a furyl nitrophenyl ketone. On the basis of the above Gilman 13) was led to believe that furan possesses superaromatic properties.

E. THE CONVERSION OF HEXOSES TO LEVULINIC ACID

The conversion of hexoses into levulinic acid was first reported in 1840 by Kalk van Mulder 14), who isolated "glucinic" acid by a sulphuric acid treatment of corn sugar. Tollens and von Grote 15), in 1873 repeated the procedure and called their product levulinic acid. In 1881 these same authors starting with sucrose were able to isolate some 8 - 9% of levulinic acid. Rischbeith 16), in 1885 obtained a yield of 13% levulinic acid from potato starch and hydrochloric acid. During the same period and by a similar procedure, levulinic acid was prepared from lactose by Rodewald and Tollens 17); from galactose by Kent and Tollens 18); from raffinose by Rischbeith and Tollens 19); and from mannose by von Grote and Tollens 20).

A synopsis of the work carried out by earlier investigators is given in the accompanying table:

TABLE I

Mode of Treatment of Various Carbohydrates in Relation to Yield of Levulinic Acid

Author			Starting Material		Yield
Grote and Tollens	(15),	1875	sucrose	400 g. sucrose; 400 g. H_2SO_4; 4300 g. H_2O. Reflux on steam bath 8 times for 2-3 days at a time.	Trace
Grote, Kehrer and Tollens	(15),	1881	sucrose	1000 g. sucrose; 1000 g. H_2O; 100 cc. H_2SO_4.	Crude 8-9%
Grote and Tollens	(15),	1875	d-fructose	Discuss d-fructose as a raw material for preparation of levulinic acid.	
Grote and Tollens	(15),	1875	inulin	11 g. inulin; 11 g. H_2SO_4; 220 cc. H_2O; refluxed 4 days.	Not given
Grote and Tollens	(15),	1881	d-glucose	50 g. glucose; 50 g. H_2SO_4; 450 g. H_2O; states that HCl gave better results.	Trace, mostly humic acid.
Rodewald and Tollens	(17),	1881	lactose	100 g. lactose; 10 g. H_2SO_4; 200 g. H_2O (14 days)	do.
Kent and Tollens	(18),	1885	d-galactose	10 g. galactose; 20 cc. HCl (5 hours)	do.

(continued)

TABLE I (cont'd)

Mode of Treatment of Various Carbohydrates in Relation to Yield of Levulinic Acid

Author			Starting Material		Yield
Rischbeith and Tollens	(19),	1886	raffinose	2 g. raffinose; 11 cc. H_2O; 1 cc. H_2SO_4 (3 hours)	Trace, mostly humic acid.
Rischbeith and Tollens	(16),	1887	starch	10 g. starch; 20 cc. 10% HCl (20 days)	13%
Conrad and Guthzeit	(21),	1885	sucrose	Show yield depends upon acid concentration.	
Conrad and Guthzeit	(21),	1885	galactose	Discussion.	
Conrad and Guthzeit	(21),	1886	d-fructose	Yields poor in all cases, fructose gave best results.	
Conrad and Guthzeit	(21),	1866	lactose	Discussion.	
Fischer and Hershberger	(22),	1889	mannose	10 g. mannose; 30 g. fuming HCl.	0.2 g.
Smith and Tollens	(23),	1900	sorbose	Discussion.	

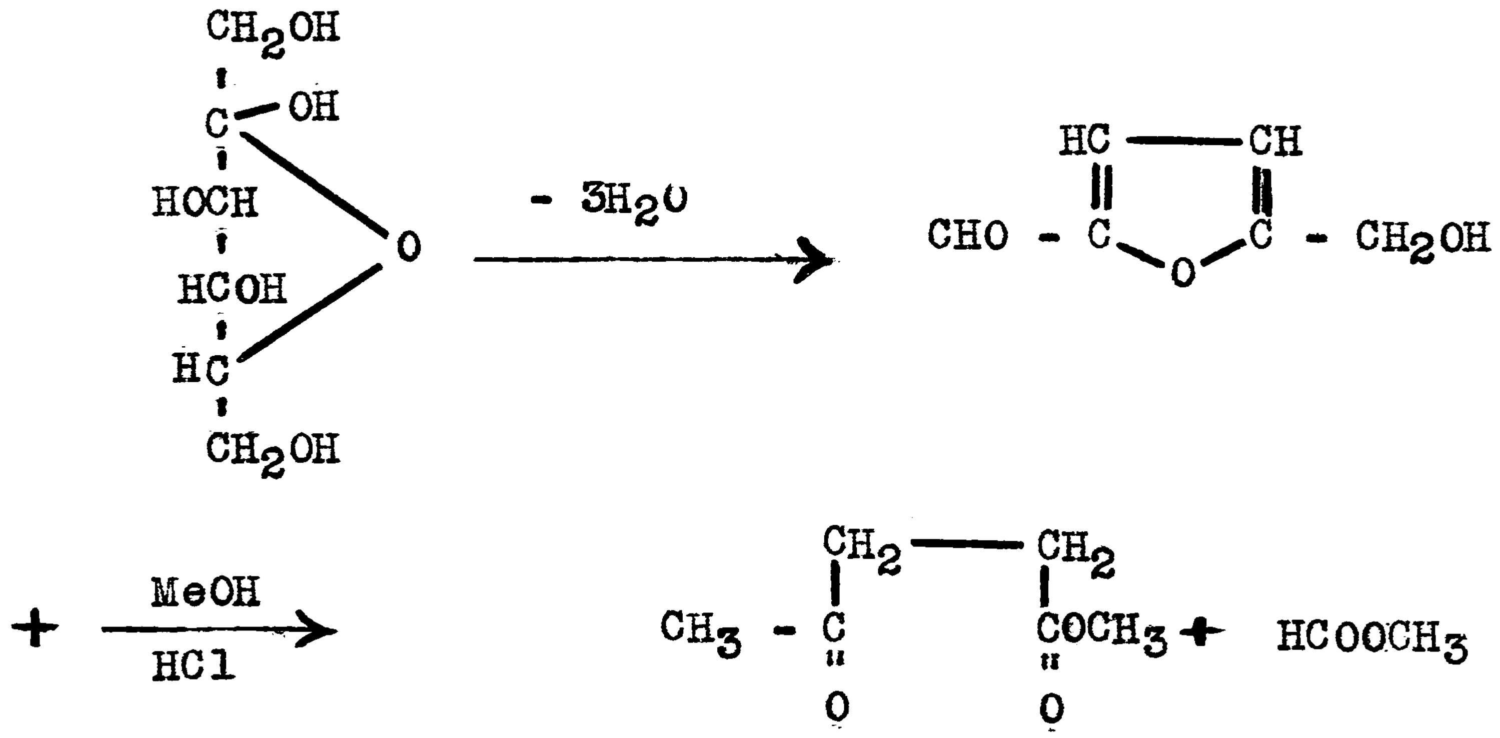
It may be seen from the above table that a variety of carbohydrates yield levulinic acid on treatment with acid, although generally in very small amount, dependent on the starting material and the conditions employed. As early as 1888 Wehmer and Tollens [24], concluded that "The formation of levulinic acid from carbohydrate materials under the influence of mineral acids, is a characteristic reaction of hexoses".

Dull [25] pointed out that an aldehyde was formed when inulin (a fructose polymer) was treated with aqueous oxalic acid. This aldehyde on further treatment with acid yielded levulinic acid. However, Kiermeyer [26] was the first to identify this aldehyde as hydroxymethyl-furfuraldehyde and he showed that this aldehyde on treatment with acid yielded 80% of levulinic acid. A much higher yield of this aldehyde has been secured from fructose in these laboratories by S. Trister [27]. No attempt was made to explain the mechanism of the change from hexose to hydroxymethyl-furfural nor from hydroxy-methyl-furfural to levulinic acid. The aldehyde is formed both from aldoses and ketoses. However, in the latter case, where the configuration of the hexose more nearly approaches that of the aldehyde, yields are much higher. E. Fischer [28] showed that the action of methanolic-HCl on glucose or glucose polymers led to the formation of the corresponding alcoholic glucoside, whereas fructose did not yield a methyl fructoside.

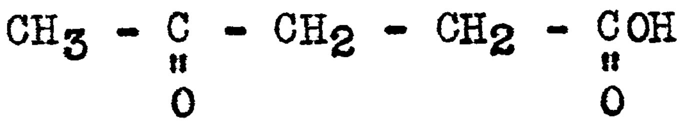
Weidenhagen and Korotkj 29) using alcoholic HCl showed that keto-hexoses were converted into the corresponding levulinic acid ester and the alkoxy-methyl-furfural whereas aldoses under the same conditions yielded only the corresponding glucoside.

However, under more drastic conditions, the levulinic acid ester and alkoxyl-methyl-furfural may also be obtained, though in poor yields, from aldoses. Increase in acid concentration increases the yield of levulinic acid and decreases the yield of hydroxymethyl-furfural.

The mechanism of conversion from hexose has not been explained up to the present and the reaction for the conversion of fructose might be written simply, as follows:



F. THE CHEMISTRY OF LEVULINIC ACID



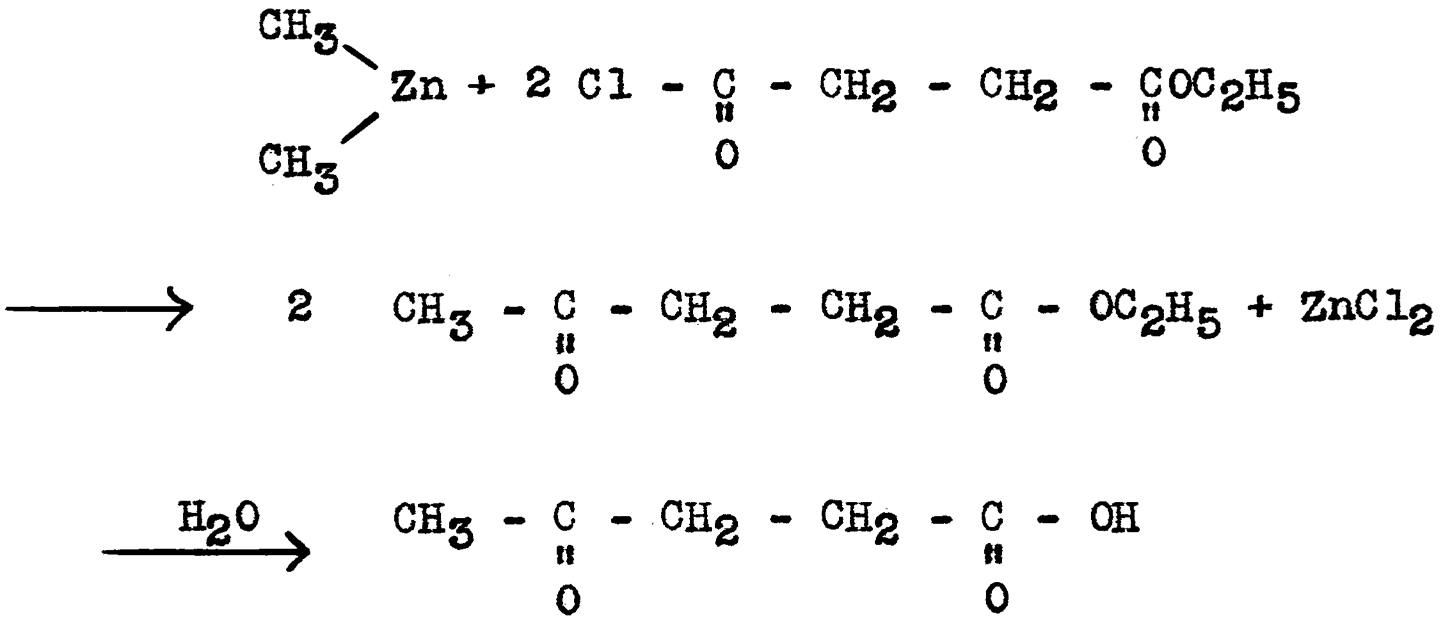
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}OH$$

γ—ketopentanoic acid

Kalk van Mulder 14) isolated a product which he termed "glucinic" acid by the action of sulphuric acid on corn sugar, and which was later identified as levulinic acid. As shown in section E, the latter is readily formed from other carbohydrate materials.

Previous Work on Constitution of Levulinic Acid

Blaise 30) treated the ethyl ester of the mono-acyl chloride of succinic acid with zinc methyl in benzene;

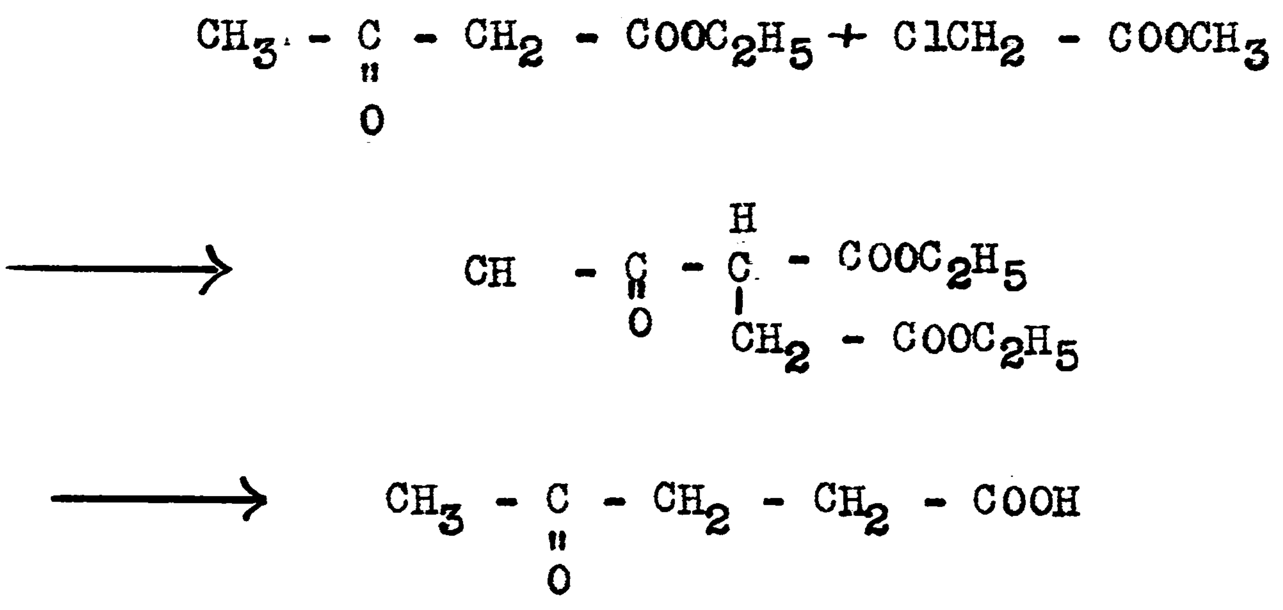


$$\begin{matrix}CH_3\diagdown\\ \quad Zn\\ CH_3\diagup\end{matrix} + 2\ Cl-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}OC_2H_5$$

$$\longrightarrow\ 2\quad CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5+ZnCl_2$$

$$\xrightarrow{H_2O}\ CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$$

and obtained levulinic acid. This was also synthesized by Harries 31) by oxidation of levulinic aldehyde with silver oxide. As a further proof of structure, levulinic acid has been prepared 32) by treatment of acetoacetic ester with an α-halogen substituted acetic acid ester followed by ketone hydrolysis thus:



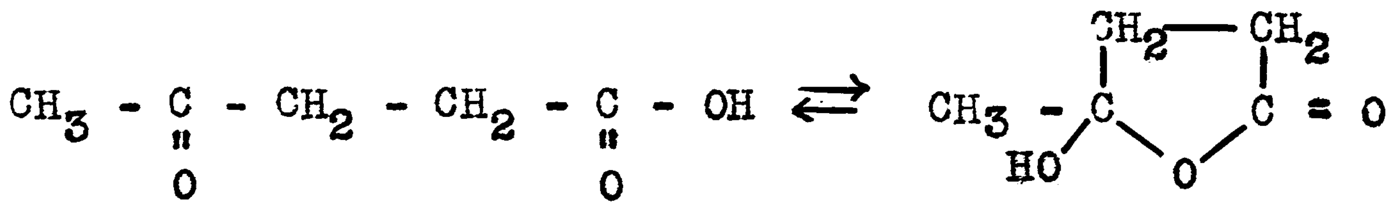
$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - COOC_2H_5 + ClCH_2 - COOCH_3$$

$$\longrightarrow CH - \underset{\underset{O}{\|}}{C} - \overset{H}{\underset{\underset{CH_2 - COOC_2H_5}{|}}{C}} - COOC_2H_5$$

$$\longrightarrow CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - COOH$$

From the above synthesis it can be seen that the structure of levulinic acid has been definitely established. By reduction to valeric acid, the structure of levulinic acid has been further proven.

It would appear that levulinic acid does not exist solely in the straight chain form. The migration of hydrogen from hydroxyl to carbonyl to form a hemiacetal is a well known reaction, and has been applied to levulinic acid thus:



$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - OH \rightleftarrows$$

It is believed that R. Anschutz [33] was the first to postulate the ring formula for levulinic acid, based on the discovery by Bredt [34], that levulinic acid with acetic anhydride gave an acetyl derivative.

Numerous other reactions of levulinic acid, namely the reduction to γ-valerolactone; the formation of chlorvalerolactone with acetyl chloride, etc., have demonstrated the existence of the ring formula. However, levulinic acid, also can form the normal ketone derivatives such as hydrazones, oximes and semicarbazones and thus must also exist in the open chain form. Any consideration of levulinic acid consequently must also take into account both forms.

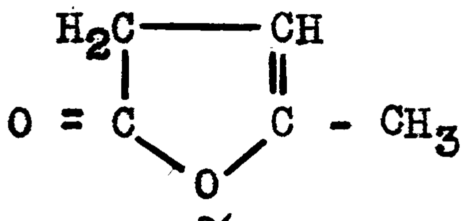
Physical Properties

Levulinic acid at room temperature consists of large glassy crystals, melting point 31 - 33.5°C., boiling point 245 - 246°C., with decomposition, at normal pressures; boiling point 154° at 24 mm. pressure and 148 - 149°C. at 15 mm. pressure. The refractive index is $n_D^{17} = 1.44050$. It is easily soluble in water and most organic solvents. With metallic hydroxides it readily forms metallic salts.

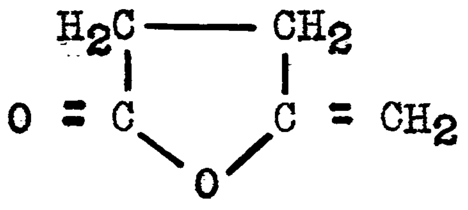
Reactions

Oxidizing reagents tend to convert levulinic acid into acetic and carbonic acids, while reduction converts it into γ-hydroxyvaleric acid or valerolactone.

Distillation under normal pressure yields acetic acid and a mixture of α- and β-angelica lactones:

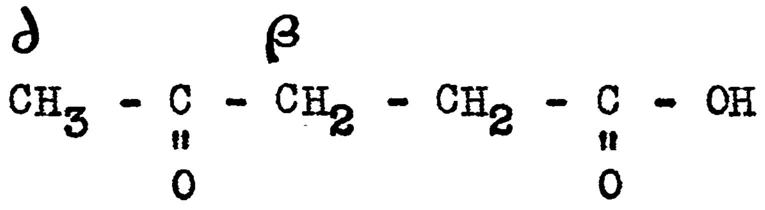


α



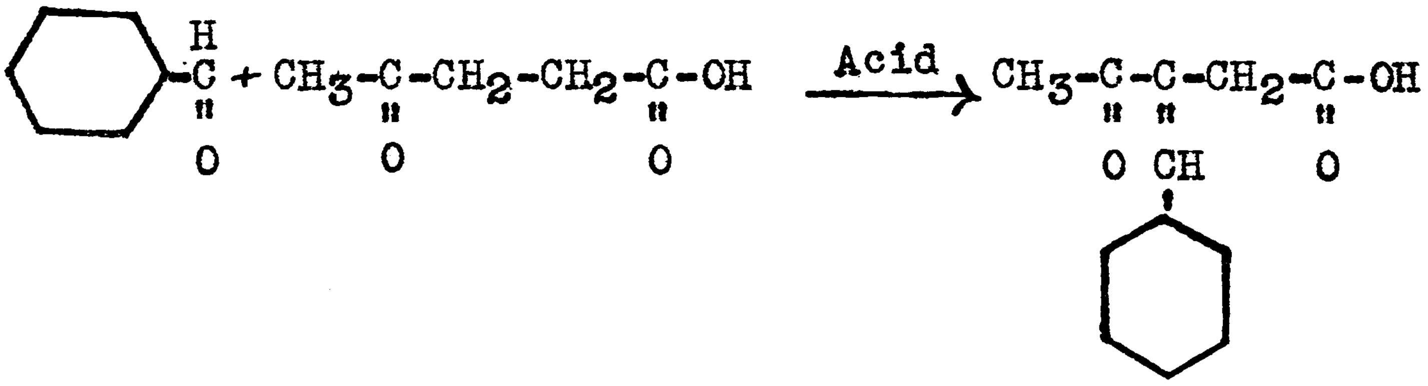
β

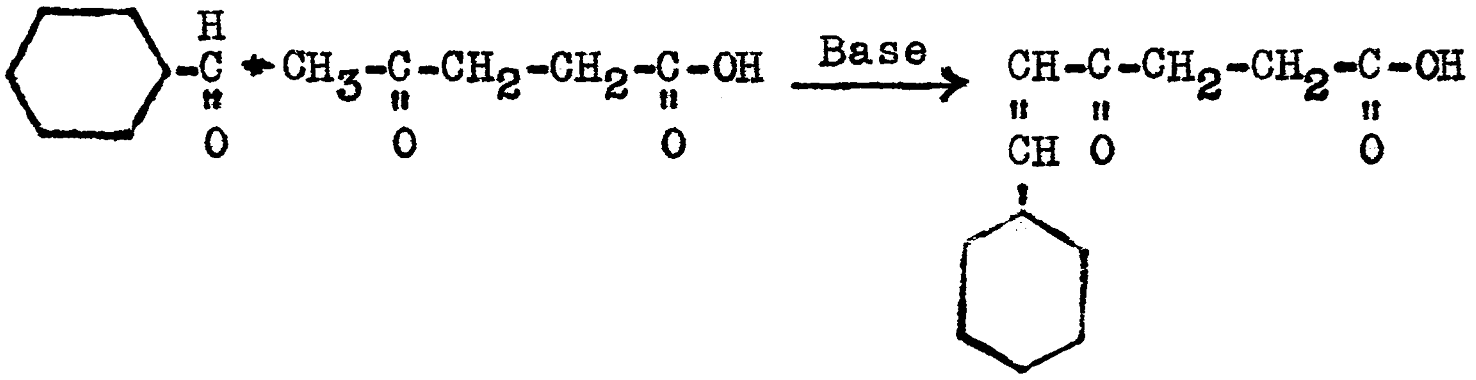
Because of the presence of a carbonyl group, and α-hydrogen atoms adjacent to it, levulinic acid exhibits the well known aldol condensation reactions:



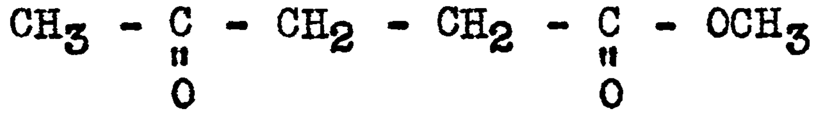
$$\overset{\delta}{CH_3} - \underset{\underset{O}{\|}}{C} - \overset{\beta}{CH_2} - CH_2 - \underset{\underset{O}{\|}}{C} - OH$$

When acid is used as the condensing agent, reaction takes place with the β-carbon, whereas in the presence of alkalis δ-condensation takes place:



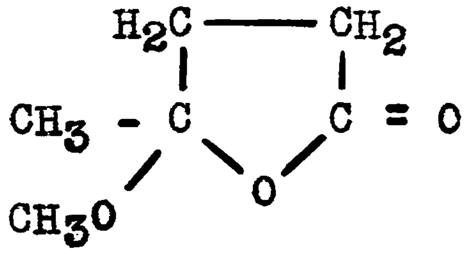


Treatment with alcoholic mineral acids readily leads to the formation of the corresponding levulinic esters. These, in turn, show the same $CH_3 - CO - CH_2 -$ reactions, etc., as does levulinic acid itself. It is possible, though improbable, that the esters also exist as combinations of the open (1.) and closed chain forms (2.):



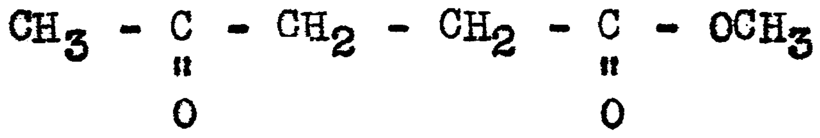
$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - OCH_3 \qquad (1.)$$

and



(2.)

G. CHEMISTRY OF METHYL LEVULINATE



$$CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - OCH_3$$

Methyl ester of γ-ketopentanoic acid

The methyl ester can be prepared by esterification of the corresponding acid and by treatment of the silver salt of the acid with methyl iodide.

It is a colorless liquid, boiling point 191 - 191.5°C. at 743 mm., boiling point 85 - 86°C. at 14 mm. The refractive index is $n_D^{15} = 1.4240$. It is soluble in water and most organic solvents. With sodium methylate it readily forms sodium levulinate.

Preparation of carbonyl condensation products is recorded by various investigators as follows: phenylhydrazone, melting point 103 - 104°C., p-nitrophenylhydrazone, melting point 136°C., 2,4-dinitrophenylhydrazone, melting point 141 - 142°C., semicarbazone, melting point 148 - 149°C.

H. THE CONVERSION OF CARBOHYDRATES TO FURANS

Treatment of carbohydrate materials by distillation with mineral acids leads to the formation of furan derivatives.

The commercial source of furfural lies in the pentosan materials which abound in oat hulls. Pyromucic acid is formed from mucic acid, which pyrone in turn is formed from carbohydrate materials.

Hydroxymethyl-furfuraldehyde has been shown to be a decomposition product of hexose materials.

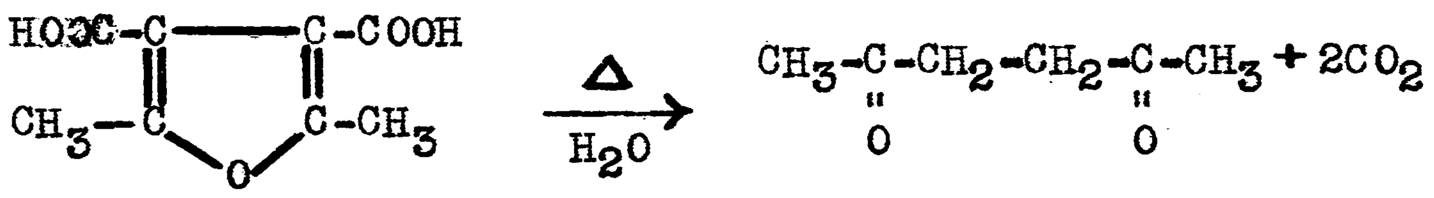
In practically every case of treatment of carbohydrate material with mineral acid, some amount of a furan derivative, generally furfural, is obtained. The conversion of these furan derivatives into simpler aliphatic materials is known and is discussed later in this thesis.

I. RING OPENING IN THE FURAN SERIES

(a) Normal Ring Opening

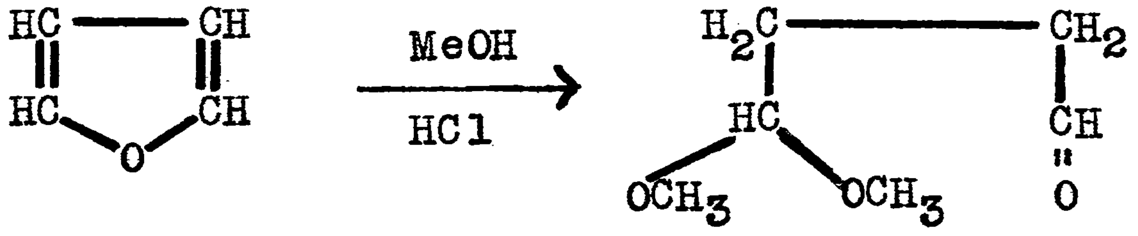
The conversion of furan derivatives to straight chain aliphatic compounds is well known and has been explained by a rupture of the oxygen bridge.

Paal 35) was the first to discover that the furan nucleus opened readily. By heating α,α-dimethyl furan dicarboxylic acid with water at 150 - 160°C., he was able to prepare acetonyl acetone:



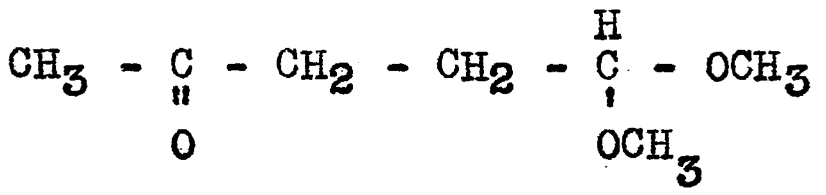
The same product was obtained from α,β-dimethyl furan by Paal and Dietrich 36).

Harries 37) converted furan into the dimethylal of succindialdehyde by heating the compound with a methanolic HCl solution:



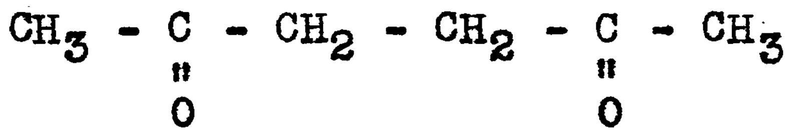
The reaction probably proceeds through the normal reaction of ring opening to give a dienol, which in turn forms the dialdehyde by ketonization yielding the dimethylal of succindialdehyde.

In a similar manner, 2-methyl furan was converted to levulinaldehyde-dimethylal [37] (1) and 2,5-dimethyl furan to acetonyl acetone [36] (2);



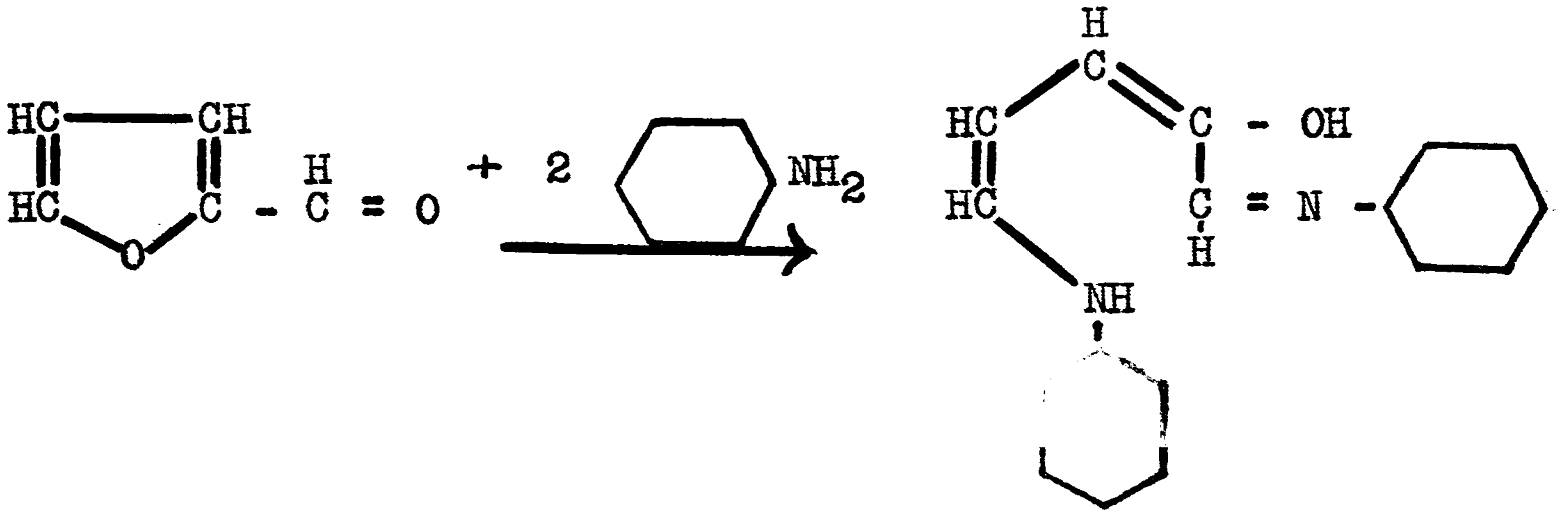
$$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_2-\overset{H}{\underset{OCH_3}{\underset{|}{C}}}-OCH_3 \qquad (1)$$

and

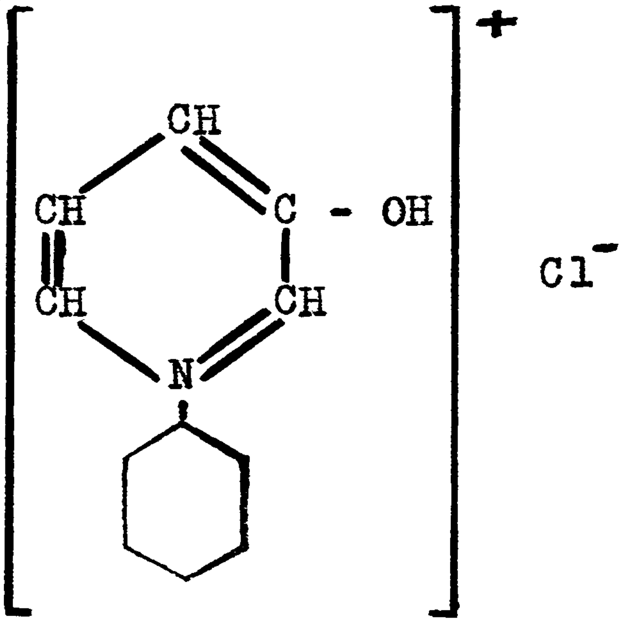


$$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_2-\underset{O}{\underset{\|}{C}}-CH_3 \qquad (2)$$

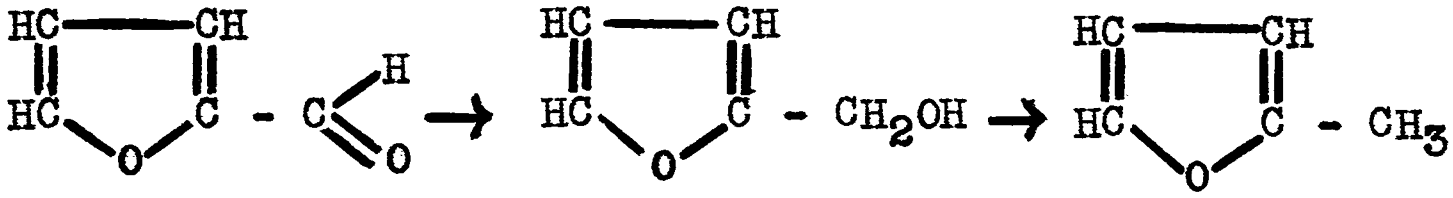
It is of interest to note that ring opening occurs in the furan system with reagents other than alcoholic solutions of acids. Thus, when furfural is treated with aniline acetate at room temperature, ring opening occurs and a pink to red colored compound is formed. This is the basis of the so-called aniline acetate test for furfural. An explanation of this phenomenon has been offered by various workers [38] as shown below:

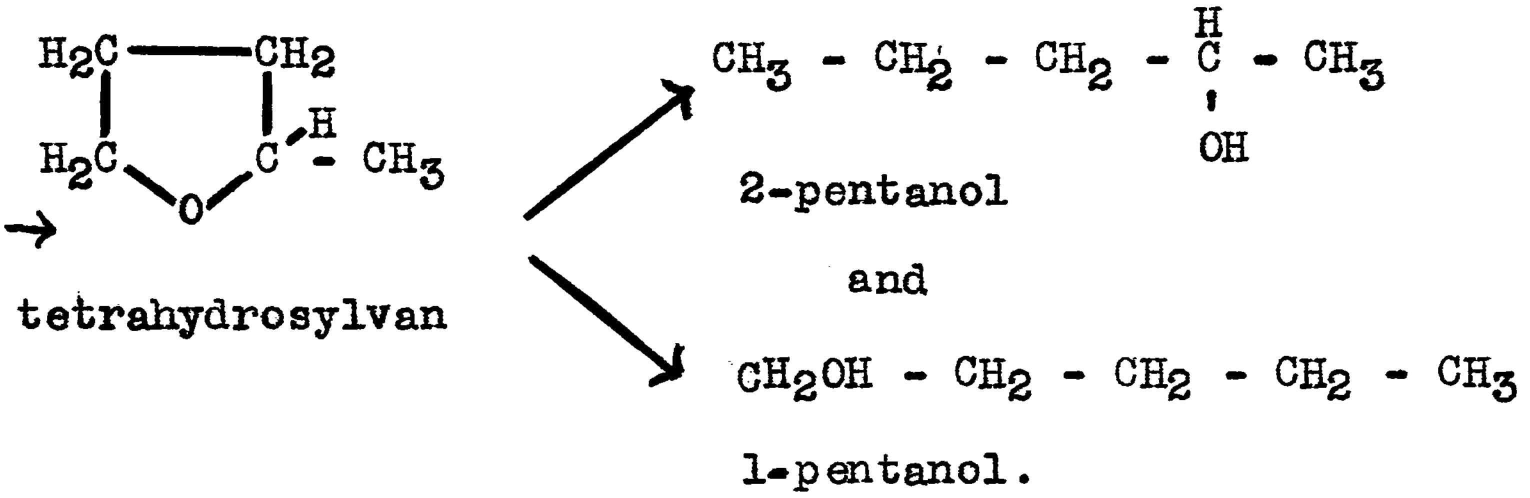

Red Compound

Its identity has been established by treatment with hydrochloric acid to form N-phenyl-β-hydroxy-pyridinium chloride:



When furfural is reduced by catalytic hydrogenation at elevated temperatures 39), the following reactions occur:


2-furfural 2-furfuryl alcohol sylvan



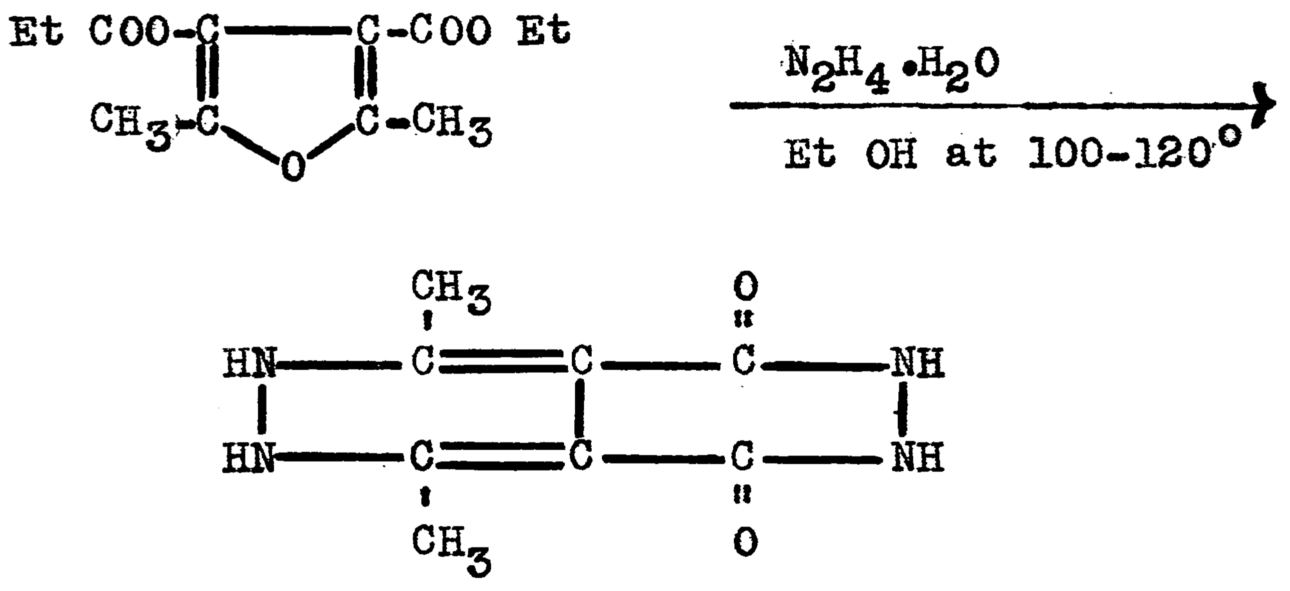
tetrahydrosylvan

2-pentanol

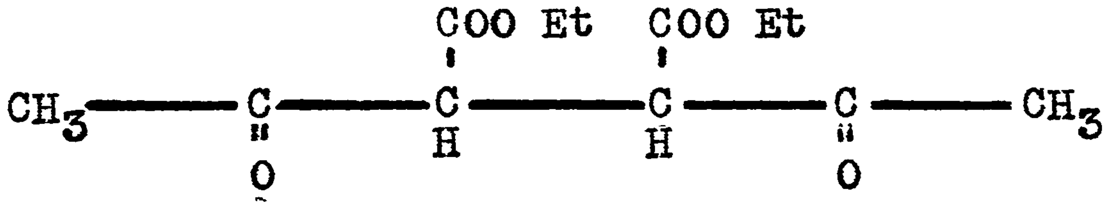
and

1-pentanol.

Treatment of substituted furans with hydrazine hydrate in ethanol at elevated temperatures 40), results in ring opening of the furan with subsequent ring closure to form a new ring system, for example:



which is the same compound as that formed from diacetyl diethyl succinate:



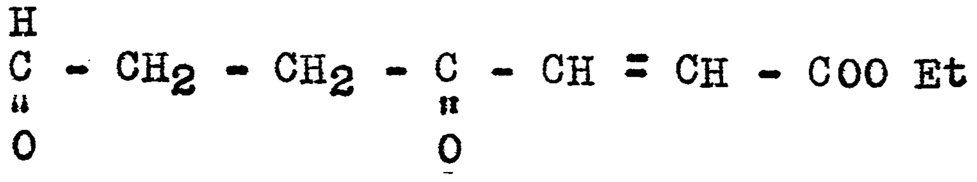
$$CH_3 - \underset{\underset{O}{\|}}{C} - \underset{H}{\overset{COO\ Et}{C}} - \underset{H}{\overset{COO\ Et}{C}} - \underset{\underset{O}{\|}}{C} - CH_3$$

The foregoing methods of ring opening are the normal methods which have been applied to furan compounds.

The method of ring opening by the use of alcoholic acid however does not always give the expected compounds and a discussion of these anomalies follows.

(b) Anomalous Ring Opening of Furans

Markwald 9) found that an alcoholic solution of furyl acrylic acid, on treatment with mineral acid, yielded the ethyl ester of hydrochelidonic acid (γ-keto-pimelic acid). Had the rupture of the furan nucleus taken place in the normal fashion,

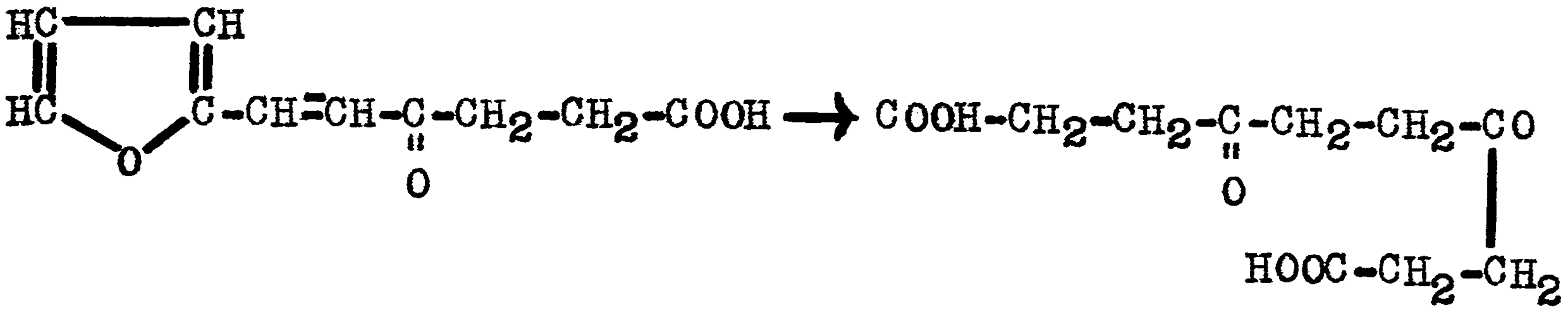


$$\underset{\underset{O}{\|}}{\overset{H}{C}} - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - CH = CH - COO\ Et$$

4-keto-7-aldehydo-heptenoic Δ 1,3 ethyl ester would have been expected as the fission product.

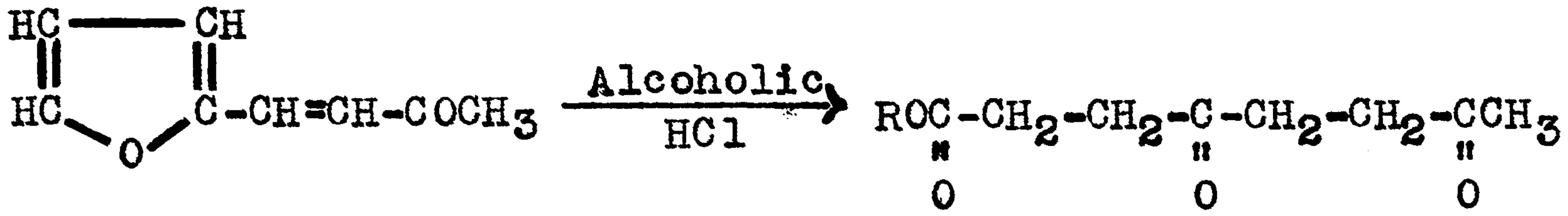
This anomaly of ring opening was found to be common to all substituted furans, having an ethylenic 37
linkage in the side chain α,β to the furan ring, e.g.;

A. Kehrer and Hofacker 41) obtained γ,γ -diketo-sebacic acid from α-furyl levulinic acid:

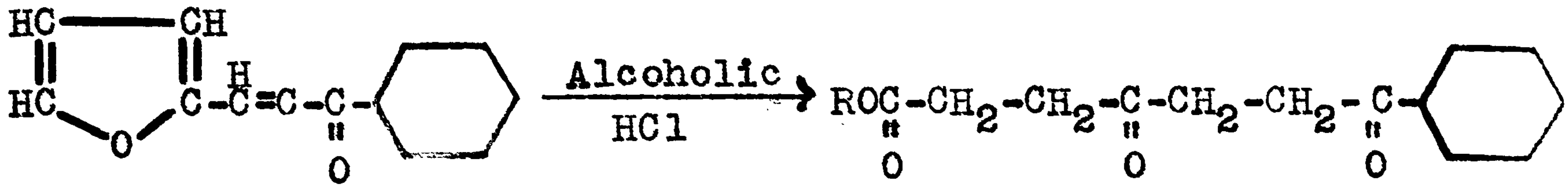


B. Kehrer and Tyler 42) prepared α-acetonyl-levulinic acid and δ-benzoyl levulinic acids from furyl acetone and furyl acetophenone respectively:

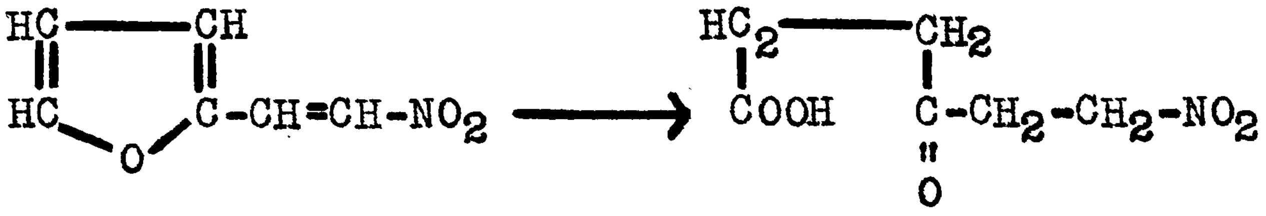
1.



2.



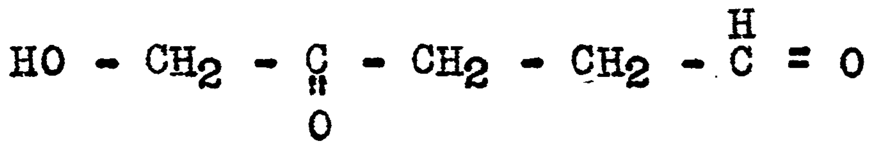
C. Thiele and Landers 43) obtained by the same method nitrohomolevulinic acid from furyl nitroethylene;



In no case was there any attempt made to explain the mechanism of ring opening to give these unexpected results.

J. THE CONVERSION OF FURANS TO LEVULINIC ACID

In 1923 Pummerer and Gump 44) attempted to explain the mechanism of conversion of furfuryl alcohol into levulinic acid, under the influence of acids. As the product formed is not that expected, this reaction represents another anomalous behavior of a furan derivative. The normal end product to be expected would be;

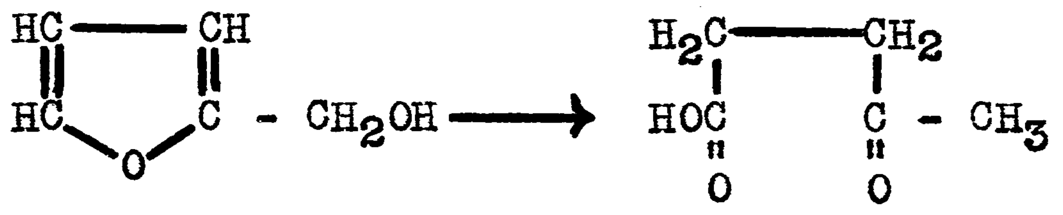


$$HO - CH_2 - \underset{\overset{\|}{O}}{C} - CH_2 - CH_2 - \overset{H}{C} = O$$

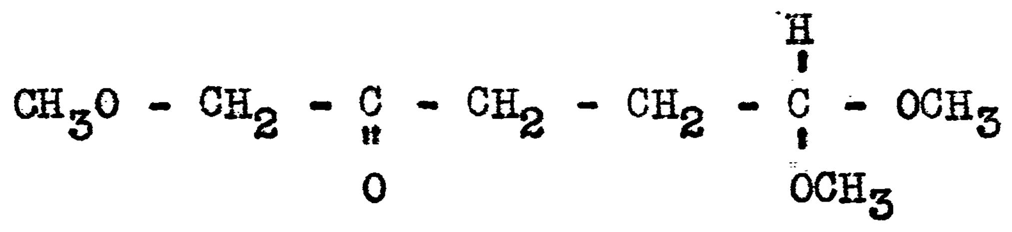
δ-hydroxy-levulinaldehyde

or an alkylated derivative of the compound. Actually if conditions are not very carefully controlled, the resulting compound is the alkyl ester of levulinic acid;

i.e.



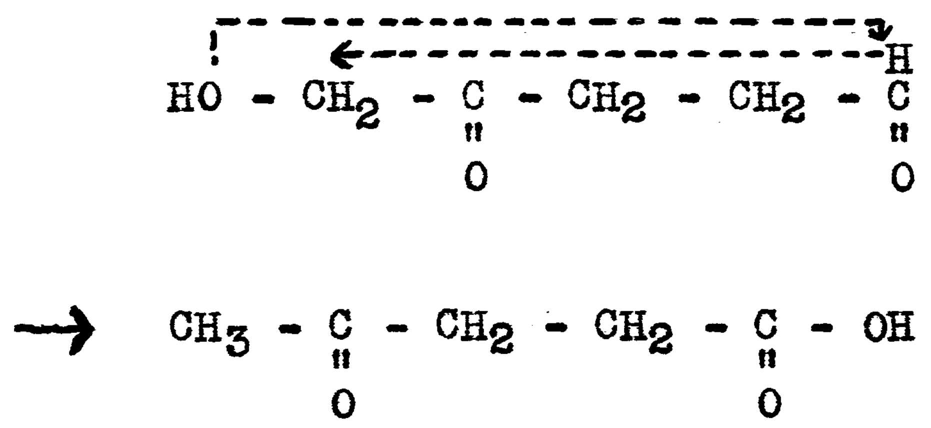
Pummerer and Gump pointed out that the hydroxy-levulinaldehyde, would probably be unstable and could not as a consequence be isolated. However, by carefully controlling the reaction by means of low concentration of furfuryl alcohol, and of mineral acid, these investigators were able to isolate a compound which corresponded on analyses for carbon and hydrogen to δ-methoxy-levulinaldehyde-dimethylal.



$$CH_3O - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - \overset{H}{\underset{OCH_3}{C}} - OCH_3$$

No methoxyl analyses were reported however.

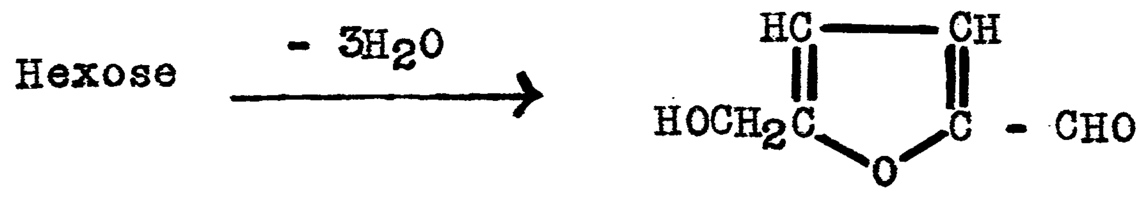
This compound on boiling with mineral acid, yielded methyl levulinate. The explanation offered by these investigators was that of a 1,5 shift of hydroxyl and a simultaneous 1,5 shift of the aldehydic hydrogen thus;



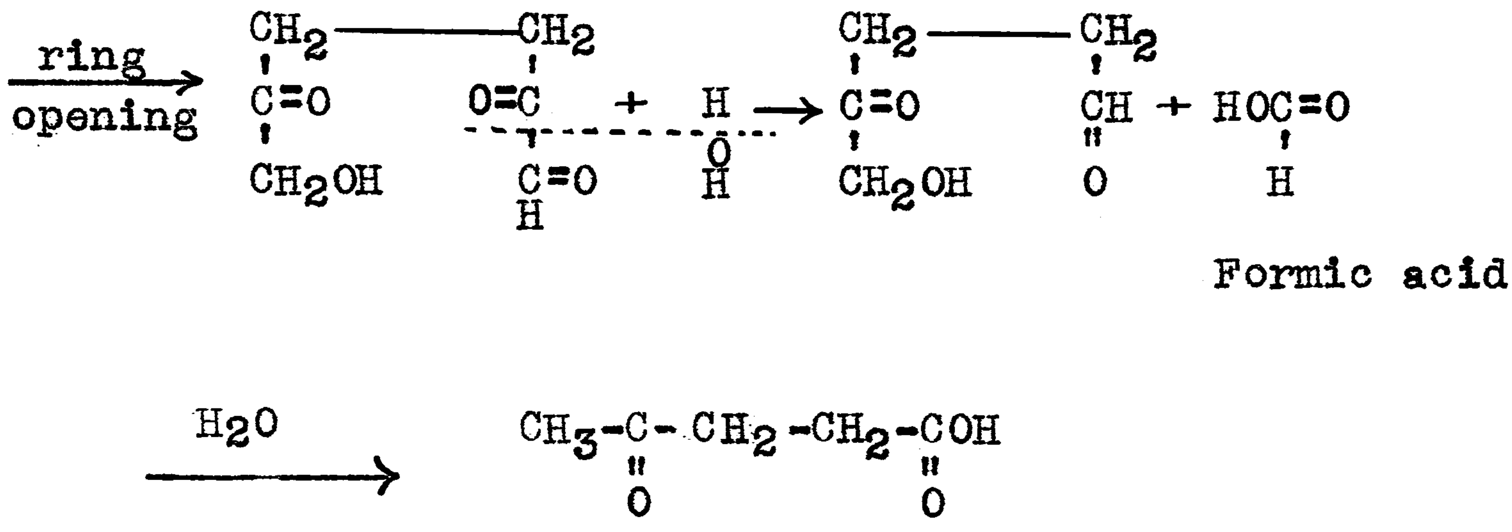
$$HO - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - \overset{H}{\underset{\underset{O}{\|}}{C}}$$

$$\rightarrow CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - OH$$

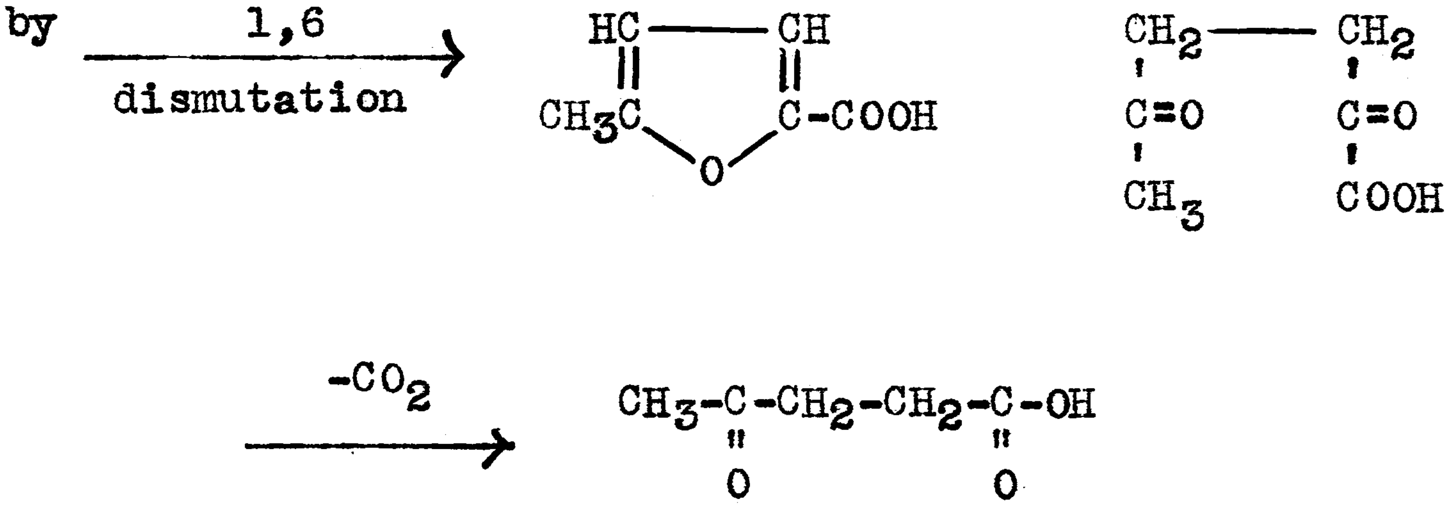
According to these authors, the conversion of hexoses to levulinic acid occurs in a similar manner:



A.



or B.



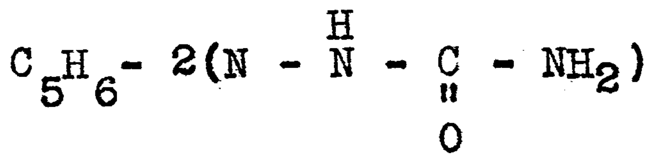
However, Pummerer points out that formic acid is formed during the reaction so that the reaction probably proceeds according to A.

To prove that an α-ketoaldehyde would readily lose formic acid on boiling with mineral acid, Pummerer refluxed pyruvic aldehyde with 0.5N H_2SO_4 for forty-four hours and secured yields of 30% of formic acid and acetaldehyde.

To show that the 1,5-dismutation of the hydroxyl group is conditioned by the keto group, and in further support of his mechanism, Pummerer reduced the δ-methoxy-levulinaldehyde-dimethylal and obtained δ-methoxy-γ-hydroxy-valeraldehyde-dimethylal. This compound was treated with 0.5N H_2SO_4 for 3 hours to give valerolactone. Thus the 1,5-dismutation occurs in this case as well.

However, it would be well to point out that Pummerer reduced his δ-methoxy-levulinaldehyde-dimethylal and treated it with methanolic-HCl and obtained valerolactone, and used this reaction as proof of structure of the original compound. Use of an unknown reaction, the same as used to convert δ-methoxy-levulinaldehyde-dimethylal to methyl levulinate does not constitute valid proof of structure of the original unreduced compound.

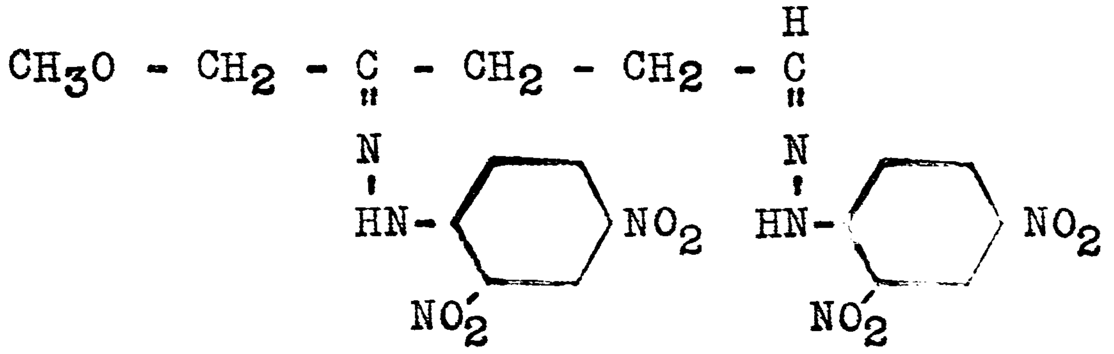
An attempt by Pummerer to secure a semicarbazone of δ-methoxy-levulinaldehyde-dimethylal, resulted in the formation of a bis-compound of the empirical formula;



$$C_5H_6-2(N-\overset{H}{N}-\underset{\underset{O}{\|}}{C}-NH_2)$$

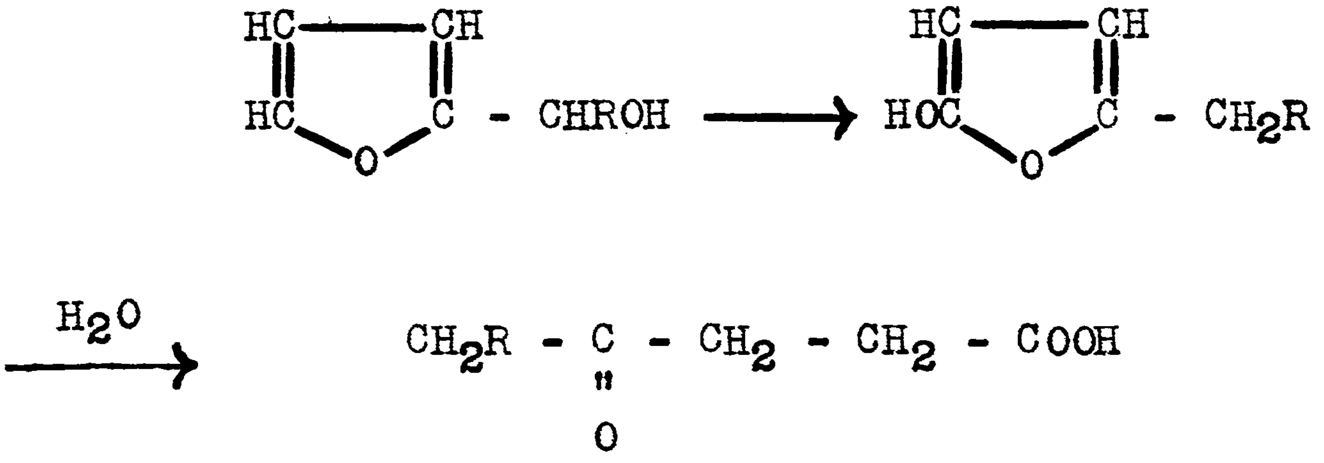
an elimination of three methoxyl groups apparently taking place in the formation of the semicarbazone.

In a later paper [44)] however, Pummerer, Guyot and Birkoffer report the formation of a 2,4-dinitrophenylhydrazone with the empirical formula $C_6H_{10}O - 2R$ and to which they assign the formula:



Also in this case no methoxyl analysis was reported.

Tchichibabine [45)] investigated the conversion of homologous furfuryl alcohols to the corresponding homologues of levulinic acid. The mechanism which he proposes is similar to that of Pummerer with one exception, namely, he assumes 1,5-dismutation of the hydroxyl group prior to ring opening thus:

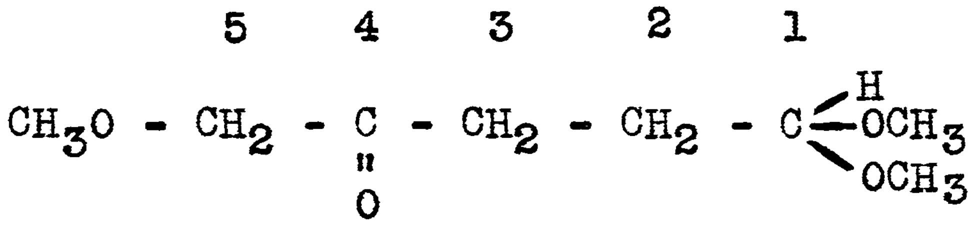


However, no proof of the prior dismutation has been offered by this author.

K. CRITICISM OF THE MECHANISM INVOLVING A 1,5-MIGRATION OF HYDROXYL

The foregoing mechanism proposed by Pummerer and co-workers involves a 1,5-migration of a hydroxyl group. No other instances of this are on record although a 1,3-migration of hydroxyl, as well as other heavy groups occurs in the phenomenon known as cationotropy 46). Conceivably the mechanism proposed by Pummerer might be correct, if two 1,3-migrations of hydroxyl are assumed to give the final result.

However, if Pummerer's intermediate is.



$$CH_3O - \overset{5}{CH_2} - \overset{4}{\underset{\underset{O}{\|}}{C}} - \overset{3}{CH_2} - \overset{2}{CH_2} - \overset{1}{C}\begin{smallmatrix}H\\OCH_3\\OCH_3\end{smallmatrix}$$

then treatment with dilute mineral acid would not be expected to remove the ether-methoxyl from the 5-carbon atom, although the adjoining keto group may conceivably exert an activating effect on the ether linkage.

Semicarbazide hydrochloride at $50^{\circ}C.$, in a buffered solution also would not be expected to remove this ether-methoxyl, while Pummerer demonstrated that semicarbazide hydrochloride does eliminate all methoxyl groups in the intermediate.

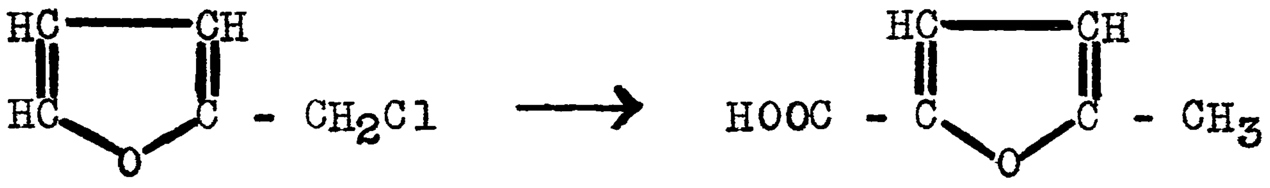
The fact that methoxyl analyses were not included for any of the compounds isolated by Pummerer, was probably an oversight on the part of this author.

Finally, Pummerer offers the similar dismutation of the reduced intermediate as proof for the mechanism of conversion. It should be pointed out that unless an intermediate is identified, or related by known structural reactions to some known compound, its assumed existence as an intermediate is not warranted, and the mechanism is not acceptable. Similarly, a reaction which follows the same course as the reaction under review, cannot be accepted as final proof of a mechanism.

In his study on the mechanism of conversion of hexoses to hydroxymethyl-furfural to levulinic acid 44), Pummerer has pointed out the formation of formic acid as a by-product, but has not established the mechanism of conversion.

L. RELATED ANOMALY OF A FURAN SYSTEM

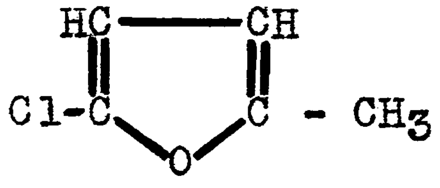
In 1930 Reichstein [47)] reported the conversion of α-furyl chloride to 2-methyl,5-pyromucic acid by treatment with NaCN;



the acid presumably resulting from hydrolysis of the corresponding nitrile.

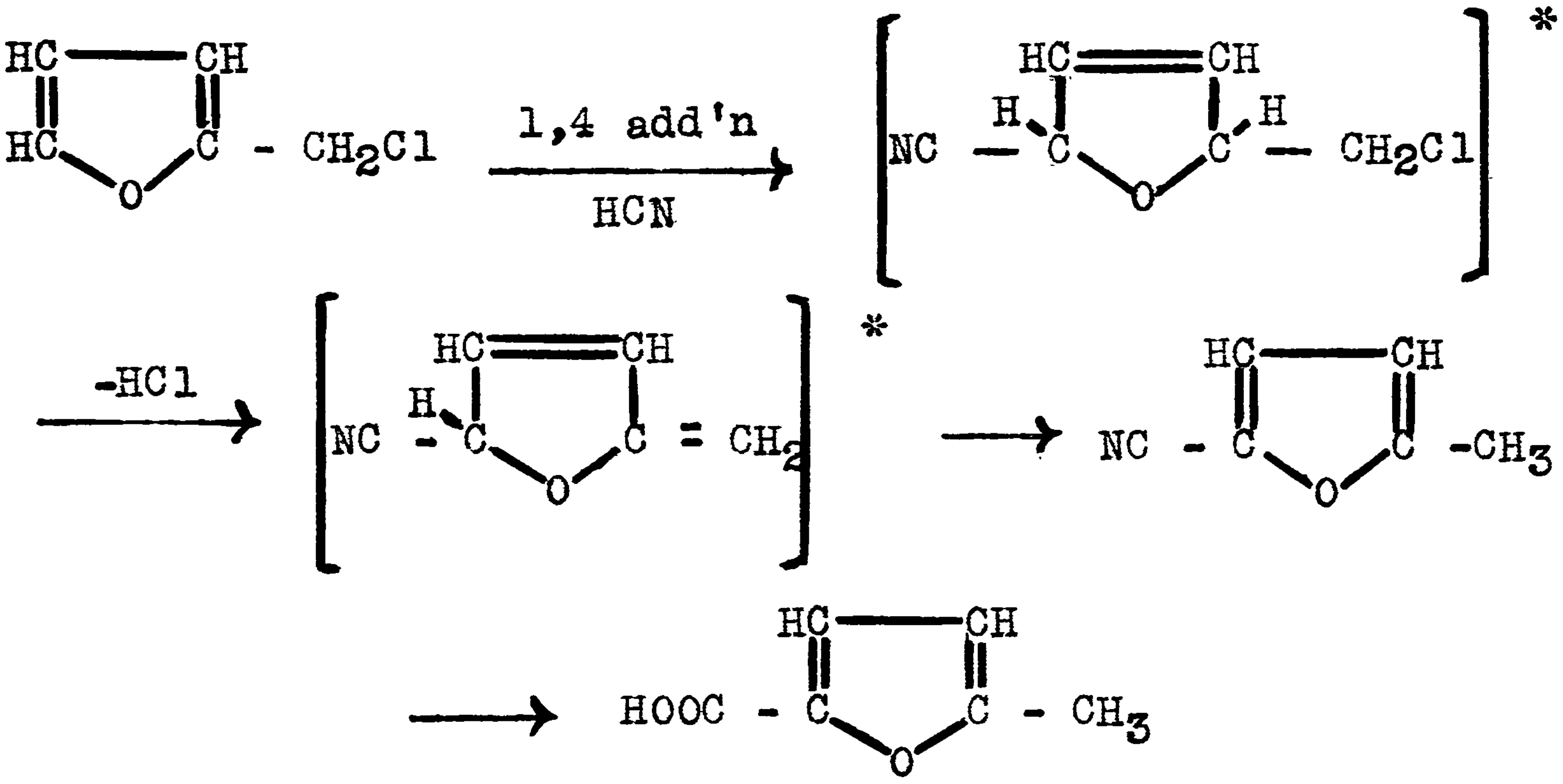
The mechanism proposed involves a primary 1,5-migration of the Cl atom, with subsequent replacement of the Cl by CN and hydrolysis.

Scott and Johnson [48)] however in 1932, proposed another mechanism for this reaction. These authors showed that the intermediate;



proposed by Reichstein, does not yield 2-methyl,5-pyromucic acid on treatment with KCN.

To account for this product, they proposed the following mechanism:



The mechanism involves 1,4-addition of HCN to the conjugated system, followed by 1,2-elimination of HCl to form a vinyl dihydrofuronitrile which in turn rearranges to form a 2-methyl, 5-furonitrile. This compound in turn is hydrolyzed to yield the acid.

The mechanism offered by these authors seems quite reasonable and is in agreement with known chemical reactions.

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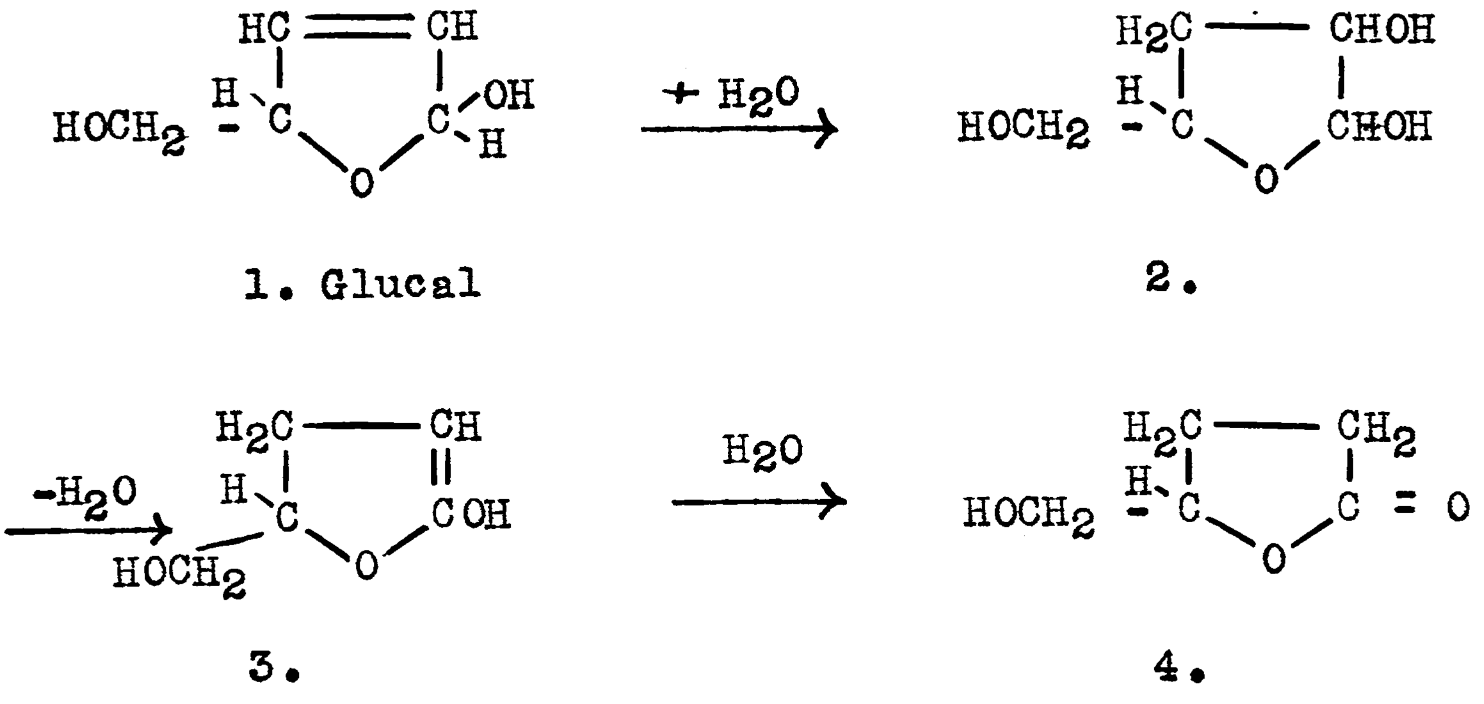
* These intermediates were not isolated.

M. THE CONVERSION OF GLUCALS TO γ-KETO ACIDS

It has been shown by P. A. Levene 49), that desoxy sugars are converted by methanolic HCl into levulinic acid. Bergmann 50) showed that methyl levulinate was obtained in high yields from pentals, by treatment with dilute HCl in methanol solution. Also that hexals and pseudo-glucal, under identical conditions were converted to δ-methoxy methyl levulinate. He believes that during conversion to levulinic acid, the desoxy sugars pass through the glucal stage.

In this work, reference is made to the mechanism postulated by Pummerer and the belief that ring opening need not necessarily take place prior to methyl levulinate formation. Bergmann offers the following mechanism for the conversion of glucal to methyl levulinate (hydroxyl is used where methoxyl should probably be used):

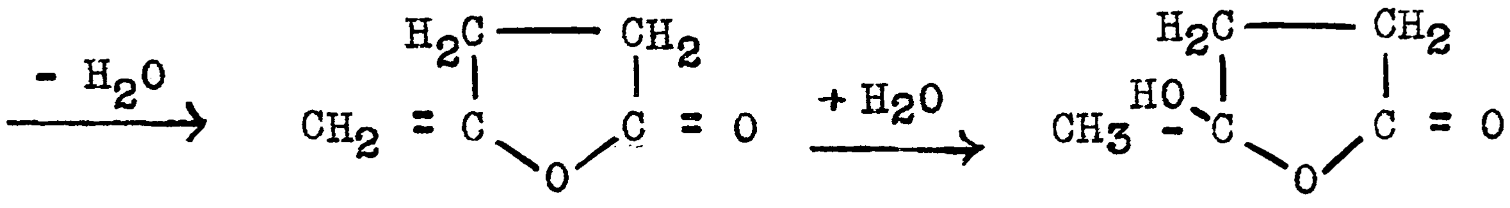


1. Glucal

2.

3.

4.



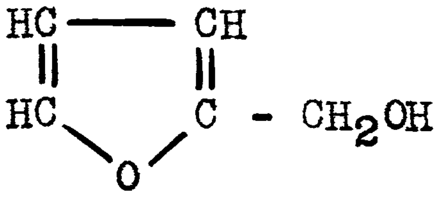
5. β-Angelica Lactone

6. Levulinic Acid

Bergmann believes that the conversion occurs as shown, and that the stages 2 - 6 need not necessarily follow as outlined, but may take place concurrently. This view agrees with the ideas put forward by Scott and Johnson, cf. page 37, for conversion of furan derivatives and will be discussed later in this thesis.

The conversion of hexals to δ-methoxy levulinic acid may take place in a similar manner.

N. THE CHEMISTRY OF FURFURYL ALCOHOL



2-furancarbinol

Furfuryl alcohol is readily formed from 2-furfuraldehyde by a controlled catalytic reduction 39) and also may be obtained by means of the Canizzarro reaction, with accompanying formation of 2-furoic acid 51).

Properties

Furfuryl alcohol is a colorless liquid of ethereal odor, boiling point 168 - 170°C. at normal pressures, boiling point 69 - 70°C. at 10 mm. pressure. The refractive index is $n_D^{25} = 1.4828$. It is assumed to exist in two modifications 52), in one modification (distilled from alkali), it is water soluble in all proportions, in the other modification (distilled from a trace of acid, or an acid salt), it is only slightly soluble in water. Physical properties of both modifications are in other respects quite similar. It is quite soluble in most organic solvents.

Reactions

In the presence of light, oxygen and traces of mineral acids, furfuryl alcohol is rapidly polymerized to a dark brown resin.

With trityl chloride in pyridine, the trityl ether is formed 53); phthalic anhydride and the sodium salt give a monofurfuryl-phthalate 54); acetic anhydride in benzene yields furyl acetate 55). With α-naphthyl-isocyanate, an α-naphthylurethane can be obtained 56).

Furfuryl alcohol may be etherified to give small amounts of furfuryl methyl ether and furfuryl ethyl ether. However, the higher ethers are quite unstable and cannot normally be formed by the usual processes of etherification.

By careful treatment with thionyl chloride, furfuryl alcohol can be converted to furfuryl chloride, which with alcohols in pyridine, gives low yields of the various ethers 57).

Furfuryl alcohol is quite stable to alkalis, but in the presence of acids, resinification, etc., (see Section J, page 30), readily takes place.

O. 2,4-DINITROPHENYLHYDRAZINE AS A CARBONYL REAGENT

The use of 2,4-dinitrophenylhydrazine as a carbonyl reagent has been pointed out by numerous investigators 58). In contrast to most ketone and aldehyde reagents, 2,4-dinitrophenylhydrazine forms the corresponding hydrazones not only in practically neutral solutions, but also in the presence of concentrated mineral acids. This may also be accomplished in aqueous or alcoholic solution, and as shown later in this thesis, in one case at least, a 2,4-dinitrophenylhydrazone may be formed by shaking a carbonyl sodium bisulphite complex with 2,4-dinitrophenylhydrazine in 50% methanol solution.

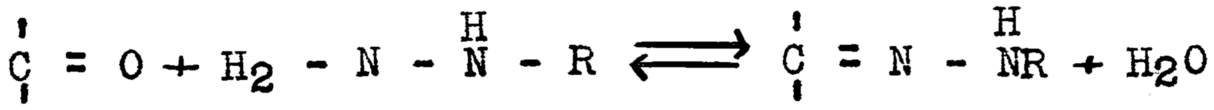
The 2,4-dinitrophenylhydrazones are well-defined crystalline compounds only slightly soluble in most organic solvents. They can be recrystallized from the common organic solvents such as methanol, chloroform,benzene, nitrobenzene, xylene, chlorbenzene, pyridine and mixtures of these solvents.

From the author's experience mixtures of different 2,4-dinitrophenylhydrazones show remarkably high depressions in melting point (of around 20°C.).

2,4-Dinitrophenylhydrazine is a very weak base, and its hydrochloride is hydrolyzed to give free HCl.

P. RECOVERY OF CARBONYL COMPOUNDS FROM 2,4-DINITROPHENYLHYDRAZONES

A number of methods for recovery of the original carbonyl compound from the 2,4-dinitrophenylhydrazone have been proposed. In each case this depends on displacement of the reaction:

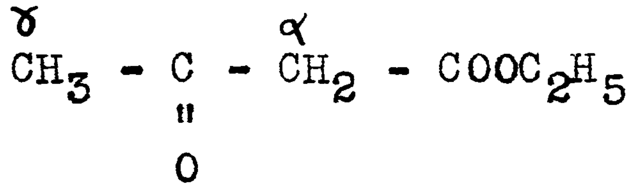


$$\overset{|}{\underset{|}{C}} = O + H_2 - N - \overset{H}{N} - R \rightleftarrows \overset{|}{\underset{|}{C}} = N - \overset{H}{N}R + H_2O$$

to the left, by some means.

Such methods involve removal of the 2,4-dinitrophenylhydrazine as a less soluble 2,4-dinitrophenylhydrazone, e.g., the use of glyoxal, pyruvic aldehyde and diacetyl 59), the use of p-nitrobenzaldehyde 60) and the use of high concentrations of simpler carbonyl compounds such as acetaldehyde 61).

Q. SOME CHEMICAL REACTIONS OF ACETOACETIC ACID ETHYL ESTER

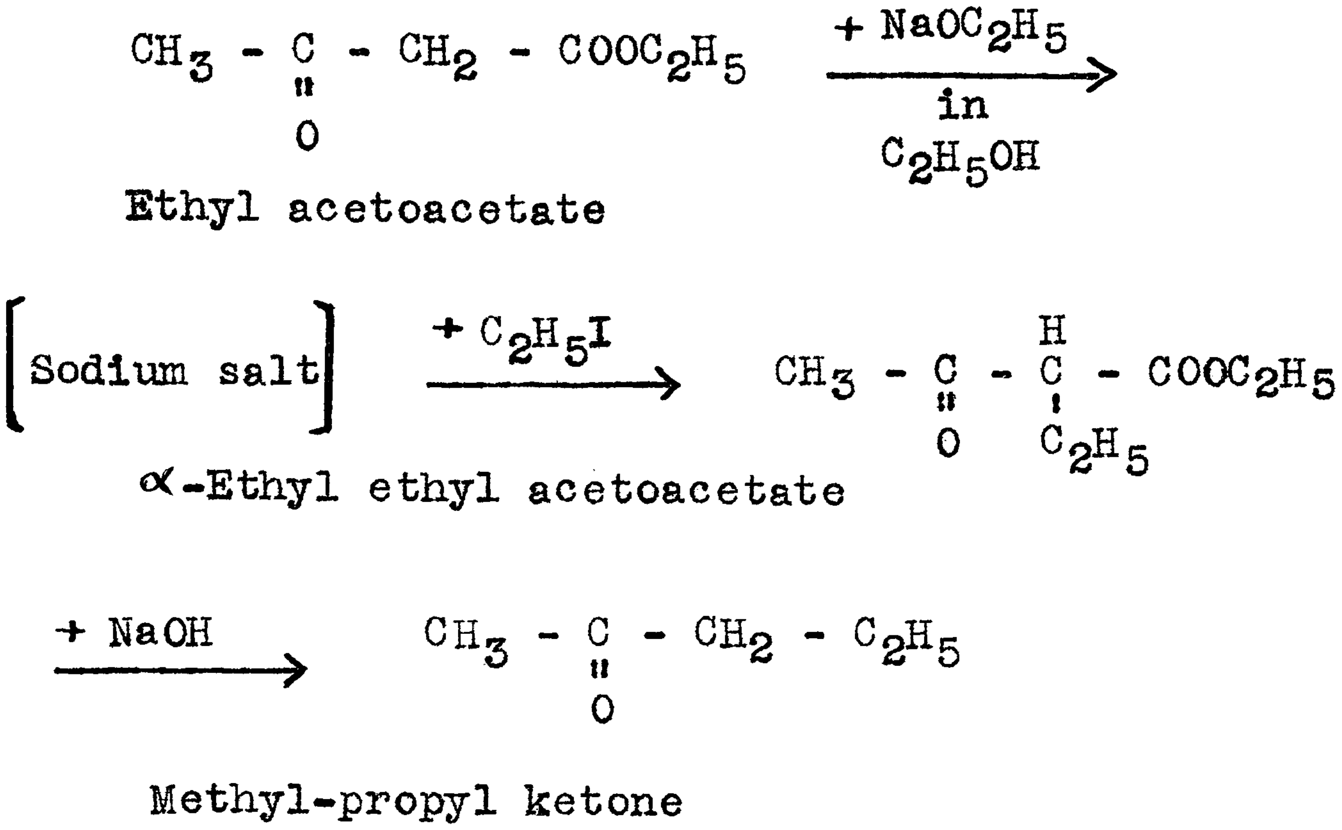


$$\overset{\gamma}{CH_3} - \underset{\overset{\|}{O}}{C} - \overset{\alpha}{CH_2} - COOC_2H_5$$

Ethyl acetoacetate

Compounds of the nature of the above which contain a carbonyl group and free α-hydrogen atoms adjacent to it, possess the property of forming sodium salts. These sodium salts are derivatives of an enol form. They possess the property of reacting with various organic halides with the elimination of sodium halide to form α-substituted acetoacetic acid esters. This property of substitution of the α-hydrogen is also a typical reaction of γ- and α-substituted acetoacetic acid esters.

Treatment of these α-substituted esters, with dilute alkali, e.g. 10% NaOH, leads to formation of the free acid which in turn loses CO_2 to yield a ketone:



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOC_2H_5 \xrightarrow[\text{in } C_2H_5OH]{+\,NaOC_2H_5}$$

Ethyl acetoacetate

$$\left[\text{Sodium salt}\right] \xrightarrow{+\,C_2H_5I} CH_3-\underset{\underset{O}{\|}}{C}-\overset{H}{\underset{\underset{C_2H_5}{|}}{C}}-COOC_2H_5$$

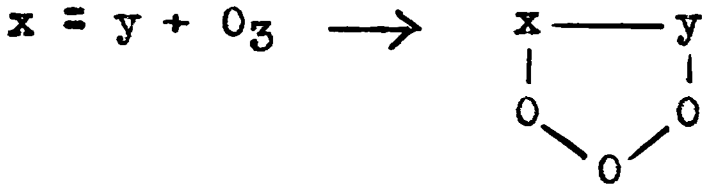
α-Ethyl ethyl acetoacetate

$$\xrightarrow{+\,NaOH} CH_3-\underset{\underset{O}{\|}}{C}-CH_2-C_2H_5$$

Methyl-propyl ketone

R. ACTION OF OZONE ON UNSATURATED COMPOUNDS

When ozone is brought under carefully controlled conditions into contact with compounds which contain an unsaturated linkage it tends to add to the unsaturated linkage [62] with formation of an ozonide:



These may then be decomposed by treatment with acid or water to form free carbonyl groups and hydrogen peroxide. In this manner it is possible to break not only carbon to carbon double bonds, but also nitrogen to carbon double bonds.

DISCUSSION OF RESULTS

PART ONE. A. GENERAL INTRODUCTION

Various investigators have postulated the existence of furan rings in the lignin molecule 63), and hydroxy-methyl-furfuraldehyde has been suggested as the building unit from which lignin is derived 64). These investigators, in some instances, have emphasized the relationship existing between furan derivatives and the hexoses from which such furans are derived, in particular, that of hydroxy-methyl-furfural to fructose.

A study of the furans thus becomes a part of the "lignin problem", especially in view of the possibility that an abnormally reactive carbohydrate or its decomposition products may be responsible for the difficulties encountered in dealing with all isolated lignins 65).

The fact that furan, and some substituted furans, undergo ring fission under the influence of mineral acids in absolute alcohol, has been shown in Section I of the historical review. However, certain anomalous products arising from the ring opening of furfuryl alcohol, as well as the unsatisfactory mechanism proposed by Pummerer and co-workers 44) for this reaction, provided the initiative for a re-investigation of this problem.

This reaction was furthermore of additional interest, since Hibbert [3) has postulated the formation of lignin in the plant as originating from condensation reactions between phenols and fructose reaction products, the latter probably consisting of furan derivatives formed under the conditions present in plant growth. The fact that fructose, under the influence of mineral acids, readily yields hydroxy-methyl-furfural as a primary decomposition product and levulinic acid as a final product, is interesting in this respect. Further, the formation of lignin-like materials from fructose (so-called fructose humic acids) and from furfuryl alcohol 27) would seem to confirm the view.

It should be pointed out at this stage, that the instability of furans, renders difficult, either a quantitative study or reproducibility of stated reactions related to ring opening. Thus, attempts to repeat certain of Pummerer's experimental work did not give identical results, this being due, most probably, to slight modifications in experimental technique or in the quality of reagents used.

B. ACTION OF METHANOLIC ACID ON FURFURYL ALCOHOL AND FURFURYL METHYL ETHER

Pummerer and Gump [44)], in their early paper dealing with the action of a boiling methanolic HCl solution on furfuryl alcohol isolated the following products, with the yields indicated:

1. Furfuryl methyl ether, boiling point 35 - 38°C. at 16 mm. pressure; yield 8%.
2. Methyl levulinate, boiling point 85 - 87°C. at 16 mm. pressure; yield 7 - 8%.
3. A fraction, boiling point 100 - 101°C. at 16 mm. pressure, assumed by Pummerer to be δ-methoxy-levulinaldehyde-dimethylal; yield 30%.
4. An unidentified product, boiling point 57 - 58°C. at 16 mm. pressure, possibly α-angelica lactone; yield 2 - 3%.
5. Resin and higher-boiling oils; yield 50%.

In a later paper the reaction was carried out by decreasing the relative concentration of furfuryl alcohol and by increasing the acid content of the solution. As a consequence, resin formation was lowered, and the yield of fraction 3 was increased.

It is evident from the above data that furfuryl alcohol is a very reactive substance and readily undergoes ring opening. Moreover, a high percentage of resinous material (presumably highly polymerized products) is formed. While there was no question as to the identity of fractions 1 and 2, no attempt was made to identify fractions 4 and 5. Also non-convincing experimental evidence was offered in proof of the identity of fraction 3 assumed to be δ-methoxy-levulinaldehyde-dimethylal. For these reasons a re-investigation of the problem was undertaken by Dr. S. Trister 27) and the results of his work may be summarized briefly as follows:

a. By using small amounts of concentrated sulphuric acid as catalyst, in the presence of a large excess of methanol, the amount of resin formation is decreased considerably (from 50 to 15%).

b. Careful neutralization of the reaction product with sodium methylate, followed by filtration of the sodium sulphate formed, and removal of the excess methanol gives a reaction product which can be readily fractionated, giving only slight amounts of resin.

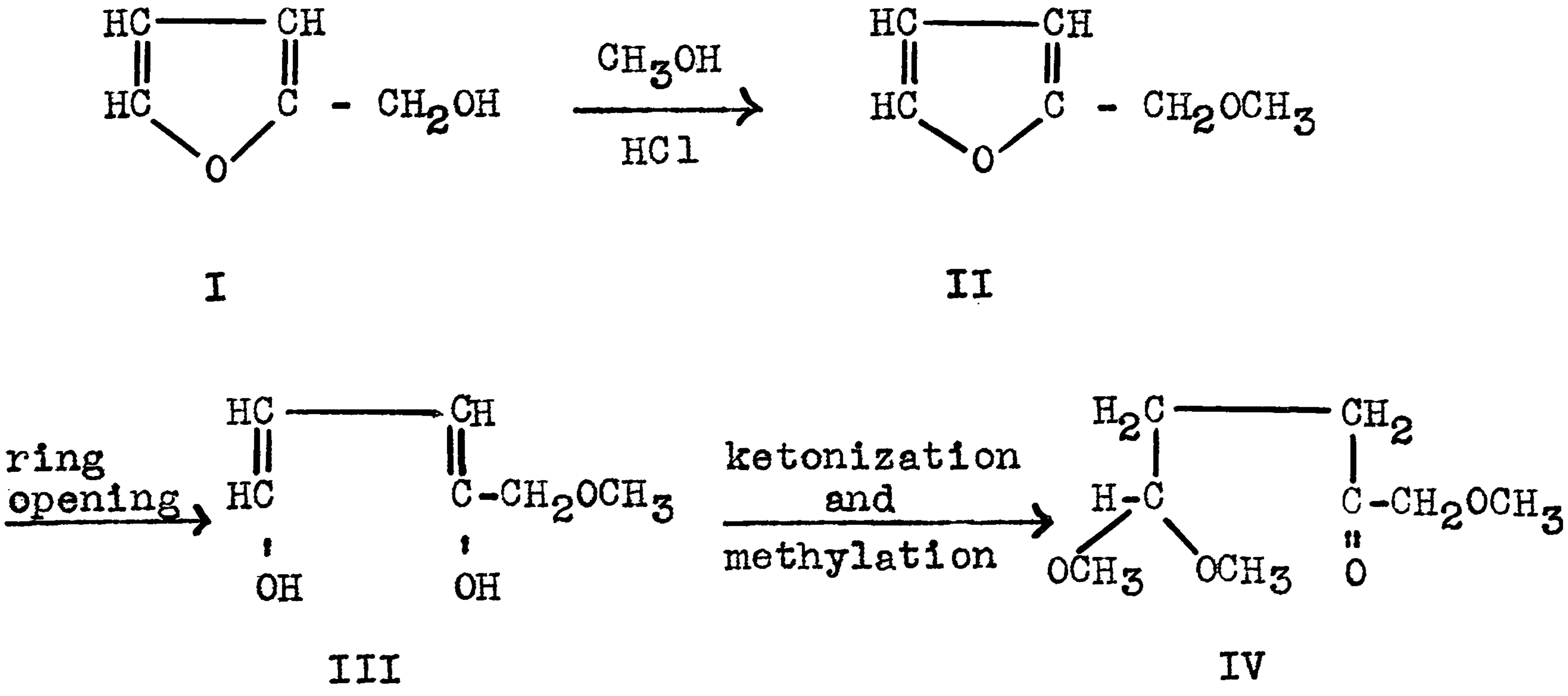
A typical experiment is shown in Experiment Two, pages 90-91. No attempt was made by Trister to ascertain the structure of Fraction A-1(d') corresponding to Pummerer's so-called δ-methoxy-levulinaldehyde-dimethylal. Results of the present investigation are in agreement with Trister's findings.

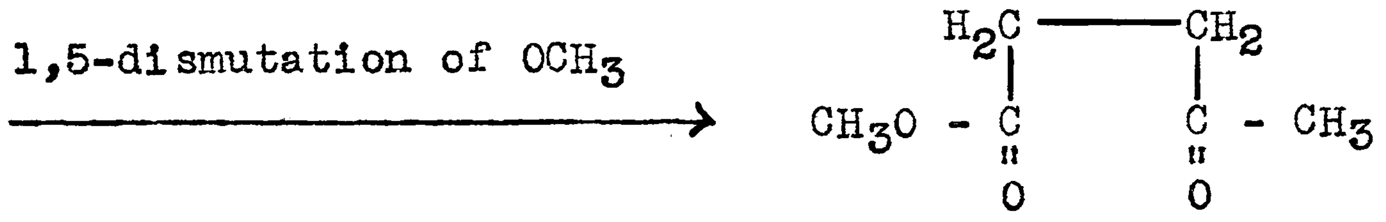
The main objects of the problem were to ascertain:

1) Confirmation or otherwise of the structure of Fraction A-1(d') as δ-methoxy-levulinaldehyde-dimethylal, and

2) A mechanism of transformation of furfuryl alcohol into levulinic acid.

The latter change, as pointed out by Pummerer, readily takes place on warming Fraction A-1(d') (Pummerer's compound) with dilute aqueous or methanolic-HCl, and in the light of this reaction the following mechanism was postulated by Pummerer:



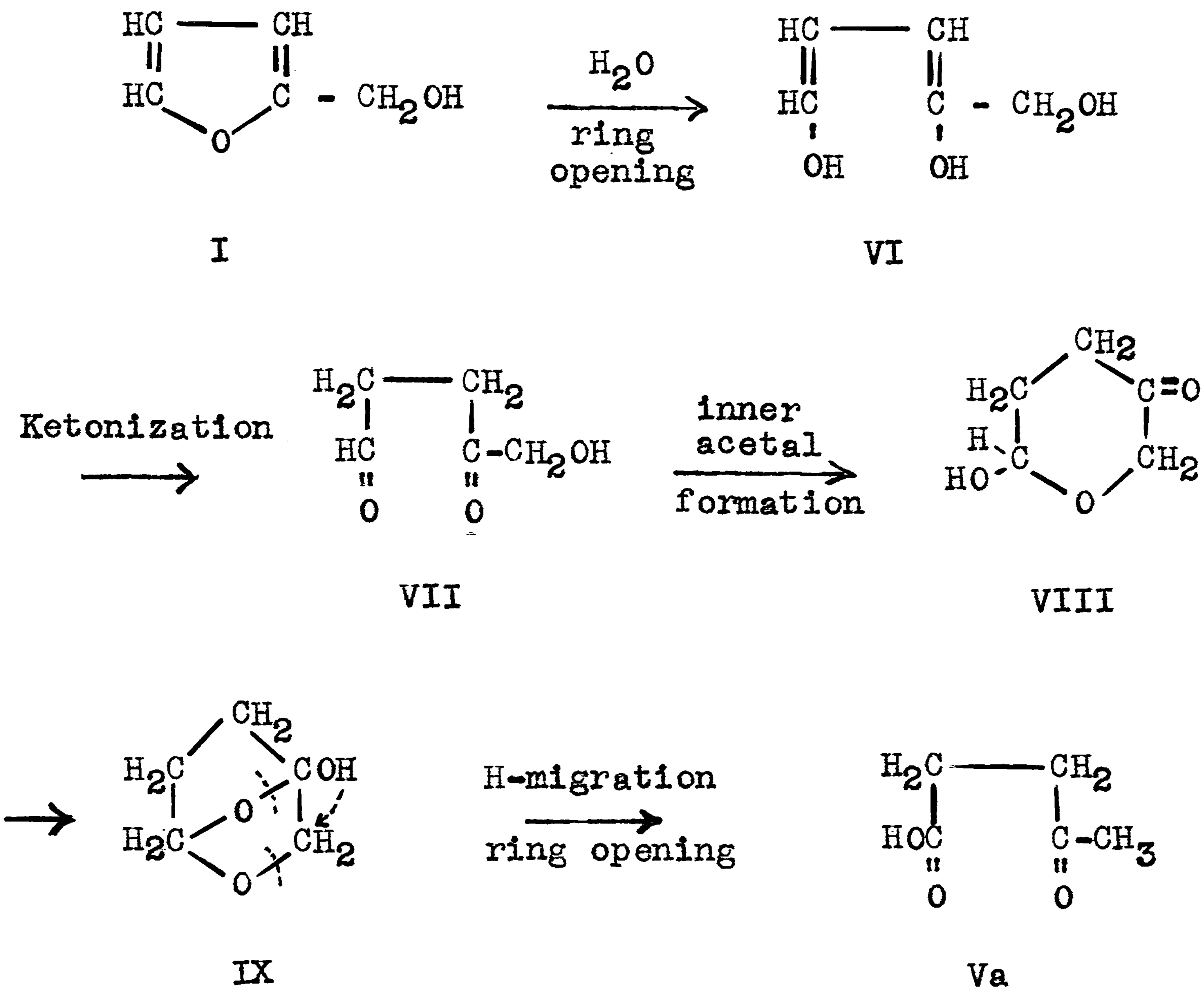


V.

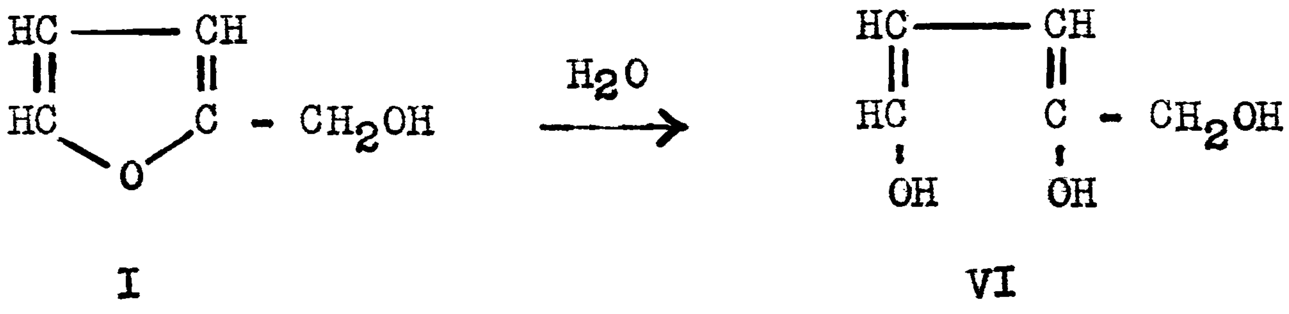
As already pointed out, (cf. pp. 35), migration of a methoxyl group in IV from a 1 to 5 carbon atom seems unlikely especially as this would involve rupture of a methyl ether bond. Conceivably, this linkage might be rendered unstable by the presence of an adjacent carbonyl group. However, when a derivative (semicarbazone) is prepared from the compound represented by IV above, complete elimination of methoxyl takes place with apparent formation of a residual grouping C_5H_6 united to two semicarbazide groups. Identical results were found using 2,4-dinitrophenylhydrazine hydrochloride in methanol solution.

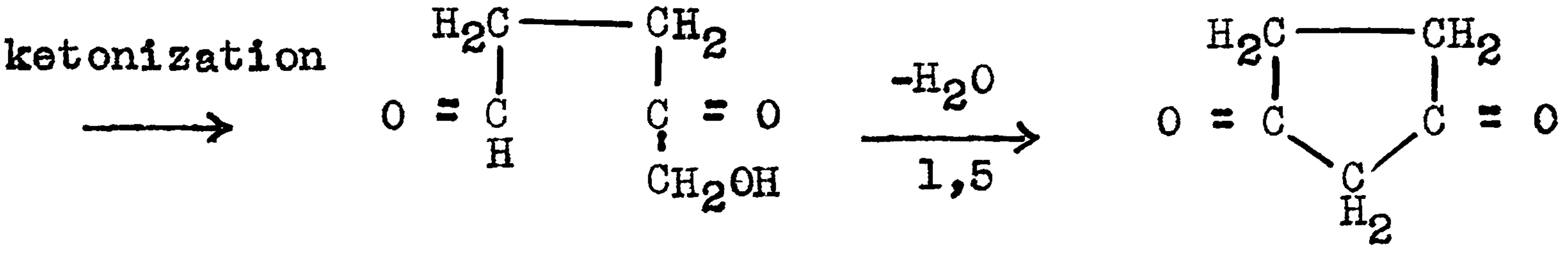
It would seem that, if Pummerer's assigned formula for IV is correct, the methyl ether bond should certainly be stable to a buffered solution of semicarbazide hydrochloride.

Two other mechanisms have been postulated in these laboratories. One by H. Hibbert, which is represented below (OH is used where OCH_3 should probably be used):

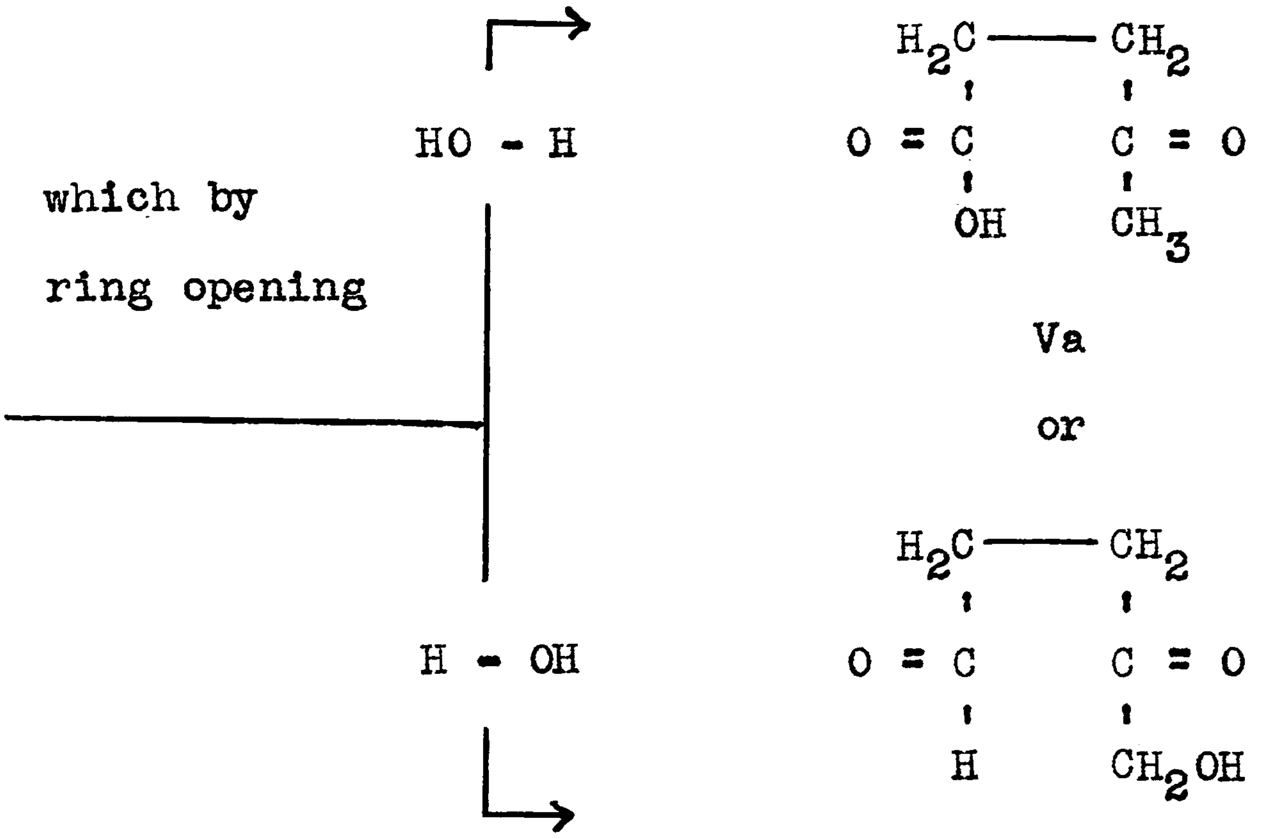


An alternative view was suggested by the writer:





VII X



Va

VII

However, neither mechanism appears to be in harmony with the experimental evidence which any proposed mechanism must account for. The facts demanding an explanation are:

1. Formation of methyl levulinate from furfuryl alcohol or furfuryl methyl ether in yields of 20 - 30% by treatment with methanolic-HCl.

2. The formation of an intermediate product having the empirical formula $C_5H_7O(OCH_3)_3$ which is easily

converted under similar conditions to methyl levulinate.

3. A structure for Pummerer's compound explaining the elimination of three methoxyl groups on formation of a bis-2,4-dinitrophenylhydrazone or a bis-semicarbazone, on treatment with the corresponding hydrochlorides in methanol, formation of the first taking place in an HCl solution, the latter in an acetic acid medium.

Action of a Methanolic Solution of H_2SO_4, at Low Temperatures, on Furfuryl Alcohol.

Following Trister's experimental procedure, it was established that the conditions of reaction used by Pummerer were too drastic (elevated temperature) and could thus have destroyed intermediates formed during the reaction. Also it was felt that the use of a reagent such as sodium bisulphite used in his purification process, might have brought about secondary reactions. It was therefore decided to follow the technique as outlined in Experiment 2, in which the modification consisted in:

1. The use of H_2SO_4, thus keeping the concentration of acid constant throughout the reaction;

2. The use of lower temperatures, 0°C. and 24°C. for longer periods of time, and

3. Separation of the various constituents by a method of fractional distillation.

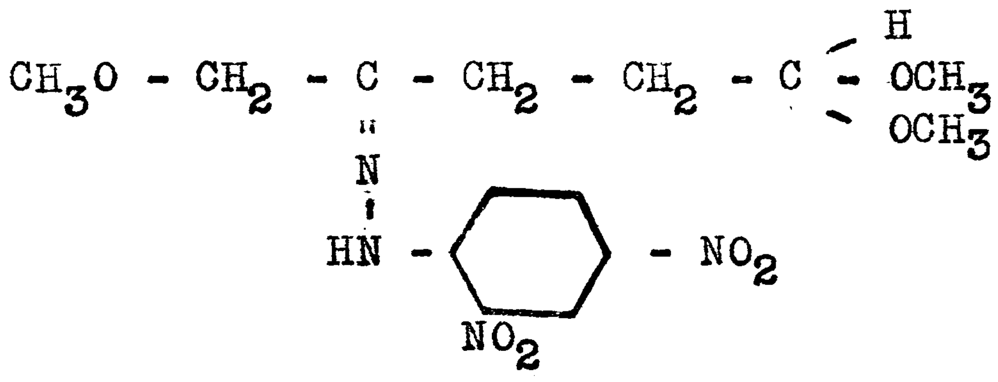
That these modifications were justified, can be seen in the results indicated in Experiment 2.

Conditions of reaction were sufficiently mild that a part of the original furfuryl alcohol was recovered unchanged, from the reaction. Resinification which takes place to 30% in the Pummerer reaction, takes place only to the extent of 12 - 13%. Volatile components, boiling point 100 - 160°C., at 12 mm. pressure, were easily separated, and the use of only physical methods in the separation of components boiling below 100°C., at 12 mm. pressure, eliminated all factors (excepting heat), liable to bring about side reactions.

Following the above technique, all of the products reported by Pummerer were isolated. The presence of his δ-methoxy-levulinaldehyde-dimethylal as a reaction intermediate, was confirmed, and this material was made the subject of the present investigation.

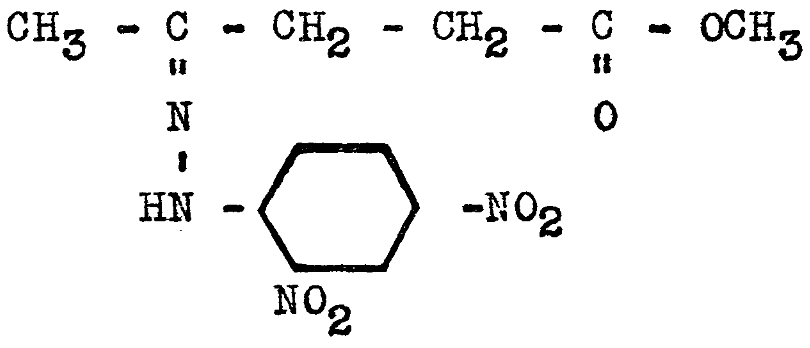
As pointed out earlier, Pummerer based his formula for this compound on two facts only; a) carbon and hydrogen analyses, and b) its conversion to methyl levulinate. Condensation reactions with amines (hydrazines; semicarbazide) yielded in all cases bis-derivatives, and in all but one case the methoxyl groups were completely eliminated in the reaction. This exception was the bis-2,4-dinitrophenylhydrazone, melting point 192 - 193°C., reported by him. It was not found possible to duplicate this reaction. He used 2,4-dinitrophenylhydrazine in H_2SO_4 (10%) at a temperature of 32°C. for 12 hours. The product contained one methoxyl group.

However, by adoption of a modified technique in which 2,4-dinitrophenylhydrazine was allowed to react with the sodium bisulphite derivative formed from Pummerer's compound, a 2,4-dinitrophenylhydrazone was isolated, containing all of the original methoxyl groups. Based on Pummerer's structure for the intermediate IV, the structural formula of this derivative would be:



XI

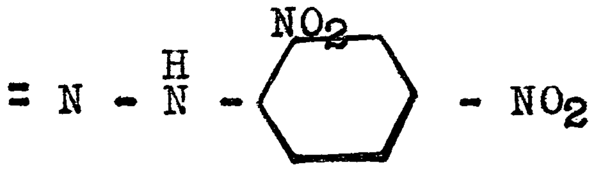
Treatment of this compound, with a boiling solution of HCl in methanol, gave the 2,4-dinitrophenylhydrazone of methyl levulinate:



XII

When the mono-2,4-dinitrophenylhydrazone was treated with an excess of 2,4-dinitrophenylhydrazine hydrochloride in methanol solution, it was converted into a bis-2,4-dinitrophenylhydrazine, which is the same compound as that formed from the Pummerer compound [original fraction (A)-1(d')] in the presence of an excess of 2,4-dinitrophenylhydrazine hydrochloride in methanol, having the empirical formula:

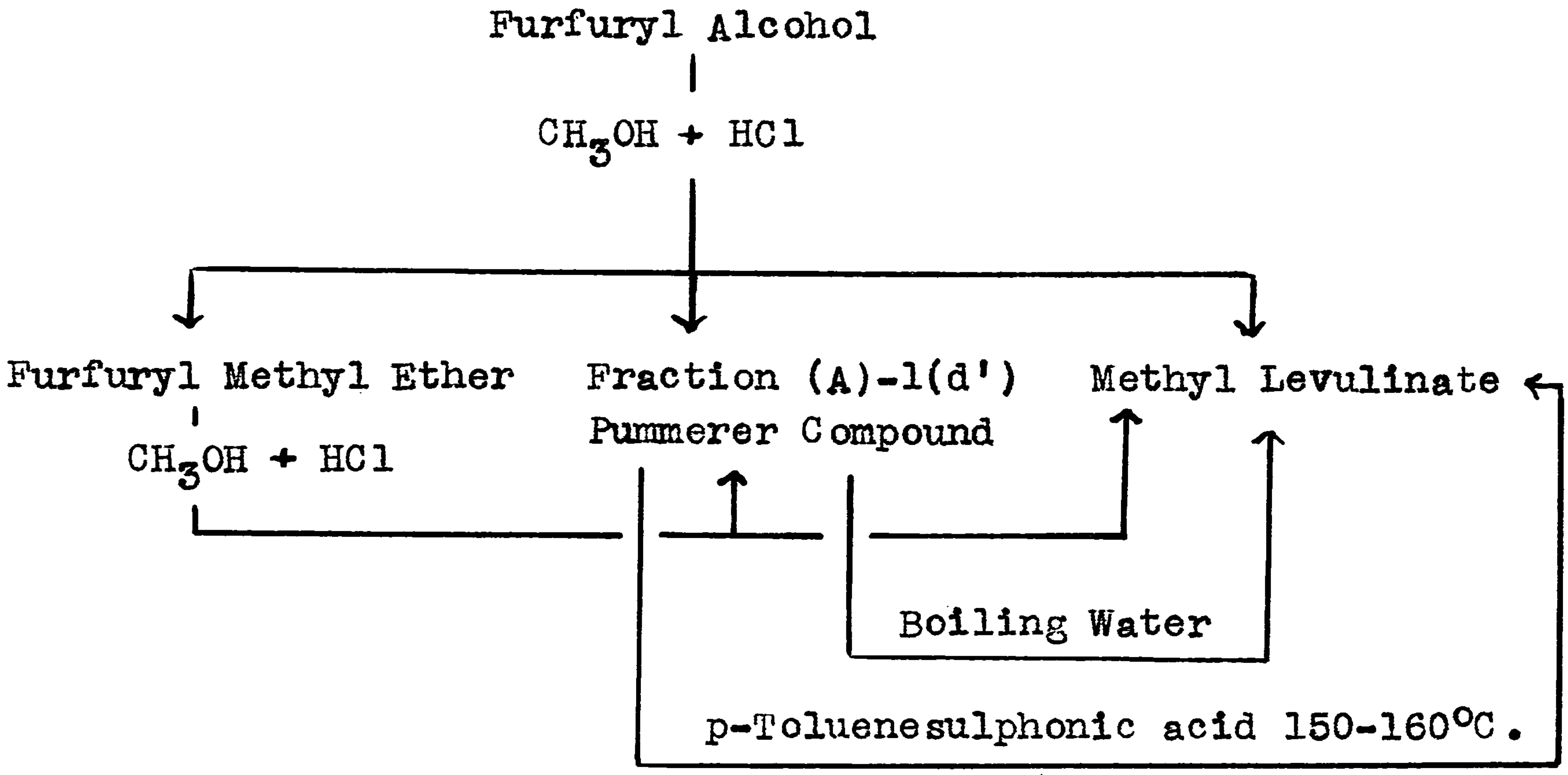
$C_5H_6 - 2R$ R is



XIII

The discovery, by the author, of this new mono-2,4-dinitrophenylhydrazone and its ease of conversion into the other final reaction products is of great importance in any discussion of the mechanism of the reaction under consideration, and, in order to permit of its true evaluation, it seems advisable to show graphically: (a) The relationship of the different products formed in the action of methanol-HCl on furfuryl alcohol (Chart I); and (b) The relationship and properties of the 2,4-dinitrophenylhydrazones from furfuryl alcohol (Chart II):

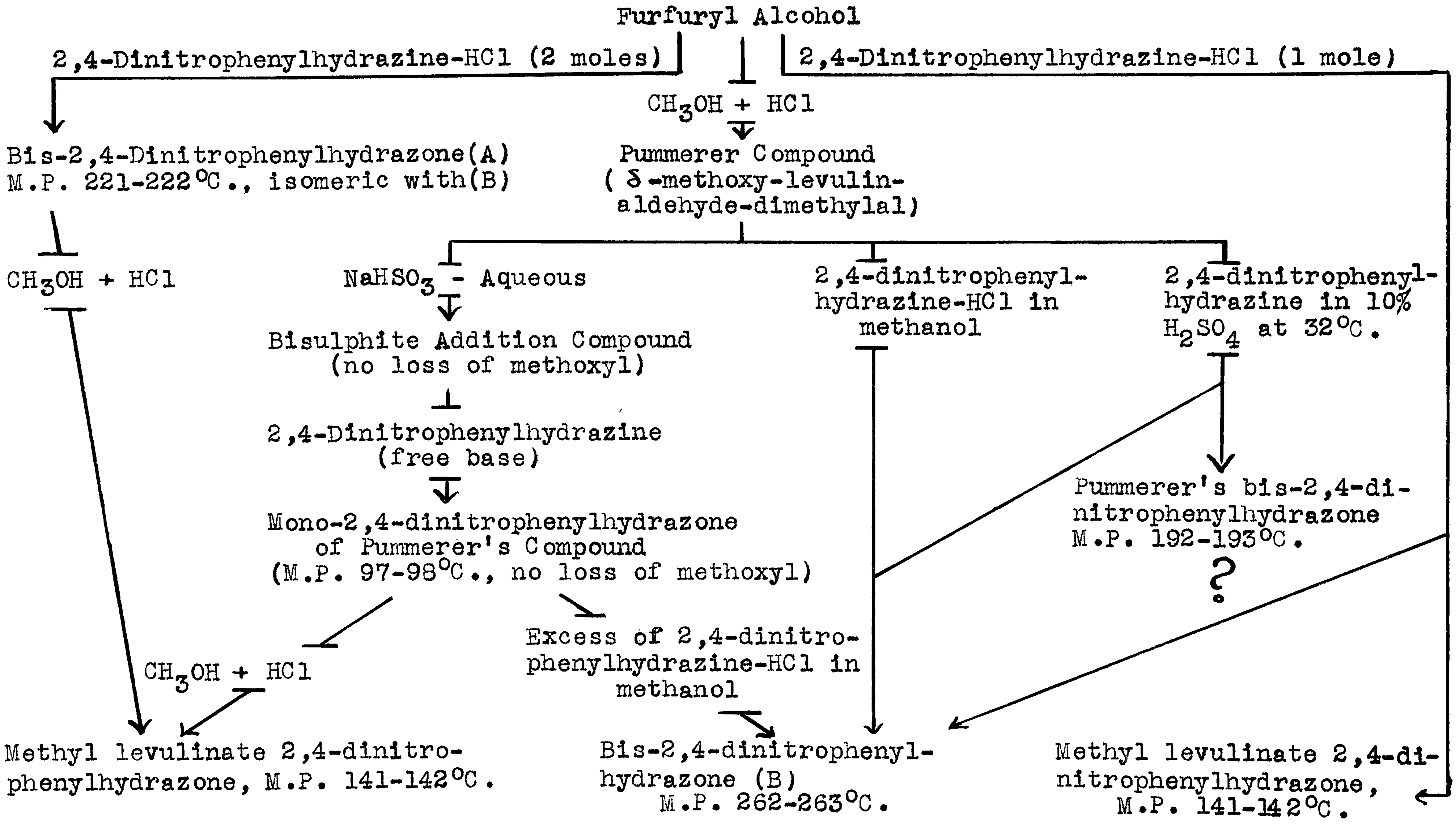
CHART I



Products are the same when CH_3OH - H_2SO_4 mixtures are used to replace CH_3OH - HCl.

CHART II

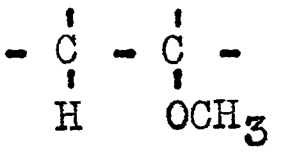
Relationship and Properties of 2,4-Dinitrophenylhydrazones from Furfuryl Alcohol



As bearing on the true structure of the Pummerer compound, the following new experimental facts, shown graphically in Charts I and II, call for consideration:

1. On steam distillation the Pummerer compound is converted quantitatively into methyl levulinate (Chart I).

2. Heating the Pummerer compound with p-toluene sulphonic acid at 150-160°C. gives methyl levulinate quantitatively and also free methanol in relatively high yield (55%). This reaction indicates the removal of methanol from the grouping



$-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{OCH_3}{|}}{C}}-$.

3. Depending on the relative quantities of furfuryl alcohol and 2,4-dinitrophenylhydrazine used, two isomeric bis-2,4-dinitrophenylhydrazones are formed, one melting at 262-263°C. (identical with that formed from the Pummerer compound) and a new bis-2,4-dinitrophenylhydrazone, melting point 221-222°C. which latter, judged from its properties, possesses a very different structure. This latter product is readily converted into methyl levulinate 2,4-dinitrophenylhydrazone by action of boiling methanol-HCl, in contrast to the inertness of the former compound (melting point 262-263°C.) under the same conditions (Chart II).

4. The most important discovery is that of a new mono-2,4-dinitrophenylhydrazone obtained from the sodium bisulphite derivative of the Pummerer compound and without involving loss of methoxyl (Chart II).

5. This new mono-2,4-dinitrophenylhydrazone when boiled with methanol-HCl yields methyl levulinate 2,4-dinitrophenylhydrazone while with an excess of 2,4-dinitrophenylhydrazine hydrochloride it is converted into the stable bis-2,4-dinitrophenylhydrazone (melting point 262-263°C.).

6. Contrary to the claims of Pummerer, treatment of the so-called δ-methoxy-levulinaldehyde-dimethylal with 2,4-dinitrophenylhydrazine in sulphuric acid (10%) at 32°C. for 12 hours gave the *stable* bis-2,4-dinitrophenylhydrazone (melting point 262-263°C.). No indication of the presence of his bis-2,4-dinitrophenylhydrazone (melting point 192-193°C.) (containing one methoxyl group) could be obtained.

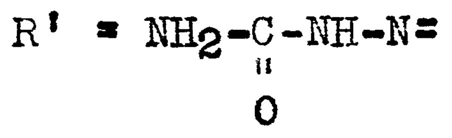
7. The new application of 2,4-dinitrophenylhydrazine hydrochloride as a reagent for determination of ring fission indicates the remarkable ease of ring opening under the influence of this reagent whereby a yield (30%) of the methyl levulinate 2,4-dinitrophenylhydrazone is obtained.

The bearing of the above experimental facts on the correctness of the structure of the Pummerer compound as δ-methoxy-levulinaldehyde-dimethylal can now be discussed.

The first important point is that the potential dicarbonyl compound from which the writer's new *stable* bis-2,4-dinitrophenylhydrazone originates is identical with that present in Pummerer's so-called δ-methoxy-levulinaldehyde-dimethylal and from which the corresponding bis-semicarbazone was obtained:

$$C_5H_6 - 2R \quad (x) \qquad\qquad C_5H_6 - 2R' \quad (y)$$

$$R = C_6H_3(NO_2)_2\text{-NH-N=}$$



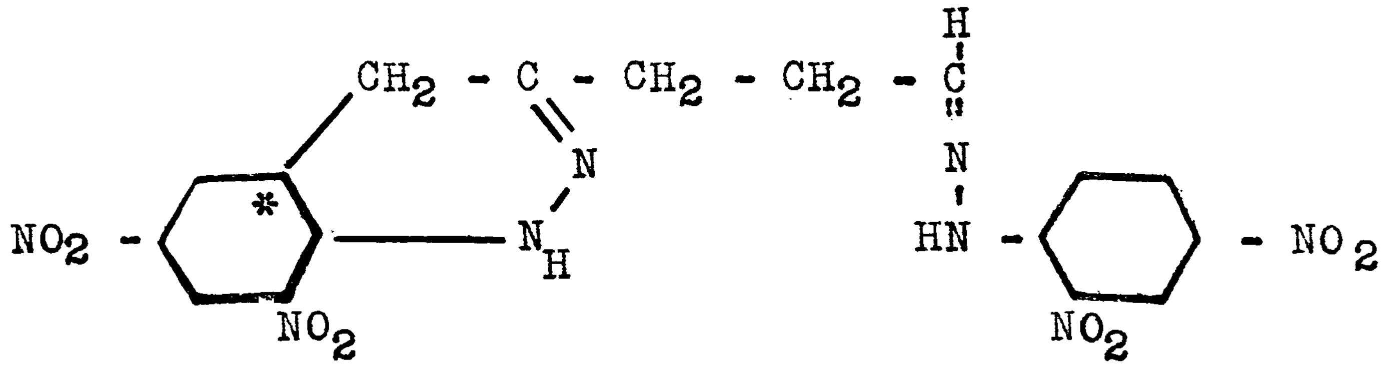
$$R' = NH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-NH-N=}$$

so that any conclusions drawn with regard to (x) apply with equal force to (y).

The greatest difficulty arising in any satisfactory interpretation of Pummerer's results is to be found in the abnormal elimination of all of the methoxyl groups in the formation of either the bis-2,4-dinitrophenylhydrazone or bis-semicarbazone from his δ-methoxy-levulinaldehyde-dimethylal.

There are several mechanisms capable of explaining this phenomenon. The first stage (common to all) consists in removal of two methoxyl groups from the acetal linkage to give a new reactive carbonyl group. The second step involving elimination of the third methoxyl group is more difficult to visualize. Three of the possibilities involve ring formation, e.g.:

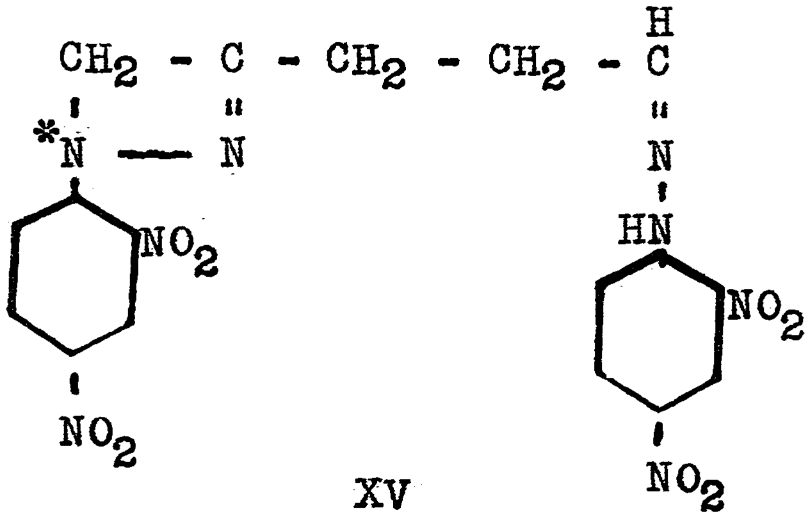
1.



XIV.

in which elimination of methanol has occurred between the δ-carbon atom and an active H * of one 2,4-dinitrophenyl nucleus;

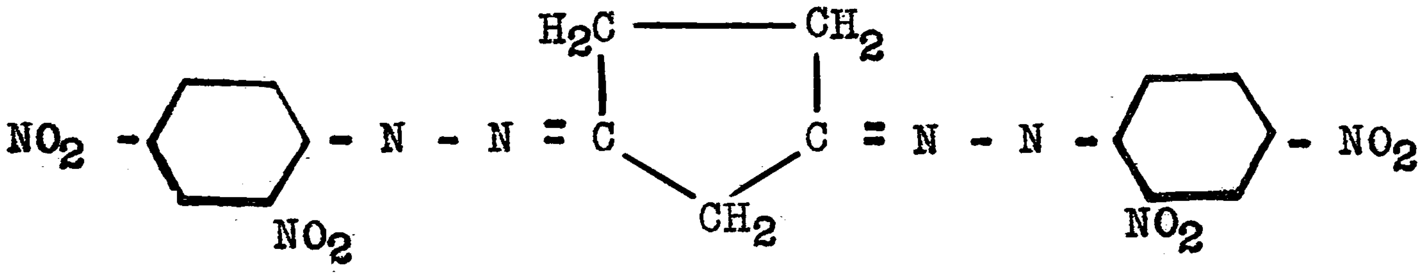
2.



XV

in which elimination of methanol has occurred between the δ-carbon atom and H * of the substituted hydrazone;

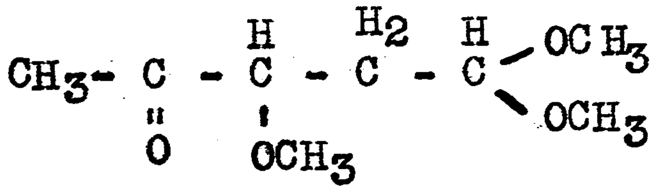
3.



XVI

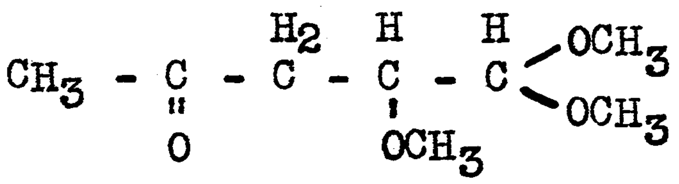
in which the 1-aldehydic group supplies the active hydrogen, and

4. Postulation of a new type of intermediate XVIII or XIX



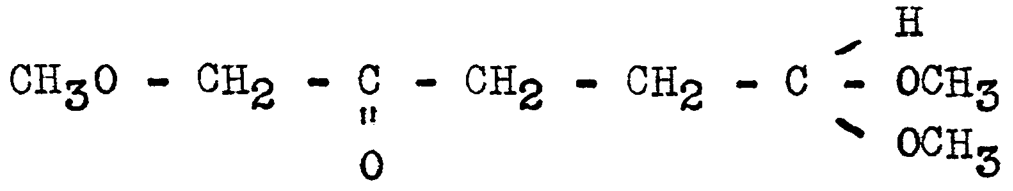
$$CH_3-\underset{\underset{O}{\|}}{C}-\overset{H}{\underset{\underset{OCH_3}{|}}{C}}-\overset{H_2}{C}-\overset{H}{C}\begin{array}{l}\diagup OCH_3\\ \diagdown OCH_3\end{array}$$

XVIII



$$CH_3-\underset{\underset{O}{\|}}{C}-\overset{H_2}{C}-\overset{H}{\underset{\underset{OCH_3}{|}}{C}}-\overset{H}{C}\begin{array}{l}\diagup OCH_3\\ \diagdown OCH_3\end{array}$$

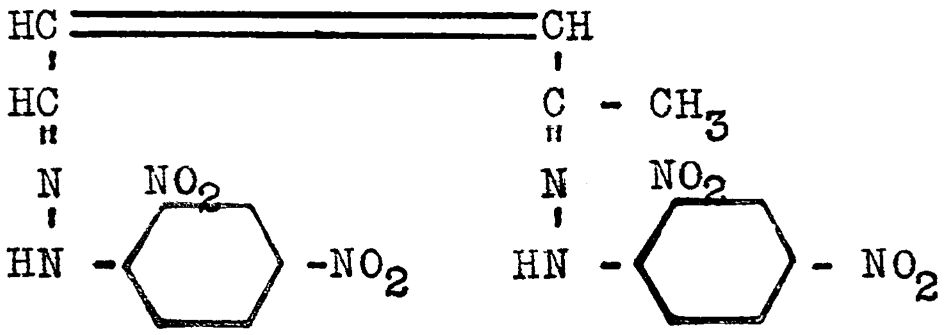
XIX



$$CH_3O - CH_2 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - C \begin{cases} H \\ OCH_3 \\ OCH_3 \end{cases}$$

XX

from which elimination, as a second step, of methanol from adjacent carbon atoms, possibly under the influence of the high molecular substituted hydrazone groups can take place to form an unsaturated derivative:



XVII

Presumably such a reaction would occur much more readily with structure XVIII than with XIX.

With regard to these various suggested structures for the completely demethoxylated stable bis-2,4-dinitrophenylhydrazone (melting point 262 - 263°C.), the first (XIV) is evidently incorrect since the bis-2,4,6-trinitrophenylhydrazone prepared from Pummerer's compound contains no methoxyl. Disproval of the second structure (XV) was shown by formation of an α, α-diphenylhydrazone from Pummerer's compound and the fact that this also contains no methoxyl. Thus there remain the possibilities (XVI) and (XVII).

With regard to (XVI), elimination of methanol involves formation of a cyclopentane ring which is considered improbable, since it should be relatively unstable to acids.

This leaves only the fourth possibility (XVII) namely, a bis-2,4-dinitrophenylhydrazone formation at the 1 and 4-carbon atoms respectively, accompanied by an elimination of methanol from adjacent carbon atoms to form an unsaturated compound. In other words, the true structure for the product, postulated by Pummerer as δ-methoxy-levulinaldehyde-dimethylal (XX) should be either (XVIII), or much more probably (XIX). Such a structure (XIX) offers a satisfactory explanation of the following experimental facts:

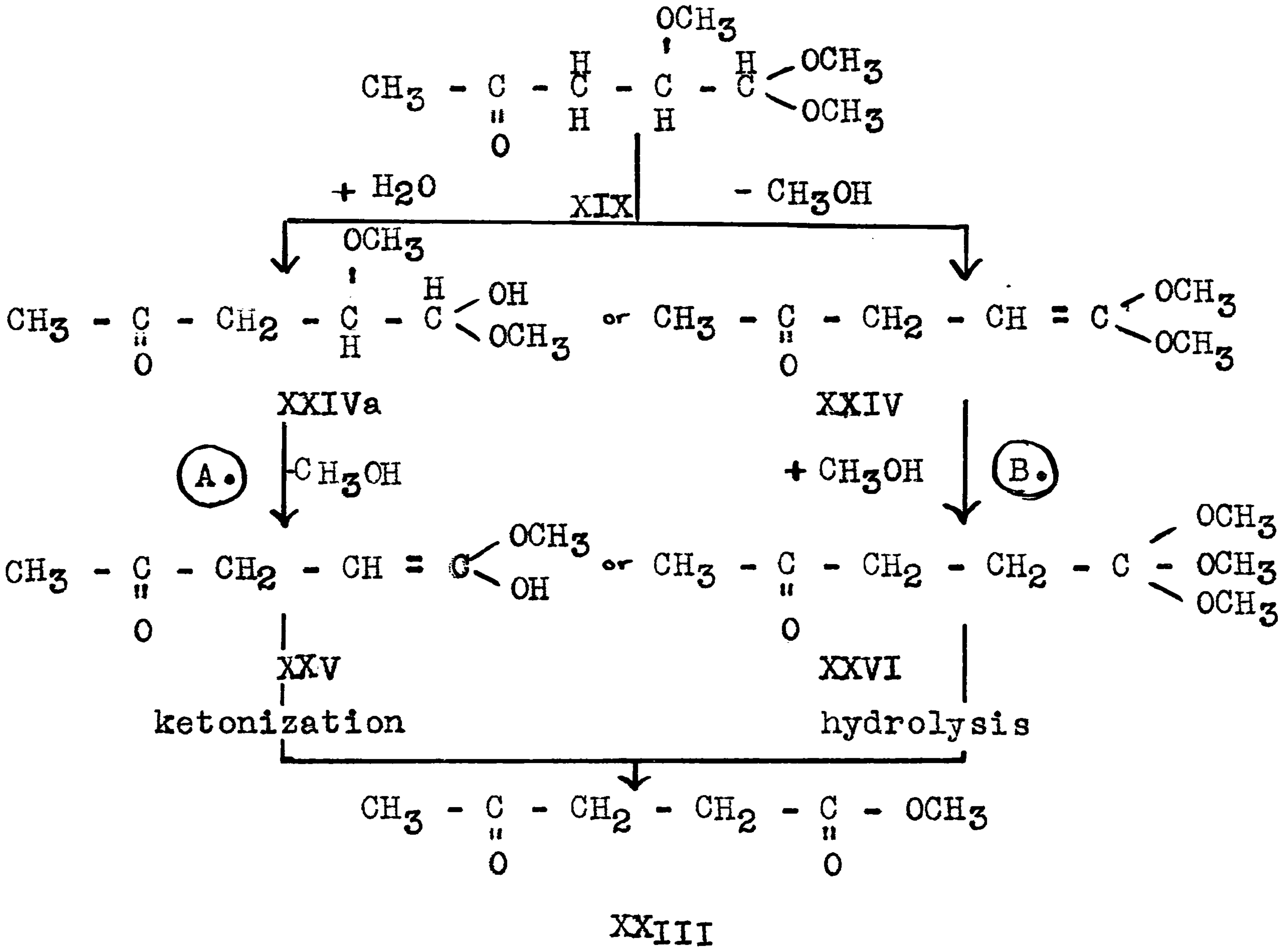
1. Formation of methyl levulinate without chain fission indicating the presence of a 5-carbon chain.
2. Ability to form a sodium bisulphite addition compound.
3. Presence of a free carbonyl group (Grignard analysis) and formation of a mono-2,4-dinitrophenylhydrazone.
4. Preparation of a bis-2,4-dinitrophenylhydrazone indicating the existence of a latent carbonyl group.
5. Methoxyl analysis showing the presence of three methoxyl groups, based on the empirical formula $C_5H_7O(OCH_3)_3$.

The presence of three methoxyl groups and one free carbonyl group in the Pummerer intermediate eliminates the mechanisms suggested by Hibbert and by the writer, since no such intermediate containing both groupings is postulated in either series of reactions, (cf. pp. 52-53).

Proposed Mechanism for Conversion of (XIX) into Methyl Levulinate.

An acceptable mechanism of conversion of (XIX) to methyl levulinate can now be offered and is indicated as follows:

All of the experimental methods used for the conversion involve subjecting the compound to conditions under which a partial hydrolysis of the acetal grouping is possible.



In the first reaction, the H atom on carbon (1), which presumably is activated spatially by the carbonyl group, undergoes elimination with methoxyl from carbon (2), to give methanol. This, if followed by partial hydrolysis with water and ketonization, would give methyl levulinate. On the other hand, a second but less probable assumption would be as in B., where primary elimination of methanol is followed by addition to give the methyl ester of ortho-levulinic acid.

The probable structure of the Pummerer product is thus shown to be (XIX) rather than ∂-methoxy-levulinaldehyde-dimethylal assumed by Pummerer.

There now remain only for discussion:

(a) The mechanism by which this product is formed from furfuryl alcohol, and

(b) The nature of the synthesis of the new bis-2,4-dinitrophenylhydrazone (melting point 221-222°C.) (Chart II).

Before proceeding with this discussion, it is necessary to consider the reactions resulting from the application of 2,4-dinitrophenylhydrazine to the determination of ease of ring opening.

C. USE OF 2,4-DINITROPHENYLHYDRAZINE FOR THE STUDY OF THE RING OPENING OF FURANS

Dr. Geo. Wright, formerly associated with this laboratory, first proposed the use of 2,4-dinitrophenylhydrazine for the study of ring opening in the furan series. The fact that the above reagent, in solutions containing a sufficient concentration of acid, brings about ring opening of furans, made this a very useful reagent for the study.

1) Behavior Toward Furfural

Treatment of furfural (which does not undergo ring opening with methanolic solutions of mineral acids), gave a derivative of furfuraldehyde, the normal 2,4-dinitrophenylhydrazone.

2) Behavior Toward Sylvan

However, treatment of sylvan (which readily undergoes ring opening with methanolic solutions of mineral acids to yield levulinaldehyde-dimethylal) gave a substantial amount of a bis-2,4-dinitrophenylhydrazone of levulinaldehyde.

3) Behavior Toward Furfuryl Alcohol

(a) By treatment of furfuryl alcohol with two parts of 2,4-dinitrophenylhydrazine hydrochloride, a new crystalline compound was obtained, (cf. page 102, Experiment 9 (a)). This derivative, purified from acetone-pet. ether, melted at 221 - 222°C. and was very unstable. The carefully purified product underwent not only a decrease in melting point, but also in the definiteness of same on storage. When boiled with a methanolic solution of HCl, it was converted into methyl levulinate-2,4-dinitrophenylhydrazone, and free 2,4-dinitrophenylhydrazine. From this it would appear that the 2,4-dinitrophenylhydrazone is formed from an unknown intermediate. It contains no methoxyl, differing in this respect from Pummerer's compound.

(b) Using a 1:1 ratio of furfuryl alcohol to 2,4-dinitrophenylhydrazine hydrochloride, two crystalline compounds, namely, methyl levulinate-2,4-dinitrophenylhydrazone (A) and a bis-2,4-dinitrophenylhydrazone (B), melting point 262 - 263°C. were obtained, (cf. page 103, Experiment 9 (b)). (B) was characterized by insolubility in methanol, and stability to alcoholic solutions of acids.

D. THE INTERCONVERSION OF, AND RELATIONSHIP BETWEEN THE VARIOUS COMPOUNDS AND THEIR 2,4-DINITROPHENYLHYDRAZONES

Since 2,4-dinitrophenylhydrazine hydrochloride was the reagent used for investigating the fission reaction, it was important to settle the relationship existing between the various 2,4-dinitrophenylhydrazones found. In the following chart (2A), the 2,4-dinitrophenyl group is represented as R, and the various 2,4-dinitrophenylhydrazones are, for sake of brevity, classified according to melting point:

(A) Melting point 97 - 98°C. This is the mono-2,4-dinitrophenylhydrazone obtained from Pummerer's compound, without elimination of methoxyl, by the action of $NaHSO_3$.

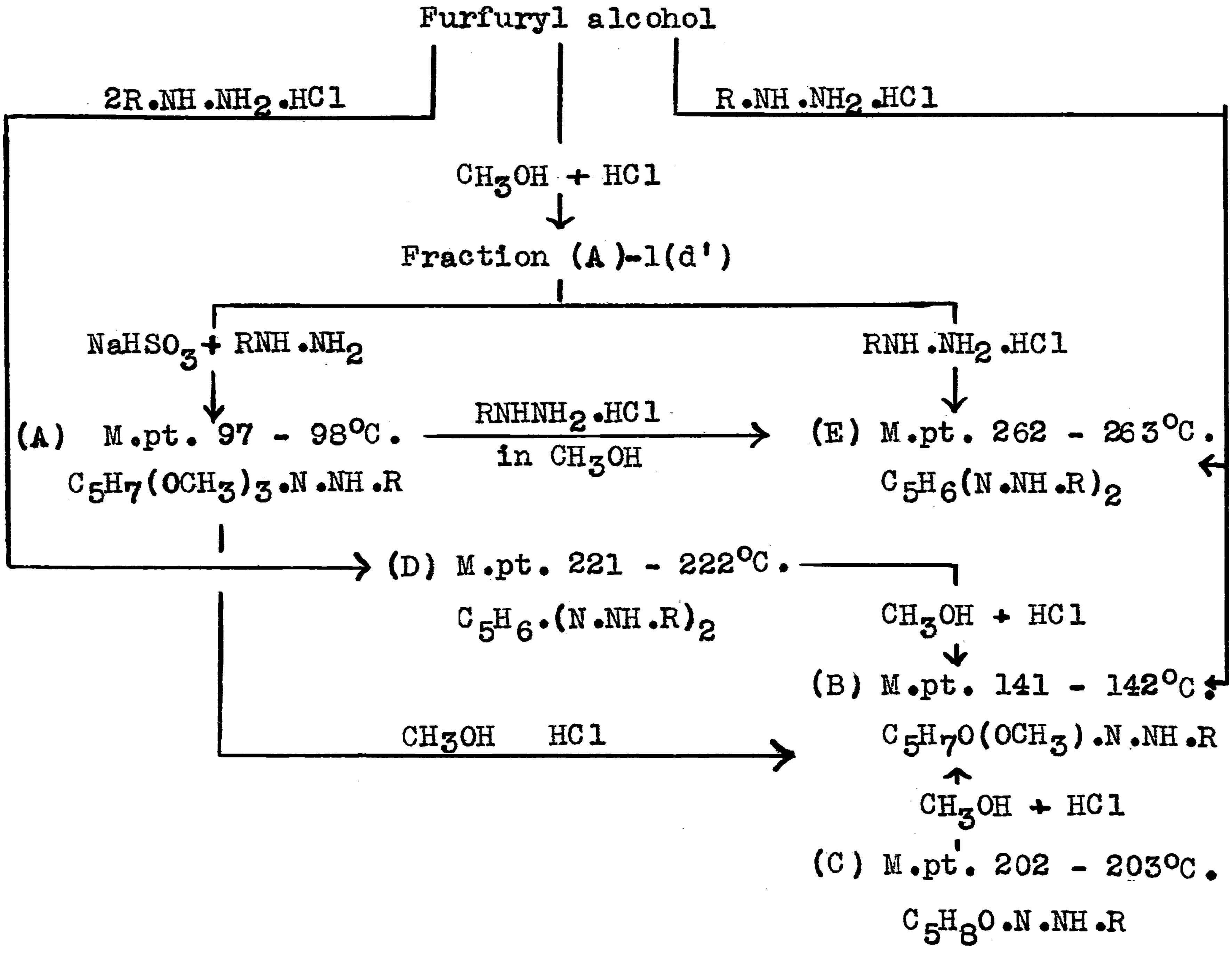
(B) Melting point 141 - 142°C. This is methyl levulinate 2,4-dinitrophenylhydrazone.

(C) Melting point 202 - 203°C. This is the 2,4-dinitrophenylhydrazone of levulinic acid.

(D) Melting point 221 - 222°C. This is the 2,4-dinitrophenylhydrazone obtained by the action of one part of 2,4-dinitrophenylhydrazine hydrochloride in boiling methanol on one part of furfuryl alcohol, (see page 102, Experiment 9 (a)).

(E) Melting point 262 - 263°C. This is the 2,4-dinitrophenylhydrazone obtained from Pummerer's compound, and also from the action of one part of 2,4-dinitrophenylhydrazine hydrochloride in methanol on one part of furfuryl alcohol,(see page 103, Experiment 9 (b)).

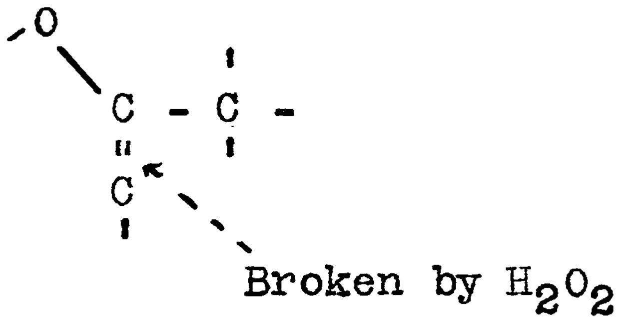
CHART 2A



From the foregoing chart, it would seem that at least two of the 2,4-dinitrophenylhydrazones are derivatives of an intermediate in the conversion reaction, viz., the product, melting point 97 - 98°C., which on further treatment is converted to methyl levulinate 2,4-dinitrophenylhydrazone; and, the derivative, melting point 221 - 222°C., which, by similar treatment, is changed to the methyl levulinate derivative. The 2,4-dinitrophenylhydrazone, melting point 262 - 263°C. is extremely stable.

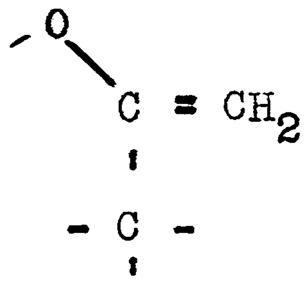
Thus a study of the 2,4-dinitrophenylhydrazones, melting point 221 - 222°C. and 262 - 263°C. was of great interest. Treatment of D and E with pyruvic aldehyde, p-nitrobenzaldehyde or an excess of acetaldehyde at elevated temperatures, did not, as anticipated, give the original carbonyl compounds, (cf. pp. 44). Methods developed by the writer such as, distillation with saturated Na_2CO_3 (aqueous), distillation with 10% NaOH, and oxidation with chromic acid, also gave negative results. The use of ozone for the recovery of carbonyl compounds, which proved valuable in the recovery of methyl levulinate from its 2,4-dinitrophenylhydrazone, gave valuable results.

The 2,4-dinitrophenylhydrazone, melting point 221 - 222°C. on ozonolysis and hydrolysis of the ozonide, yielded formaldehyde in appreciable quantity (one-half of one group per mole). Use of different solvents showed this did not originate from them. Furthermore, boiling the 2,4-dinitrophenylhydrazone directly with 1% hydrogen peroxide, gave similar yields of formaldehyde. This high yield of formaldehyde by ozonolysis, served to demonstrate the presence of a $CH_2=$ group. Also the recovery of formaldehyde from a hydrogen peroxide oxidation points to the presence of a grouping similar to that found in some of the anthocyanins 66), where hydrogen peroxide is known to attack an ethylenic double bond:

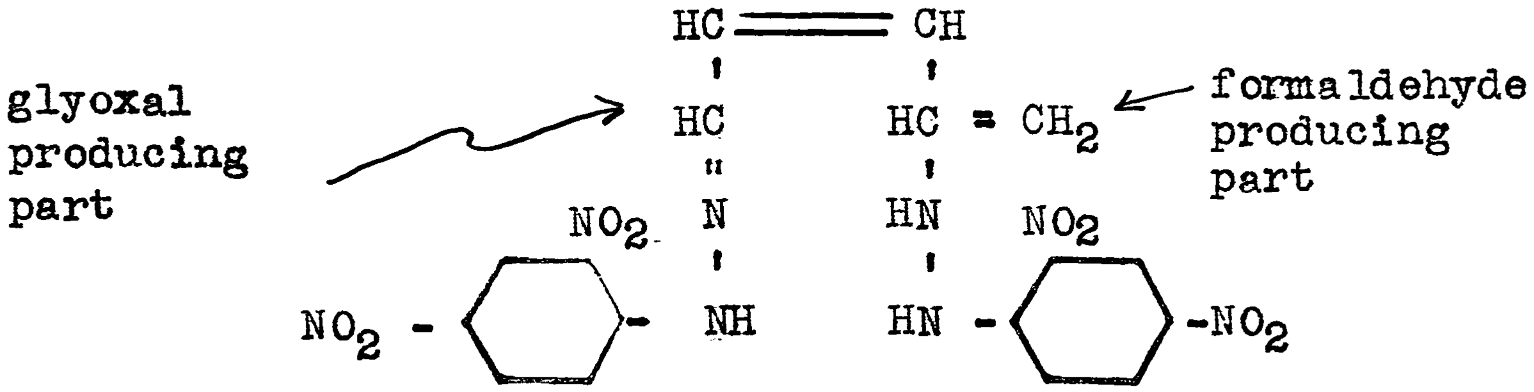


Broken by H_2O_2

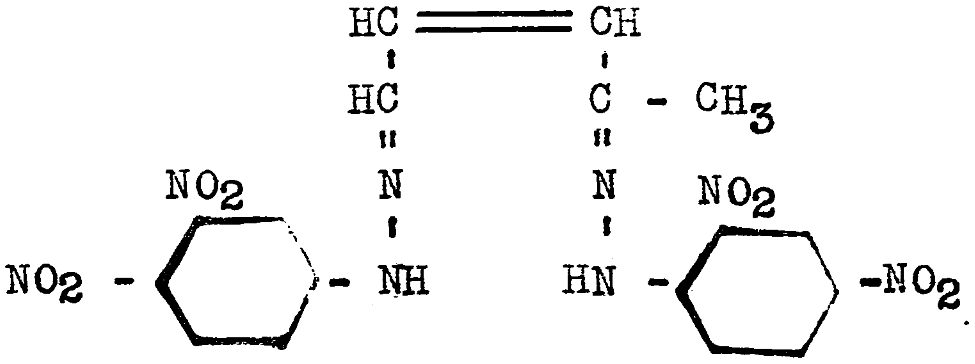
Presumably, the grouping present in the 2,4-dinitrophenylhydrazone giving rise to formaldehyde, is:



Based on this assumption, as well as on the empirical analyses for carbon and hydrogen (which are admittedly in only poor agreement), as well as the indicated formation of glyoxal-2,4-dinitrophenylosazone as an accompanying ozonolysis product, it can be seen that XXVII represents a possible structure for the 2,4-dinitrophenylhydrazone (D):



On the other hand, ozonolysis of (E) gave no formaldehyde, and only small yields of glyoxal-2,4-dinitrophenylosazone. The carbon and hydrogen analysis indicated the presence of a C_5H_6-group attached to two 2,4-dinitrophenylhydrazine residues. Thus, a possible formula for this would be:

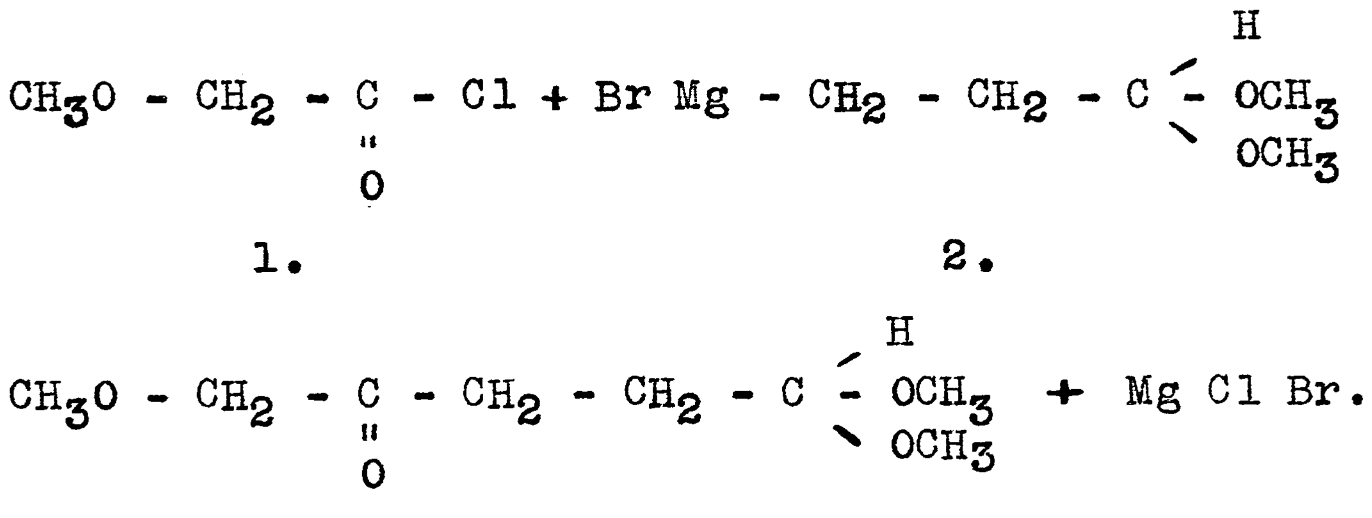


Neither of these postulated structures would be correct in the event that the glyoxal derivative was shown to actually arise from the 2,4-dinitrophenylhydrazine residue. However, no glyoxal-2,4-dinitrophenylosazone could be isolated by ozonolysis of the 2,4-dinitrophenylhydrazone of methyl levulinate.

E. THE ATTEMPTED SYNTHESIS OF DERIVATIVES OF δ-METHOXY-LEVULINALDEHYDE-DIMETHYLAL

Since the writer was satisfied that the structure postulated by Pummerer 44) for the intermediate was not the correct one, and since this was not based on identity with any known compound, it seemed desirable to synthesize δ-methoxy-levulinaldehyde-dimethylal by known chemical reactions.

Various methods of synthesis were unsuccessfully attempted, the most promising one of which was that involving a condensation between methoxy acetyl chloride and the magnesium addition compound from β-brom propionaldehyde dimethylal:



$$CH_3O - CH_2 - \underset{\overset{\|}{O}}{C} - Cl + BrMg - CH_2 - CH_2 - C\begin{smallmatrix} H \\ - OCH_3 \\ OCH_3 \end{smallmatrix}$$

1. 2.

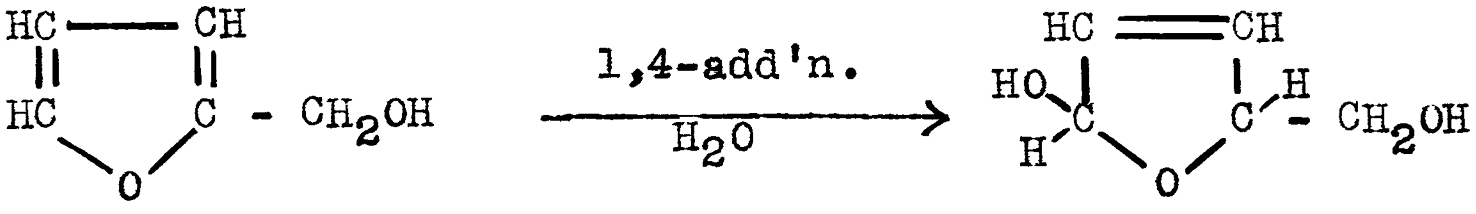
$$CH_3O - CH_2 - \underset{\overset{\|}{O}}{C} - CH_2 - CH_2 - C\begin{smallmatrix} H \\ - OCH_3 \\ OCH_3 \end{smallmatrix} + MgClBr.$$

However, it was found impossible to form the Grignard reagent from the latter, either in ether or benzene solution even with the aid of catalysts such as iodine or mercuric chloride. The use of the zinc-copper couple (Reformatsky reaction) in a mixture of benzene and ethyl acetate (1:2), was not successful. In the absence of a solvent it was possible to prepare a zinc addition product in small yields, but attempts to condense this reagent with methoxy acetyl chloride did not give the desired compound.

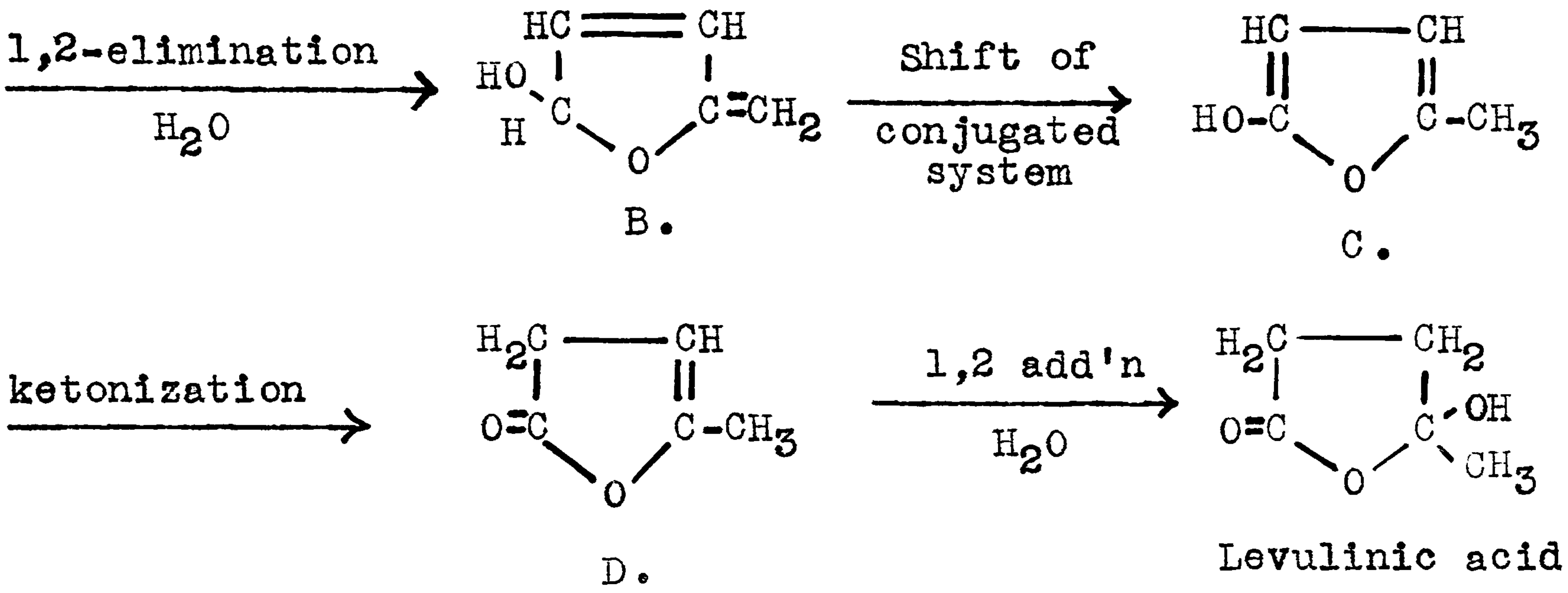
F. THE PROBABLE MECHANISM OF CONVERSION OF FURFURYL ALCOHOL TO METHYL LEVULINATE

Since the mechanism proposed by Pummerer seems somewhat doubtful, much consideration has been given to the possibility of postulating another type capable of explaining in a more satisfactory manner the conversion of furfuryl alcohol into methyl levulinate.

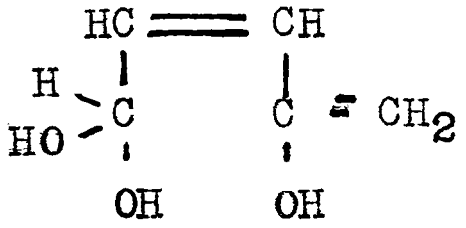
In this connection it should be pointed out, in the first place, that it is not necessary to postulate an actual ring opening for such changes. In harmony with the ideas of Bergmann 50) and of Scott and Johnson 48), and in view of the isolation and identification by the writer, of the two 2,4-dinitrophenylhydrazones, (1. Melting point 221 - 222°C. and 2. Melting point 262 - 263°C. obtained by the reaction of 2,4-dinitrophenylhydrazine hydrochloride in methanol with furfuryl alcohol in ratios of 2:1 and 1:1 respectively), the following alternative mechanism is suggested as a more probable explanation:



A.

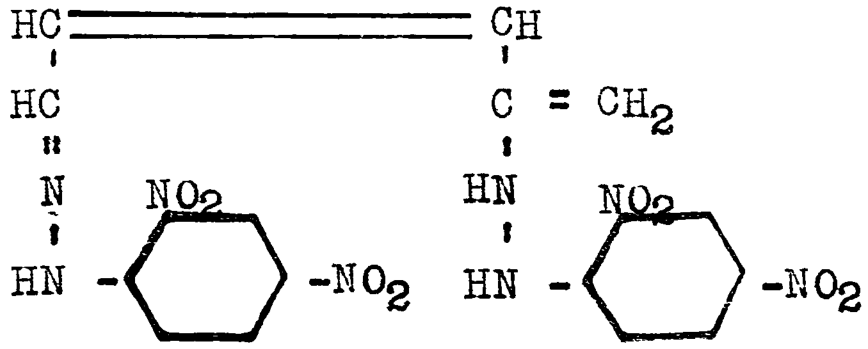


The intermediate A. shown above is Bergmann's glucal, cf. pp. 39, which is known to undergo conversion into methyl levulinate. Ring opening of the intermediate B. could possibly give a derivative as shown below:



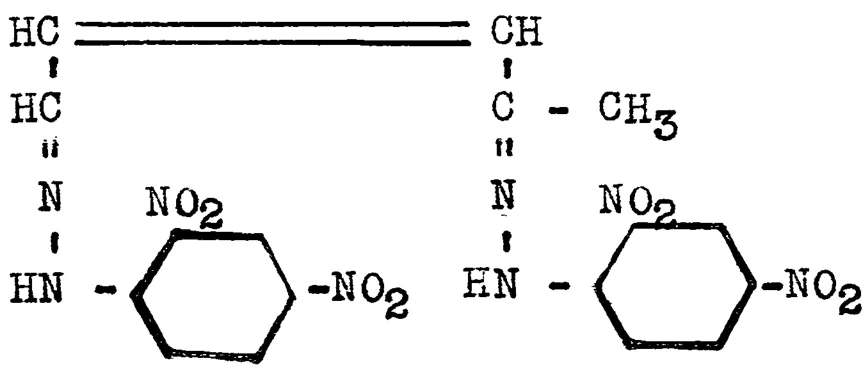
E.

which with 2,4-dinitrophenylhydrazine hydrochloride could yield a 2,4-dinitrophenylhydrazone, 2,4-dinitrophenylhydrazide:



F.

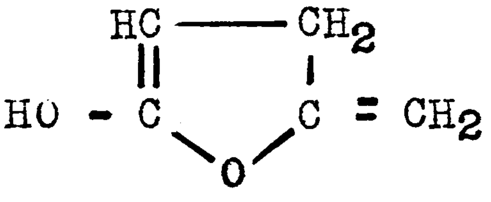
which is the formula postulated for the compound, melting point 221 - 222°C. secured from furfuryl alcohol, cf. pp. 102. The compound, melting point 262 - 263°C., cf. pp. 103, formed from furfuryl alcohol, would, according to this mechanism, probably be the 2,4-dinitrophenylhydrazone synthesized from the keto form of structure E:



G.

The derivatives C. and D. are interconvertible forms of α-angelica lactone which is known to add water on boiling to give levulinic acid 67).

Another possible mechanism of conversion from B. to levulinic acid could occur from a 1,3 shift of H with consequent shift of a double bond to give:



H.

which is β-angelica lactone. This, in turn, is also known to give levulinic acid on boiling with water.

Both α- and β-angelica lactones are formed from levulinic acid on heating at atmospheric pressure.

The mechanism proposed above serves to explain in a satisfactory manner, the conversion of furfuryl alcohol to levulinic acid by certain intramolecular rearrangements, which have already been established as highly probable in other similar rearrangements. These involve:

1. A 1,4-addition of water or methanol to a conjugated system.

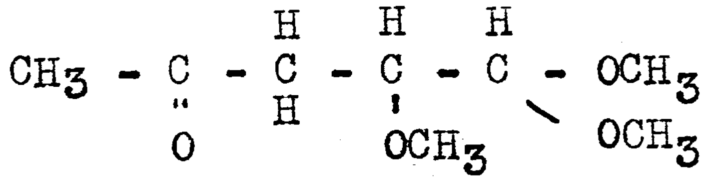
2. A 1,2-elimination of water, methanol or HCl.

3. Shift of a conjugated system into a ring system.

4. Addition of water or methanol, or ring opening to give methyl levulinate.

The experimental evidence for the mechanism suggested, admittedly is not complete, but is in fair agreement.

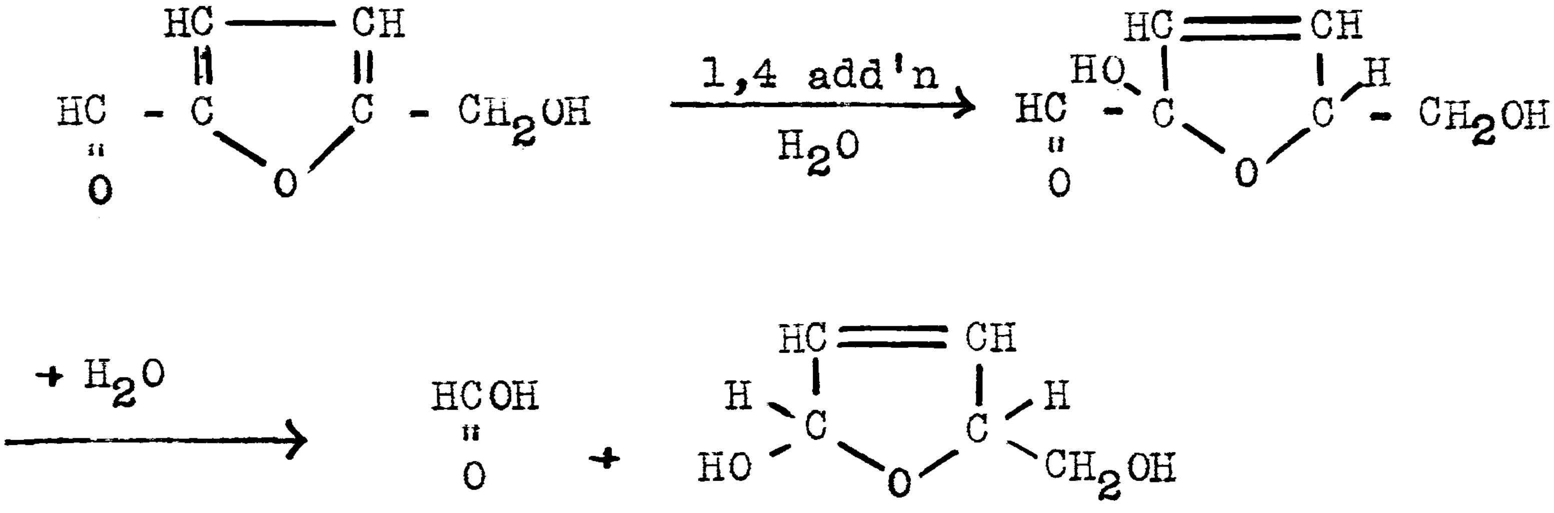
As has been shown the two isomeric bis-2,4-dinitrophenylhydrazones secured from furfuryl alcohol could have come from form B. Similarly B on ring opening, accompanied by methanol addition to the double bond could give the compound:



$$CH_3 - \underset{\underset{O}{\|}}{C} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{\underset{OCH_3}{|}}{C}} - \overset{H}{C} \begin{matrix} - OCH_3 \\ \diagdown OCH_3 \end{matrix}$$

which was postulated earlier (cf. pp. 65-66) as the proper structure for the Pummerer compound.

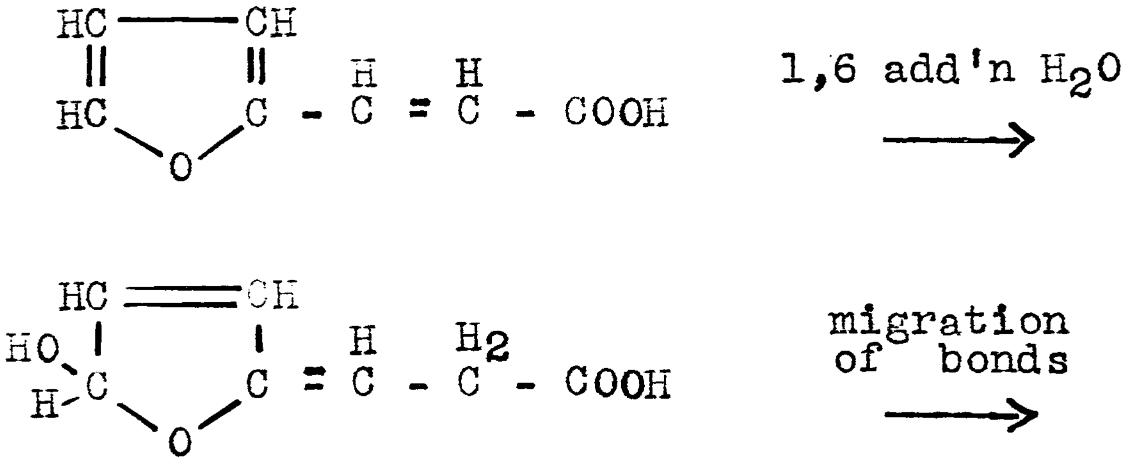
On the basis of the above postulated mechanism, ring opening of hydroxy-methyl-furfural may be explained as follows:

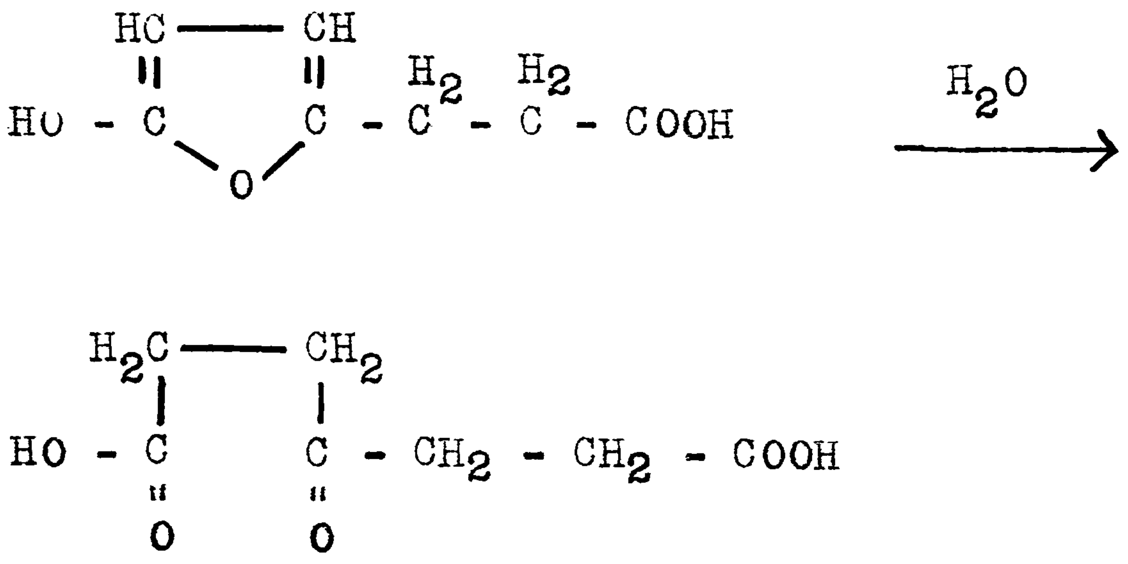


A.

the same intermediate as secured from furfuryl alcohol.

On the same basis ring opening of furyl acrylic acid could yield γ-ketopimelic acid:





The 1,6-addition shown above may possibly be a 1,4-addition to the ring system with simultaneus 1,2-addition of water to the ethylenic double bond, followed by 1,2-elimination of water to give a new conjugated system.

It can be seen that the mechanism postulated above is thus capable of explaining quite satisfactorily, all of the anomalous reactions of ring opening in the furan nucleus.

G. THE RELATIONSHIP OF FURANS TO LIGNINS

Since it has been postulated by Hibbert 3) that lignin is composed of simple building units, formed from a degradation product of fructose, and a phenolic material such as guaiacol or pyrogallol 1,3-dimethyl ether, the possibility exists that these degradation products are furan in nature.

On the basis of the mechanism postulated for ring opening of hydroxy-methyl-furfural, it can be seen that there are a number of extremely active compounds formed which could condense with the phenolic material. The nature of these possible condensations is discussed later in Part Two of this thesis.

PART ONE SUMMARY

1. The interaction of a methanolic solution of H_2SO_4 with furfuryl alcohol, has been studied.

2. By use of milder conditions of reaction and of isolation, it has been established that no products are formed other than those reported by Pummerer (using similar reagents).

3. A new reagent, 2,4-dinitrophenylhydrazine hydrochloride, has been used to study the mechanism involved in the ring fission of furan derivatives.

4. Two new isomeric 2,4-dinitrophenylhydrazones of intermediates, formed in the conversion of furfuryl alcohol to methyl levulinate, have been prepared, and structures assigned to them.

5. A mono-2,4-dinitrophenylhydrazone has been prepared from Pummerer's so-called δ-methoxy-levulinaldehyde-dimethylal, without any loss of methoxyl.

6. A new mechanism has been proposed to account for the anomalous products of ring opening in the furan series.

7. Several new compounds have been synthesized, viz., β-brom propional-dimethylal, methoxy acetyl chloride.

8. A new structure has been proposed for Pummerer's assumed δ-methoxy-levulinaldehyde-dimethylal which is in better agreement with the facts than the formula assigned by Pummerer.

9. Some methods of recovery of carbonyl compounds from their derivatives, have been applied to 2,4-dinitrophenylhydrazones..

PART ONE EXPERIMENTAL

EXP. 1. THE ACTION OF METHANOLIC HCl ON FURFURYL ALCOHOL

It was thought desirable, in the first place, to repeat carefully the procedure followed by R. Pummerer 44).

Ninety grams of freshly distilled furfuryl alcohol was dissolved in 900 cc. of absolute alcohol. To this mixture was added, at the boiling point, 100 cc. of absolute methanol containing 6 g. of gaseous HCl. The mixture was heated under reflux for 3 hours, cooled, 15 g. of powdered K_2CO_3 added, and the mixture stirred until the solution was no longer acid to moist litmus. It was then filtered with suction to remove K_2CO_3 and KCl.

The methanol was removed under reduced pressure leaving 100 g. of a dark brown oil which on distillation at 10 mm. pressure gave 73 g. of a yellow oil, boiling point 35 - 100°C. There remained in the flask 25 g. of a dark brown resinous material.

The pale yellow oil was added, with cooling, to 185 cc. of saturated aqueous $NaHSO_3$, and the mixture shaken for 2 hours. It was then extracted nine times with ether, the ethereal extract dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure leaving 10 g. of a dark brown oil (A). This was carefully fractionated at 12 mm. pressure:

(A) Fraction	1.,	0.5 g.	Boiling	point	35 - 38°C.
"	2.,	1.0 g.	"	"	65 - 70°C.
"	3.,	5.0 g.	"	"	78 - 79°C.
"	4.,	2.0 g.	"	"	80°C. +

The extracted sodium bisulphite solution was cooled, and neutralized with 10% NaOH (aqueous). Decomposition was accomplished by saturating the solution with solid Na_2CO_3, the resulting solution then extracted nine times with ether, the ethereal extract dried over anhydrous Na_2SO_4, and the ether removed under reduced pressure leaving 40 g. of a pale yellow oil (B).

This was then fractionated at 15 mm. pressure:

(B) Fraction	1.,	0.5 g.	Boiling	point	$<$ 80°C.
"	2.,	30.0 g.	"	"	83.5 - 89°C.
"	3.,	4.0 g.	"	"	89 - 93°C.
"	4.,	1.0 g.	"	"	93 - 94°C.
"	5.,	4.0 g.	"	"	$>$ 100°C.

The above procedure is the same as that reported by Pummerer. Six similar experiments gave about the same yields of the corresponding fractions. In no case was it possible to isolate the fraction (boiling point 98 - 99°C. at 16 mm. pressure) reported by Pummerer and to which he assigns the structure of δ-methoxy-levulinaldehyde-dimethylal.

EXP. 2. THE ACTION OF 2% METHANOLIC H_2SO_4 ON FURFURYL ALCOHOL *

To a solution of 250 g. freshly distilled furfuryl alcohol, dissolved in 1250 cc. of absolute methanol, there was added at -5°C., during a period of 5 hours, a solution of 50 g. concentrated H_2SO_4 in 1250 cc. of absolute methanol (prepared by adding the acid to well-cooled methanol). The resulting solution was kept at 0°C. for 15 hours, and then at 24°C. for an additional 24 hours.

To the greenish colored solution sodium methylate (26 g. of sodium in 600 cc. absolute methanol) was then added until the solution changed to a cherry red color and was barely alkaline to moist litmus. The solution was filtered to remove Na_2SO_4, and concentrated under reduced pressure to a volume of one liter. To this was added 500 cc. of

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* This method was first developed by S. Trister and H. Hibbert (unpublished results) and later improved by the author.

diethyl ether, in order to precipitate sodium methyl sulphate, which was removed by filtration.

The ether and methanol were removed under reduced pressure leaving about 280 g. of a reddish oil (A), which was distilled at 7 mm. pressure to give the following fractions:

(A)	Fraction 1.	182 g.	Boiling point		< 120°C.
	" 2.	69 g.	"	"	120 - 150°C.
	" 3.	30 g.	Residual resin.		

Fraction (A)-1. was re-distilled at 7 mm. pressure:

(A)-1.	Fraction (a)	35 g.	Boiling point		25 - 65°C.
	" (b)	57 g.	"	"	65 - 80°C.
	" (c)	61 g.	"	"	80 - 100°C.
	" (d)	14 g.	"	"	> 100°C.

A loss of 14 g. occurred during removal of methanol.

Eight subsequent re-fractionations of fraction (A)-1. gave the following results:

(A)-1. Fraction	(a')	16 g.	Boiling point		< 65°C.	at 8 mm.
"	(b')	18 g.	"	"	68 - 70°C.	" " "
"	(c')	2 g.	"	"	75 - 78°C.	" " "
"	(d')	55 g.	"	"	88 - 92°C.	" " "
"	(e')	12 g.	"	"	92 - 150°C.	" " "
"	(f')	22 g.	"	"	153 - 156°C.	" " "

The lower boiling fractions were now re-distilled for analysis and the results were as follows:

Analysis of Materials from the Above Experiment

Fraction (A)-1.(a')

This fraction consisted mainly of furfuryl methyl ether. As this material was investigated and definitely identified by Pummerer, it was not investigated further.

Fraction (A)-1.(b').

This fraction, boiling point 68 - 70°C. at 8 mm. pressure, was re-distilled and gave a main fraction, boiling point 72°C. at 12 mm. pressure. It was identified as furfuryl alcohol, and as shown below contained only traces of methoxyl.

Analysis

0.01981 g. required 0.15 cc. $Na_2S_2O_3$, 0.04748N; OCH_3, 0.17

0.02034 g. " 0.15 cc. " " ; " , 0.16

This material gave an α-naphthylurethane[56] melting point 128°C. (the literature value for the α-naphthylurethane of furfuryl alcohol is 128°C.). There was no depression in melting point on mixing.

Fraction (A)-1.(c')

The material was shown to be methyl levulinate by preparation in a quantitative yield, of the 2,4-dinitrophenylhydrazone, melting point 141 - 142°C., mixed melting point with an authentic sample was 141 - 142°C.

Fraction (A)-1.(d')

The fraction was re-distilled to give a liquid, boiling point 98°C. at 15 mm. pressure. This corresponds to R. Pummerer's δ-methoxy-levulinaldehyde-dimethylal.

Analysis

Calculated for $C_5H_7O(OCH_3)_3$; OCH_3, 52.8

0.01879 g. required 38.62 cc. $Na_2S_2O_3$, 0.04748N; OCH_3, 52.7

0.01539 g. " 31.75 cc. " , " ; " , 52.4

Fractions (A)-1.(e'), and (A)-1.(f') were not investigated further, but were probably polymers of the simpler materials.

YIELDS OF THE VARIOUS PRODUCTS

Fraction (A)-1.(a')	- Furfuryl methyl ether	6.2%
" " " (b')	- Furfuryl alcohol	7.1%
" " " (c')	- Methyl levulinate	1.0%
" " " (d')	- δ-Methoxy-levulinaldehyde-dimethylal	22.0%
" " " comprising (e')+(f')+(A)-2.	Volatile Polymers (?)	50.0%
" " -3.	Resins	12.0
	Total	98.3%

EXP. 3. Five duplicate preparations gave approximately the same yields and indicated absence of any other fractions in the material boiling below 100°C. (7 mm. pressure).

EXP. 4. FURFURYL α-NAPHTHYLURETHANE

This compound was prepared by the standard method by allowing equimolecular quantities of furfuryl alcohol and α-naphthyl-isocyanate to react at room temperature for 36 hours. The reaction product was a white crystalline compound. Recrystallized from petroleum ether (boiling point 100 - 110°C.) it gave colorless needles, melting point 128°C., (literature value 128°C.).

EXP. 5. FURFURYL ALCOHOL AND SEMICARBAZIDE HYDROCHLORIDE

All attempts to secure a reaction product from furfuryl alcohol and semicarbazide hydrochloride in methanolic, ethanolic or buffered aqueous media resulted only in a quantitative recovery of the original semicarbazide hydrochloride. The same result was found using the acetate.

EXP. 6. FURFURYL ALCOHOL AND DIMEDON

Treatment of furfuryl alcohol with dimedon (dimethyl-dihydroresorcinol) in a 5% sodium acetate buffered solution at 60°C. led to a quantitative recovery of the furfuryl alcohol and the dimedon.

EXP. 7. METHYL LEVULINATE SEMICARBAZONE

The semicarbazone of methyl levulinate was prepared by the standard method, namely treatment of methyl levulinate with an equimolecular proportion of semicarbazide hydrochloride and sodium acetate in aqueous media; yield, almost quantitative, of colorless crystals; purified from methanol, melting point 148°C. (literature value 148°C.).

EXP. 8. THE REACTIONS AND PROPERTIES OF FRACTION (A)-1.(d') FROM EXPERIMENT 2.

The following experiments (a) to (l) were all carried out with the same material. (Pummerer's assumed δ -methoxy-levulinaldehyde-dimethylal).

The fraction was soluble in water, methanol, ethanol, petroleum ether, benzene, etc., in all proportions.

(a) Physical Properties

Boiling point 86 - 87°C. at 4.5 mm. pressure; 97 - 98°C. at 15 mm.; on cooling to -60°C. it freezes to a glass-like product; $n_D^{23} = 1.4276$.

(b) Action with Saturated Aqueous Sodium Bisulphite

It is readily soluble, on shaking, and the addition compound on treatment with sodium carbonate is reconverted into the original material.

(c) Action of Aqueous Semicarbazide Hydrochloride

Treated with semicarbazide hydrochloride in an aqueous solution, buffered with sodium acetate, for one hour at 60°C., a yellowish colored semicarbazone was obtained which on recrystallization from glacial acetic acid at 90°C. *, followed by recrystallization from

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* When glacial acetic acid is used as a solvent for recrystallization of semicarbazone, it should not be used at temperatures above 90°C.

boiling water, melted at 222 - 223°C. with decomposition, and was identical with the bis-semicarbazone isolated by R. Pummerer 44), from his δ -methoxy-levulinaldehyde-dimethylal

Analysis

Calculated for $C_7H_{12}N_6O_2$; C, 39.6; H, 5.7; N, 39.6
1.519 mgms. gave 2.225 mgms. CO_2; 0.774 mgms. H_2O; C, 39.9; H, 5.7
1.352 " " 1.988 " CO_2; 0.704 " H_2O; C, 40.0; H, 5.7
2.544 " required 3.62 cc., 0.020032N, H_2SO_4; N, 39.5
1.930 " " 2.77 cc., " " ; N, 39.7

(d) Action of Semicarbazide Acetate in Methanol Solution

Treatment with semicarbazide acetate in methanol for 24 hours at room temperature gave the same semicarbazone as from (c).

(e) Action of 2,4-Dinitrophenylhydrazine Hydrochloride in Methanolic Solution

Use of an excess of 2,4-dinitrophenylhydrazine hydrochloride in methanol solution at room, or at elevated temperatures, gave a red crystalline material which on purification from boiling pyridine melted at 262 - 263°C., with decomposition. The same product was obtained by heating a buffered acetate solution.

Analysis

Calculated for $C_{17}H_{14}N_8O_8$; C, 44.5; H, 3.0; N, 24.6

1.644 mgms. gave 2.690 mgms. CO_2, 0.433 mgms. H_2O; C, 44.6; H, 2.9

1.180 " " 1.920 " " , 0.328 " " ; C, 44.4; H, 3.0

3.444 " required 3.01 cc., 0.020032N, H_2SO_4; N, 24.6

3.332 " " 2.96 cc., " " ; N, 24.6

(f) Action of 2,4-Dinitrophenylhydrazine in 10% Aqueous Sulphuric Acid at 32°C.

Pummerer 44) claims, by using this method, to have isolated a crystalline 2,4-dinitrophenylhydrazone melting at 192 - 193°C., from δ-methoxy-levulinaldehyde-dimethylal.

It was not found possible to duplicate this result in spite of numerous attempts. In no case could his 2,4-dinitrophenylhydrazone be isolated. On the contrary, the compound, invariably found, was the bis-2,4-dinitrophenylhydrazone, melting point 262 - 263°C. as prepared in (e).

(g) The Action of 2,4,6-Trinitrophenylhydrazine Hydrochloride in Methanol Solution

To a solution of 1.4 g. of 2,4,6-trinitrophenylhydrazine hydrochloride in 50 cc. of boiling methanol, was added 0.5 g. of the fraction. After two minutes a reddish-brown precipitate settled out (0.5 g.) and was removed by filtration.

This material was recrystallized by extraction with chloroform in a Soxhlet extractor, giving red needles, melting point 247°C., with decomposition.

A micromethoxyl analysis indicated the absence of methoxyl.

(h) The Action of α, α-Diphenylhydrazine

An α, α-diphenylhydrazone was obtained as an oil following the standard procedure. This, on recrystallization was obtained as pink-colored crystals, melting at 16 - 17°C.

A micromethoxyl determination indicated the absence of methoxyl.

(i) Action of 2,4-Dinitrophenylhydrazine and a Trace of Hydrochloric Acid on the Sodium Bisulphite Complex Prepared from this Fraction [(A)-1(d')].

To 10 cc. of saturated aqueous sodium bisulphite was added 0.5 g. of the fraction and the resulting solution shaken for 30 minutes. There was added 10 cc. of methanol (a white precipitate resulted), 0.5 g. of 2,4-dinitrophenylhydrazine and 4 drops of concentrated HCl.

The resulting suspension was shaken overnight when a yellow crystalline precipitate was formed, which was removed by filtration, yield 0.3 g. This material was recrystallized twice from methanol and once from chloroform-pet. ether giving yellow needles, melting point 97 - 98°C.

Analysis

1.800 mgms. required 9.86 cc. 0.00923N, $Na_2S_2O_3$; OCH_3, 26.1
Calculated for $C_{11}H_{11}N_4O_4(OCH_3)_3$; OCH_3, 26.1

The analysis is in agreement with the structure of a mono-derivative of the type $C_5H_7(R)(OCH_3)_3$ from fraction (A)-1(d') in which none of the methoxyl groups had been removed.

(j) Action of p-Toluenesulphonic Acid

To five g. of the fraction, heated to 150 - 160°C. in a distilling flask fitted with a condenser, was added in small amounts, over a period of 5 hours, 0.5 g. of p-toluenesulphonic acid, and the distillate collected. At the end of this time the residue in the flask was distilled to give 3 g. of a liquid, boiling point 78 - 82°C. at 8 mm. pressure. This was identified as methyl levulinate by preparation and comparison of the semicarbazone with an authentic sample.

The original distillate boiled at 63°C. and was identified as methanol by oxidation to formaldehyde, isolated as the dimedon derivative. The yield of methanol was 1.0 g., which, on the basis of a molecular weight for the fraction of 176, and a methoxyl content of three groups, would correspond to a yield of 55%.

(k) Treatment with Boiling Water

Treatment of 0.5 g. of the fraction by solution in water and steam distillation, converts the product almost quantitatively into methyl levulinate, identified as the 2,4-dinitrophenylhydrazone.

(l) Grignard Analysis

Molecular weight used (Pummerer's and author's results) = 176, 5 cc. of xylene used as solvent.

Weight of sample taken	0.1620 g.
Active Hydrogen	
RMgX added	2.97 cc.
Volume of gas at N.T.P.	6.34 cc.
Found per gram mole.	0.3
Additive Value	
Water added	2.00 cc.
Volume of gas at N.T.P.	23.45 cc.
Found carbonyl per gram mole.	0.95

EXP. 9. ACTION OF 2,4-DINITROPHENYLHYDRAZINE HYDROCHLORIDE ON A METHANOL SOLUTION OF FURFURYL ALCOHOL (2:1)*

(a) To a solution of 6.0 g. (1 mole) of 2,4-dinitrophenylhydrazine and 3.0 cc (1 mole) of concentrated HCl in 200 cc. of boiling methanol was added 1.8 g. of furfuryl alcohol. The mixture was refluxed and at the end of 20 minutes, a curdy yellow precipitate had formed. Heating was continued for 1 hour, the mixture cooled and filtered to give 4.2 g. of a yellow crystalline compound, which on recrystallization from acetone-pet. ether, melted at 221 - 222°C.

Attempts to isolate a further product from the filtrate were unsuccessful.

Analysis

Calculated for $C_{17}H_{14}N_8O_8$; C, 44.5; H, 3.0; N, 24.6

1.382 mgms. gave 2.234 mgms. CO_2; 0.430 mgms. H_2O; C, 44.1; H, 3.4

1.796 " " 2.876 " CO_2; 0.536 " " ; C, 43.6; H, 3.3

1.904 " required 1.64 cc. 0.02020N, H_2SO_4; N, 24.4

1.339 " " 1.19 cc. 0.02020N, H_2SO_4; N, 24.4

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* The procedures followed in 9(a), and 9(b) were first developed by Dr. Geo. Wright in these laboratories. It remained for the writer to investigate these reactions.

A qualitative micromethoxyl analysis indicated the absence of methoxyl.

(b) This experiment is a duplicate of Experiment 9(a). The only variation was in the use of a 1:1 ratio of 2,4-dinitrophenylhydrazine hydrochloride to furfuryl alcohol, instead of 2:1.

To a boiling solution of 0.54 g. 2,4-dinitrophenylhydrazine and 0.5 cc. of concentrated HCl in 50 cc. of methanol was added 0.3 g. of furfuryl alcohol. The mixture was heated under reflux for four hours. While the mixture was still hot it was filtered to remove 0.3 g. of an insoluble red compound (A), which on recrystallization from boiling pyridine melted at 262 - 263°C. Addition of water to the filtrate precipitated 0.1 g. of an orange colored compound (B), which on recrystallization from methanol yielded orange crystals, melting point 141 - 142°C., mixed melting point with the 2,4-dinitrophenylhydrazone of methyl levulinate, 141 - 142°C.

<u>Analysis of (A)</u>

Calculated for $C_{17}H_{14}N_8O_8$; C, 44.5; H, 3.0; N, 24.6

1.180 mgms. gave 1.920 mgms. CO_2; 0.328 mgms. H_2O; C, 44.4; H, 3.0

1.644 " " 2.690 " " ; 0.433 " " ; C, 44.6; H, 3.0

1.148 " required 1.00 cc. 0.02020N, H_2SO_4; N, 24.6

2.146 " " 1.86 cc. " " ; N, 24.5

(c) The Action of 2,4-Dinitrophenylhydrazine Hydrochloride on Furfuryl Methyl Ether

The procedure followed, using a ratio of 2:1, was identical with that indicated in 9(a). Yields were the same of the identical product (mixed melting point).

(d) The Action of 2,4-Dinitrophenylhydrazine Hydrochloride on Furfuryl Methyl Ether

In this experiment the ratio was altered to 1:1. The procedure followed was identical with that indicated in 9(b). Yields were the same of the identical products (mixed melting points).

(e) The Action of 2,4-Dinitrophenylhydrazine Hydrochloride on a Methanolic Solution of Sylvan

To a solution of 4.44 g. of 2,4-dinitrophenylhydrazine and 2.2 cc. of concentrated HCl in 100 cc. of methanol, 1.0 g. of sylvan was added at boiling point. After 4 hours at the same temperature, a finely-divided brown crystalline precipitate started to form. At the end of 24 hours the precipitate was filtered off, recrystallized from pyridine, melting point 235.5 - 236°C. Yield 1.0 g.

The melting point reported in the literature for the bis-2,4-dinitrophenylhydrazone of levulinaldehyde is 235 - 236°C.

(f) The Action of 2,4-Dinitrophenylhydrazine Hydrochloride on a Methanolic Solution of Furfural

Following the procedure outlined in (e) and using furfural a red crystalline compound was obtained, which on recrystallization from pyridine and pet. ether, melted at 224 - 225°C.

Analysis

Calculated for $C_{11}H_8N_4O_5$; C, 47.8; H, 2.9; N, 20.3
1.997 mgms. gave 3.438 mgms. CO_2; 0.524 mgms. H_2O; C, 47.4; H, 2.9
2.086 " " 3.622 " " ; 0.540 " " ; C, 47.4; H, 2.9
4.066 " required 2.97 cc. 0.020032N, H_2SO_4; N, 20.2
4.463 " " 3.27 " " " ; N, 20.3

From the above series of experiments it can be seen that ring opening occurred both with furfuryl alcohol and sylvan under the same conditions of reaction, but not with furfural; in the latter case formation of a condensation product with the aldehyde group and hydrazine took place.

EXP. 10. THE RECOVERY OF CARBONYL COMPOUNDS FROM THEIR 2,4-DINITROPHENYLHYDRAZONES

(a) Preparation of Cyclohexanone 2,4-Dinitrophenylhydrazone

To a solution of 2,4-dinitrophenylhydrazine hydrochloride in boiling methanol, was added an excess of cyclohexanone. On cooling, there was deposited from the solution golden platelets; recrystallized twice from methanol, melting point 159 - 160°C.

Analysis

Calculated for $C_{12}H_{14}N_4O_4$; C, 51.8; H, 5.0; N, 20.2

2.612 mgms. gave 4.961 mgms. CO_2, 1.178 mgms. H_2O; C, 51.8; H, 5.0

2.422 mgms. equivalent to 1.73 cc., 0.0202N, HCl; N, 20.2

(b) Treatment of Cyclohexanone 2,4-Dinitrophenylhydrazone With Aqueous Sodium Carbonate

The 2,4-dinitrophenylhydrazone (0.2 g.) was dissolved in a solution containing 20 cc. saturated Na_2CO_3 and 20 cc. of water. The resulting solution was then distilled. The first 20 cc. of distillate, on treatment with 2,4-dinitrophenylhydrazine hydrochloride yielded 0.1 g. of a yellow compound; recrystallized from methanol, melting point at 159 - 160°C. Mixed melting point with the authentic material was 159 - 160°C. Yield was 50% of the theoretical.

(c) Treatment of Furfural 2,4-Dinitrophenylhydrazone With 5% Sodium Hydroxide

Treatment of the 2,4-dinitrophenylhydrazone of furfural with boiling 5% sodium hydroxide and distillation of the aqueous solution resulted in a 60% recovery of furfural, identified as the 2,4-dinitrophenylhydrazone, melting point 224°C.

(d) Oxidation of Methyl Levulinate 2,4-Dinitrophenylhydrazone

One gram of the above compound was stirred at room temperature for 16 hours with 0.75 g. of a solution of CrO_3 in glacial acetic acid. The acetic acid was removed under reduced pressure, the residual mixture extracted with benzene, and the benzene removed under reduced pressure leaving 0.2 g. of a liquid, boiling point 75 - 80°C. (7 mm.), which was identified as methyl levulinate by preparation of the 2,4-dinitrophenylhydrazone, melting point 141 - 142°C. Recovery of methyl levulinate was 54%.

(e) Ozonization of Methyl Levulinate 2,4-Dinitrophenylhydrazone

Ozone was passed into a cooled (0°C.) solution of 0.5 g. of the above hydrazone in 25 cc. of chloroform, until absorption ceased. The chloroform was removed under reduced pressure, and the viscous liquid remaining decomposed by boiling with water. The solution contained a carbonyl compound which was isolated as the 2,4-dinitrophenylhydrazone (0.27 g.), melting point 203 - 204°C. A mixture with an authentic sample of levulinic acid 2,4-dinitrophenylhydrazone showed no melting point depression.

(f) Action of Sodium Carbonate on the Bis-2,4-Dinitrophenylhydrazone, Melting Point 221°C.

No carbonyl containing compounds were obtained on heating this compound with aqueous sodium carbonate.

(g) Action of Sodium Carbonate on the Bis-2,4-Dinitrophenylhydrazone, Melting Point 262 - 263°C.

Treatment with aqueous sodium carbonate gave no carbonyl-containing compounds.

(h) Action of Boiling Sodium Hydroxide on the Bis-2,4-Dinitrophenylhydrazone, Melting Point 221°C.

With aqueous sodium hydroxide (0.5 - 10%) no carbonyl containing compounds were found.

(i) Action of Hot Sodium Hydroxide on the Bis-2,4-Dinitrophenylhydrazone, Melting Point 262 - 263°C.

Attempts to decompose the above compound by means of aqueous or aqueous-pyridine solutions of sodium hydroxide, gave no carbonyl-containing compounds.

(j) Oxidation of the Bis-2,4-Dinitrophenylhydrazone, Melting Point 221°C.

Oxidations with chromic acid (Section (d) above), and with alkaline potassium permanganate did not yield identifiable products.

(k) Oxidation of the Bis-2,4-Dinitrophenylhydrazone, Melting Point 262 - 263°C.

No identifiable products were obtained on treatment similar to (j).

EXP. 11. OZONOLYSIS OF 2,4-DINITROPHENYLHYDRAZONES

(a) Cinnamaldehyde 2,4-Dinitrophenylhydrazone

(1) The above compound was ozonized at 0°C. in chloroform suspension with an excess of ozone. The ozonide was hydrolyzed with boiling water and yielded benzaldehyde (64%), identified as the phenylhydrazone and the 2,4-dinitrophenylhydrazone.

(2) Ozone was passed into a solution of 0.2 g. of the above 2,4-dinitrophenylhydrazone in 75 cc. of

chloroform at -20°C. until the first marked decrease in ozone absorption was observed. The chloroform was removed and the ozonide decomposed by boiling with water at 100°C. for five minutes. On cooling there crystallized out 0.12 g. of an orange-coloured compound, which on recrystallization from acetone melted at 167 - 168°C. No analysis was made but this compound was probably the half-2,4-dinitrophenylhydrazone of glyoxal.

Treatment of this compound with a methanolic solution of 2,4-dinitrophenylhydrazine hydrochloride gave a crystalline compound, melting point above 290°C. This compound was not investigated further but was probably glyoxal-2,4-dinitrophenylosazone (melting point reported 326°C.).

(b) Bis-2,4-Dinitrophenylhydrazone From Furfuryl Alcohol, Melting Point 221 - 222°C. (Experiment 9 (a).)

Ozone was passed (at -10°C.) into a suspension of 0.5 g. of this compound in 100 cc. of ethyl acetate (specially purified) at a rate of 98 cc. per hour, for 3 hours and 25 minutes. At the end of this time the ethyl acetate was removed under reduced pressure, and there was added 60 cc. of water. The mixture was heated to boiling and 40 cc. distilled over into a solution of 2,4-dinitrophenylhydrazine hydrochloride, giving 0.12 g. of a crystalline compound, which on recrystallization from methanol, had a melting point of 156 - 157°C. There was no depression in the melting point on mixing with an authentic sample of formaldehyde-2,4-dinitrophenylhydrazone. The yield of formaldehyde was 0.016 g. corresponding to 0.030 g. if there was one $CH_2=$ group, in the original compound.

The residual solution, containing some solid material, was treated with an excess of 2,4-dinitrophenylhydrazine hydrochloride and yielded an orange-coloured compound, melting point 317 - 318°C. A mixed melting point with the 2,4-dinitrophenylosazone of glyoxal showed no depression.*

(c) Bis-2,4-Dinitrophenylhydrazone, Melting Point 262 - 263°C. From Furfuryl Alcohol (Experiment 9 (b).)

Treatment of an equal quantity of this compound in ethyl acetate under the identical conditions used in Experiment 11 (b) gave no carbonyl containing compounds

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* Because of the small amount of this material isolated, and the possibility that it could have come from the benzene nucleus, it was not investigated further. At the moment, however, it appears that this compound may have a distinct relationship to the structure of the above compound.

in the distillate, and the same product (the 2,4-dinitrophenylosazone of glyoxal) in the residual solution.

(d) The use of other solvents such as dioxane, acetone and chloroform in the two preceding experiments gave identical products.

(e) Action of Aqueous 1% Hydrogen Peroxide on the Bis-2,4-Dinitrophenylhydrazone Prepared From Furfuryl Alcohol, Melting Point 221 - 222°C. Experiment 9 (a).

A suspension of the compound in 50 cc. of 1% aqueous hydrogen peroxide was heated to boiling and 50 cc. distilled into a solution of 2,4-dinitrophenylhydrazine hydrochloride in water. There resulted a yellow compound which on recrystallization from methanol, melted at 156 - 157°C., identical with the compound secured in Experiment 11 (b). Five-tenths gram gave 0.12 g. of the formaldehyde derivative, equivalent to 0.008 g. $=CH_2$ (55%).

EXP. 12. THE INTERCONVERSION OF THE VARIOUS 2,4-DINITROPHENYLHYDRAZONES FROM FURFURYL ALCOHOL

(a) Attempts were made to convert the 2,4-dinitrophenylhydrazone of levulinic acid into one or other of the derivatives obtained by action of 2,4-dinitrophenylhydrazone on furfuryl alcohol. For this purpose it was treated with an excess of furfuryl alcohol in one case, and 2,4-dinitrophenylhydrazine hydrochloride in aqueous solution in the other. In both cases the original product was recovered unchanged. However, by boiling the 2,4-dinitrophenylhydrazone with a methanolic solution of HCl, it was recovered quantitatively in the form of its methyl ester.

(b) Attempts to convert the 2,4-dinitrophenylhydrazone of methyl levulinate into one or other of the derivatives, by any of the methods tried above, yielded only the unchanged original derivative.

(c) Mono-2,4-Dinitrophenylhydrazone From Fraction (A)-1(d') Experiment 8(i). (Pummerer Compound)

The product isolated by fractionation of the fission product of furfuryl alcohol (use of CH_3OH-H_2SO_4) was used for the following experiment.

Treatment of the derivative with methanolic HCl at 60°C. for a period of one hour, gave a quantitative yield of methyl levulinate-2,4-dinitrophenylhydrazone, melting point 141 - 142°C.

Treatment with an excess of 2,4-dinitrophenylhydrazine hydrochloride in methanol gave a quantitative yield of a reddish crystalline compound, melting point 262 - 263°C. which was identical with the derivative obtained in Experiment 9 (b).

(d) Bis-2,4-Dinitrophenylhydrazone, Melting Point 221 - 222°C. Prepared from Furfuryl Alcohol (Experiment 9 (a).)

To a suspension of 0.4 g. of the above product in 30 cc. of methanol there was added 20 cc. of 0.64N, HCl in absolute methanol. The mixture was refluxed for 3 hours when all material appeared to go into solution. The solution was concentrated to 20 cc. and set aside to crystallize. An orange-coloured compound (0.25 g.) separated out, which on recrystallization from methanol, melted at 141 - 142°C., and was identified as the 2,4-dinitrophenylhydrazone of methyl levulinate.

Removal of the solvent left 0.1 g. of a residue. Recrystallization from chloroform gave a red-coloured crystalline product, melting point 194 - 195°C., which on mixing with 2,4-dinitrophenylhydrazine showed no depression in the melting point.

(e) Bis-2,4-Dinitrophenylhydrazone, Melting Point 262 - 263°C. From Furfuryl Alcohol, Experiment 9 (b).

A suspension of this material in a concentrated (5%) solution of HCl in methanol was heated under reflux for 24 hours. The original material was recovered quantitatively.

EXP. 13 PROPERTIES OF THE TWO MODIFICATIONS OF FURFURYL ALCOHOL

Variety	Water Soluble	Water Insoluble
Weight of sample taken	0.1220 g.	0.1353 g.
Active Hydrogen		
RMgX added	2.97 cc.	3.00 cc.
Volume of gas at N.T.P.	26.50 cc.	29.20 cc.
Found per gram mole.	0.96	0.95
Additive Value		
Water added	2.00 cc.	2.00 cc.
Volume of gas at N.T.P.	41.70 cc.	42.60 cc.
Found per gram mole.	0.05	0.03

In all experiments carried out, no difference was obtained in the chemical or physical properties (with the exception of the solubility in water) of the two modifications.

EXP. 14. ATTEMPTED SYNTHESIS OF δ-METHOXY-LEVULINALDEHYDE-DIMETHYLAL

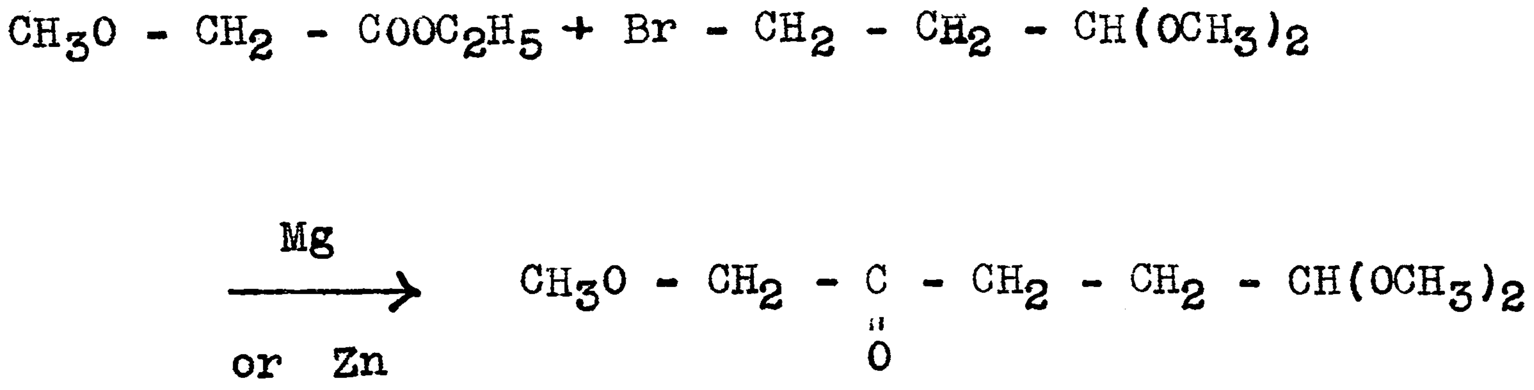
Three different modes of synthesis were attempted, but due to experimental difficulties, and lack of time available, none of them could be brought to a successful conclusion.

Synthesis I consisted of the following steps:

a) Preparation of methyl methoxy acetate.

b) Preparation of β-brom-propional-dimethylal.

c) Condensation of a) and b) by a Grignard or Reformatsky reaction.



$$CH_3O - CH_2 - COOC_2H_5 + Br - CH_2 - CH_2 - CH(OCH_3)_2$$

$$\xrightarrow[\text{or Zn}]{\text{Mg}} CH_3O - CH_2 - \underset{\overset{\|}{O}}{C} - CH_2 - CH_2 - CH(OCH_3)_2$$

(a) Preparation of Methyl Methoxyacetate *

To a solution of 261 g. of sodium hydroxide (technical) in 1450 cc. of boiling methanol (storeroom) was added with stirring a solution of 322 g. of chloracetic

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* The method used to prepare methoxyacetic acid was kindly supplied by Eastman Kodak Co., Organic Chemicals Division.

acid (practical) in 580 cc. of methanol. Addition was carried out at such a rate as to maintain the solution at boiling point. After addition was complete, the methanol was removed by distillation at normal pressures, the sodium chloride formed during the reaction was removed by filtration, and was washed well with methanol, which was added to the filtrate. Removal of the methanol was continued by distillation and the final traces were removed by passing steam into the solution.

To the cooled aqueous solution was added slowly and with cooling, 170 g. of concentrated sulphuric acid. The resulting solution was placed in a continuous extractor and was extracted with diethyl ether for 12 hours, the solution was dried and the ether was removed under reduced pressure. Distillation of the residue gave 185 g. of a main fraction, boiling point 91 - 92°C. at 7 mm. pressure; yield 70% of the theoretical.

To a solution of 183 g. of methoxyacetic acid in 200 g. methanol was added anhydrous gaseous HCl to saturation. The mixture was allowed to stand 12 hours, and to it was added a saturated solution of sodium carbonate to neutrality. The methoxyacetic acid methyl ester separated as an overlying layer which was separated, dried over anhydrous magnesium sulphate and distilled to yield 150 g. of a colorless liquid, boiling point 131 - 132°C. at 753 mm. pressure; yield 72% of the theoretical.

(b) Preparation of β-Brom-propional-Dimethylal

The method adopted for this preparation was similar to that outlined by K. U. Nef [68], for the preparation of β-brom-propional-diethylal. J/

To 135 cc. of a saturated solution of HBr in methanol, was added at 0°C. with stirring, 56 g. of acrolein. The mixture was stirred at 0°C. for 1 hour and allowed to come to room temperature. Solid sodium carbonate was added, followed by 150 cc. of diethyl ether. The ethereal solution was washed with saturated sodium carbonate to remove HBr, with saturated sodium bisulphite to remove any unreacted acrolein or β-brom-propionaldehyde, then washed with water, dried over anhydrous magnesium sulphate and the ether removed under reduced pressure. The residual dark oil was distilled yielding a colorless oil, boiling point 51 - 53°C. as the main fraction. Yield was 51.5 g. or 29% of the theoretical.

(c) Attempts to Prepare the Grignard Derivative of β-Brom-propional-Dimethylal

Attempts to prepare the Grignard reagent of the above compound in ether and in benzene using iodine and mercuric chloride as catalysts, were not successful.

(C') Action of β-Brom-Propional-Dimethylal on Methyl Methoxy-Acetate in the Presence of Zn-Cu Couple

Attempts to prepare δ-methoxy-levulinaldehyde-dimethylal using equimolecular quantities of the above three reagents, at a temperature of 100°C., led to solution of the zinc-copper couple but it was impossible to isolate the anticipated compound. It would appear that the zinc couple was formed, but that addition of the reagent to the carbonyl of the ester grouping did not take place.

Synthesis II consisted in the preparation of

a) γ-Methoxy ethyl acetoacetate.
b) γ-Methoxy α-allyl ethyl acetoacetate.
c) Ketone saponification to give methoxymethyl butenyl Δ, 1,2-ketone.

This latter on ozonolysis would be expected to give the desired aldehyde.

Unfortunately in the time available and due to the very small yields in step I, it was impossible to complete the synthesis, although indications were quite promising.

Synthesis III consisted in the preparation of

a) Methoxy acetyl chloride.

b) β-Brom-propional-dimethylal.

c) Condensation of a) with a Reformatsky reagent prepared from b).

By use of Zn and β-brom-propional-dimethylal at 100°C., it was possible to secure a small amount of a Reformatsky reagent which was soluble in benzene-ethyl acetate (1:2). However, an attempted condensation of this reagent with methoxy-acetyl chloride did not give the desired compound.

(a) Preparation of Methoxy Acetyl Chloride

To one mole of methoxy acetic acid was added 1.2 moles thionyl chloride. The resulting mixture was heated under reflux for 5 hours, and was then distilled at normal pressures to give a 95% yield of methoxy acetyl chloride, boiling point 112 - 113°C.

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PART TWO.

SOME FISSION PRODUCTS OF LIGNIN

PART TWO. CLAIM TO ORIGINAL RESEARCH

1. An investigation of the products isolated by the action of sodium hydroxide on waste sulphite liquors from soft wood and hard wood respectively, has been carried out. Guaiacol was isolated and identified as a decomposition product of the former, and guaiacol, pyrogallol 1,3-dimethyl ether and acetosyringone of the latter.

2. Acetovanillone and guaiacol have similarly been isolated and identified as the fission products of spruce lignin sulphonic acid (Sodium hydroxide treatment), thus proving the presence of this grouping in the lignin complex.

3. Acetosyringone, guaiacol and pyrogallol 1,3-dimethyl ether have likewise been isolated and identified as true fission products of birch lignin sulphonic acid (Sodium hydroxide treatment).

4. The long chain dioxyphenyl-propane condensation theory postulated by Freudenberg for the structure of lignin has been shown to be untenable.

HISTORICAL REVIEW

PART TWO A. GENERAL INTRODUCTION

The complex substance or substances known to botanists and chemists alike as Lignin, the name applied to the encrusting material in plant bodies containing cellulosic tissue, is one of the most common, and the least understood, of all of the naturally occurring high molecular weight compounds.

The number of scientific workers who have interested themselves in this substance in the long period between its definition 1) 2), and isolation 3) by Payen as far back as 1837 and the present day, has been very great. Isolated lignin as a substance, or class of substances, has yielded but little information to these investigators because of its complex nature, sensitivity in the "native state" to chemical reagents, high molecular weight and relative insolubility. Up to the present time it has been impossible to determine whether lignin belongs to any one class of organic compounds. The question as to the nature of this material has not, and cannot be settled on the basis of available evidence. The question whether it is entirely of aromatic or aliphatic nature, or of a mixed nature, must remain unanswered until such time as a higher yield of lignin degradation products from treatment of an unchanged native lignin can be prepared and identified.

It is first questionable whether the lignin, which is secured at the present time by any method such as acid hydrolysis, alcoholysis or cuprammonium solution of the cellulose present in the wood, represents unchanged lignin as present in the wood. Many investigators have put forward the opinion that there is present in the plant a simple substance to which they assign the name primary lignin. This substance, when treated with the reagents commonly used for its isolation, is assumed to undergo rapid condensation and polymerization to give the complex substance known as lignin.

The question still exists as to whether the primary lignin present in the plant exists as a separate entity, or whether it exists in combination with the carbohydrate materials present in the plant. Some investigators 4) 5) have assumed that an ester-like union exists between an acid group in the lignin and the carbohydrate material, whereas other investigators 6) 7) 8) have postulated an ether-like linkage. A further idea 9) has been suggested that lignin is combined with carbohydrates in an acetal-like union.

In contrast with these views the original postulation of Payen 3) has received support from a number of workers. Payen believed that the lignin in the plant is present simply as an encrusting material and that no chemical combination existed between lignin and the carbohydrate materials in the plant tissue.

The more modern concept as to union or lack of union is to be found in the researches by Norman 10) on the cell wall. His results may be summarized briefly as follows:

1. The various materials constituting the cell wall of the plant, consist of cellulose, hemicelluloses, xylans, pectins, lignin, etc.

2. Because of the difficulty of separating some of these constituents, it would appear that part of the association in the cell wall consists of a true chemical combination between various constituents.

3. Though the evidence for the existence of a lignin-hemicellulose complex, is not direct, in the sense that such a compound can be isolated and characterized, the weight of indirect evidence is considerable. Evidence is given to show that there is a definite solubility relationship between hemicelluloses and lignin. Treatment of wood by hydrolytic reagents renders soluble a

part of the hemicellulose and a part of the lignin present. However, all of the lignin and hemicellulose need not be combined, either one, if it is in excess, can exist in the free state.

4. Any method of isolating lignin must then provide hydrolysis of the existing complex, prior to extraction.

It will be impossible to determine the correctness of these various views until such time as investigators have determined the nature of the plant precursor of lignin, the mode of formation of lignin, and to some extent the chemical constitution.

B. THE GENESIS OF LIGNIN

The question of the plant material giving rise to lignin has been attacked by numerous workers. It has been of greatest interest since, if the basic substance which leads to its formation were known, it should be possible to assign a formula to lignin. It has been suggested 11) 12) 13) that cellulose in the plant is the parent substance, and evidence is offered for some similarities in physical properties, e.g. double refraction in the polarizing microscope. However, the difficulty of synthesizing aromatic substances from cellulose and the well established fact 14) that such form a part of the lignin complex renders such a theory untenable.

Klason 15) and Rassow 16) have advanced the idea, that lignin is formed in the plant from pentoses or pentosans, a view based on the assumed reciprocal relationship between pentosans and lignin.

Numerous other investigators, among them Schrauth 17) Schmidt 18), von Euler 19), Oden 20), Jonas 21) and more recently Hilpert 22), have suggested that lignin is formed from soluble carbohydrates such as pentoses, methyl pentoses and hexoses. Hilpert goes further and suggests, that lignin does not exist as such in the plant but, that it is formed from simple carbohydrate materials in the process of extraction. If this latter were true, it would be difficult to explain the isolation of vanillin, acetovanillone, and various organic acids secured as degradation products of lignin preparations.

Another view has been put forward that lignin is derived from pectins in the plant 23) 24). However, on the basis of the above postulations and the well-known difficulty of conversion of carbohydrate to aromatic substances, it would be logical to assume that lignin, if it were formed solely from carbohydrates, cellulose, pentosans or pectins (the latter galacturonic acid polymers) would be solely aliphatic in nature. It will be shown later that this is not true.

Freudenberg 25) and Klason 26) hold the view that lignin is derived in the plant wholly from an aromatic precursor. Such a substance as coniferyl alcohol or coniferyl aldehyde could, as they have indicated, be polymerized in the plant to give derivatives which are wholly aromatic. It has been pointed out by Klason that this polymerization readily takes place outside the plant in vitro, and that polymerized coniferyl alcohol has properties similar to those of isolated lignin. However, these two theories of polymerization postulate a wholly aromatic structure for lignin, which again is not in accordance with the facts.

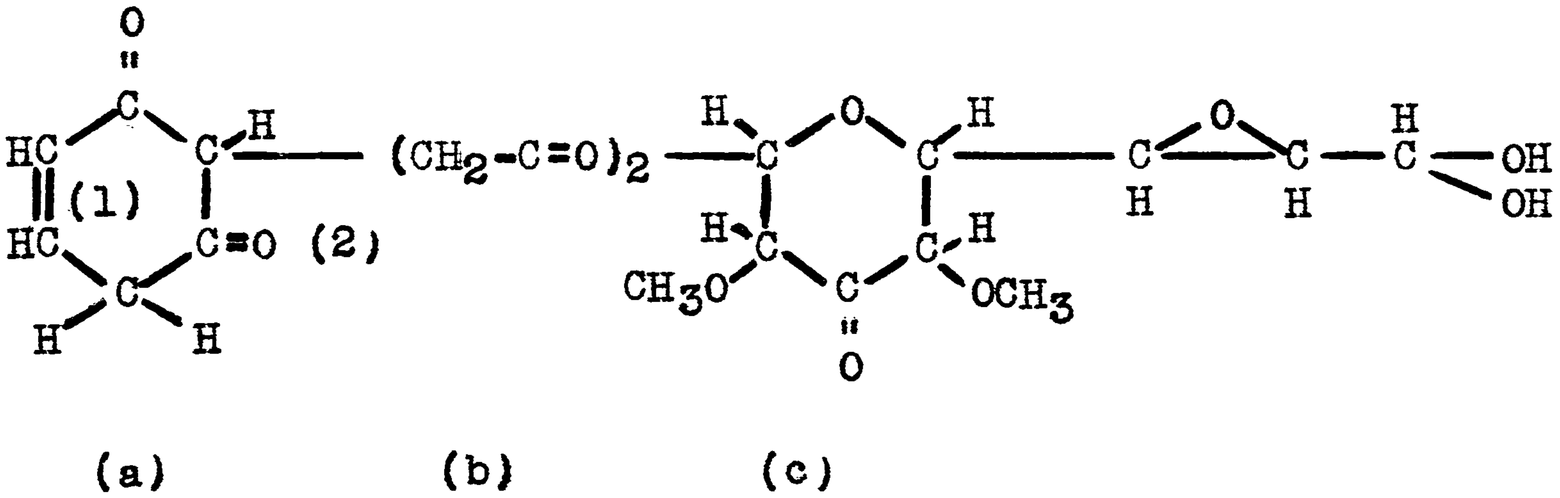
None of the proposals which have been made so far, seems to take into account sufficiently, the chemical nature and properties of lignin. Each theory takes into consideration only part of the known facts, and others detrimental to the idea are temporarily forgotten. In the latter part of this thesis under discussion of results, there is given what, it is believed, is a more complete theory of the plant synthesis of lignin. Complete proof cannot be offered for the same, but it is believed it explains much more satisfactorily than others the known experimental facts, viz.; the mode of plant synthesis, the nature of a variety of new degradation products, and finally the behavior of lignin to various reagents.

C. THE GENERAL THEORIES AS TO STRUCTURE OF LIGNIN

Older Views

Before discussing recent views, it might be well to review the various structures proposed for lignin.

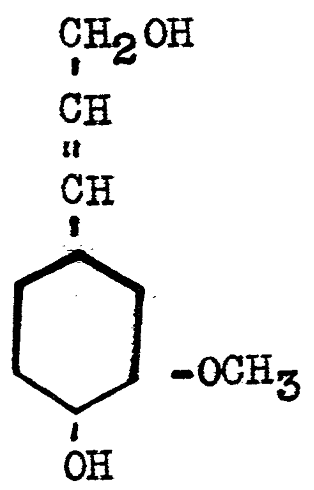
The somewhat fanciful formula proposed by Cross and Bevan 27) as shown below, takes into account some of the reactions of lignin, but is based on very meager experimental evidence:



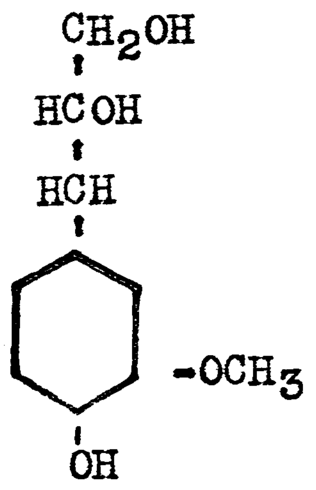
This is in reality a structural representation indicative of various groups known or assumed to be present in lignin, in a simple formula. Chlorination could take place at (1) in (a) to give pyrogallol forming derivatives, which have not been isolated as yet in spite of many attempts. The formula shows methoxyl groups present in lignin; also free hydroxyl groups which are known to be present, and a possible enolic hydroxyl at (2). It also shows an ethylene oxide ring, which on treatment with sodium bisulphite solution could open to give a sulphonic acid, and a hydropyran ring which, under the influence of alkali could give a soluble sodium salt. The group (b) is assumed to be present on the basis of acetic acid formation from lignin. The existence of a hydropyran ring, is based on the formation at high temperatures, of maltol and acetone. This however is not necessarily true as these compounds can be obtained from compounds which do not contain the hydropyran ring. The existence of a group containing a hydrated aldehyde also would hardly be expected in a compound of this type.

However this formula accounts for a number of known reactions of lignin and is useful to that extent.

Klason 26) assumed that lignin is a mixture of condensation products from coniferyl alcohol (A) and oxyconiferyl alcohol (B):

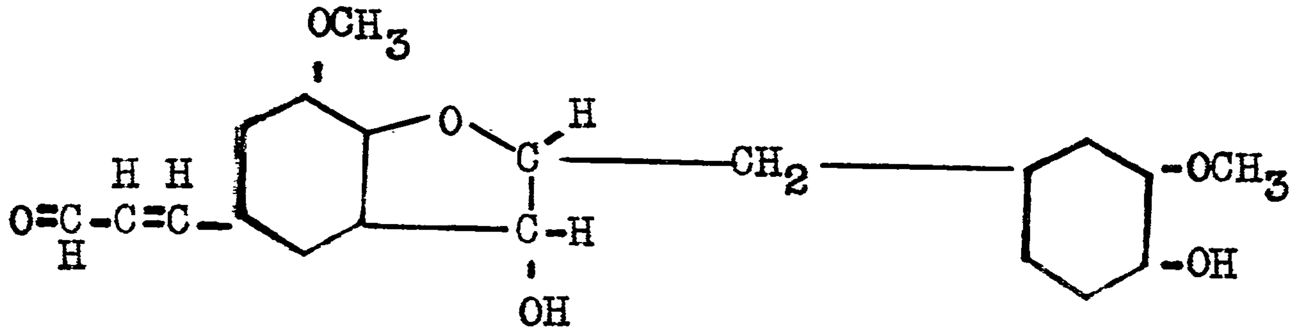


(A)

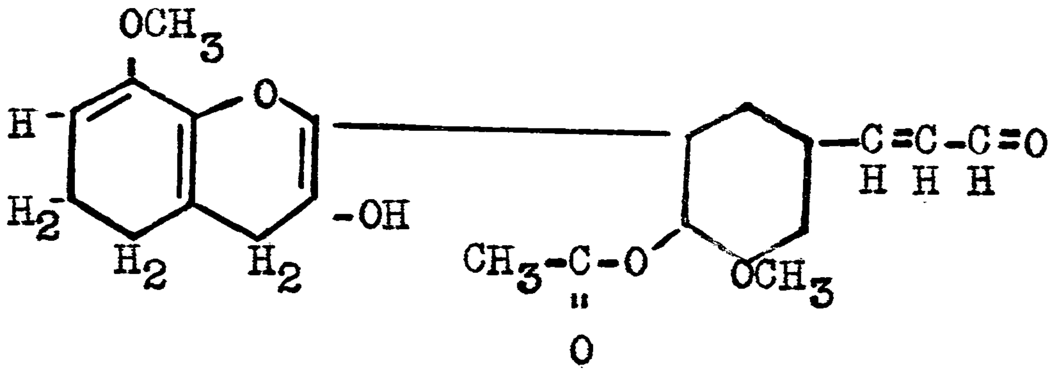


(B)

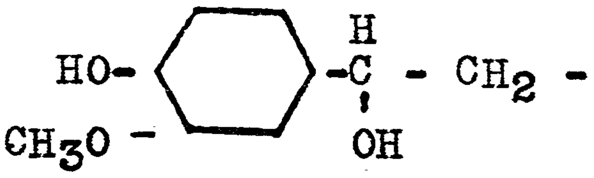
and the two formulae which he proposed 28) are shown below:



and



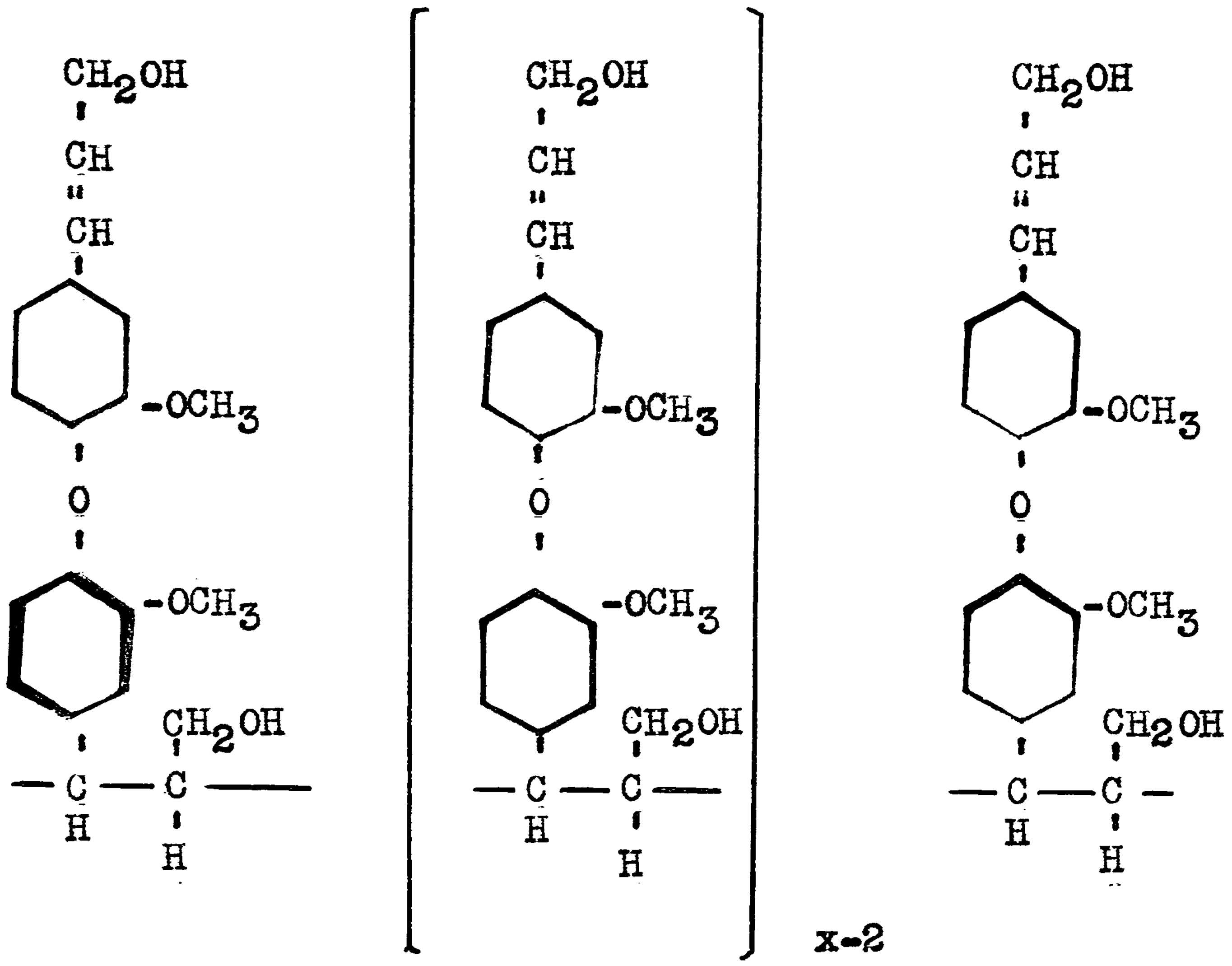
However, he modified this to some extent later 29) and assumed the existence of the complex;



in lignin.

Klason's conclusions are based essentially on analyses and properties of fractionated lignin sulphonic acids and comparison of these with a coniferyl aldehyde polymer. However, results of alkali fusions, dry distillations, zinc dust distillations of other lignin preparations and sodium hydroxide treatment of fractionated lignin sulphonic acids, tend to some extent to support this theory. Undoubtedly the guaiacyl residue does exist in lignin as indicated in the isolation of n-propyl guaiacol and vinyl guaiacol by Philips and Goss 30) 31) from a distillate obtained from a zinc dust distillation of alkali isolated corn cob lignin and as proved by the isolation of vanillin from lignin sulphonic acid by Tomlinson and Hibbert 14) and by the isolation of aceto-vanillone in this research. However this theory is based primarily on the presence of about 3% of coniferyl derivatives in the sap of conifers in the springtime, and on the similarity of polymerized coniferyl derivatives (Ultimate analyses, Methoxyl analyses) to lignin sulphonic acid.

Kürschner's view 32) that lignin is a polymer of the glucoside coniferin is of interest in view of the recent work proving definitely the presence of glucosidic linkage and a carbohydrate complex. Later however, he proposed 33) as did Klason that lignin is a polymerized coniferyl alcohol as shown below:



involving an ether union through the phenolic hydroxyls. This formula was proposed to account for his yields of vanillic acid, secured by thermal degradation of lignin 30). However, if his view was correct the yields of vanillin 14) should be much higher than the eight percent secured. Moreover this formula indicates the possibility of numerous double bonds which certainly do not exist in lignin, and also does not account for the free phenolic hydroxyls and glucosidic linkages present in the latter.

Schrauth 17) proposed to formulate lignin as a condensed furan system containing furan rings, hydroaromatic rings and aromatic rings, all formed from the condensation of 5-hydroxymethylfurfural. Though the formula does not explain the reactions of lignin, the possibility (as will be discussed later) exists that hydroxymethylfurfural is one of the building components of lignin.

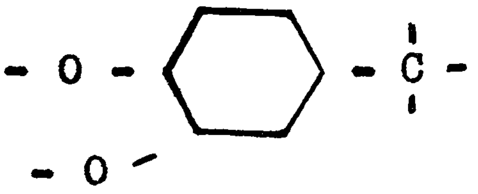
D. THE FREUDENBERG CONCEPT OF LIGNIN

Freudenberg, in his book "Tannins, Cellulose and Lignin", made an attempt in 1933 to assign a formula to lignin, and at the same time to account for its presence in wood. He based this formula on a large amount of chemical data and on the preceding work of Klason and of Kürschner.

Freudenberg insists primarily, that lignin, as isolated, is a high molecular weight polymer. He does not state whether it is a homopolymer (polymer of identical units) or a hetero polymer (polymer of various units). Elementary analyses for carbon and hydrogen and the carbon - hydrogen ratio indicate there exists in the polymer a condensed unsaturated ring system which he believes to be essentially of the benzene type. Adsorption spectra measurements 34) indicate the presence of 10, 20 or 60% of benzene nuclei in lignin. A benzofuran or benzopyran type might also be present.

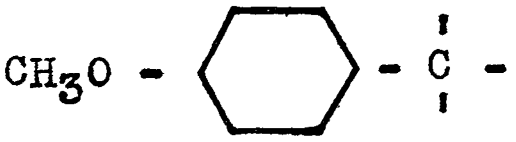
The formation of vanillin in a yield of 2% led Freudenberg to accept, in a modified form, the Klason formula 26) for lignin, namely a condensation product of coniferyl alcohol. Inasmuch as the latter is found in the cambium sap of certain conifers, it could be regarded as the basic component of lignin.

The earlier work on the isolation of minute quantities of protocatechuic acid by alkali fusion 35) served to demonstrate the presence of a group of the nature:



However, the fact that monocarboxylic acids of substituted benzenes, for example veratric and protocatechuic acid were isolated does not prove that these acids are formed primarily, since some dicarboxylic acids readily lose CO_2 to form mono-acids. Fischer, Schrader and Friedrich 36) among others, demonstrated the formation of benzene polycarboxylic acids by oxidation treatment of lignin.

Phillips and Goss 37) showed the presence of the complex:



by their oxidation of lignin degradation products to give anisic acid.

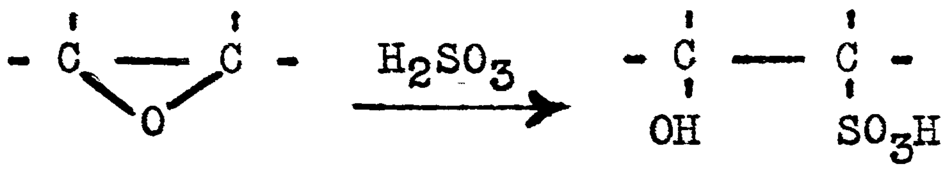
The presence of methoxyl groups and their marked resistance to acid and alkali showed that the methoxyl groups in lignin were neither ester nor acetal-methoxyls, but were present in the form of ethers. The formation of formaldehyde from lignin in yields of from 0.9 - 1.2% under the same conditions as from piperonyl derivatives, is seen by Freudenberg as proof of the presence of the dioxymethylene group.

The nature of the free hydroxyl groups in lignin has been well covered in other publications 38) from this department and no attempt will be made here to develop the nature of these hydroxyls.

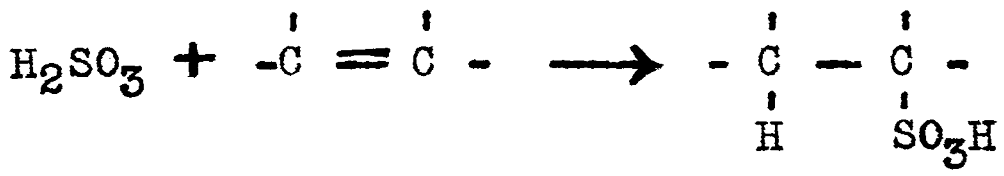
The other oxygen atoms in the lignin are assumed to be present in the form of ether-oxygen groupings, and treatment by hydriodic acid indicates that one valency of the oxygen bond is attached to a benzene nucleus; the nature of the other valency is unknown. It may be either aliphatic or aromatic in character.

Before indicating Freudenberg's structure of lignin, some of the possible mechanisms of sulphonation and Freudenberg's concept of this process will be discussed.

As mentioned earlier (the Cross and Bevan formula), the idea has been advanced that sulphonation could occur at an ethylene oxide ring to give a sulphonic acid and a free hydroxyl 39):

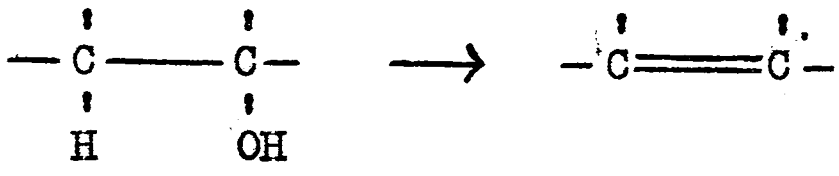


This is likewise true of the heterocyclic carbon oxygen rings. The idea, that the reaction of lignin with acid bisulphites involves the formation of a simple additive aldehyde or ketone complex, seems fallacious, since it has been shown 40) that, in concentrations of SO_2 such as those used in the manufacture of sulphite pulp, the aldehydo bisulphite complex formed from aqueous sulphurous acid would break down. The formation of a lignin sulphonic acid by addition to a double bond 41):



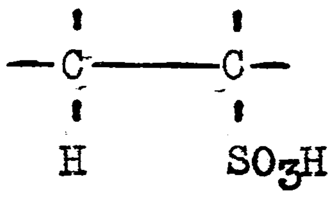
$$H_2SO_3 + -\overset{|}{C} = \overset{|}{C} - \longrightarrow -\underset{H}{\overset{|}{C}} - \underset{SO_3H}{\overset{|}{C}} -$$

has been postulated by Peter Klason and is quite possible. Freudenberg however, until quite recently, postulated sulphitation as occurring in the aromatic nucleus 35). Although this explanation of sulphitation could explain the formation of lignin sulphonic acids, it serves no purpose, since it, in itself, does not explain concurrent reactions. However, in this connection it might be well to mention that the existence of a double bond 42) in native lignin is still quite doubtful 43). Treatment of wood with benzoyl peroxide indicates some unsaturation which presumably disappears in the polymerization products. Freudenberg 43), and later Hibbert and Tomlinson 14) overcame this objection by postulating the formation of a double bond formed by the primary elimination of water from two adjacent carbon atoms ;



$$-\overset{|}{\underset{\overset{|}{H}}{C}}-\overset{|}{\underset{\overset{|}{OH}}{C}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}-$$

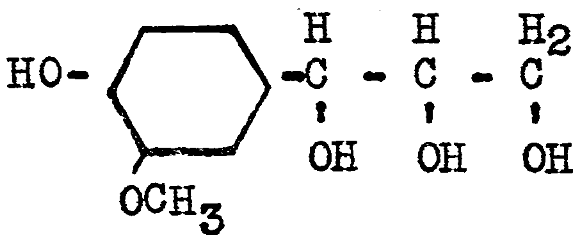
which in turn could add on H_2SO_3 to give :



$$-\overset{|}{\underset{\overset{|}{H}}{C}}-\overset{|}{\underset{\overset{|}{SO_3H}}{C}}-$$

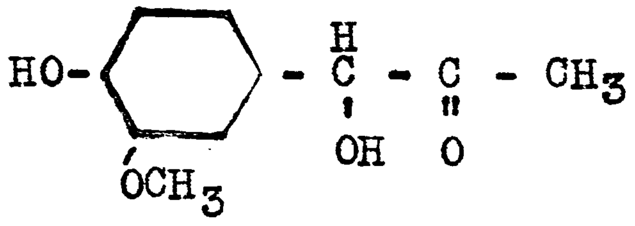
Oxidation of lignins 35) with ozone has yielded 1 - 2% of acetic acid. Yields of acetic acid as high as 6% have been secured by the use of chromic acid 25). Oxidation technique as applied by various investigators has also yielded oxalic acid, malonic acid, succinic acid and carbon dioxide.44).

To explain these chemical properties and reactions, Freudenberg postulates the formulation of lignin as primarily a condensation polymer of simpler building units of the type of 3-methoxy-4-hydroxyphenyl glycerols:



or its

biochemical equivalents;



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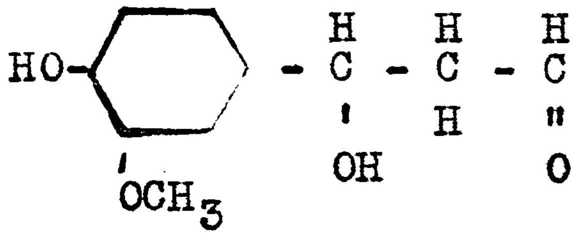
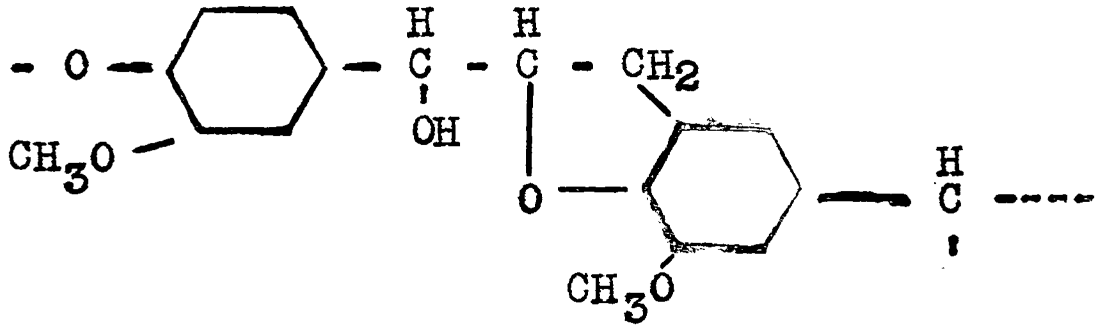
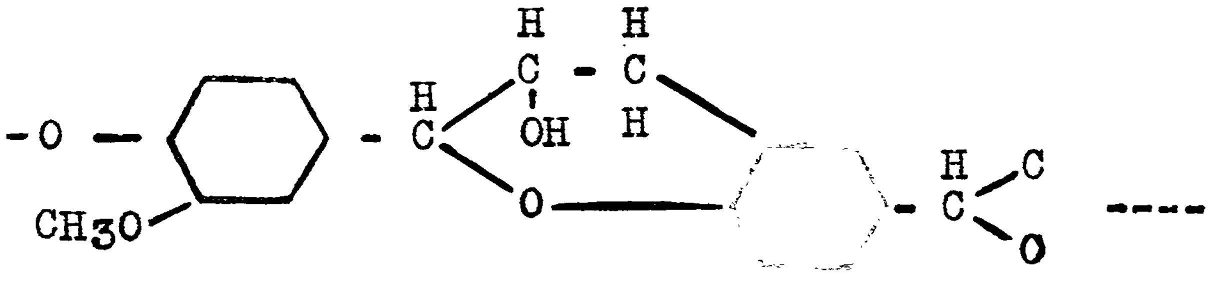


Condensation could take place in many ways, and to explain the various degradation products and reactions of lignin he had to select certain of these condensation reactions, a few of which are listed below:



(1)



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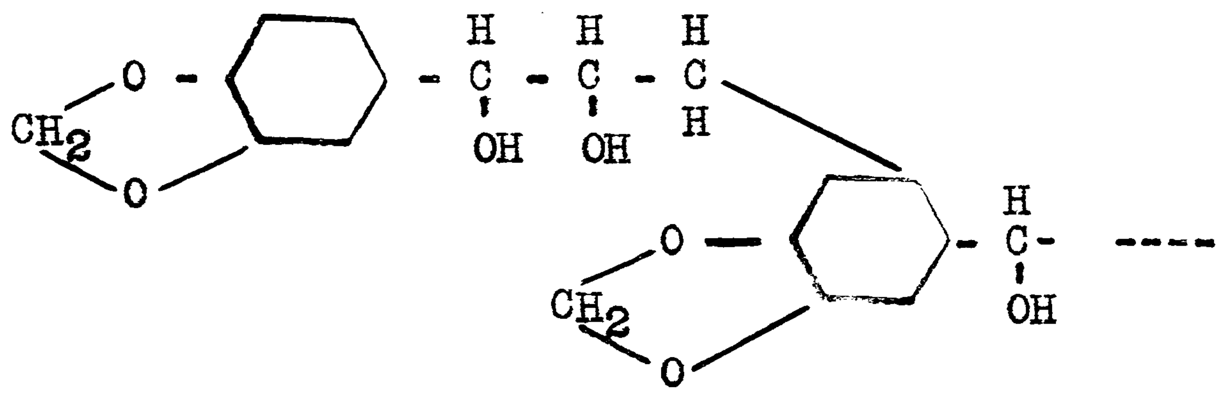

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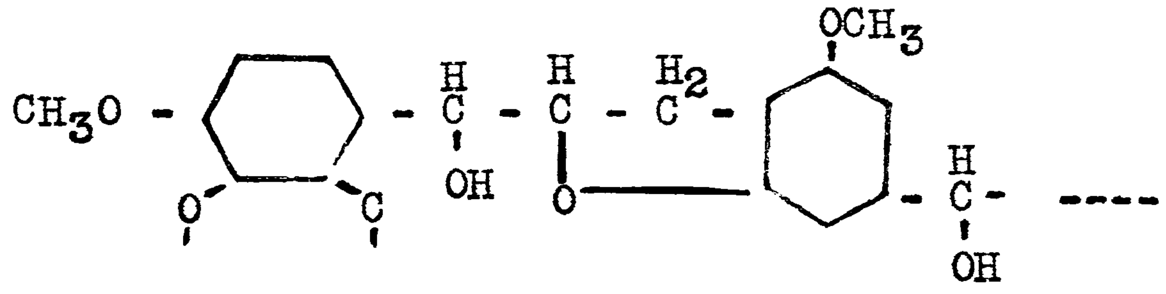

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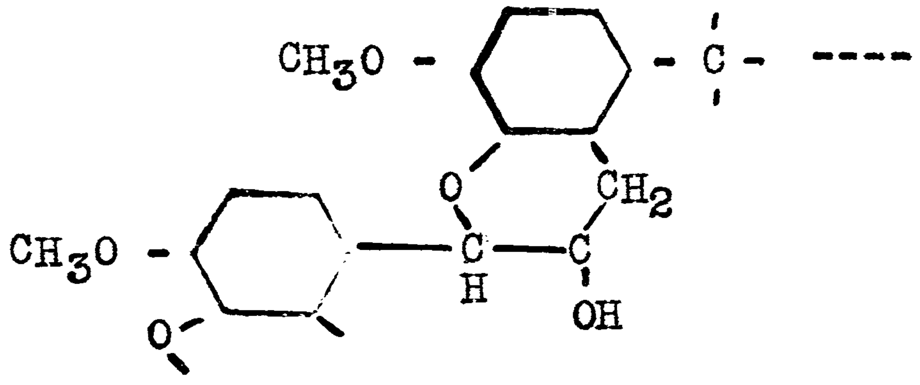

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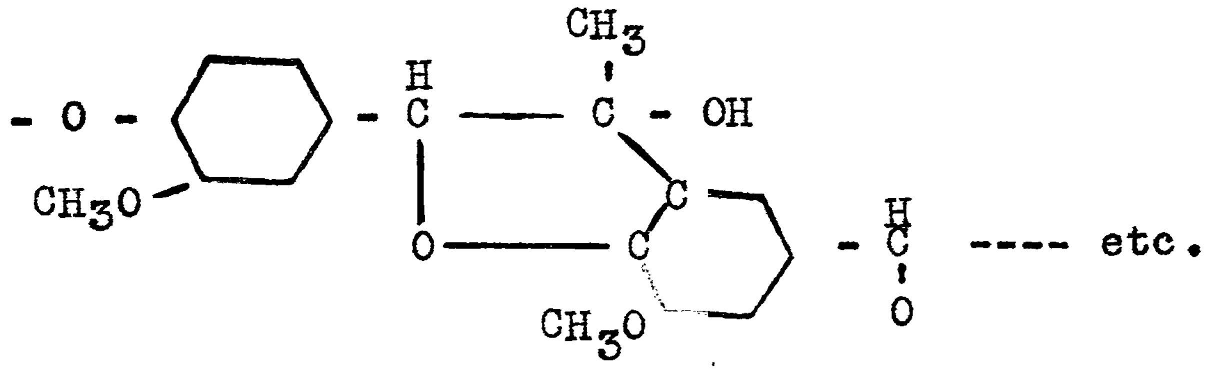

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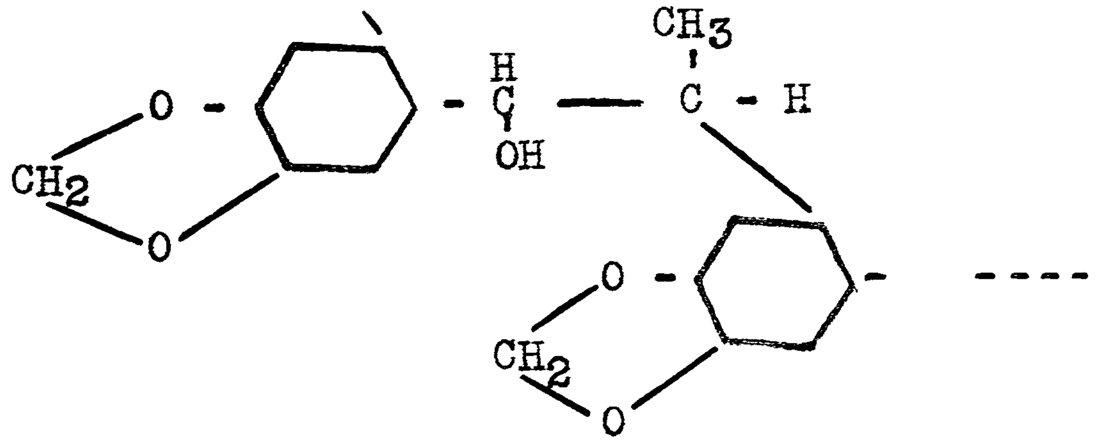
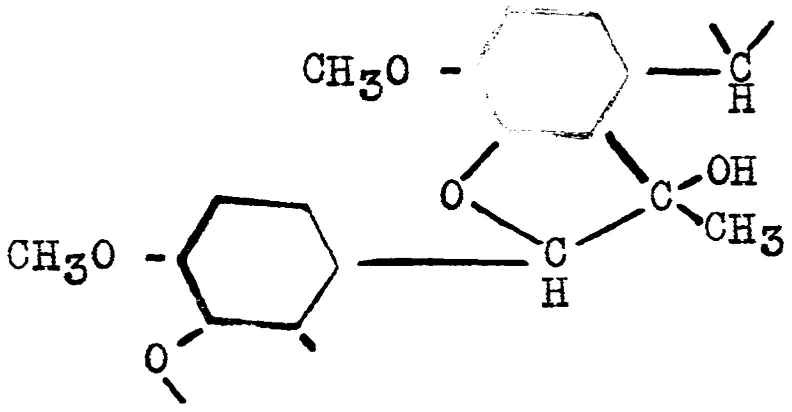


(7)

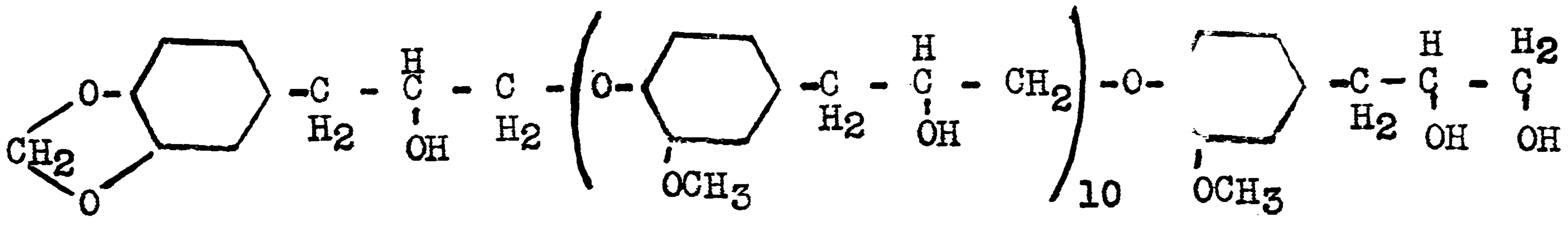
and



---- (8)

The total number of possible condensations is high, since the vanillin, piperonyl, and isovanillin types could condense with aliphatic hydroxyl groups to give mixed ethers. In addition to this there is the possibility that a condensation of an aliphatic hydroxyl with an aromatic nuclear hydrogen could take place. Of those suggested, the types 6, 7 and 8 would explain satisfactorily, the formation of acetic acid by oxidation, but possess a disadvantage in that they involve condensation with the benzene nucleus.

For the formation of so-called "primary lignin", Freudenberg favors a simple long chain condensation polymer formed from one of the substituted dioxyphenyl glycerols, and also assumes the presence of an end group of a dioxymethylene substituted benzene nucleus:



This polymer, in turn, is converted in the plant post-mortally, or during the process of isolation into a condensation polymer known as lignin, i.e. $x\,A \rightarrow (A)_x - y\,H_2O$. Freudenberg postulates ring closure and methylation occurring concurrently with the condensation.

It must again be emphasized that these views are based entirely on the following limited experimental evidence:

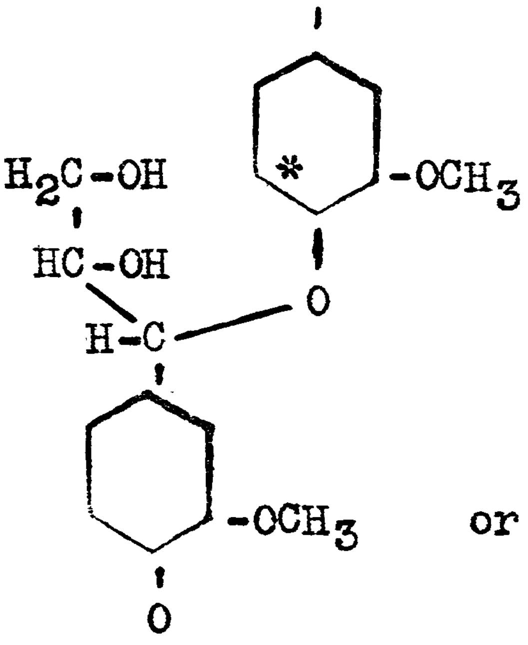
1. The formation of small yields of formaldehyde (0.9 - 1.2%) on distillation with acid,
2. The formation of protocatechuic acid (13) by sodium hydroxide fusion,
3. The properties and analyses of lignin sulphonic acids.

In a more recent paper 45) however, Freudenberg clarifies his ideas of lignin and at the same time offers more evidence for his formula. He takes into consideration the results of oxidation experiments, which he has carried out, and the results of model researches carried out by others. He gives a good summary of the recent work by Hibbert and co-workers 14) in which vanillin and syringic aldehyde were isolated from lignin sulphonic acids. In addition he attempts to show why lignins prepared by alcoholysis do not yield similar products to those secured from lignin sulphonic acids.

He regards lignin as a polymer built up from simple units through dehydration leading to ether formation. The building units which he gives as possibilities are those put forward by him in 1933, namely the dioxyphenyl nucleus attached to a side chain of glycerol or a biochemically equivalent type.

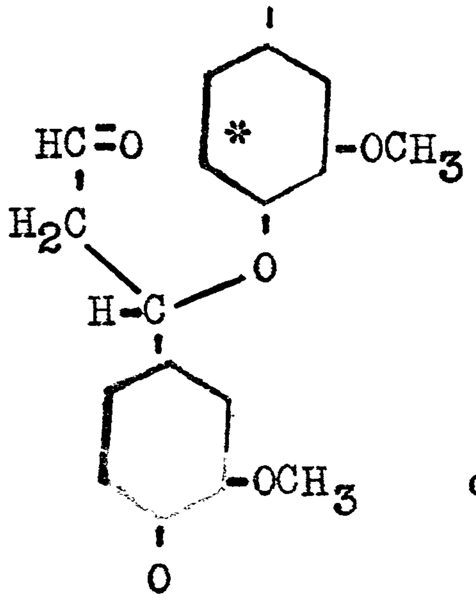
Polymerization takes place by ether formation accompanied by secondary condensation reactions either in the plant, or due to the chemical treatment used for isolation. Thus in lignin there may exist Benzo-pyran or Benzo-furan systems.

Formerly, up to 1937, he had assumed that ether formation resulted from a condensation between the primary hydroxyl of the side chain and the phenolic hydroxyl. The basis of this was the absence of any group in lignin, which could be oxidized to give a carboxyl. In his later paper however, he believes that the first idea was probably erroneous and suggests that the union between the building units is as depicted below:



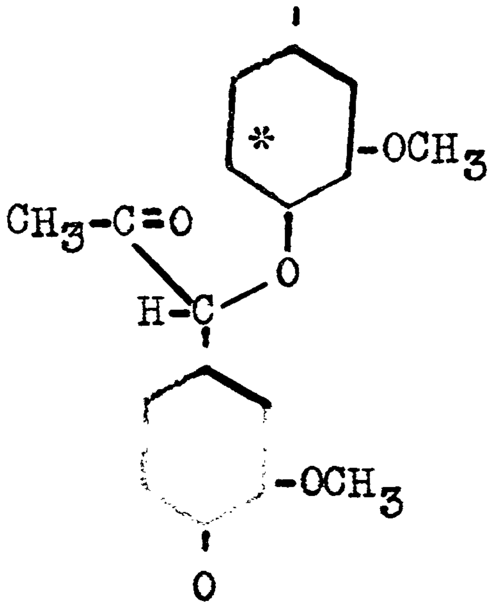
A

or



B

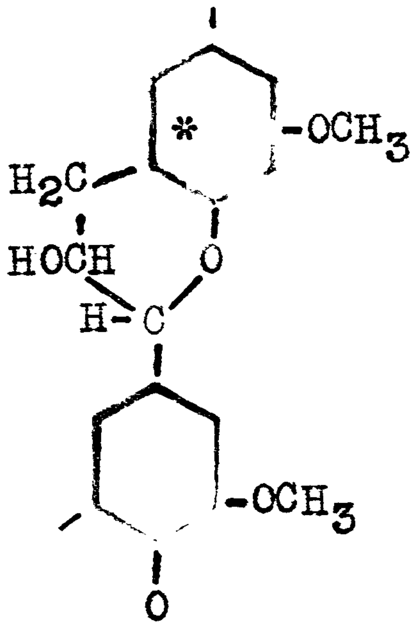
or



C

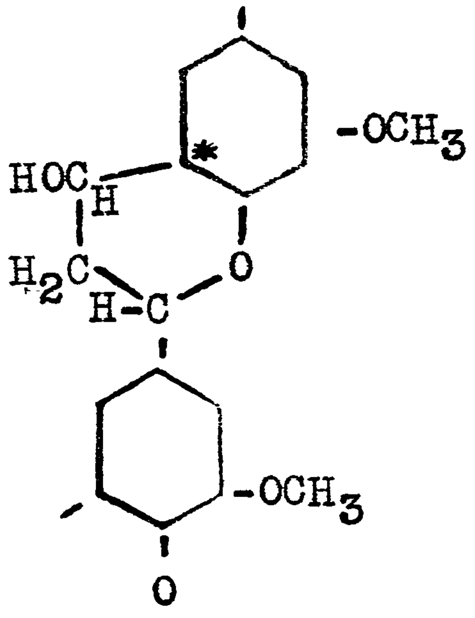
for the three biochemically similar types.

The further condensation (Freudenberg's secondary reaction) may then be understood. The hydrogen in the position * is necessarily active since it is ortho to oxygen and meta to an aliphatic side chain, and in formula A, could condense with the primary hydroxyl with the elimination of water to form a pyran system, as shown below:

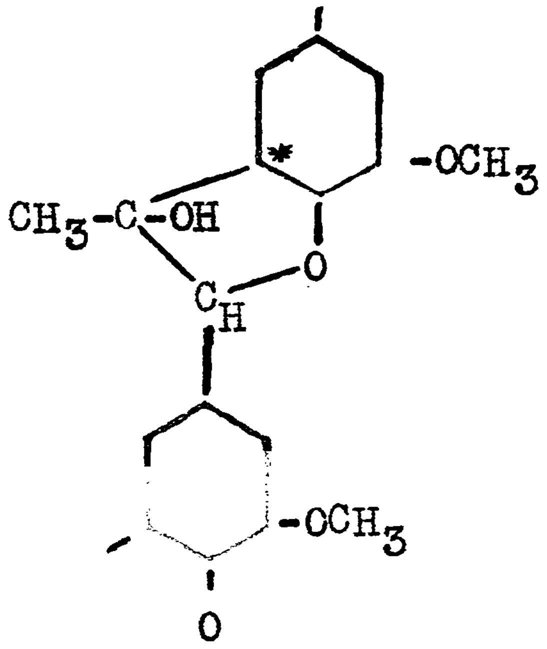


D

In the case of B and C, the active hydrogen could migrate to the carbonyl giving 1,2-addition to the carbonyl with the resulting formation of a pyran system as shown in E and a furan system as shown in F:



E



F

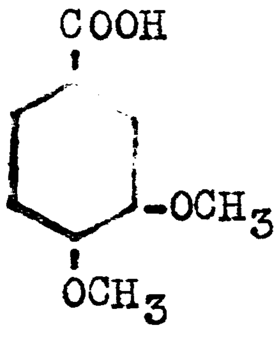
The original yield (1.2%) of formaldehyde secured from lignin has been doubled recently by E. Hägglund 46), and indicates that instead of one in every twelve units containing a piperonyl residue, this would be contained in one in seven.

Thus Freudenberg regards spruce lignin as consisting of a linear polymer of various units of the type A, B, or C, preferably one of the two latter. This lignin contains seven such units, of which the terminal one contains a piperonyl group, primary lignin being formed in this manner in the cell wall.

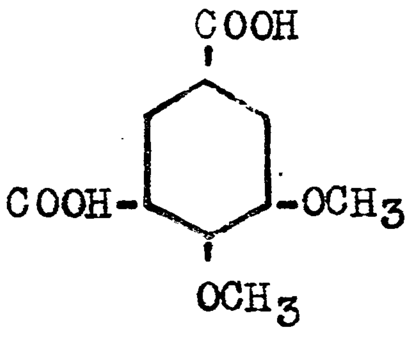
Subsequent condensations of D, E and F can then occur either in the wood postmortally or during isolation under the influence of reagents to yield more complex polymers. Other condensations might also occur to yield large three dimensional polymers.

The evidence which Freudenberg offers for this theory of the formation of lignin is described below in some detail since it would be unfair to criticize his formula unless all the evidence offered is considered.

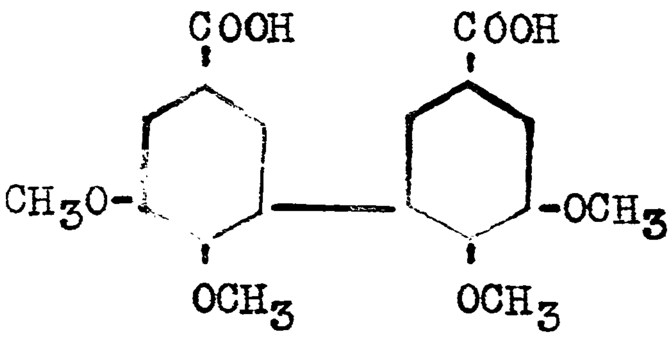
An isolated lignin (Phosphoric acid method) was fused with hot alkali, the decomposed material methylated and then oxidized with potassium permanganate giving veratric acid (10%), isohemipinic acid (4%) and some dehydrodiveratric acid (3%), (the latter however, was only obtained in one experiment and so far, has been found impossible of duplication):



G



H



I

By subjecting these compounds to the action of the same reagents, and comparing yields, Freudenberg shows that the actual combined yield of the above compounds G, H and I should have amounted to over 20%.

The facts raise the following questions:-

1. Possible existence of the diphenyl bond in lignin,

2. Formation of isohemipinic acid or dehydrodiveratric acid as true lignin degradation products.

The Diphenyl Complex

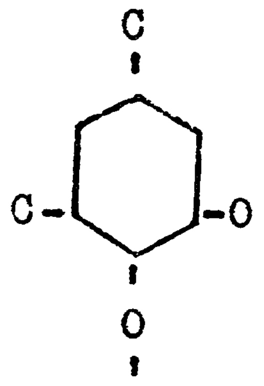
The method of isolating the lignin by means of phosphoric and hydrochloric acids could not result in a dehydrogenation. However, the latter could have occurred by oxidation during the alkali treatment, as evidenced by formation of a tetrahydroxydiphenyl from resorcinol under the same conditions. Eugenol and vanillin on the other hand did not yield any diphenyl derivative on similar alkali treatment 45). In Freudenberg's opinion oxidation takes place during the alkali decomposition, but he found later that in a nitrogen atmosphere, he was still able to secure the same quantity of dehydrodiveratric acid. The use of diazomethane for methylation obviated the possibility that dehydrogenation took place under the influence of the alkali during methylation.

If the diphenyl grouping were present, Freudenberg has shown that the amount of dehydrodiveratric acid obtained would be the theoretical quantity, as demonstrated by treatment of dehydrodiveratric acid under identical conditions, when recovery of the acid was practically 100%. Treatment of dimethyl-dehydrodivanillin and dehydrodiveratric acid, under the same conditions gave 90 - 97% of dehydrodiveratric acid.

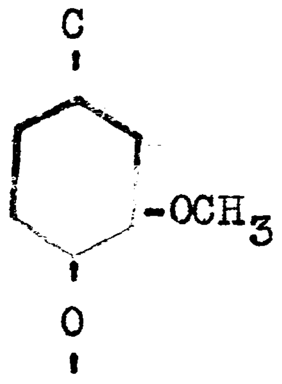
5-Substituted Vanillyl Grouping

If the isohemipinic acid found was formed from the diphenyl derivative, there should have been a much higher ratio of dehydrodiveratric acid to isohemipinic acid. In the case of methylated lignin sulphonic acid and lignin thioglycollic acid, whilst isohemipinic acid was secured, no dehydrodiveratric acid was obtained.

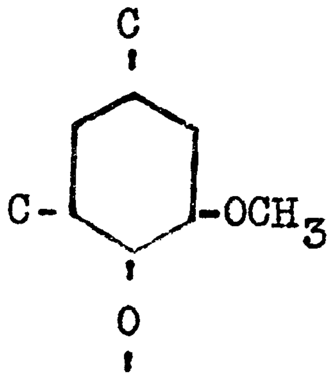
For these reasons, Freudenberg concludes that though the diphenyl derivative may have been synthesized from the veratric acid, there does not seem to be much doubt that the isohemipinic acid came from the structure J as shown below, and on the basis of the above work assigns the following formulae to representative building units of lignin:



J

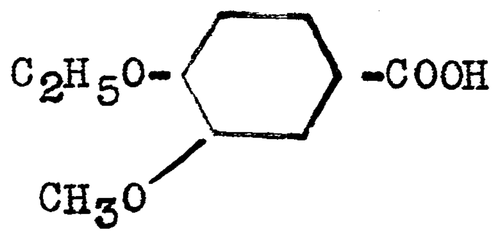


K



L

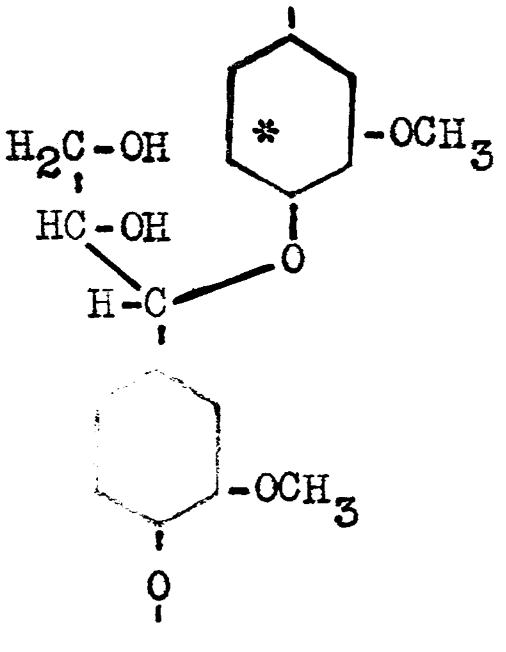
It is known that alkaline treatment of lignin sulphonic acid yields vanillin 14). When Freudenberg "ethylated" instead of methylating prior to oxidation he obtained a 10% yield of the corresponding ethyl ether of vanillic acid M, instead of obtaining a 10% yield of veratric acid:



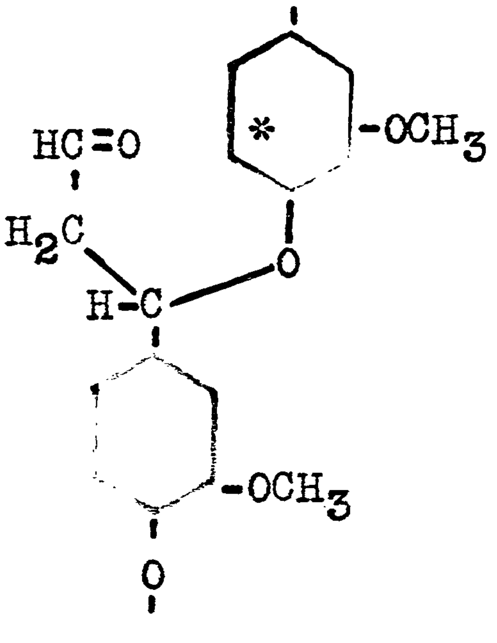
M

thus proving that the unit K exists as such in the lignin molecule. However, a formula corresponding to L must not necessarily be excluded.

A lignin sulphonic acid purified by precipitation with quinoline and then electrodialysed, yielded under Freudenberg's technique, small quantities of veratric and isohemipinic acids. This is regarded by him as additional proof of the existence of types A and B in the lignin molecule:

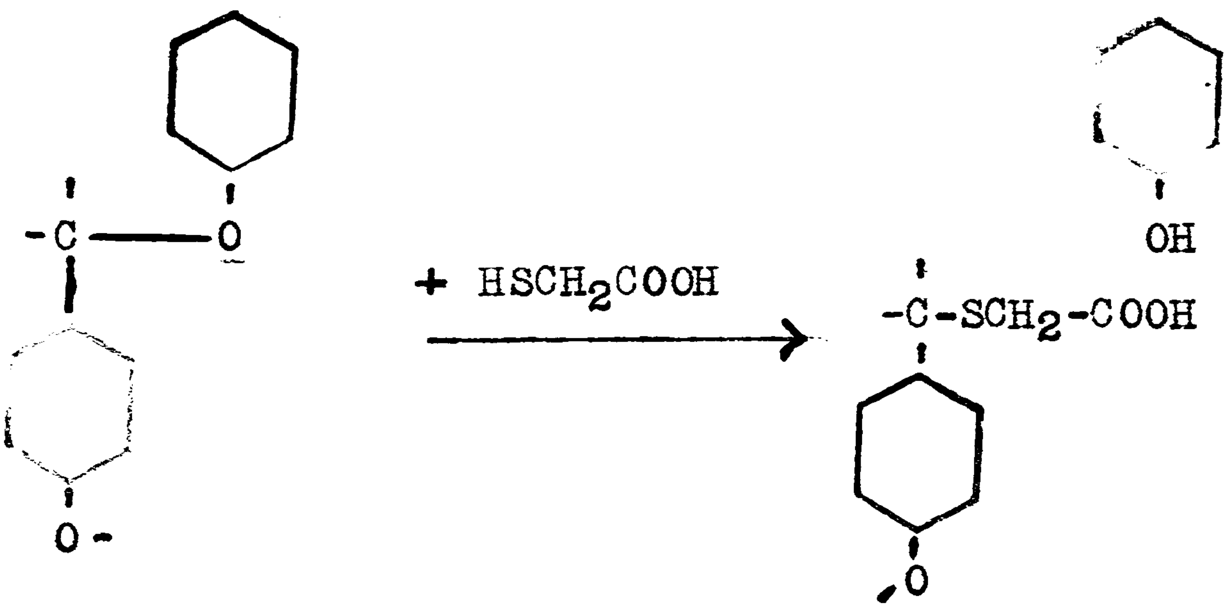


A

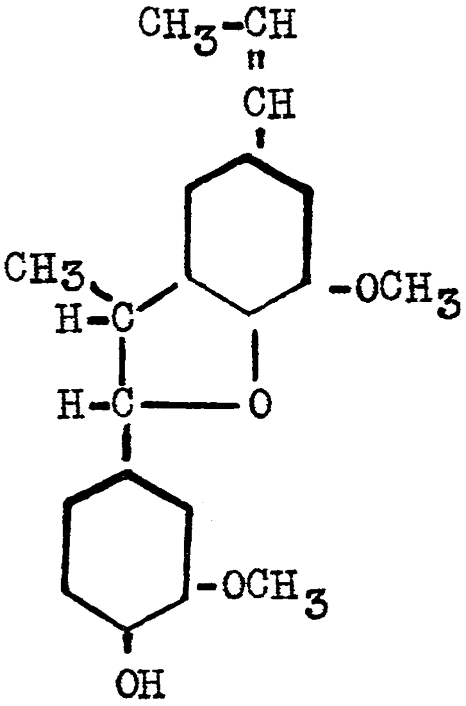


B

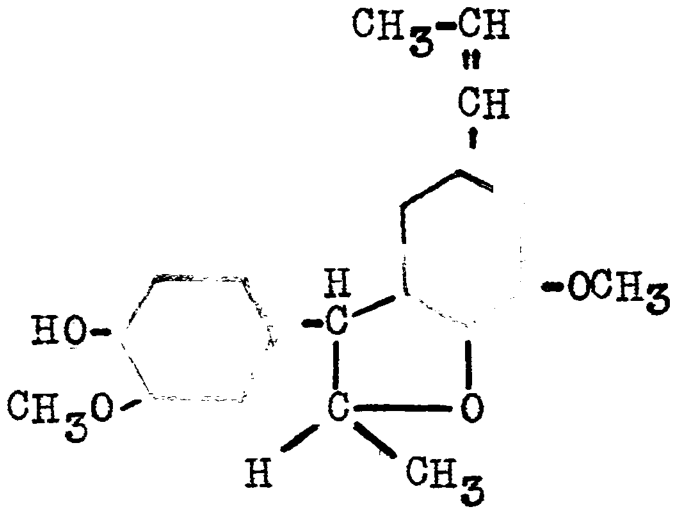
The newly developed method of Bror Holmberg 47) for the isolation of lignin by the use of thioglycollic acid gives interesting results. Some of the oxygen, which exists in the form of ether oxygen under the action of thioglycollic acid, apparently forms free phenolic hydroxyl groups as shown below:



In his most recent paper 45) Freudenberg reviews his interesting experimental results of certain model compounds for some of the structures he postulated in his lignin molecule, for example, dehydrodiisoeugenol, formulated as either N or O:

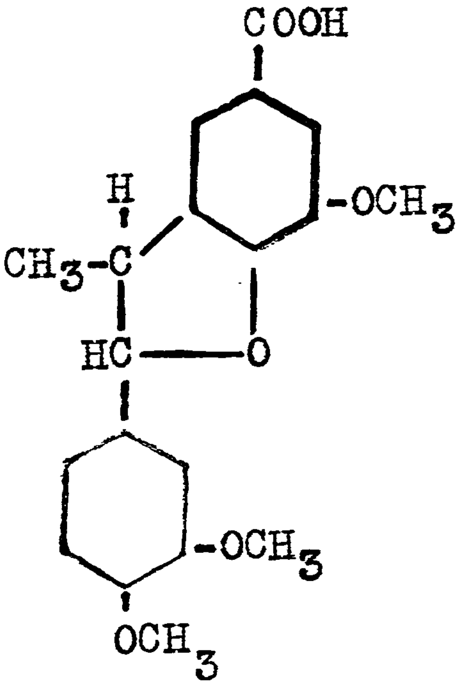


N



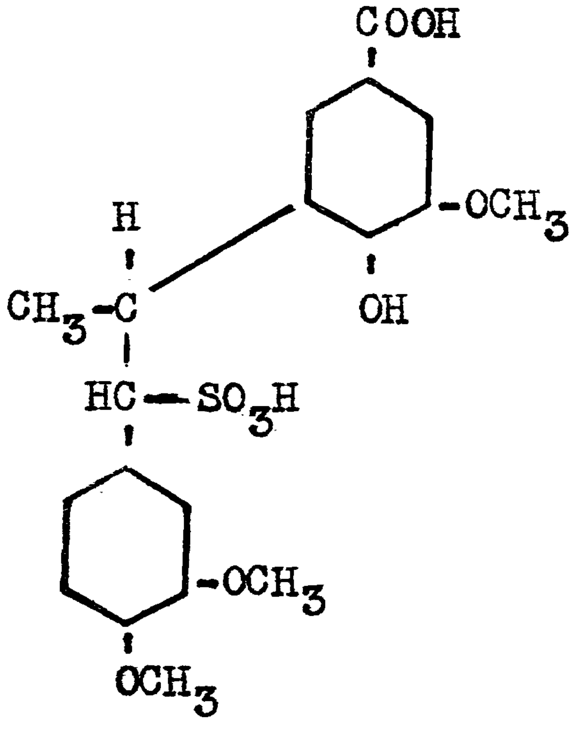
O

Methylation and oxidation yielded Erdtmann's acid [48) (P):

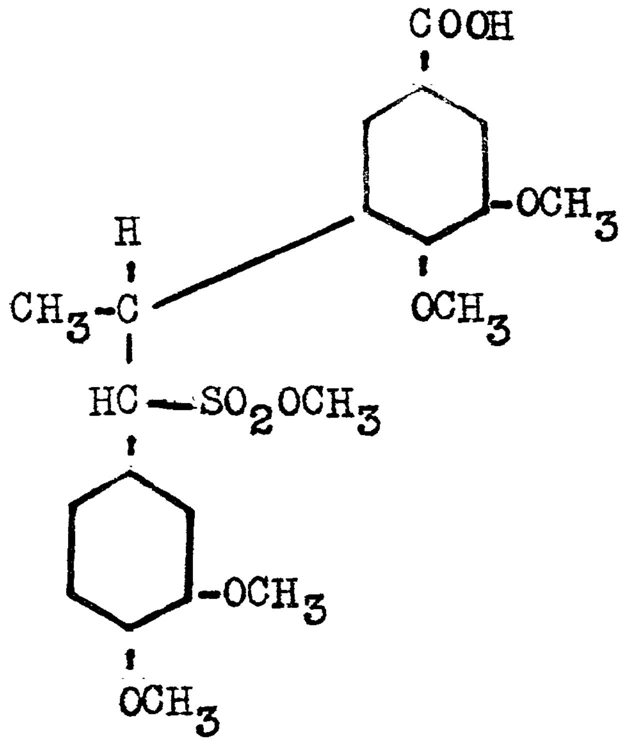


P

which, on further treatment gave only veratric acid, but on prior treatment with sodium hydroxide, methylation with diazomethane and subsequent oxidation, gave yields of veratric and isohemipinic acid corresponding in amount to the yields obtained from lignin. Treatment with acid sodium bisulphite under the conditions of the sulphite cook, yielded an amorphous sulphonic acid to which the structure Q was assigned. The latter, on methylation with diazomethane was converted into an amorphous product R:



Q



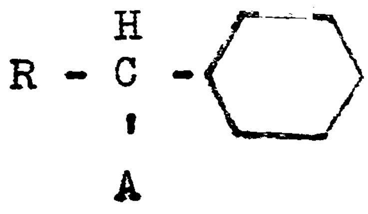
R

Oxidation of R gave percentage yields of veratric and isohemipinic acids corresponding to those from lignin.

The corresponding yield of isohemipinic acid from lignin sulphonic acid is not known, which is understandable since only a small part of the lignin molecule may be in the form R above.

A thioglycollic acid derivative in which the SO_3H group is replaced by SCH_2COOH of Erdtmann's acid gave, using Freudenberg's experimental conditions, a smaller yield of veratric acid than did the sulphonic acid. The yield of isohemipinic however, was about the same. The thioglycollic acid derivative of lignin, in contrast to lignin sulphonic acid, yielded isohemipinic acid under Freudenberg's conditions.

In Freudenberg's concept of Holmberg's work, the oxygen bridge in Erdtmann's acid represents an α-phenyl carbinol ether. Formula N has a bridged oxygen atom which is closer to the benzene nucleus and which is consequently probably more reactive than the one shown in the formula O. Furthermore, according to Freudenberg and Holmberg, if this ring were ruptured a secondary hydroxyl would be formed. It has been shown that the secondary alcohols, phenyl methyl carbinol and diphenyl carbinol react with acid sulphite, thioglycollic acid and alcoholic mineral acid to form derivatives of the type S:

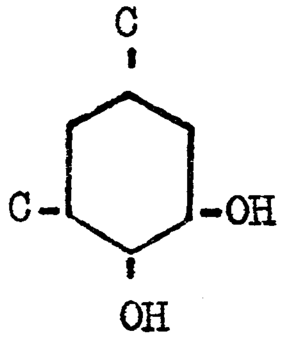


S

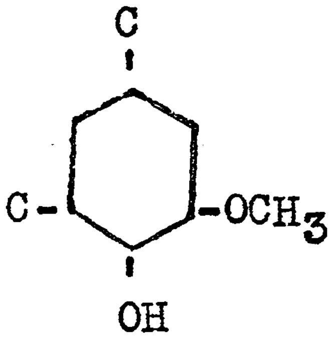
where R = CH_3 or φ , and A = SO_3H, SCH_2-COOH, OC_2H_5 etc. 47). Holmberg also showed that the ethers corresponding to the above alcohols will react with thioglycollic acid in the presence of mineral acids to break the ether bond with the formation of compounds of the form S above.

Freudenberg summarizes the above data as follows: Oxidation of lignin which has been methylated with diazomethane or dimethyl sulphate gives only small yields of veratric acid and no isohemipinic acid. However, if lignin is given a preliminary treatment with alkali and then methylated and oxidized, there can be obtained much larger yields of veratric acid (15%) and in addition isohemipinic acid may be secured. Using a blank determination on the amount of veratric acid, it is possible to re-isolate this after treatment with NaOH; he estimated that the decomposition of lignin with NaOH yields 30% of aromatic compounds.

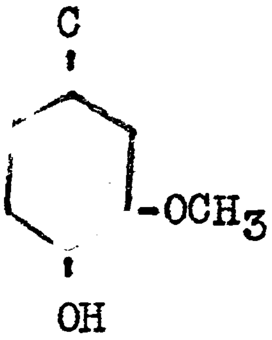
One of these fragments is the piperonyl residue. Another part could be obtained from the forms D, E, or F by ring opening at the position *. Judging from the small yield of isohemipinic acid obtained, he believes that possibly half of the aromatic nuclei are in the forms T or U:



T



U

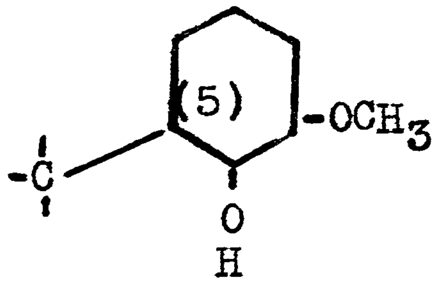


V

The fact that ethylation, subsequent to alkali treatment, and prior to oxidation yielded the ethyl ether of vanillic acid, he states, serves as an indication that a large part of the veratric acid results from the form V.

Hägglund and Carlsson 39) showed that a hydroxyl group is formed during sulphonation of lignin. It has been established that the hydroxyl group formed was "phenolic" in nature. This then accounts for the yield of isohemipinic acid. Sulphitation of a group of the type D and E, could take place by a reaction similar to that occurring with Erdtmann's acid, to give ring opening. Thus, there would result a form capable of yielding isohemipinic acid on oxidation. The veratric acid is obtained by oxidation of the α-sulphonate formed during sulphitation.

Tomlinson and Hibbert 14) have shown that veratric acid may be secured by an alkali treatment of methylated lignin sulphonic acid. Freudenberg states that this is in accord with the idea that a free "phenolic" hydroxyl group is formed during the process of sulphitation. The synthesis of vanillin by the above authors from an alkali treatment of lignin sulphonic acid, which was confirmed by Hägglund, agrees well with the formation of veratric acid demonstrated by Freudenberg. However, Freudenberg states that the vanillin residue possibly may have come from a chain rupture by alkali at the 5-position:



He admits the probability that the sulphonic acid is in a position α to the benzene nucleus. This is in agreement with Hägglund, with Klason and with Hibbert, and is a modification of his former theory of a β-sulphonic acid linkage. The fact that the sulphonic acid group is in the α-position is in harmony with the assumed rupture of a coumarane or chromane ring to form the sulphonic acid.

In the process of sulphitation, Freudenberg states that three to five oxygen bridges have reacted with sulphurous acid to form sulphonic acid groups and free phenolic hydroxyls. He shows that the views of Hibbert, which assume a sulphonic acid radical attached in the α-position of an aliphatic side chain are in agreement with the fission products arising from the splitting of his hydropyran or hydrofuran rings, the aldehyde thus formed being free to form a bisulphite compound or to condense with a neighbouring side chain, as in A, B or C. Freudenberg believes that these aliphatic carbonyls undergo condensation with neighbouring side chains during sulphitation. As a proof of this, he points to the formation of an insoluble lignin sulphonic acid from the soluble form by treatment with mineral acid.

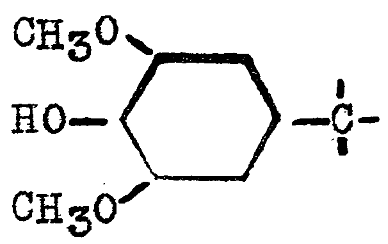
The reactions of lignin thioglycollic acid are interpreted similarily. Its analysis indicates that for every seven building units, two have reacted like Erdtmann's acid (c.f. pp. 158), and two have reacted like Holmberg's carbinol (c.f. pp. 160).

Freudenberg offers some new views on the interaction of lignin with alcohols in presence of mineral acids. According to Bror Holmberg's work, it is possible to etherify the secondary hydroxyl (the one adjacent to the benzene nucleus) by means of ethanol and HCl, and this etherification is probably part of the reaction, the other probably being one of ether splitting, during which the phenolic group is removed from the molecule, thus decreasing its size. He also points out that methanol lignin yields 10% veratric and 3% isohemipinic acid after methylation and oxidation.

When a lignin is isolated by treatment of wood with benzyl alcohol and a small amount of mineral acid, there is secured a brown colored substance which is soluble in alkali and organic solvents. If this is treated in a ball mill with benzyl chloride the resulting benzyl lignin contains three to four benzyl groups for every five methoxyl groups. The benzyl lignin is a cream colored substance insoluble in all solvents.

E. SUMMARY OF FREUDENBERG'S VIEWS

The reactions described seem to explain the color reactions of lignin and the tendency to form branched chain molecules (the three dimensional arrangement in isolated lignin). Moreover, Freudenberg states that his views apply equally well to beech lignin in which the syringyl radical,



is a building unit. The fact that the vanillyl radical occurs along with the syringyl radical can be explained by the chain theory of ether linkages in the lignin molecule. Since he has postulated only two forms of union, namely the ether linkage and nuclear condensation, and since the latter cannot occur with the syringyl residue, he finds it necessary to assume the presence of some other type of linkage in beech lignin.

Finally, Freudenberg states that these views of lignin and its properties, indicate the way in which "proto-lignin" condenses to form the isolated lignin. In the main however, they are concerned with the ether linkage and with the carbinol grouping formed on breaking this bond.

F. CRITICISM OF FREUDENBERG'S CONCEPT

Freudenberg 25), Peter Klason 26) and Kurschner 32) have reported the occurrence of about 3% of coniferyl alcohol in the spring sap of conifers. It is on this basis they assume the formation of primary lignin as a polymer of coniferyl aldehyde.

The possibility exists that this coniferyl alcohol has been formed as a degradation product of lignin. As will be shown later under discussion of results, this is a distinct possibility. The existence of numerous other simple organic materials in the plant cell wall might just as well be taken as an indication that these other materials are the precursors of lignin. If coniferyl alcohol is the precursor of lignin in the plant, it is to be expected that the yields of degradation products of lignin would contain large amounts of aromatic compounds. In no case have yields of more than 20% of aromatic compounds been reported. Freudenberg 45) reports yields corresponding to 20% of aromatic derivatives from his alkali degradation. A repetition of this work by A.B. Cramer (unpublished results) indicates that these yields are much too high. This would indicate that the aromatic nucleus does not necessarily form the major portion of the lignin molecule.

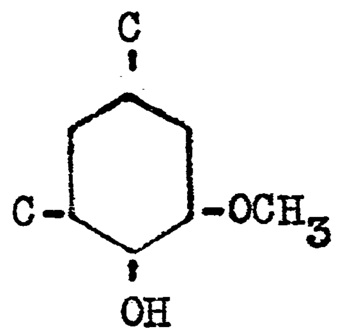
The yield of formaldehyde obtained by Freudenberg [45], and assumed to come from a dioxymethylene group, does not necessarily mean that the latter is present in lignin. Hunter, Wright and Hibbert [49] have shown that formaldehyde may be formed from a large variety of carbohydrate and furan derivatives, and most isolated lignins have now been shown to contain carbohydrate material. These, when treated with 15% hydrochloric acid yield formaldehyde, identified as its dimedon derivative, and furfural, identified as its 2,4-dinitrophenylhydrazone. As a result of this work, it would appear that the basis of Freudenberg's postulation of the dioxymethylene group is inadequate.

Freudenberg believes that none of the free hydroxyl groups occurring in lignin is phenolic in type. This view is based on the alkali insolubility of isolated lignin and its behaviour towards p-toluene sulphonic acid. He has shown that p-toluene sulphonic esters of phenolic hydroxyls react with hydrazine to form p-toluene sulphinic acids, and that this reaction does not occur with the p-toluene sulphonic acid ester of lignin.

It has been shown in these laboratories by Hibbert and co-workers that at least part of the free hydroxyl groups present in lignin are phenolic or enolic [51] [52]. The work of Hibbert and Tomlinson [14] has demonstrated the presence of at least one free phenolic hydroxyl in lignin sulphonic acid. Freudenberg himself has confirmed this view. According to Hibbert and Tomlinson, diazomethane methylation of lignin sulphonic acid and subsequent treatment with alkali yields veratric aldehyde, whereas treatment of the unmethylated lignin sulphonic acid yields vanillin. Freudenberg showed that if lignin sulphonic acid was decomposed with alkali and ethylated previous to oxidation, there was obtained a yield of the ethyl ether of vanillic acid similar to that of veratric acid, obtained by following his methylation technique. Although the free phenolic hydroxyl might have been formed during Freudenberg's treatment with alkali, it seems more likely that it was present in the lignin sulphonic acid. However, the possibility is not excluded, that the free phenolic hydroxyl is formed during sulphonation. Bell, Wright and Hibbert in "Studies on Lignin and Related Compounds, XXXIV", have shown that the hydroxyl groups reacting with acetic acid in acetic birch lignins are probably phenolic or enolic in type. This does not agree with Freudenberg's postulation that all of the free phenolic hydroxyl groups in lignin are united as ethers. He overlooks the point that they may be present glycosidically united to carbohydrates.

The formation of isohemipinic acid as shown by

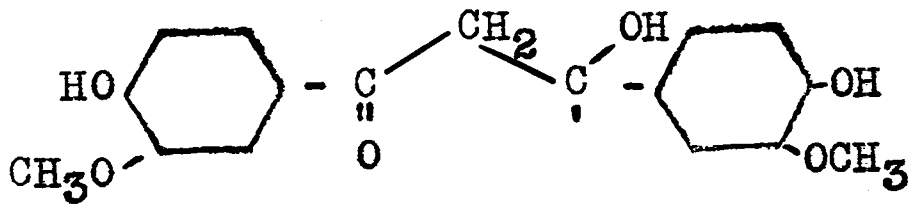
Freudenberg is very interesting. It is quite probable, as he asserts, that this acid is formed from the grouping;



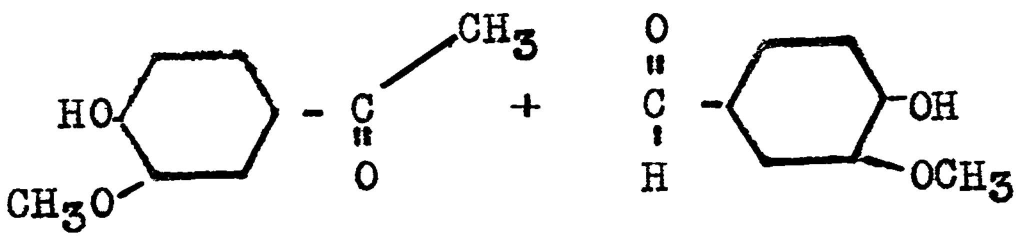
which could conceivably exist in the lignin complex.

The isolation of acetovanillone from waste sulphite liquor and of the same compound from potassium lignin sulphonate throws some doubt on the coniferyl alcohol theory of lignin formation postulated by Freudenberg. Two possible forms could give acetovanillone under the influence of alkali:

I.

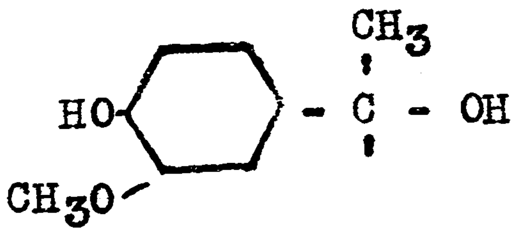


by a reversed aldol with migration of hydrogen to yield:



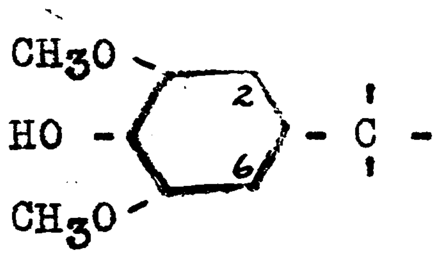
and a linkage of the type:

II.



which by the same process could yield acetovanillone. These structures do not seem possible on the basis of Freudenberg's formula. However, they will be considered later in the "Discussion of Results".

On the basis of the work of Hawkins, Hibbert and Wright 14), which established the formation of syringic aldehyde as well as vanillin from birch and beech lignin sulphonic acids, if the syringyl radical is present in the same lignin molecule as the vanillyl radical, the possibility of nuclear condensation occurring with this radical seems remote because of the relative inactivity of the 2 and 6 hydrogen atoms;



Freudenberg's postulation of the possible mechanism of sulphonic acid and thioglycollic acid formation seems quite plausible, and the evidence offered for this mechanism is very good indeed. However, it seems strange that the compound secured by sulphitation of Erdtmann's acid Q and by methylation of Q, (R), should be amorphous. Analyses indicate the structure postulated, but no evidence is offered that this structure is correct. It is possible that other reactions than those shown have occurred.

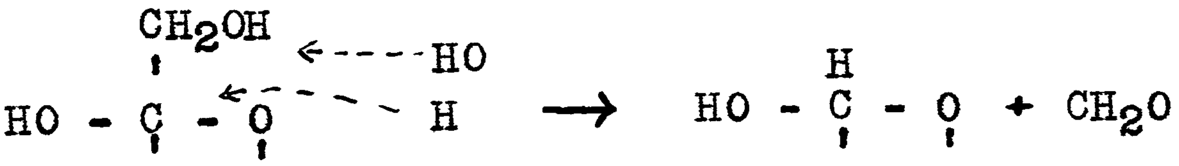
G. RECENT PAPERS FROM THIS LABORATORY

Reference has already been made to the presence of carbohydrate material in all of the lignin preparations studied heretofore. Bell, Wright and Hibbert 51) recently have extracted yellow birch with glacial acetic acid in which partial acetylation took place with free hydroxyl groups. The material so secured was treated by a process of differential solubility and separated in this way into various fractions. The fractions, so obtained, all contained carbohydrate material. This was shown, by a subsequent treatment with formic acid which eliminated the carbohydrate material, and removed most of the acetyl groups which were apparently attached to the carbohydrate residue.

A portion of the acetyl was not eliminated, and it is believed that this is present as an ortho-acetate. Removal of the latter without removing the carbohydrate liberated two hydroxyl groups, methylateable with diazomethane.

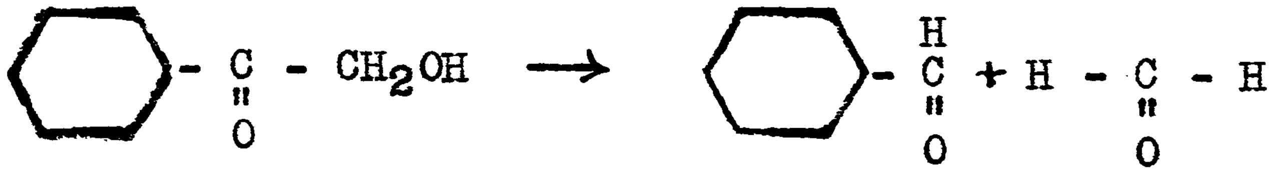
Removal of the carbohydrate material also according to these authors results in the formation of acidic hydroxyls. On the basis of these observations, they postulate a phenol glycoside as part of the lignin complex, and show that treatment with cold 5% alkali increased the amount of free phenolic (or enolic) hydroxyl in lignin, by removal of a part of the carbohydrate material. They believe that in Freudenberg and Willstätter lignin the free phenolic hydroxyls may be tied up with the carbohydrate residue. This is demonstrated by the insolubility of these lignin preparations in alkali.

Hunter, Wright and Hibbert 49) have shown that the formaldehyde yields secured by Freudenberg, Sarkov and Hägglund from spruce and birch lignin by treatment with acid, need not necessarily have come from the dioxymethylene group. These authors (Hunter, Wright and Hibbert) find that furfural as well as formaldehyde is formed by treating lignin preparations with 12% hydrochloric acid or with 28% sulphuric acid. Formaldehyde has been reported frequently from carbohydrate materials under treatment with the above reagents, and these authors have demonstrated that formaldehyde may be formed from the grouping:



$$HO - \underset{|}{\overset{\overset{CH_2OH}{|}}{C}} - \underset{|}{O} \cdots H \;\; \overset{\leftarrow \cdots HO}{} \longrightarrow HO - \underset{|}{\overset{H}{C}} - \underset{|}{O} + CH_2O$$

by hydrolysis. This occurs readily with hexoses. That this probably also occurs with aromatic compounds has been assumed by Hanaeus and Zincke 52) who isolated benzaldehyde but not formaldehyde from α-hydroxyacetophenone:



Formic acid lignin which does not contain carbohydrate materials yields only faint traces of formaldehyde and no furfural. It would thus seem likely that the formaldehyde reported by Freudenberg results not from the dioxymethylene group, but from hexose carbohydrate materials which are present in the lignin preparations, in a chemically combined state.

Bell, Cramer, Wright and Hibbert 53) have reported that no veratric acid can be isolated from the oxidation of fructose humic acid, which to some extent, contradicts Hilpert's theory that lignin is formed from carbohydrate materials. Furthermore, these authors have reported that both ethyl iodide and methyl iodide are formed on treating formic acid lignin with hydriodic acid. Mild treatment of lignin with hydriodic acid yields only methyl iodide. The ethyl iodide was isolated and identified as the ethyl pyridinium iodide.

Tieman 54) has demonstrated that both ethyl and methyl iodides can be secured by treating coniferyl alcohol in a bomb tube with hydriodic acid. Doubtless there must exist within the lignin molecule some structure which will yield ethyl iodide on drastic treatment with hydriodic acid.

The above authors 53) believe that in the process of lignin formation, glycoside formation takes place between the phenolic hydroxyl of the "protolignin" and carbohydrate materials present in the plant. This is in agreement with the recent paper of Bell, Wright and Hibbert 51), who have demonstrated that most of the hydroxyl groups in acetic acid birch lignin are phenolic or enolic, and in a later paper, have also shown the existence of a carboxyl group in lignin 55), susceptible to lactone formation. Treatment of one of the dimethylsulphate-sodium hydroxide methylated fractions of acetic acid birch lignin with sodium methoxide led to the formation of a chloroform and water soluble sodium salt of the acid. These authors present evidence which indicates that during dimethylsulphate methylation the carboxyl group is present as a lactone, but that this lactone ring is broken during diazomethane methylation to give a compound with a higher methoxyl content. This has now been shown by Wright 56) to be a general reaction. Grignard analyses for active hydrogen and addition seem to confirm these views.

A recent paper by Hawkins, Wright and Hibbert 14) reports the isolation of syringic aldehyde and vanillin in equal quantities from sodium hydroxide treatment of hard wood lignin sulphonic acids, the occurrence of the former thus accounting for the higher methoxyl content of hard wood lignins. It is not clear yet whether the syringyl radical and the vanillyl radical are identical parts of separate lignins or whether these radicals both form parts of the same lignin complex.

It is of interest to note that the combined quantities of syringic aldehyde and vanillin amount to approximately the value found for vanillin from the soft wood lignins.

A recent paper by Bell, Wright and Hibbert 57) shows that there is present in birch formic acid lignin a grouping which yields acetone superoxide on ozonization in anhydrous medium. In the case of both the formic and acetic acid lignins of birch, a permanganate oxidation yields acetone thus showing the presence of either the isopropylidene group, or some grouping capable of giving rise to acetone under the experimental conditions.

Buckland, Tomlinson and Hibbert 58), have shown that waste sulphite liquor which has been treated at 150° C. for 8 hours with 9% sodium hydroxide, will on suitable treatment yield acetovanillone. The author and H. Hibbert in a recent paper [59] have shown that acetovanillone is a direct degradation product of lignin sulphonic acid. In addition, it has been pointed out that in the degradation products from birch lignin sulphonic acid, acetovanillone is not present, but that acetosyringone may be secured in yields which are much higher than those of acetovanillone.

H. SUMMARY OF THE RECENT PAPERS FROM THIS LABORATORY

In the later work published by Hibbert and co-workers, a number of interesting facts have been uncovered.

1. It has been shown that carbohydrate material is attached chemically as part of the "protolignin" complex.

2. The presence of this carbohydrate material may explain the formation of formaldehyde from lignin preparations, demonstrated by the fact that formic acid lignin which does not contain carbohydrate materials, does not yield formaldehyde on treatment with acid.

3. The presence of orthoacetyl groups has been shown in acetic acid lignin.

4. Removal of these orthoacetyl groups liberates free phenolic hydroxyl groups.

5. Ethyl iodide has been shown to be a hydriodic acid degradation product of lignin.

6. A carboxyl group has been found present in lignin probably in the form of a lactone.

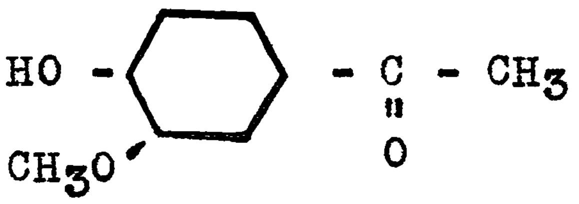
7. The isopropylidene group or a complex closely related to the same, has been demonstrated in birch formic

acid lignin.

8. A group which can give acetone on oxidation has been shown to be present in birch formic and acetic acid lignins.

9. Syringic aldehyde, acetovanillone and acetosyringone have been identified as degradation products of lignin sulphonic acids.

I. THE CHEMISTRY OF ACETOVANILLONE



The root of the Canadian Hemp (Apocynum Cannabinum) possesses the property of retarding the heart in systole, and is used as a remedy for dropsy and heart troubles. In 1883, Schmiedeberg 60) obtained from this material two substances which he called apocynin and apocynein respectively.

The former had the physiological properties of Apocynum, but as it was a resinous product it was not examined further. The so-called apocynin of the pharmacologist is the product obtained by precipitating the alcoholic extract of the Canadian Hemp root and drying the resulting precipitate.

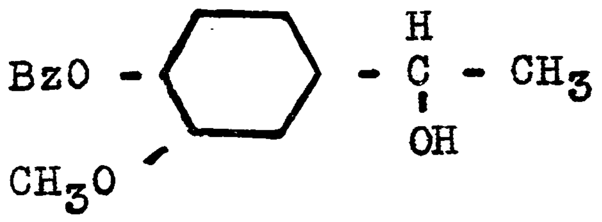
Wood 61) reported the existence of a definite crystalline compound in the alcoholic extract above.

In 1891 Tiemann 62), isolated a compound which he called acetovanillone, in small yields from the oxidation of acetoeugenol followed by hydrolysis. The properties of this compound were studied by Tiemann 62) and Neitzel 63) and modes of synthesis were developed by the latter author and by Otto 64).

It remained however for Finnemore 65) to establish the identity of the crystalline material isolated by Wood 61), as acetovanillone.

Various methods have been used to synthesize the latter. Neitzel 63) heated a mixture of vanillic and acetic acids with calcium carbonate and obtained very poor yields. Otto 64) prepared it, also in poor yield, from guaiacol, acetic acid and zinc chloride - aluminum chloride mixture at 140 - 150°C.

Finnemore 65) adopted a method involving the application of Grignard technique. As the starting material used contained a phenolic hydroxyl it was necessary to protect this hydroxyl during the reaction. Finnemore started with vanillin and prepared the benzoyl ester. This was treated in turn with methyl magnesium iodide to yield a so-called benzoyl apocynol;



Oxidation of the above compound with potassium dichromate and sulphuric acid, followed by hydrolysis, gave synthetic acetovanillone.

A more recent synthesis has been developed 66). A cooled mixture of guaiacol acetate is stirred, with a solution of anhydrous aluminum chloride in nitrobenzene. After twenty-four hours the aluminum chloride is hydrolyzed and the acetovanillone may then be separated by a process of extraction, distillation and crystallization. Yields are very good, 50% of theoretical.

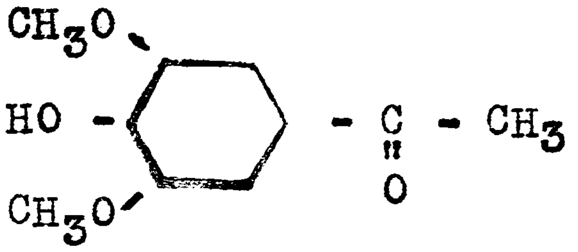
Acetovanillone is an almost colorless crystalline solid, melting point 114 - 115°C., boiling point 295 - 300°C. However, it may be sublimed under 1 - 25 microns pressure below the melting point. It is quite soluble in benzene, ether, alcohol and hot water. It is only slightly soluble in ligroin and cold water. It may be purified by recrystallization from benzene-petroleum ether, alcohol-petroleum ether or hot water. It is stable to 10% sodium hydroxide at 110°C. It does not react with bisulphites even at 125°C.

With potassium hydroxide at 170°C. it yields protocatechuic acid, and with strong hydrochloric acid at 140 - 150°C., is converted to acetopyrocatechol. Permanganate oxidation of the methyl ether yields veratric acid. It reacts readily with hydrazines and semicarbazide but not with acid bisulphite.

Condensed with tetra-acetyl bromo-glucose it yields a tetra-acetyl glucoside, which by shaking with cold barium hydroxide (5%) gives acetovanillyl glucoside 67). Acetovanillone with ferric chloride solution gives a bluish violet color which disappears on boiling, due to dehydrodiacetovanillone formation.

In pyridine, as solvent, a Grignard analysis 68) indicates that acetovanillone is present 25% as the enol form. In the other solvents, for example, dioxane, acetovanillone reacts normally.

J. THE CHEMISTRY OF ACETOSYRINGONE



Acetosyringone was first isolated and named by Mauthner 69) in 1928. It was prepared by a rearrangement at 0°C., of the acetyl derivative of pyrogallol 1,3-dimethyl ether by the use of anhydrous aluminum chloride. It is a colorless, crystalline solid, melting point 121 - 122°C. It may be sublimed under reduced pressure at temperatures above the melting point. It is soluble in ether, alcohol, benzene, petroleum ether, and hot water, only slightly soluble in cold water, readily soluble in dilute sodium hydroxide, sodium carbonate and sodium bicarbonate, and gives, with an alcoholic solution of ferric chloride, a deep blue color.

Acetosyringone reacts with substituted hydrazine but not with $NaHSO_3$.

K. THE CHEMISTRY OF GUAIACOL AND PYROGALLOL 1,3-DIMETHYL ETHER

These compounds have been isolated from various wood tars; guaiacol from soft wood and hard wood tars, and pyrogallol 1,3-dimethyl ether from hard wood tars.

From the configuration of these compounds it can be seen that the hydrogen atom para to the free hydroxyl group, is active. Michael,70) in 1883, carried out considerable work on the condensation of phenols with aldehydes, and in his papers gives a good review of earlier work. The mechanism of this condensation has been explained by Michael as a probable aldol condensation followed by dehydration. In each case condensation was brought about by traces of acid (mineral or organic) or by traces of alkali. It is interesting in the light of recent views on the mode of formation of lignin to quote from the above paper:

"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.

DISCUSSION OF RESULTS

PART TWO A. GENERAL INTRODUCTION

Buckland, Tomlinson and Hibbert 58) have shown that acetovanillone can be isolated by the action of alkalis on waste sulphite liquor obtained from soft woods. Since the waste sulphite liquor used by these authors was a commercial by-product obtained by an acid sulphite cook of conifers, it was desirable to determine whether acetovanillone formation resulted from "resin decomposition" or is a direct fission product of lignin.

Consequently, special precautions were observed, such as a pre-extraction of the sulphite liquor with the identical solvent (benzene) prior to isolation of the acetovanillone, thus eliminating the possibility of formation of the latter from resins, etc.

Finally, it was necessary to treat a purified derivative of lignin sulphonic acid with alkali, and to isolate the acetovanillone as a degradation product. A satisfactory identification of acetovanillone from resin-free soft wood and from a purified potassium lignin sulphonate could thus be taken as very good evidence, not only of its origin, but also that other aromatic substances were also lignin degradation products, both in the case of hard and soft woods.

Buckland, Tomlinson and Hibbert 58) also reported the isolation of volatile phenols from waste sulphite liquor by their alkaline treatment. It was of interest to investigate this volatile fraction further, to establish the identity of its constituents, and to determine whether this fraction was present when a sulphite liquor from a bisulphite cook of resin-free wood was treated with alkali.

B. ACETOVANILLONE AS A LIGNIN DEGRADATION PRODUCT

The soft wood used in this investigation was a sample of black spruce. This was selected since the pulpwood treated by Buckland, Tomlinson and Hibbert 58) consisted of a mixture of approximately 75% spruce and 25% balsam.

The wood used was a mixture of heart wood and sap wood. It was ground in a Wiley mill fitted with a 1 mm. punched brass screen. As a result, the wood-meal was fine enough that it could all be passed through a 20 mesh screen. In order to free the wood of resins, fats, waxes and tannins, a process was adopted of continuous extraction with organic solvents and finally extraction with water. The time of contact with the extractants used was sufficient to remove all extractable material.

The process of sulphite cooking was modified to some extent, from the process in use in the industry. Sodium bisulphite was used in place of calcium bisulphite, and the time of preheating the wood-meal with the sulphite liquor was decreased. This was possible since the time required for penetration of the wood-meal is less than for wood chips, and the wood to liquor ratio was decreased in order to secure a higher concentration of sodium lignin sulphonate.

In respect to concentration of available and combined SO_2, time and temperature of cook, the process was much the same as the industrial process. The charge was removed from the digester and the pulp was filtered, washed well with water and air-dried. The washings were added to the filtrate. At this point it was deemed unnecessary to separate the pure lignin sulphonic acid. It was found that extraction with benzene removed a negligible amount of material,(less than 5 mgms. from three litres of sulphite liquor), so that no non-lignin material was present. Carbohydrate materials and polysaccharides are insoluble in benzene and thus are not removed.

Following this, the required amount of sodium hydroxide was added to the clear sulphite liquor and the lignin sulphonic acids decomposed by the method of Buckland, Tomlinson and Hibbert 58), following carefully their conditions for alkalinity, time and temperature, and the reaction product then extracted with benzene, and the vanillin removed by extraction of the latter with aqueous sodium bisulphite. After washing with water, the benzene solution was evaporated leaving a light brown viscous oil containing some crystalline material. This was fractionated by a combined distillation and sublimation technique. On distillation under reduced pressure, a volatile oil distilled from the mixture at a temperature below 100°C.

(7 mm. pressure). As soon as the bath temperature reached 120°C. a colorless liquid distilled over, which crystallized in the side arm of the distilling flask. At this point the capillary tube in the distillation apparatus was changed and it was replaced by a cold finger, on which the liquid then deposited as a crystalline sublimate. This was identified by melting point and mixed melting point with synthetic compound, as acetovanillone. Further confirmation was found in the identity of the semi-carbazones.

C. ACETOVANILLONE AS A DEGRADATION PRODUCT OF PURIFIED POTASSIUM α-LIGNIN SULPHONATE

From the preceding it is evident that acetovanillone is a degradation product of lignin sulphonic acid, and to prove this definitely a sample of a pure potassium salt of α-lignin sulphonic acid, prepared and purified by Dr. Gray King 71), by a process of quinoline precipitation and electrodialysis, was subjected to the same treatment.

Acetovanillone was obtained in small quantity and identified by melting point, and mixed melting point.

Its isolation from 4.5 grams of potassium lignin sulphonate required very careful work and about one half of the anticipated material formed was isolated in the crude state. Purification was accomplished by micro methods of sublimation and crystallization.

D. BASIS OF CALCULATION OF YIELDS

In order to determine the amount of lignin in solution, it was necessary to know the amount of lignin present in the original wood, the original weight of wood, the amount of lignin remaining in the pulp and the weight of the pulp remaining after the sulphite cook.

The yield of vanillin was determined by precipitation of this compound as the m-nitrobenzoyl hydrazone. The yield of acetovanillone was taken as the weight of pure material isolated.

Thus calculations could be made as to the amount of lignin in solution and the amount of vanillin and acetovanillone secured from this lignin. (See Experimental, page 223.)

The yield of vanillin was the same as that secured by Tomlinson and Hibbert 14), i.e. 6 - 7% on the basis of lignin. The yield of acetovanillone was of the same order as that reported by Buckland, Tomlinson and Hibbert 58). Their acetovanillone to vanillin ratio was 1:20, whereas that found by the author was 1:24. This is good agreement when it is considered that the latter work was done on the micro scale.

E. IDENTITY OF ACETOSYRINGONE, GUAIACOL AND PYROGALLOL 1,3-DIMETHYL ETHER AS LIGNIN DEGRADATION PRODUCTS

Since it is possible to isolate acetovanillone not only from resin-free woods, but also from a pure potassium salt of an α-lignin sulphonic acid, the conclusion can be drawn, that this is a true degradation product of lignin sulphonic acid from soft woods, and the same remarks also apply to the newly-discovered fission products, namely; guaiacol from spruce lignin sulphonic acid, and acetosyringone, guaiacol and pyrogallol 1,3-dimethyl ether from birch lignin sulphonic acid.

F. ACETOSYRINGONE AS A DEGRADATION PRODUCT OF BIRCH LIGNIN SULPHONIC ACID

Since vanillin and acetovanillone are true degradation products of spruce lignin sulphonic acid, and vanillin and syringic aldehydes of lignin sulphonic acids from hard woods, it was of interest to determine whether acetovanillone and acetosyringone are also degradation products of the latter.

Alkali treatment of sulphite liquor from resin-free yellow birch, yielded only acetosyringone and no acetovanillone. A methoxyl determination on the crude sublimate, which it was expected would contain both acetovanillone and acetosyringone showed 27.6% methoxyl (acetovanillone OCH_3, 18.6; acetosyringone, 31.6%). From this high methoxyl content, the probable absence of acetovanillone was predictable and confirmed by an almost quantitative recovery of pure acetosyringone from the crude product.

The yield of acetosyringone was much higher (calculated on the basis of lignin) than the yield of acetovanillone from spruce. It was identified by melting point, methoxyl analysis and mixed melting point with synthetic acetosyringone prepared from pyrogallol dimethyl ether (2,3-dimethoxy, 1-hydroxybenzene). Further proof was secured by preparation of the p-nitrophenylhydrazone and melting point, methoxyl analysis and mixed melting point of this derivative with the corresponding derivative of synthetic acetosyringone.

G. GUAIACOL FROM SOFT WOOD WASTE SULPHITE LIQUOR

Buckland, Tomlinson and Hibbert 58) reported the existence of volatile phenolic materials in the benzene extract from an alkali cook of waste sulphite liquor.

It was of interest to determine whether this phenolic material consisted of one material or of a mixture of materials. To this end a sample was secured of the vanillin-free benzene extract containing not only this material, but also acetovanillone, etc.

Preliminary distillation, and fractionation of this phenolic material, indicated that it was guaiacol, contaminated by very small amounts of other material. The guaiacol was purified by fractionation, and identified by melting point, methoxyl analysis and the comparison of the p-nitrobenzoyl and p-toluenesulphonyl esters with those secured from an authentic sample of guaiacol.

H. GUAIACOL AS A SPRUCE LIGNIN DEGRADATION PRODUCT

The volatile material secured from treatment of resin-free black spruce with sulphite liquor, subsequent alkali treatment, removal of vanillin, extraction and distillation was identified as guaiacol.

The yield was very small, 0.07% on the basis of lignin. The identification of this material even in such low yields however, leads to interesting theoretical conclusions as shown later.

I. GUAIACOL AND PYROGALLOL 1,3-DIMETHYL ETHER AS FISSION PRODUCTS OBTAINED FROM HARDWOOD SULPHITE LIQUOR

Hardwood waste sulphite liquor, on treatment with alkali, yields in addition to vanillin and syringic aldehyde, acetosyringone, guaiacol and pyrogallol 1,3-dimethyl ether.

Acetosyringone was identified by comparison with the synthetic material. Identification of both guaiacol and pyrogallol 1,3-dimethyl ether was accomplished by conversion into the corresponding p-nitrobenzoyl esters, analyses and comparison with authentic samples.

Further confirmation of the pyrogallol 1,3-dimethyl ether was secured by preparation of its cörulignon oxidation product 73) and comparison with authentic material.

Yields are reported, but are not significant, since the pulpwood used was a mixture; the concentration of the liquor was not known, and the quantity of materials secured was small.

J. GUAIACOL AND PYROGALLOL 1,3-DIMETHYL ETHER AS DEGRADATION PRODUCTS OF BIRCH LIGNIN SULPHONIC ACID

Guaiacol was identified as a degradation product of resin-free birch sulphite liquor by preparation of the p-nitrobenzoyl ester and comparison with an authentic sample.

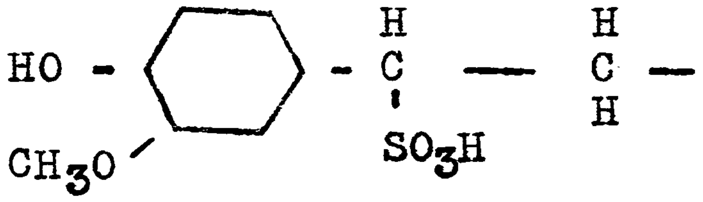
Pyrogallol 1,3-dimethyl ether was identified by comparison with an authentic sample, and by comparison of the p-nitrobenzoyl ester and corulignin oxidation products, with those secured from an authentic sample.

On the same basis as acetosyringone, the two products secured from resin-free birch may be considered as lignin degradation products. Isolation of these in as small yields as reported seems significant.

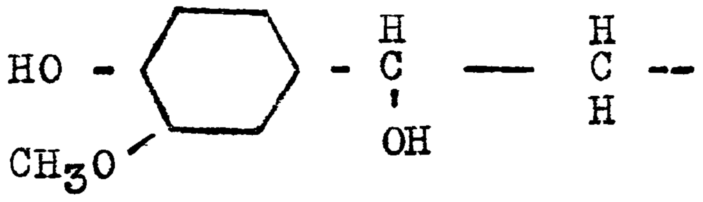
K. THEORY OF THE FORMATION OF ACETOVANILLONE AND GUAIACOL FROM LIGNIN SULPHONIC ACIDS

Vanillin has been isolated as a degradation product of lignin sulphonic acid, in a yield of 6 - 7% 14) by Hibbert and Tomlinson, who believe it is formed in the following manner:

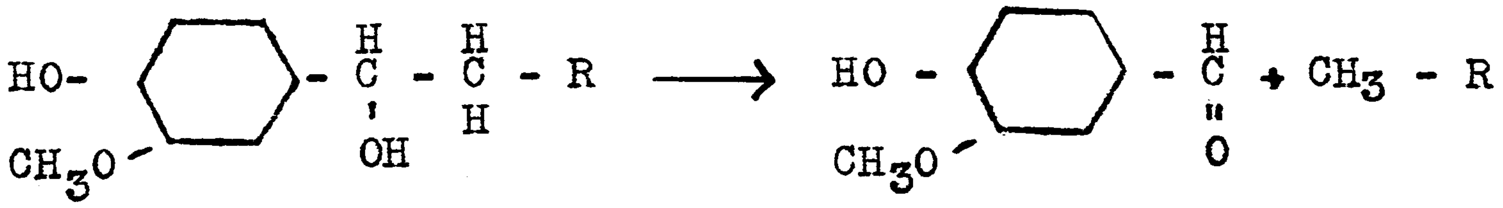
Sulphonation of lignin leads to the formation of a group of the following constitution;



in which the sulphonic acid group is present as a substituent on a carbon atom α to the benzene nucleus. Treatment of this product with sodium hydroxide results, first in replacement of the sulphonic group with a hydroxyl group giving:



which then, as the result of a reversed aldol condensation gives vanillin in the following manner:

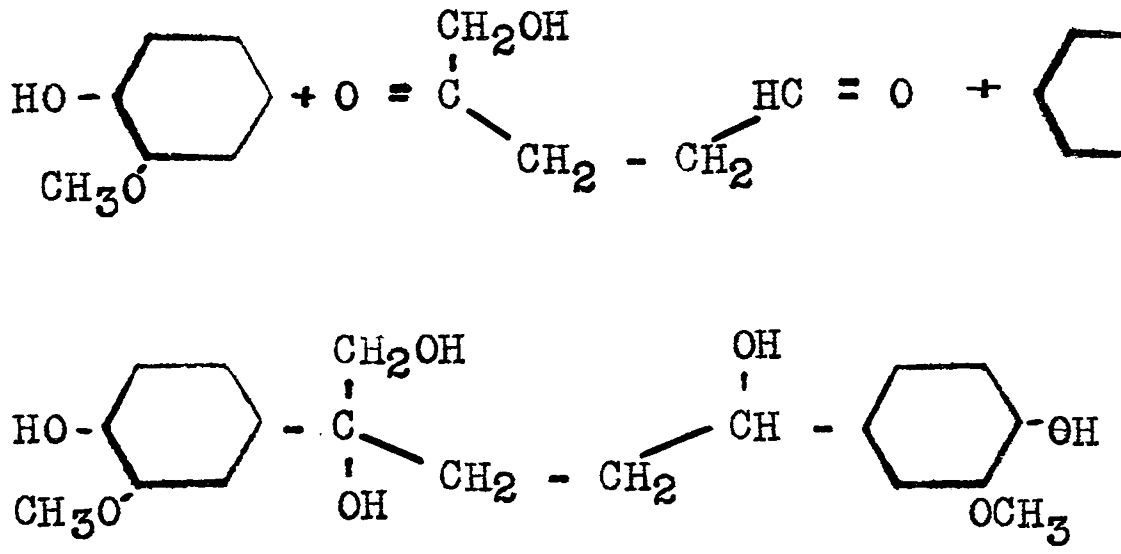


This conclusion has been accepted by other workers in the field of lignin chemistry, and as already shown, has necessitated the revisal by Freudenberg of his earlier views in which sulphonation was assumed to take place in the aromatic nucleus. His later theory of a chain condensation occurring with the α-carbon atom of the side chain is likewise irreconcilable with this work.

There is not, in Freudenberg's latest theoretical formula for lignin, any group which can possibly give acetovanillone by treatment of the lignin sulphonic acid with alkali.

The recent discoveries in these laboratories by Hibbert and co-workers, of a number of aromatic fission products of lignin sulphonic acids, have thrown new light on the structure of lignin.

Thus the isolation of vanillin 14) and acetovanillone 59) by the alkali fission of lignin sulphonic acids from conifers (soft woods); and of vanillin 14); syringic aldehyde 14); and acetosyringone 59), from sulphonic acids from hard woods, led Hibbert, recently, to formulate a new theory of the structure of lignin 72). This, in brief, assumes that lignin is synthesized in the plant as the result of nuclear condensations between guaiacol (in the case of soft woods) and a condensation product of fructose. The identity of the latter is uncertain but is regarded as being one or more of a number of biochemically equivalent substances, which in their final form, give rise to reactions, based on their functioning in a large measure, as 2-keto-pentanal groupings. Thus hydroxy-levulinaldehyde can condense with two molecules of guaiacol as shown below, to give, what Hibbert regards as a simple building unit of the lignin complex:



I.

It is known that glucose, fructose and mannose are all formed in the course of plant synthesis and, in the light of the well-known Lobry de Bruyn equilibrium, in slightly alkaline medium are readily transformed into one another.

The glucose is transformed further into cellulose, and the mannose into mannan, while the fructose disappears as such, due to its enormous reactivity as compared with the other two hexoses. It is remarkable that this property of fructose should have been so almost entirely overlooked by the plant chemist and botanist. The only marked exception to this statement is to be found in the research of Wislicenus 74) carried out on the analysis of plant sap of different species of wood, in which he showed that the hexose which underwent the greatest fluctuation in concentration at the time of maximum plant metabolism (Spring-time) was fructose. From his analyses of the sap, in particular the sugar content, and of the behaviour of same to chemical agents, he was led to conclude that the progenitor of isolated lignin was to be found in hydroxy-methyl-furfural itself, a condensation product of fructose. He believed that lignin was not to be regarded as a single definite substance, but rather, was to be considered as "The sum of all colloidally dissolved substances of high molecular weight which are precipitated from the cambial sap by adsorption on the surface of cellulose fibers".

Apart from this statement, little or no further experimental work has been carried out to establish a relationship between fructose and lignin.

This question was taken up some three years ago in these laboratories, by the initiation of researches dealing with the properties of fructose decomposition products.

It was shown by Trister 75) that high yields of hydroxy-methyl-furfural could be obtained from fructose by mild acid hydrolysis and that this product readily underwent, under the influence of catalysts such as $SnCl_4$, concentrated H_2SO_4, etc., a series of condensation reactions to give "fructose humic acids" having in many ways, similar properties to lignin.

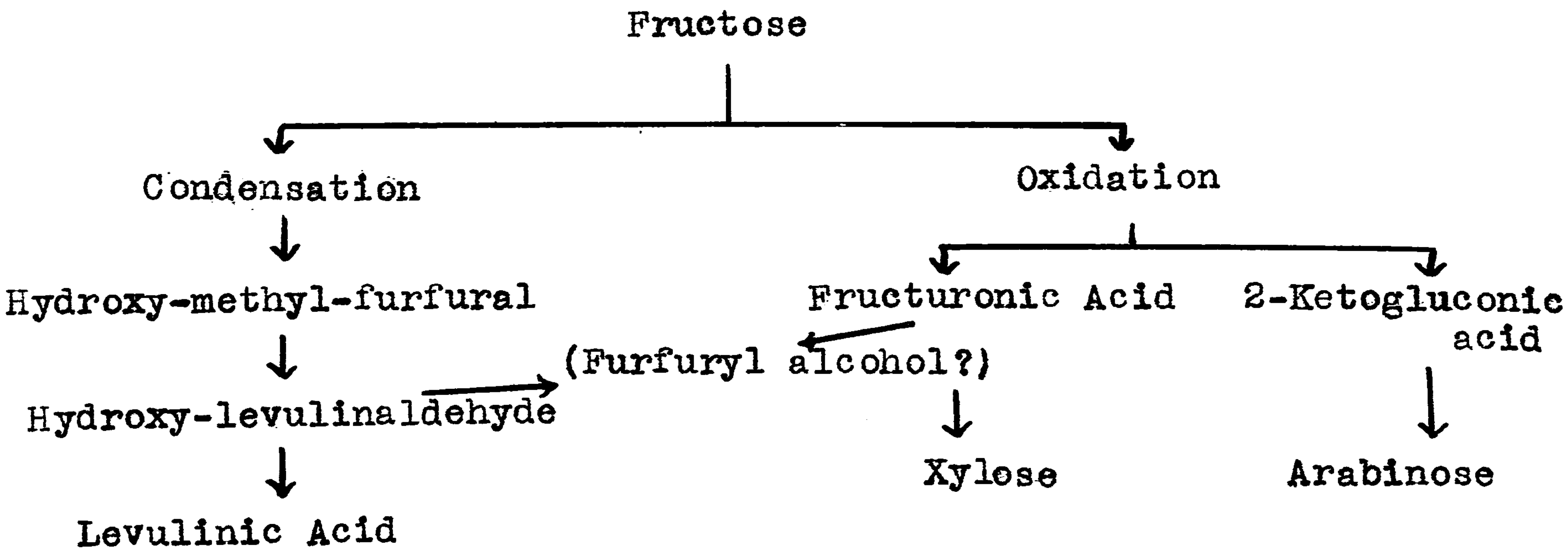
Work was then directed towards the mechanism of the conversion of furfuryl alcohol into methyl levulinate, using, in preliminary experiments, furfuryl alcohol dissolved in a large excess of anhydrous methanol and a small amount of concentrated H_2SO_4 as catalyst. Trister was able to obtain a higher yield of γ-methoxy-levulin-aldehyde-dimethylal, than that found previously by Pummerer 76) while the amount of resin formation was lowered very appreciably from 30 to 13%.

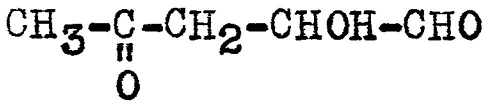
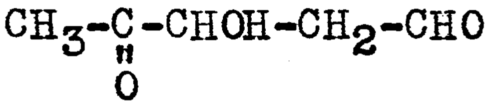
This preliminary investigation threw no light, however, on the mechanism involved in the change although indicating clearly the ease of ring opening.

The problem was undertaken, at this stage, by the writer, and the results of his investigations are given in Part One.

The fact that fructose disappears in the course of plant synthesis implies that it has been transformed into other products, and this being the case, the question arises as to the nature of the latter.

It is evident that fructose can readily pass into hydroxy-methyl-furfural, and also, presumably into furfuryl alcohol. Of the two uronic acids derivable from fructose, namely 2-keto-gluconic acid and fructuronic acid, only the former has been isolated in the pure state. Both are very reactive substances, far more so than other hexuronic acids. The changes shown below, represent, therefore, relatively simple changes when viewed from the chemical standpoint:



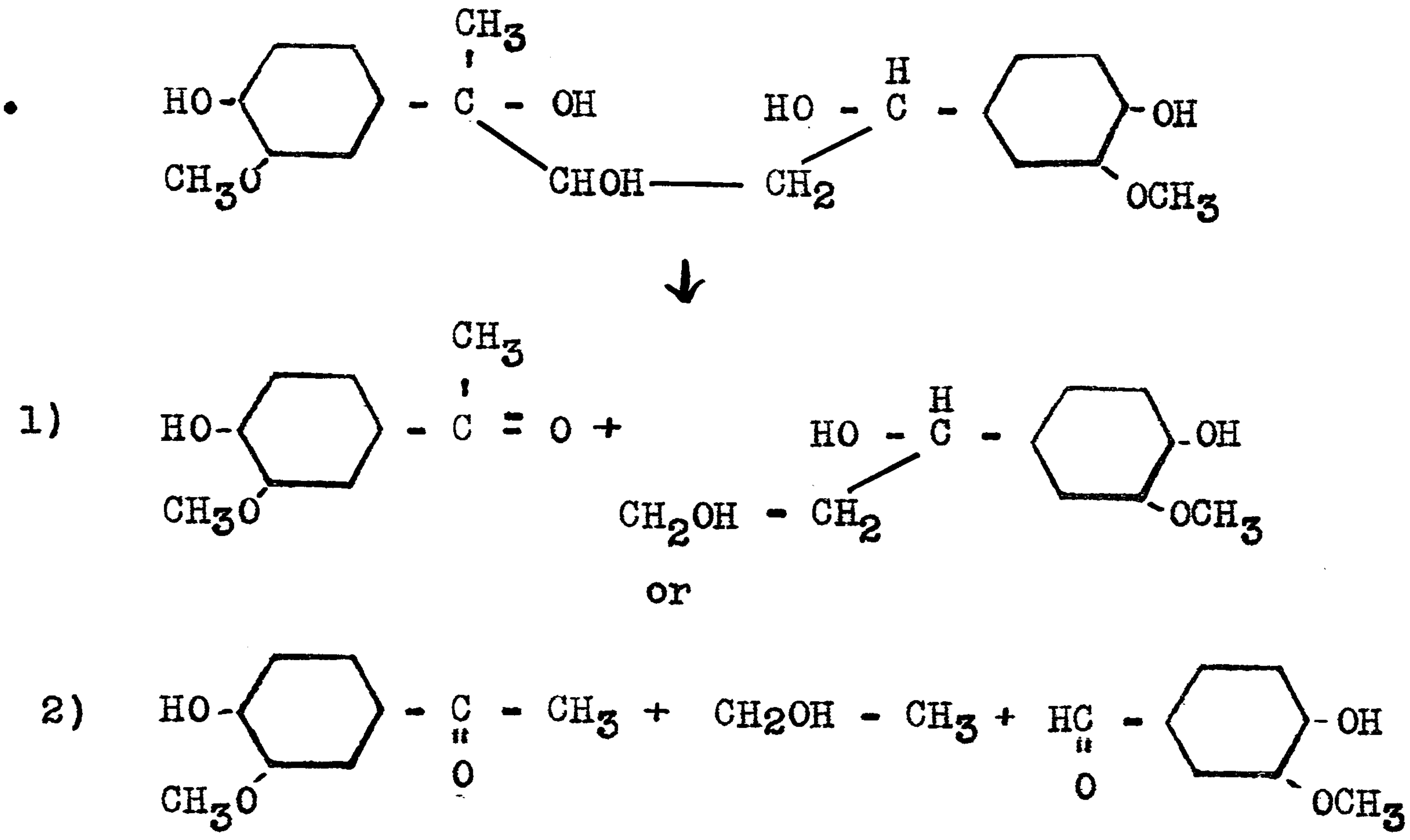
If the assumption is made that plant enzymes are capable of transforming fructose into such very reactive substances as the biochemically equivalent products, namely furfuryl alcohol; δ-methoxy-levulinaldehyde; levulinic acid; angelica lactone; and the isomeric 2-keto-pentanals, namely,  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CHOH-CHO$ and  $CH_3-\underset{\underset{O}{\|}}{C}-CHOH-CH_2-CHO$ it is apparent that nuclear condensation could readily occur with phenols, assuming such were present in the plant sap.

Baeyer 77) was the first to show that phenols readily yield resinous condensation products with aldehydes under the influence of strong mineral acids, while some years later Michael 70) found that these changes readily took place under very mild conditions, namely at room temperature, under the influence of dilute acids. His results led Michael to conclude, some forty-five years ago "It is 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".

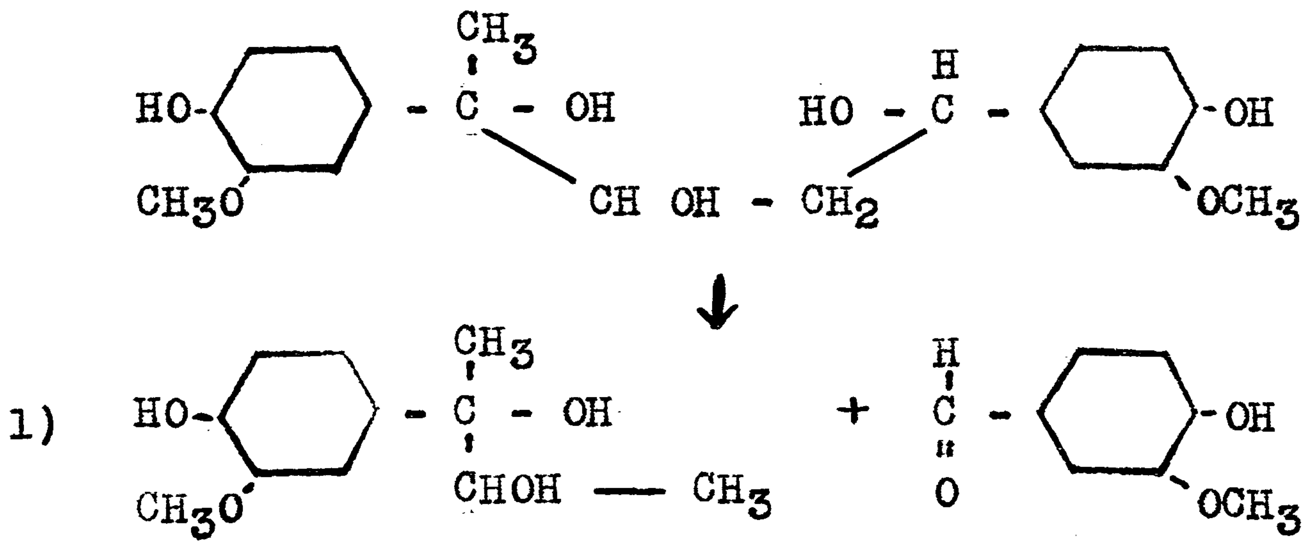
According to the recent views of Hibbert, lignin is synthesized in the plant by condensation reaction between a phenol and fructose, or one or other of its condensation products. The phenol is assumed to be guaiacol in the case of soft woods, and a mixture of guaiacol and pyrogallol 1,3-dimethyl ether in the case of the hard woods.

Typical instances of such condensations are those shown below; under (A) and (B):

A.



B.



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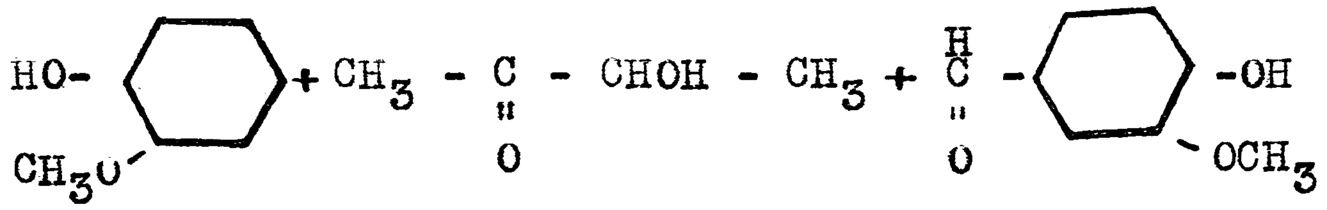
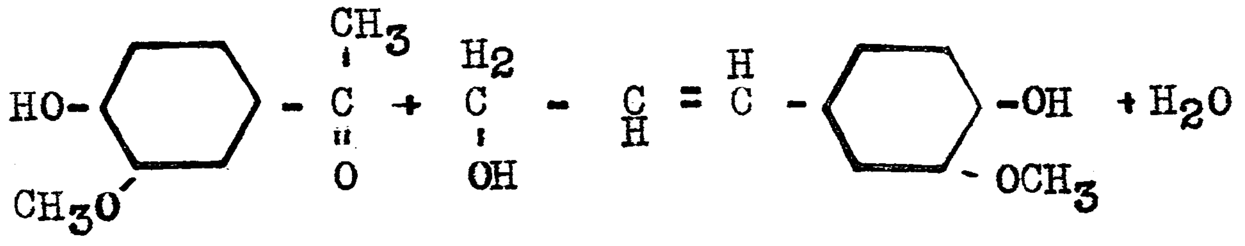
2)



or

3)

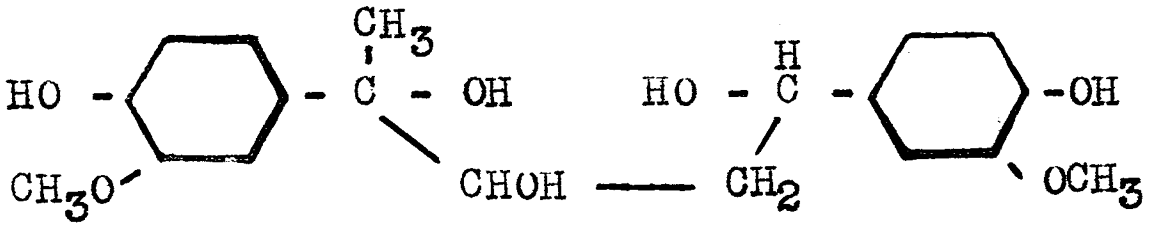


Taking model A as an example, it can be seen that this could readily undergo fission, as indicated, into acetovanillone, ethanol and vanillin. Similarly B, on chain fission could yield guaiacol; 2-hydroxy-ethyl-methyl-ketone, vanillin, acetovanillone and coniferyl alcohol, as indicated under 1, 2 and 3. In fact, it seems highly probable that this alcohol may actually be formed in this manner in the course of plant synthesis, and is not, as assumed by Klason and Freudenberg, the source of lignin formation.

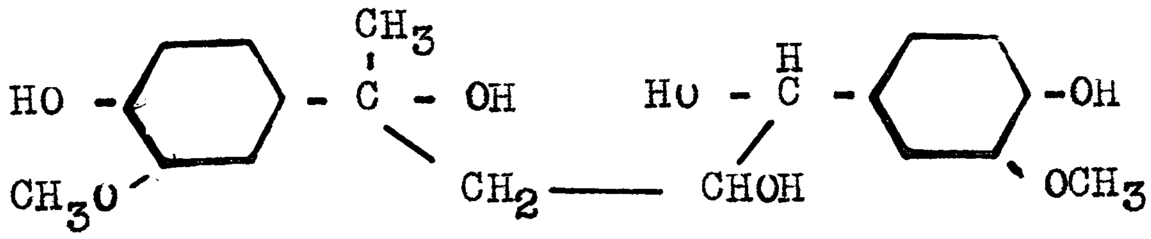
The discovery by the writer, that lignin sulphonic acids from soft wood, on alkali fission yield not only vanillin 14), but also guaiacol and acetovanillone, while those from hard woods yield, in addition to syringic aldehyde 14), also acetosyringone and pyrogallol 1,3-dimethyl ether lends strong support to the views of Hibbert on the structure of lignin.

In the writer's opinion it seems highly probable that the carbohydrate intermediate postulated, is a direct transformation product (either cyclic or open chain) of furfuryl alcohol.

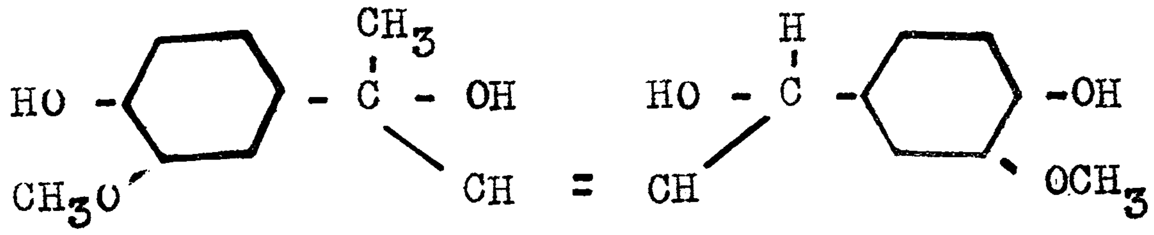
The results obtained in this investigation can readily be explained on the basis of alkali fission of the products (in soft woods) such as:



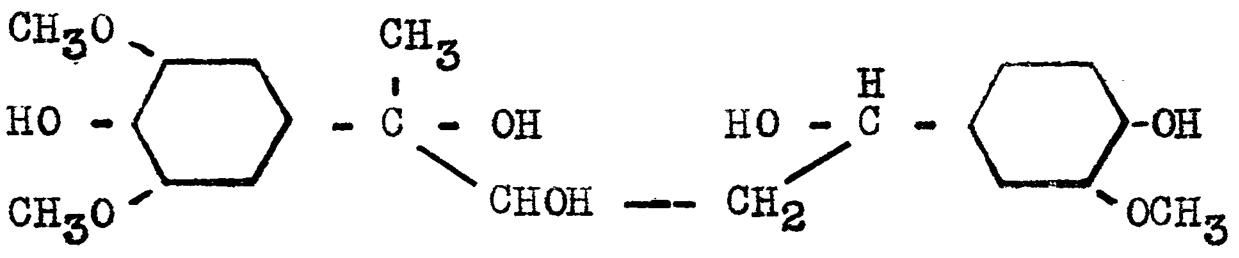
or



or



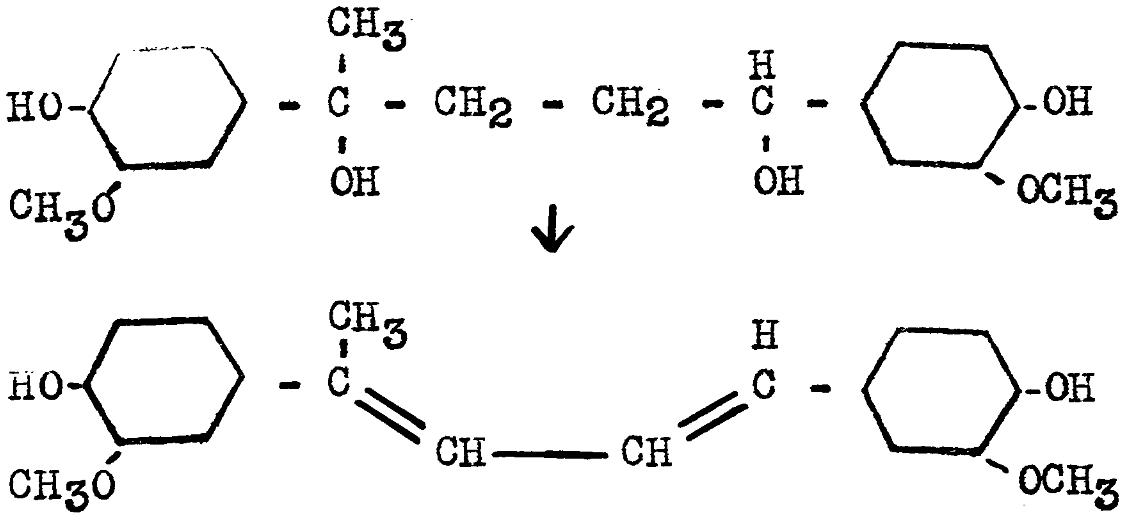
In the case of hard woods some of the guaiacyl radicals, are replaced by the syringyl radical, e.g.:



According to this new theory of plant synthesis, lignin as present in the woody tissue, is a relatively simple substance, a mixture of nuclear condensation products of a phenol (guaiacol, pyrogallol 1,3-dimethyl ether) with one or other carbonyl-containing fructose condensation product . The latter represent extraordinarily reactive substances, readily undergoing condensation and polymerization reactions under the influence of very mild chemical reagents, and thus yielding extracted lignins of a much more highly complex character.

An example of this is shown below:(C):

C.



which could polymerize to give much more complex products. A lignin aggregate consisting of the units indicated, would give all of the typical lignin reactions and would yield all of the known lignin degradation products with the exception of acetone superoxide (obtained as an ozonization product).

It was interesting to determine whether a condensation was possible between guaiacol and furfuryl alcohol. By simple treatment of guaiacol with water-soluble furfuryl alcohol in the presence of a trace of mineral acid, there was secured a lignin-like condensation product. This contained methoxyl to the extent of about 5% indicating about 18% of aromatic nuclei in the condensation product. No further experimental work was carried out on this condensation, on account of lack of time. Such reactions as the effect of sulphite liquor, oxidizing agents, sodium hydroxide, etc., would serve to demonstrate the similarity between these condensation products and preparations from "proto lignin".

PART TWO. SUMMARY

1. Acetovanillone and guaiacol have been identified as alkali fission products of spruce lignin sulphonic acid.

2. Acetosyringone, guaiacol and pyrogallol 1,3-dimethyl ether have been identified similarly as alkali fission products of birch lignin sulphonic acids.

3. On the basis of these results the Freudenberg theory of lignin formation is shown to be untenable.

4. The formation of the above products finds a satisfactory explanation in the light of the new theory of Hibbert, on the nature of plant synthesis, and the formation of lignin as the result of condensation reactions between a phenol (guaiacol, pyrogallol 1,3-dimethyl ether) and one or other condensation product from fructose.

5. The structures proposed in this thesis, and arising out of these conceptions, are found capable of explaining in a remarkable way, a large number of the reactions of lignin and lignin preparations. Those referred to in this thesis are merely degradation reactions for products of this type.

6. A synthetic lignin-like product was obtained by condensing guaiacol with furfuryl alcohol.

7. The product regarded as dimethoxy phenyl acetic acid, isolated by Phillips and Goss from the pyrolysis products obtained from corn cob lignin was, most probably, acetosyringone.

PART TWO. EXPERIMENTAL

A. History of Black Spruce Used in This Investigation

The soft wood used in this investigation was a seven inch Black Spruce log, about sixty-five years of age. It was cut for the Forest Products Laboratory of Canada and was stored in their stockroom for five years. The log was very dry and cracked.

History of Yellow Birch Used in This Investigation

The hard wood used in this investigation was a fourteen inch Yellow Birch log, of about one hundred and twenty-five years of age. It was secured as a "wet log" from the Howard Smith Paper Mills Limited, at Windsor Falls, Quebec.

History of Hard Wood Waste Sulphite Liquor

The sulphite liquor used for the extraction of guaiacol and pyrogallol 1,3-dimethyl ether was a semi-concentrated material obtained from a mixture of hard woods (maple, birch and beech) and kindly supplied by the Brown Company, Rumford Falls, Maine.

History of Material from Waste Sulphite Liquor

The material used for the investigation on isolation of acetovanillone and guaiacol from waste sulphite liquor was secured from the vanillin plant of Howard Smith Chemicals Limited at Cornwall, Ontario. This company was kind enough to supply fifty gallons of benzene solution, which had been freed of vanillin by their commercial process.

B. Isolation of Acetovanillone from Black Spruce

Preparation of Wood

A black spruce log was stripped of its bark, and the knots removed from it by means of a drill. The log was then shaved by means of a mechanical planer, and the whole of the shavings passed through a Wiley mill fitted with a one millimeter screen.

The resulting woodmeal was placed in a continuous extractor and first extracted with a 1:1 ethanol-benzene mixture for forty-eight hours. This was followed by a continuous extraction with ethanol for thirty-six hours and finally with water for thirty-six hours. The meal was removed, dried by centrifuging, washed with methanol and air-dried, giving a woodmeal free of resins, tannins, waxes, etc.

Preparation of Sulphite Liquor

To thirty litres of water, there was added 450 g. of sodium hydroxide (technical) and gaseous sulphur dioxide then passed into the resulting solution, this being titrated from time to time for combined and total sulphur dioxide.

Analysis of Final Liquor

Combined SO_2 was determined by acidimetric methods using 0.443 N. NaOH and different indicators and 1 cc. of sulphite liquor.

Indicator phenolphthalein	NaOH	=	1.06 cc.
" methyl orange	NaOH	=	0.20 cc.
Combined SO_2	NaOH	=	0.86 cc.
% SO_2 combined			1.22

The total SO_2 was determined by the iodometric method using 0.1 N, iodine solution.

Volume of I_2 consumed	18.38 cc.
% SO_2 total	5.90

Preparation of "Spruce Lignin Sulphonic Acid"

Thirteen hundred and fifty grams of air dried extracted wood meal was placed in a stainless steel autoclave * and to this was added 11.4 litres of the sulphite liquor prepared above. The autoclave was sealed and heated by means of an oil bath. The time of the cook was eight hours at a temperature of approximately 125°C.

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* The author wishes to express his thanks to the Howard Smith Chemicals Ltd., for the use of their laboratory and equipment.

At the end of this time the pressure was released and the contents allowed to cool overnight. The pulp slurry was removed, filtered and washed with water yielding 810 grams of oven-dried product. Two litres of the resulting filtrate on extracting six times with benzene yielded no extractable material. The resulting liquor was used for the next procedure.

Sodium Hydroxide Decomposition of Sulphite Liquor

The liquor from the above process amounted to 9.0 litres, and to this there was added 810 grams of sodium hydroxide (technical). The solution was then placed in a stainless steel autoclave, and heated for six hours at 150 - 155°C. (58 lbs. pressure). The autoclave was allowed to cool overnight. The liquor from this process amounted to 9.5 litres.

Removal of Vanillin

Three litres of the alkali treated liquor was neutralized carefully with concentrated HCl to pH, 8.4 (colorimetric). A gray colored flocculent precipitate immediately settled out. The mixture was heated to 85°C. and the temperature was maintained there for 1 hour. The amorphous precipitate was removed by filtration and the resulting solution acidified carefully to pH 7.0. The liquor was then placed in a 3 litre continuous extractor, and extracted with benzene continuously for 5 days.

The benzene extract (500 cc.) was concentrated under reduced pressure to 150 cc. It was then freed from vanillin, by shaking for one hour with two 150 cc. portions of 20% sodium bisulphite (aqueous). The vanillin was removed by this process as a water-soluble bisulphite addition compound.

Analysis for Vanillin

The sodium bisulphite solution so obtained was acidified and an aliquot part used for a quantitative determination (1:45.4 of the original volume),

The vanillin was precipitated as the m-nitrobenzoyl hydrazone, by treatment, (first buffering the acid solution with sodium acetate and then heating for six hours at 60°C.) with m-nitrobenzoyl hydrazide.

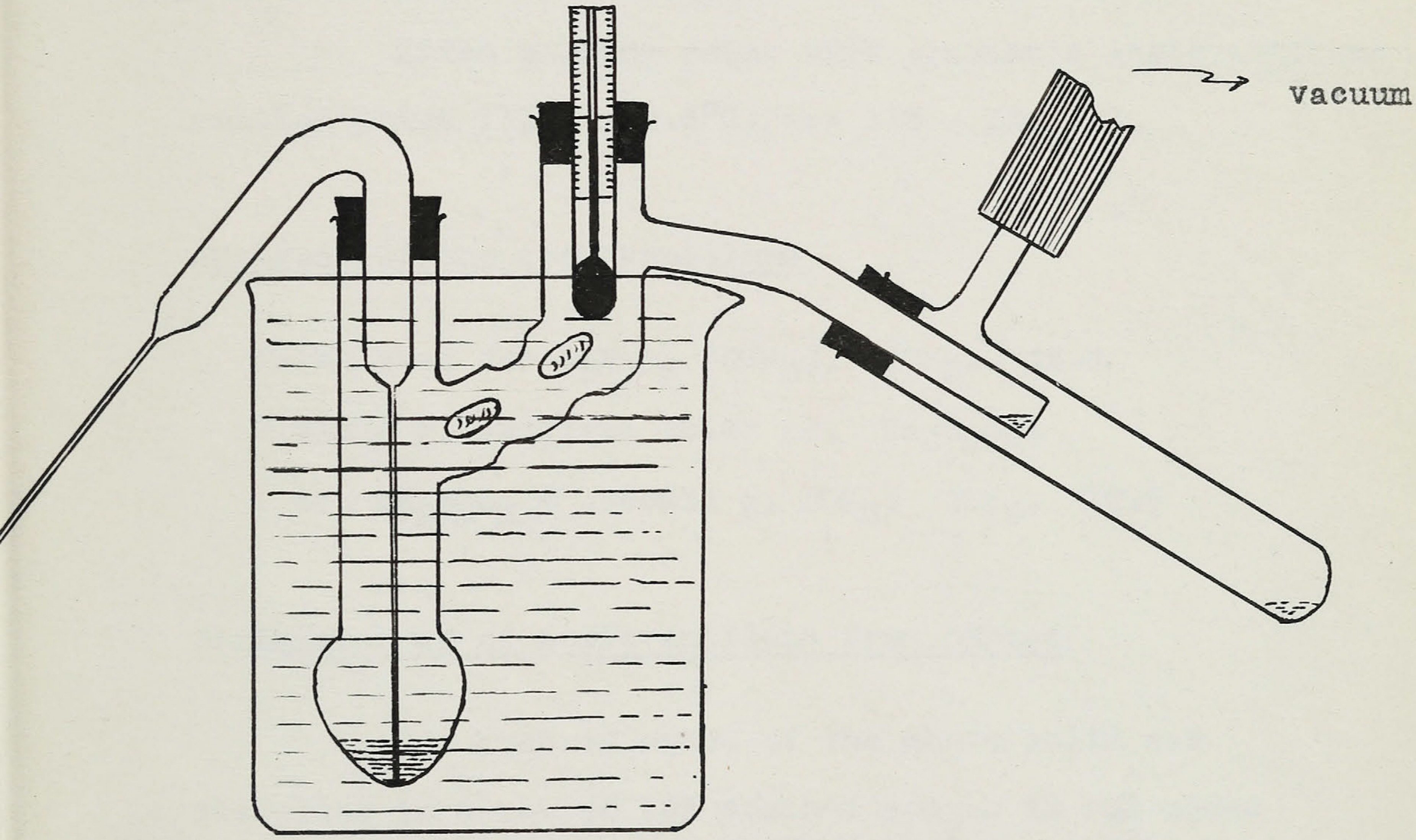
Weight of hydrazone found	0.3256 g.
Total weight of hydrazone (x 45.5)	14.8148 g.
Weight of vanillin (14.815 x .4829)	7.154 g.

Isolation of Acetovanillone

The bisulphite-extracted benzene solution was dried over anhydrous magnesium sulphate, and the benzene removed under reduced pressure giving 900 mgms. of a residual dark viscous material. This was transferred to a micro-distillation set-up and distilled under reduced pressure.

MICRO DISTILLATION APPARATUS

Scale 1 : 1



About 50 - 60 mgms. of a phenolic oil distilled over into the receiver below 100°C. (7 mm. pressure). As the bath temperature reached 130°C. the distillate began to solidify in the side arm. The capillary tube was then removed and a cold finger inserted. 300 mgms. of a crystalline solid, melting point 105-108^{o}C.,was isolated at this temperature. The bath was then raised to 200^{o}C. but no further distillate or sublimate was obtained. The residue in the flask amounted to 450 mgms.

C. Identification of Acetovanillone

The crystalline material separating on the cold finger in the preceding run was recrystallized from benzene-petroleum ether twice giving colorless crystals, melting point 112 - 114.5°C. It was then recrystallized from ligroin yielding colorless crystals, melting point 113 - 114.5°C.

Mixed melting point with synthetic acetovanillone , melting point 113 - 114.5°C.,was 113 - 114.5°C.

Analysis of the Acetovanillone

Calculated for $C_8H_7O_2$ (OCH_3); OCH_3, 18.6

0.91370 g. required 10.85 cc. $Na_2S_2O_3$;

1 cc. $Na_2S_2O_3$ = .000234 g. OCH_3; OCH_3, 18.5

Semicarbazone of Acetovanillone from Spruce

One hundred mgms. of the above solid was dissolved in 4 cc. of 50% ethanol and to it was added 70 mgms. of semicarbazide hydrochloride and 0.3 cc. of 25% sodium acetate solution.

After forty-eight hours there were obtained 50 mgms. of a crystalline solid, which on recrystallization from 75% methanol (after decolorizing with charcoal) gave colorless crystals, melting point 165.5 - 166.5°C.

Mixed melting point with the semicarbazone of synthetic acetovanillone, melting point 164.5 - 165.5°C., was 165.5 - 166.5°C.

Analysis of Acetovanillone Semicarbazone *

Calculated for $C_9H_{10}N_3O_2$ (OCH_3): OCH_3, 13.9

1.676 mgms. required 4.87 cc., 0.00946N $Na_2S_2O_3$; OCH_3, 13.90

0.981 mgms. required 2.78 cc., 0.00946N $Na_2S_2O_3$; OCH_3, 13.86

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* The author wishes to thank Mr. Cyril Marks for the micromethoxyl analyses.

D. Calculation of Yields

Yields of Acetovanillone and Vanillin

Original weight of wood (air dried)	=	1350 g.
Lignin content of wood (air dried)* 27.6%	=	373 g.
Weight of pulp (ovendried)	=	810 g.
Lignin content of pulp (ovendried)** 2.6%	=	21 g.
Weight of lignin in solution	=	352 g.
Total volume of solution	=	9.5 l.
Volume of solution used	=	3.0 l.
Weight of lignin used	=	111 g.
Weight of vanillin - see page 218	=	7.154 g.
% Vanillin yield (lignin basis)	=	6.40%
Weight of acetovanillone	=	300 mgms.
% Acetovanillone yield (lignin basis)	=	0.27%
Acetovanillone to Vanillin ratio was		1:24

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* This value for the lignin content of resin-free, air-dried spruce was supplied by Mr. L. Hawkins.

** This value was determined by the standard 72% sulphuric acid method employed in this laboratory:

2.1488 g. of pulp gave	0.0565 g. of lignin
Lignin content was	2.6%

E. Isolation and Identification of Acetovanillone from Potassium Lignin Sulphonate

A sample of the potassium salt of α-lignin sulphonic acid prepared by Dr. G. King [71) was used in this experiment.

Analysis for OCH_3

1.628 mgms. required 4.11 cc. of .00946N $Na_2S_2O_3$; OCH_3, 12.3
1.322 mgms. required 3.31 cc. of .00946N $Na_2S_2O_3$; OCH_3, 12.2

Analysis for S

.32184 g. gave .1240 g. $BaSO_4$; S, 5.3

Action of Sodium Hydroxide on Potassium Lignin Sulphonate

To a solution of 36 g. sodium hydroxide in 150 cc. of water, was added 4.5 g. of the potassium salt of α-lignin sulphonic acid. The resulting solution was heated under reflux, in a nitrogen atmosphere for 12 hours. The mixture was then allowed to cool and to it was added concentrated sulphuric acid to give a solution of pH 8.4. A brown flocculent mass was precipitated. The mixture was heated to 85°C. for one hour and the suspended material removed by filtration. The resulting yellowish colored filtrate was then acidified with concentrated sulphuric acid to a pH of 7.0. The solution (200 cc.) was placed in a continuous extractor and extracted with benzene continuously for four days.

Removal and Estimation of Vanillin

The benzene solution was concentrated under reduced pressure to 25 cc., shaken for 1 hour with 20 cc. of 20% sodium bisulphite solution and then for the same time interval with 15 cc. of bisulphite solution.

Estimation of Vanillin

This was carried out as already described.

Weight of m-nitrobenzoyl hydrazone	- 0.4265 g.
Weight of vanillin 0.4265 x .4828	- 0.2059 g.
% yield of vanillin basis potassium lignin sulphonate	- 4.6%

Isolation of Acetovanillone

The benzene solution after removal of the vanillin was dried over anhydrous magnesium sulphate and the benzene removed under reduced pressure. The resulting dark-brown viscous residue was transferred to a small side-arm test tube, a cold finger inserted, and the material distilled under reduced pressure, yielding about 10 mgms. of material on the cold finger. This consisted of some solid material and a liquid. The latter was removed by washing the cold finger rapidly with petroleum ether (30 - 50°C.) leaving about 3 mgms. of a crystalline solid.

Identification of Acetovanillone

The crystalline material so obtained was purified first by sublimation, and then by recrystallization from benzene-petroleum ether mixture to give colorless crystals, melting point 112 - 113°C.; mixed melting point with synthetic acetovanillone, melting point 113 - 114.5°C. was 113 - 114.5°C.

F. Isolation of Acetosyringone from Yellow Birch

(a) Preparation of Wood

A yellow birch log was stripped of its bark, chipped by hand and was ground in a Wiley Mill fitted with a one millimeter screen.

The resulting woodmeal was freed from resins, fats, waxes, etc., by the method already described for spruce wood.

(b) Sodium Bisulphite Treatment of Yellow Birch

The liquor used in the sodium bisulphite cook was identical with that used for Black Spruce, cf. Experimental, Section B, page 216.

Eleven hundred and fifty grams of the previously extracted wood was placed in a stainless steel autoclave and treated with 10 litres of acid sodium bisulphite cooking liquor. The charge was treated as in Experimental, Section B, page 216, to yield 640 g. of oven-dried pulp and 9 litres of clear liquor.

(c) Removal of Vanillin and Syringic Aldehydes

The liquor from the foregoing process amounted to 9 litres.

Three litres of this liquor was neutralized and extracted, following the procedure outlined for black spruce, Experimental Section B, page 216. The benzene solution was concentrated to 150 cc. under reduced pressure, and the combined aldehydes were removed by shaking for 1 hour with two 150 cc. portions of 20% sodium bisulphite solution.

(d) Analysis for Aldehydes

The two aldehydes in the sodium bisulphite solution were precipitated as the m-nitrobenzoyl hydrazones.

Weight of m-nitrobenzoyl hydrazones - 6.802 g.
Weight of combined aldehydes x 0.50 - 3.401 g.

(e) Isolation of Acetosyringone

The bisulphite extracted benzene solution was treated similarly to the black spruce.

The fractions obtained were as follows:

1. A volatile oil, b.p. 40-100°C. at 7 mm	100 mgms.
2. A crystalline sublimate, b.p. 120-200°C. at 7 mm	500 mgms.
3. A non-volatile resin	800 mgms.

(f) Identification of Acetosyringone

The crystalline sublimate was purified by sublimation, followed by recrystallization twice from water, and once from benzene-petroleum ether to yield colorless crystals, melting point 121 - 122.5°C.

Analysis

Calculated for $C_8H_6O_2\ (OCH_3)_2$; OCH_3, 31.6
1.263 mgms. require 8.22 cc. 0.00946N $Na_2S_2O_3$; OCH_3, 31.8
1.147 mgms. require 7.49 cc. 0.00946N $Na_2S_2O_3$; OCH_3, 31.8

(g) Preparation of the p-nitrophenylhydrazone

To a solution of 50 mgms. of the above compound in 1.5 cc. methanol there was added 100 mgms. of p-nitrophenylhydrazine hydrochloride. The mixture was heated to the boiling point and then 1.5 cc. methanol added, and set aside to crystallize. There settled out 75 mgms. of yellowish colored needles. This p-nitrophenylhydrazone was filtered off, recrystallized twice from methanol and once from chloroform; golden needles, melting point 194 - 195°C.

Analysis

Calculated for $C_{14}H_{11}N_3O_3(OCH_3)_2$; OCH_3, 18.7
0.928 mgms. require 3.63 cc. 0.00923N $Na_2S_2O_3$; OCH_3, 18.7

G. Synthesis of Acetosyringone

Five g. of pyrogallol 1,3-dimethyl ether (E. K. Co.) was dissolved in 15 g. of acetic anhydride containing 1 drop concentrated hydrochloric acid. The mixture was heated under reflux for 3 hours, cooled, poured onto cracked ice, and the aqueous mixture extracted with chloroform. The chloroform extract was washed with aqueous sodium bicarbonate, and dried over anhydrous magnesium sulphate. Removal of the chloroform left 4 g. of the acetate as a pale yellow oil which was used directly for the following reaction:

To the pale yellow oil, there was added, with stirring and cooling, a solution of 5 g. of anhydrous aluminum chloride in anhydrous nitrobenzene. The mixture was stirred for 24 hours at room temperature and was then poured on to cracked ice, and the resulting solution extracted three times with diethyl ether. The ether solution was extracted several times with aqueous sodium bicarbonate, the bicarbonate solution neutralized with hydrochloric acid and then extracted three times with ether. The ether solution was dried over anhydrous magnesium sulphate. Removal of the ether left 1 gram of a white crystalline material, which on recrystallization, first from benzene-petroleum ether and then twice from water, yielded colorless needle-shaped crystals, melting point 121 - 122°C., corresponding to the literature 69), 121 - 122.5°C.

Analysis

Calculated for $C_8H_6O_2(OCH_3)_2$; OCH_3, 31.6

2.694 mgms. require 17.99 cc. 0.00923N $Na_2S_2O_3$; OCH_3, 31.9

p-Nitrophenylhydrazone of Acetosyringone

The method of preparation was identical with that used with the acetosyringone from yellow birch; golden-colored needles, melting point 194°C.*

Analysis

Calculated for $C_{14}H_{11}N_3O_3(OCH_3)_2$; OCH_3, 18.7

1.676 mgms. require 6.54 cc. 0.00923N $Na_2S_2O_3$; OCH_3, 18.6

Identity of Synthetic Acetosyringone with the Material from Birch Sulphite Liquor

A mixed melting point of 121 - 122°C. was obtained, thus showing no depression.

A mixed melting point of the two p-nitrophenylhydrazones showed 193 - 194°C., indicating no depression.

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* The melting point reported for the p-nitrophenyl hydrazone in the literature is 189 - 190°C.

H. Calculation of Yields

Yield of Acetosyringone to Combined Vanillin-Syringic Aldehyde Fraction

Original weight of wood (air dried) = 1150 g.

Lignin content of wood (air dried)[*] 20.5% = 235.5 g.

Weight of pulp (oven dried) = 680 g.

Lignin content of pulp (oven dried)[**] 8.6% = 58.5 g.

Weight of lignin in solution = 187.0 g.

Total volume of solution = 9.0 l.

Volume of solution used = 3.0 l.

Weight of lignin used = 59.0 g.

Weight of combined aldehydes, see page 228 = 3.401 g.

% Combined aldehyde yield (lignin basis) = 5.76%

Weight of acetosyringone = 500 mgms.

% Acetosyringone yield (lignin basis) = 0.84%

Ratio of acetosyringone to combined aldehydes 1:7

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[*] This value for the lignin content of the resin-free, air dried birch was supplied by Mr. L. Hawkins.

[**] This value was determined by the standard 72% sulphuric acid method employed in this laboratory:

2.2344 g. of pulp gave 0.1924 g. of lignin
Lignin content was 8.6%

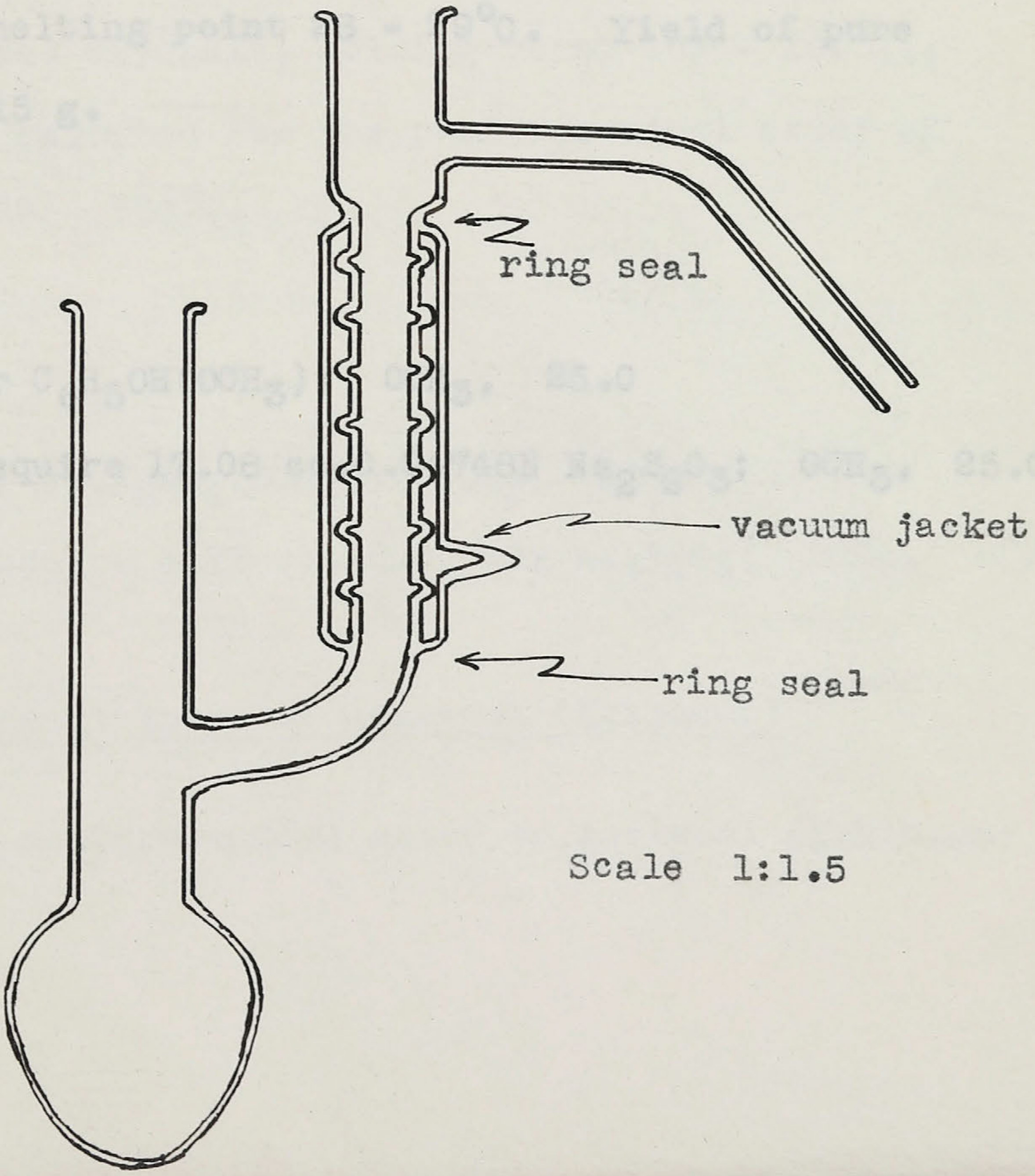
I. Isolation of Guaiacol from Waste Sulphite Liquor

(a) Raw Materials

The tarry residue, left in the benzene extract after removal of vanillin from alkali-treated waste sulphite liquor, was secured from Howard Smith Chemicals Ltd.

(b) Isolation of Guaiacol

The tarry residue was placed in a 500 cc. distilling flask and distilled under reduced pressure, yielding 20 g. of a yellowish foul-smelling liquid, boiling point 70 - 90°C. at 7 mm. This material was redistilled in the 25 cc. high-vacuum jacketed distilling flask shown below:



Scale 1:1.5

All of the material distilled between 79 and 80°C. at 4.5 mm. It was then purified by dissolving in 2% sodium hydroxide solution and extracting the alkaline solution with ether. This solution was then acidified with hydrochloric acid, extracted three times with ether, and the ether extract dried over anhydrous magnesium sulphate.

Removal of the ether left a pale yellow liquid, which on re-distillation in the same apparatus gave a colorless liquid, boiling point 85 - 86°C. at 10 mm. The liquid was seeded with a crystal secured by cooling one drop with scraping, in a test tube immersed in a dry-ice cooling mixture. The whole mass gradually became crystalline, melting point 28 - 29°C. Yield of pure guaiacol was 15 g.

Analysis

Calculated for $C_6H_5OH(OCH_3)$; OCH_3, 25.0

18.24 mgms. require 17.08 cc.,0.04748N $Na_2S_2O_3$; OCH_3, 25.0

J. Identification of the Guaiacol from Waste Sulphite Liquor

(a) p-Nitrobenzoyl Ester

To a solution of 100 mgms. of pure p-nitrobenzoyl chloride in 3 cc. of pyridine there was added 2 drops of the isolated guaiacol and the mixture set aside overnight. The solution (containing precipitated crystalline material) was poured on to a mixture of concentrated hydrochloric acid and cracked ice, giving a white curdy precipitate which was filtered off under suction, washed with water, and then stirred for 1 hour with 4% sodium hydroxide.

The solid remaining in suspension was filtered off, washed with water and recrystallized from ethanol, giving colorless crystals, melting point 103 - 104°C.; melting point reported for the p-nitrobenzoyl ester of guaiacol is 103 - 104°C.

Analysis

Calculated for $C_{13}H_8NO_4(OCH_3)$; OCH_3, 11.6

1.929 mgms. require 4.75 cc. 0.00923N $Na_2S_2O_3$; OCH_3, 11.7

(b) p-Nitrobenzoyl Ester of Guaiacol (Kahlbaum)

The p-nitrobenzoyl ester of guaiacol (Kahlbaum) was prepared as described above; colorless crystals, melting point 103 - 104°C.

A mixed melting point of the two showed no depression.

(c) p-Tosyl Ester of Guaiacol Isolated from Waste Sulphite Liquor

The procedure followed using tosyl chloride, was identical with that used for the preparation of the p-nitrobenzoyl ester.

The tosyl ester (colorless crystals), melted at 84 - 85°C.

Analysis

Calculated for $C_{13}H_{11}SO_3(OCH_3)$; OCH_3, 11.1

1.490 mgms. require 3.44 cc. 0.00923N $Na_2S_2O_3$; OCH_3, 11.0

(d) p-Toluene Sulphonic Ester of Guaiacol (Kahlbaum)

The same product was obtained, melting point 84 - 85°C.

A mixed melting point of the two p-toluene sulphonic esters above showed no depression.

K. Guaiacol from Resin-Free Spruce Meal

The volatile fraction, (page 219) secured from resin-free spruce woodmeal, and amounting to 50 - 75 mgms., was treated with p-nitrobenzoyl chloride to yield colorless crystals, melting point 103 - 104°C.

Analysis

Calculated for $C_{13}H_8NO_4(OCH_3)$; OCH_3, 11.6

0.915 mgms. require 2.23 cc. 0.00923N $Na_2S_2O_3$; OCH_3, 11.7

A mixed melting point with the p-nitrobenzoyl ester from an authentic sample of guaiacol showed no depression.

L. ISOLATION OF GUAIACOL, PYROGALLOL 1,3-DIMETHYL ETHER AND ACETOSYRINGONE FROM HARD WOOD WASTE SULPHITE LIQUOR

Three liters of concentrated waste sulphite liquor * prepared from a mixture of hard woods (beech, birch and maple) of specific gravity 1.26 was diluted to 10 liters and mixed with 900 g. of sodium hydroxide (technical).

The resulting solution was heated under pressure, neutralized, and extracted, etc., as applied to sulphite liquor obtained from resin-free spruce for the isolation of vanillin [14]. Following the same procedure, the vanillin and syringic aldehyde was removed from the benzene solution of the reaction product by use of bisulphite and the benzene solution then evaporated under reduced pressure leaving a tarry material.

This was distilled under reduced pressure and gave the following fractions:

Fraction	1.	Wt.	250 mgms.,	Boiling point $<$ 100°C. at 7 mm. pressure
"	2.	"	900 mgms.,	Boiling point 105 - 110°C. at 0.025 mm. pressure
"	3.	"	1.8 g.	Crystalline product subliming at 120 - 180°C. at 0.025 mm. pressure
"	4.	"	7.0 g.	Residual tarry material.

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* Supplied through the kindness of the Brown Company, Rumford Mills, New Hampshire, U.S.A.

M. IDENTIFICATION OF GUAIACOL AND PYROGALLOL 1,3-DIMETHYL ETHER FROM HARD WOOD WASTE SULPHITE LIQUOR

Fraction 1 was acylated with 350 mgms. of p-nitrobenzoyl chloride dissolved in 2 cc. pyridine following the customary procedure.

Recrystallization of the crude mixture of esters was effected by solution in 25 cc. of hot ethanol, and cooling. The crystalline material which separated was recrystallized twice from ethanol, giving 50 mgms. of colorless crystals, melting point 155 - 156°C. On mixing with the p-nitrobenzoyl ester of pyrogallol 1,3-dimethyl ether (Eastman Kodak Co.) there was no depression of the melting point; calculated yield of pyrogallol 1,3-dimethyl ether was 25 mgms.

Analysis

Calculated for $C_{13}H_7NO_4(OCH_3)_2$; OCH_3, 20.4
1.112 mgms. required 4.74 cc., 0.00923N, $Na_2S_2O_3$; OCH_3, 20.34

The alcoholic filtrate from the above recrystallization was allowed to evaporate slowly, to a volume of about 25 cc., when a second crop of crystals was deposited and removed by filtration, melting point 110 - 140°C., weight = 20 mgms. Because of the small amount of this material, separation into its components was not attempted.

Further evaporation of the solvent to 5 cc. gave 150 mgms. of a crystalline compound, which was recrystallized twice from ethanol to give colorless crystals, melting point 104 - 105°C. On mixing with the p-nitrobenzoyl ester of guaiacol (Kahlbaum), there was no depression of the melting point; calculated yield of guaiacol = 70 mgms.

Analysis

Calculated for $C_{13}H_8NO_4(OCH_3)$; OCH_3, 11.6

1.928 mgms. required 4.76 cc., 0.00923N, $Na_2S_2O_3$; OCH_3, 11.8

Fraction 2: The p-nitrobenzoyl ester prepared from this material melted at 155 - 156°C., and on mixing with the ester of an authentic sample showed no depression of the melting point; calculated yield = 100 mgms.

Oxidation of 10 mgms. of the fraction with aqueous ferric chloride, gave steel blue crystals of cörulignin 73), which gave a characteristic blue solution in concentrated sulphuric acid.

In contact with air, the pyrogallol 1,3-dimethyl ether secured above became red in color.

N. Identification of Acetosyringone From Hard Wood Waste Sulphite Liquor

Fraction 3, isolated from hard wood waste sulphite liquor was recrystallized three times from water to give colorless needles, melting point 121 - 122°C. which on mixing with synthetic acetosyringone showed no depression in the melting point. The yield of finally purified material was 1.0 g.

O. Yields of Various Fractions to Combined Vanillin-Syringic Aldehyde Yield

Due to practical difficulties involved in the isolation of these fission products, and the fact that a commercial sulphite liquor was used, it is not possible to give an accurate estimate of the relative ratio of the products formed. A very rough estimate would indicate a ratio for guaiacol : pyrogallol 1,3-dimethyl ether : acetosyringone : total aldehydes (vanillin and syringic aldehyde) of 1:4:40:320.

P. IDENTIFICATION OF GUAIACOL AND PYROGALLOL 1,3-DIMETHYL ETHER FROM RESIN-FREE BIRCH

The volatile material isolated by a similar alkaline treatment from 6 liters of birch lignin sulphonic acid obtained from a solvent-extracted birch wood meal was fractionated and yielded:

Fraction 1. Wt. 50 mgms., Boiling point 100°C. at 7 mm. pressure.

Fraction 2. Wt. 200 mgms., Boiling point 105 - 110°C. at 0.025 mm. pressure.

There was present, also, 1.0 g. of acetosyringone and 3.0 g. of non-volatile resin.

Fraction 1 was concerted to a p-nitrobenzoyl ester, melting point 104 - 105°C., which on mixing with the p-nitrobenzoyl ester of guaiacol (Kahlbaum) showed no depression on the melting point.

Fraction 2 was identified as pyrogallol 1,3-dimethyl ether, by a similar process to that applied to pyrogallol 1,3-dimethyl ether, secured from hard wood waste sulphite liquor, viz.:

1. Melting point of p-nitrobenzoyl ester 155 - 156°C., showing no depression of the melting point when mixed with an authentic sample of the material.

2. Blue coloration, on solution of the ferric chloride oxidation product (cörulignin) in concentrated sulphuric acid.

The ratio of guaiacol to pyrogallol 1,3-dimethyl ether : acetosyringone was roughly 1:5:20. On the basis of lignin yields these represent 0.04, 0.2 and 0.8% respectively.

Q. Investigation of the Acetovanillone Fraction from Waste Sulphite Liquor

After removal of the guaiacol from the tar, c.f. page 233, the residual material was sublimed using a cold finger. A yellowish colored solid was obtained, melting point 108 - 110°C; yield 62.5 g.

This material was recrystallized by extracting with five successive portions of boiling water. Each fraction was decolorized separately, with animal charcoal and on cooling, yielded pale-yellow crystals, the melting points of which are shown below:

Extraction No. 1 - m.p. 111 - 112°C.
Extraction No. 2 - m.p. 113 - 113.5°C.
Extraction No. 3 - m.p. 113.5 - 114.5°C.
Extraction No. 4 - m.p. 113.5 - 114.5°C.
Extraction No. 5 - m.p. 113 - 114°C.

Mixed melting points of the combined fractions were as follows:

Fraction 1 and 2 - 113 - 113.5°C.
Fraction 3 and 4 - 113.5 - 114.5°C.
Fraction 1, 2, 3 and 4 - 113.5 - 114.5°C.

All fractions were thus identical and so were combined and given a final recrystallization from water;

pale lemon colored crystals, melting point 113 - 114.5°C.

An extraction of the mother liquors yielded a further crop of acetovanillone, melting point 113 - 114.5°C.

R. Treatment of Guaiacol with Furfuryl Alcohol (Preparation of a Synthetic Lignin)

To a mixture of 5 g. of guaiacol and 2.5 g. of furfuryl alcohol, was added three drops of concentrated hydrochloric acid. There was an immediate formation of a dark green color, and after 10 to 15 minutes, considerable evolution of heat and formation of droplets in the solution. The mixture was set aside for a period of five weeks, at room temperature. The resulting dark-colored viscous liquid was dissolved in 50 cc. of acetone, the solution dried over anhydrous magnesium sulphate, and dropped, with stirring, into 250 cc. petroleum ether (30 - 50°C). The black amorphous solid precipitating out was redissolved in acetone and then precipitated from diethyl ether as a greyish flocculent precipitate. This was washed three times with diethyl ether and three times with petroleum ether, separated by the use of the centrifuge and dried. The grey amorphous material showed marked electrostatic properties, similar to some lignins.

Solubilities were as listed below; soluble in acetone, dioxane and pyridine; insoluble in water, ether, petroleum ether, ethanol, methanol and dilute (5%) sodium hydroxide.

Analysis

0.01189 g. requires 2.35 cc. 0.04529N, $Na_2S_2O_3$; OCH_3, 4.6

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