HIGH-PRESSURE HYDROGENATION OF WOOD AND RELATED CARBOHYDRATES

by

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CLAIMS TO ORIGINAL RESEARCH

1. A new type, highly efficient, low cost, easily constructed, laboratory fractionating column has been designed and built.

2. Maple holocellulose has been hydrogenated for the first time. From a comparison of the carefully fractionated hydrogenation products with those obtained from maple wood (30) by similar treatment, it has been established that the propylcyclohexyl derivatives isolated from the latter are of lignin and not of carbohydrate origin.

3. A new propylcyclohexyl derivative, 3-cyclohexylpropanol-1, has been isolated from the hydrogenation products of maple wood, spruce wood, and various maple lignin fractions, and has been identified by direct synthesis. The structural significance of this material to the lignin nucleus is important, in that it provides the first evidence for the presence of a high percentage of terminal $-CH_2-O-$ groupings in the side chain of the lignin propyl phenol nucleus.

4. Propyl phenol derivatives are shown to be absent in 2 to 3 weeks old spruce tips and present only to a very limited extent in 3½ to 4 months old spruce, showing the slow development of lignin during the growth of spruce.

5. N-pentanol has been isolated and identified as a new hydrogenation product from maple wood.

6. N-octadecanol has been isolated and identified as a hydrogenation product from young spruce tips (3 weeks old and 4 months old).

7. β-hydroxypropiovanillone has been hydrogenated in dioxane medium over CuCrO catalyst and shown to yield 4-n-propylcyclohexanol and 3-cyclohexylpropanol-1 in a minimum yield of 81%. These products were present in the percentage ratio of 24:76.

I. Historical Review of Lignin Structure

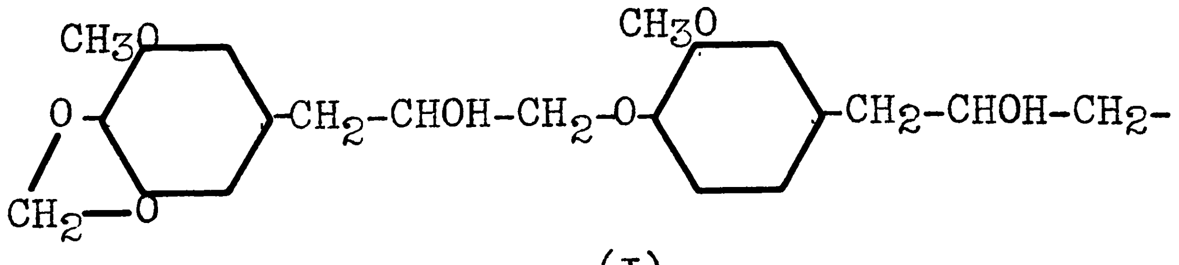
Early Developments in Lignin Chemistry

Recent reviews on the structure of lignin by von Wacek (1) Freudenberg (2), Erdtman (3) and Hibbert* (4) have emphasized the essentially aromatic character of lignin and its relationship to coniferyl types.

During the period 1897 (5) to 1936 (6), Klason's original "coniferyl-oxyconiferyl alcohol hypothesis", in which polymers of coniferyl alcohol, coniferyl aldehyde, guaiacol aldol, etc. were included, underwent various modifications. This theory, which may be regarded as constituting the first phase of lignin research, was based (i) on the universal occurrence of coniferyl alcohol in young plant tissue (7), (ii) on data derived from the ethanolysis of the spruce lignin sulfonic acids and from solvent-extracted material (spruce wood) presumably containing both polymerized coniferyl and oxyconiferyl alcohol, and (iii) on the occurrence of products such as catechol, guaiacol and protocatechuic acid in the lignin alkali-fusion reaction mixture (8).

In the second phase of lignin research (1926-1932) emphasis was laid on new methods for the isolation of lignin from wood and on identification of functional groups (methoxyl, hydroxyl, carbonyl, aromatic nucleus) in the extracted lignins. In this connection, methods were employed involving the use of concentrated acids such as sulfuric acid (9), hydrochloric acid (10), and mixtures of hydrochloric and phosphoric acids (11), as well as much milder procedures such as alcoholysis (4) by the use of alcohols, glycols, glycerol and glycerol chlorhydrin.

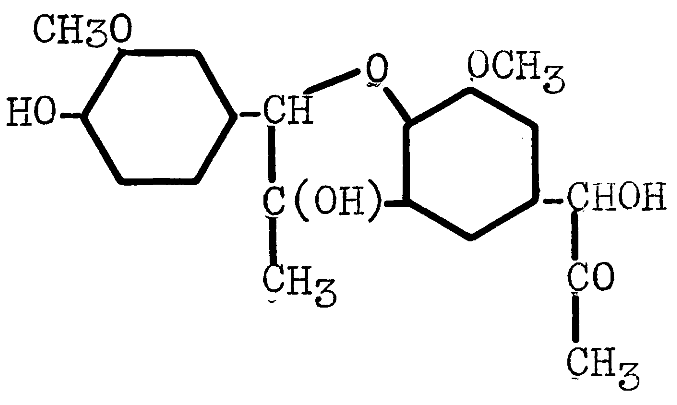
Freudenberg's earlier theory of the structure of lignin (12) was based essentially on the isolation of small amounts of catechol, protocatechuic acid and formaldehyde from spruce hydrochloric acid lignin, and on analyses of this lignin. These results indicated (a) aromatic character and absence of free phenol groups; (b) attachment of the methoxyl groups to aromatic nuclei; and (c) presence of aliphatic hydroxyl groups in side chains attached to the benzene nucleus. Freudenberg's modification of Klason's view of lignin as a propylphenol derivative differed only in the type of side chain envisaged and in the assumption that the building units were joined through ether linkages to give a "linear type" condensation polymer (12, page 134). Such a polymer, however, should readily undergo



(I)

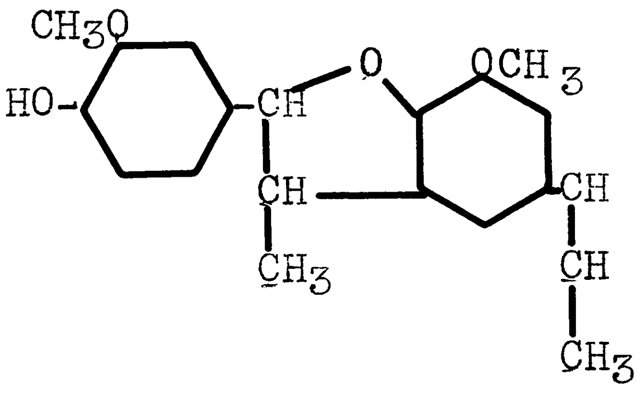
degradation by hydrolytic action into simple molecular units, and, this not being the case, Freudenberg found it difficult to postulate transformation into "secondary lignins" (12, page 135). The assumed presence of the dioxymethylene group was based on the liberation of a small amount of formaldehyde (up to 1.2 per cent) (13,14,15). The side chains visualized by Freudenberg were R-CHOH-CHOH-CH$_2$OH, R-CH$_2$-CHOH-CH$_2$OH, R-CHOH-CH$_2$-CHO and R-CHOH-CO-CH$_3$ (12, page 135). According to his definition these compounds are "biochemically identical" (12, page 137); this expression, however, has, scientifically, no biochemical significance and can only be assumed to imply they are in equilibrium with each other, at least <u>in vivo</u>.

On the basis of the studies on alkali degradation of spruce lignin, followed by methylation and oxidation (16,17,18), Freudenberg has abandoned the ether-type linkage of assumed propylphenol units and now considers the union to be of a carbon-to-carbon type involving oxygen-ring formation between side chains and aromatic nuclei (2, page 95) (II).



(II)

(from two moles of R-CHOH-CO-CH$_3$)



(III)

It can be seen that this structure (II) is similar to the dimer resin-type polymer (e.g. dehydrodiisoeugenol, (III) suggested by Erdtman (19)).

One of the chief objections to this new Freudenberg conception has been the assumed presence of the dioxymethylene group either on terminal, (12, page 134) or (in his later theory) centrally disposed (2, pages 95, 109) aromatic nuclei, to the extent of 25 per cent of the spruce lignin structure. This theory has been seriously criticized (4), especially from the point of view of the non-isolation of piperonyl units. Furthermore the inclusion of such nuclei as centrally-located units in a dehydrodiisoeugenol type of polymer implies a new and unusual form of condensation. It is also of importance to note that such a condensation polymer (II) could not be formed with syringyl derivatives where the five position (ortho to the phenol group) is blocked by a methoxyl group.

Recent Developments in Lignin Chemistry

The recent developments (constituting the third phase) which have led to a clearer understanding of the structure and origin of protolignin are those connected with studies on (i) alkaline oxidation of lignin, wood, and lignin sulfonic acids; (ii) high pressure hydrogenation of wood and lignin; and (iii) early experiments on the alcoholysis of wood. The results of these studies have provided experimental support for (i) the above mentioned theoretical conception of lignin originally proposed by Klason and extended by Freudenberg and (ii) the modern theory of plant respiratory catalysts as lignin progenitors developed by Hibbert (4).

A. Alkaline Oxidation of Lignin and Lignin Derivatives

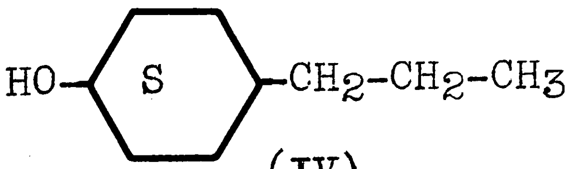
The action of alkali on lignin sulfonic acids has been investigated extensively following earlier observations (4, page 37) regarding the presence of vanillin, at least in small quantities, in the reaction mixture. With spruce lignin sulfonic acid a yield of 6-7 per cent of vanillin (20) and smaller amounts of acetovanillone (21) and guaiacol (22) are obtained, while, with oak lignin sulfonic acid, in addition to these there are present syringaldehyde (23), acetosyringone (24), and 1,3-dimethoxypyrogallol (23). The addition of an oxidizing agent such as metanitrobenzene sulfonic acid, in small quantity, to the alkaline spruce lignin sulfonic acid mixture gave a lower yield of aldehyde (25). More recently Freudenberg and coworkers have developed an alkali-nitrobenzene oxidation technique by which yields of 20-25% of vanillin from spruce wood and spruce lignin sulfonic acid are obtained. (26).

Although yields of 25% vanillin appear to be the maximum obtainable from soft woods, an extension of this method to maple and aspen woods gave yields of 46 and 48% respectively of mixtures of vanillin and syringaldehyde (27). If it be assumed that these aldehydes are derived from propylphenol units similar to those obtained by the ethanolysis of maple wood, these yields indicate that approximately 58-62% of the protolignin in angiosperms is aromatic in nature, and, thus, the validity of Klason's assumption that lignin has a fundamentally aromatic structure is established.

Lautsch and Piazolo (28) oxidized a brominated spruce lignin with alkali and nitrobenzene and obtained 6-bromovanillin (8 per cent), a product which cannot be prepared directly from vanillin. This result is assumed to prove that the units in lignin are united with each other by etherification at the 4-position. Attempts to increase the yield of aromatic lignin oxidation products by substituting certain metallic oxides (29) for the nitrobenzene were unsuccessful.

B. Hydrogenation of Wood and Lignin

A more complete survey of this subject will be given in a later section of this introduction. Complete liquefaction of maple wood (30), however, has been effected by application of hydrogenation technique, the protolignin being converted, in part, to 4-n-propylcyclohexanol (IV) and 3-(4-hydroxycyclohexyl)-propanol-1 (V) in yields of 19.5 and 5.8 per cent respectively (based on the Klason lignin content of wood). Using the carbon content of these isolated units



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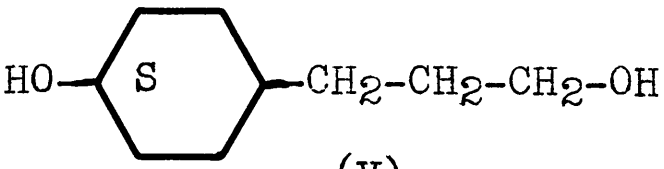


(V)

and of the "methoxyl-free protolignin" in the wood as a basis for calculation, the combined yield of propylcyclohexane derivatives represents a recovery of 36 per cent (30).

Examination of the yields of hydrogenation products from various amorphous fractions of a maple lignin isolated by ethanolysis (31) indicates that, for a given series of such fractions, increasing solubility and increasing susceptibility to depolymerization into simple, monomolecular propylphenol units by ethanolysis are paralleled by an increasing yield of the water-insoluble propylcyclohexanol hydrogenation products. This observation is thought to indicate the prevalence of -C-O-C- bonds between the propylphenol "lignin building-units" in those lignin fractions which are readily-soluble and are easily cleaved by ethanolysis and hydrogenolysis and, conversely, an increasing incidence of -C-C-C- bonds in lignin fractions having these characteristics to a lesser extent.

Hatihama et al. (32) hydrogenated hydrochloric acid lignin in the presence of several less active catalysts, particularly nickel, and obtained a 50% yield of ether-soluble aromatic oils containing pyrocatechin and n-propylguaiacol. Similar results have been reported by Freudenberg and co-workers (33) who, following earlier work by Bobrov and Kolotova (34), extended the investigations to sulfite liquor. More recently, Freudenberg and Adam (35) have developed a procedure which consists of the simultaneous dry distillation and catalytic hydrogenation of isolated lignins on the surface of which various metallic catalysts had been precipitated. In this manner ether-soluble, tarry fractions (20-50% yield) containing, among other products, phenols and phenolic ethers were obtained.

In addition to establishing the foregoing evidence for the presence of the propylphenol unit in lignin, hydrogenation studies have shown that a relatively large proportion of the propylcyclohexane derivatives obtained from wood (30) and certain lignins (31,36,37) contain oxygen atoms attached to the terminal carbon atom in the propyl side chain. This result provides the only experimental proof of the presence of oxygen in that position in protolignin.

A further contribution of the hydrogenating technique to lignin chemistry has been the classification of lignins according to their relative complexities (based on the yield and nature of hydrogenation resins). The results of Adkins and co-workers (37,38) have shown that sulfuric acid, soda and alkali lignins are more complex than either protolignin (30) or alcoholysis lignins (31,36).

C. Alcoholysis of Wood

The fourth phase in the elucidation of lignin structure may be regarded as that associated with the more recent contributions of Hibbert and co-workers on the action of ethanolic hydrogen chloride on various plant materials.

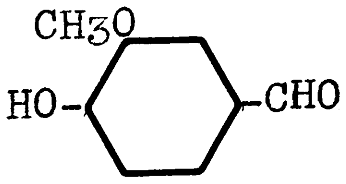
The belief that proto- and extracted lignins exist only as highly polymerized, complex substances led investigators to conclude that the amorphous water-insoluble product obtained by customary extraction methods was the only form in which lignin could be isolated. Precipitation into water from concentrated alcohol, acetic acid, or other solutions has been almost an invariable step in the isolation or purification of lignin.

Prior to the recent developments of the ethanolysis lignin extraction process by Hibbert and co-workers, the aqueous precipitating liquors had been examined on only two occasions, namely, by Friedrich and Brüda (39) (methanolysis of beech) and by Brauns and Hibbert (40) (methanolysis of spruce). The former investigators isolated a small amount of lignin which apparently had been suspended in the water as a sol, and only minute traces of methoxyl-containing material were found in true solution in the concentrated aqueous liquors. Brauns and Hibbert also found only a small quantity of methoxyl-containing material in their work.

When it was observed, however, that the sum of the weights of the amorphous water-insoluble lignin and of the Klason lignin remaining in the alcoholysis wood residue was almost always considerably less than the weight of the Klason lignin in the untreated wood, Hibbert became interested in the cause of this discrepancy. The explanation of this was found when Cramer, Hunter and Hibbert (41) showed that the loss in weight was due (in the case of the ethanolysis of spruce and maple woods) to the water solubility of a large proportion (12% of the Klason lignin, spruce; 30%, maple) of the methoxyl-containing materials.

As a result of this important observation an extensive series of investigations was started immediately in these laboratories to determine (a) the structure of the components of the water-soluble fraction; (b) the factors involved in their isolation, especially those relating to their actual presence as such in the wood or their appearance as stabilized end-products derived from more complex polymers and/or more reactive simple units; (c) the significance of the simple units in relation to the structure of the amorphous, water-insoluble ethanol lignin;and (d) the significance of the simple units in relation to photosynthesis, plant respiration and the formation of protolignin.

To date, over one-third (14% of Klason lignin content) of the water-soluble oils from maple wood has been shown to be composed of α-ethoxypropiovanillone (VIII) (41a) and its syringyl analog (IX) (41b); vanilloyl methyl ketone (X) (42) and its syringyl analog (XI) (43); vanillpropanone-2 (XII) (44) and its syringyl analog (XIII) (44); vanillin (VI) (45) and syringaldehyde (VII) (45). In addition 1-vanill-1-ethoxypropanone-2 (XIV) (46) has been isolated from spruce wood water-soluble oils.



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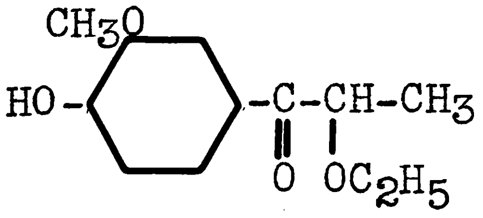

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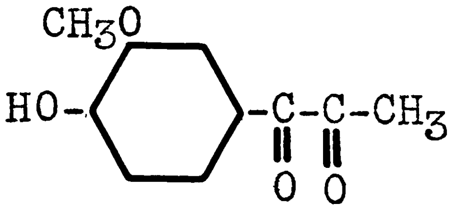
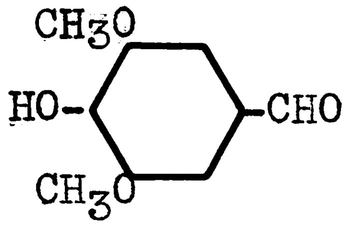
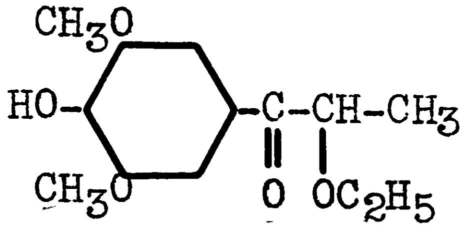


(X)



(VII)



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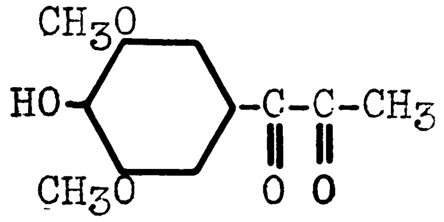

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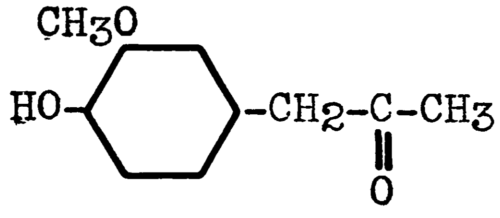
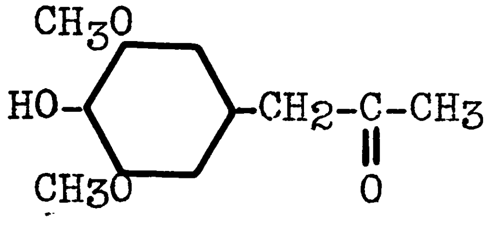


(XII)



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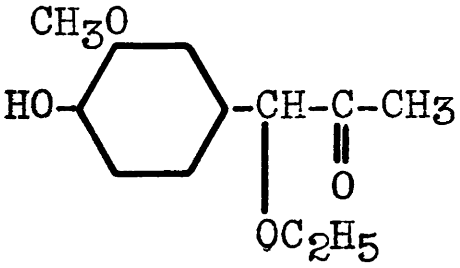


(XIV)

An actual relationship between these monomeric units and extracted lignins has been established by Peniston, McCarthy and Hibbert (47). These investigators refluxed an acetylated oak lignin with anhydrous ethanolic hydrogen chloride (2%) for 15 hours. The crude, water-soluble oils thus obtained (36% of the acetyl-free lignin content of the starting material) were separated into four fractions whose characteristics were very similar to those obtained by the action of ethanolic hydrogen chloride on maple wood.

As a direct result of the isolation and identification of the propyl phenol derivatives and of 3-(4-hydroxycyclohexyl)-propanol-1 (V) (by means of hydrogenation) interest has been centered on the potential significance of related compounds such as β-hydroxypropiovanillone (XV), 1-vanillo -3-hydroxy-propanone-2 (XVI) and their corresponding syringyl derivatives.

$R\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}OH$ (XV)

$R\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}OH$ (XVI)

D. Biochemical Aspects of Protolignin Formation

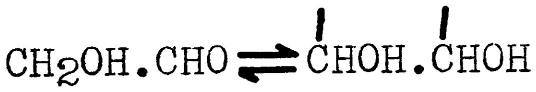
Mechanism of Plant Synthesis of Propylphenol Derivatives

(1) Synthesis of Simple Phenols- Various theories concerning the synthesis of phenolic compounds in plants have been based on assumed transformation of hexoses (48, 49), while a more recent theory (4) considers the phenolic substances as being formed from intermediate photosynthetic and/or plant respiratory products.

(i) Free Radical Theory (50)- Specific types are assumed to be present in the active stages of plant growth (formic acid (XVII), glycollic aldehyde (XVIII), and acetaldehyde (XIX)), in equilibrium with the corresponding enol-radicals:

$HCOOH \rightleftharpoons \overset{|}{\underset{|}{C}}(OH)_2$

(XVII)



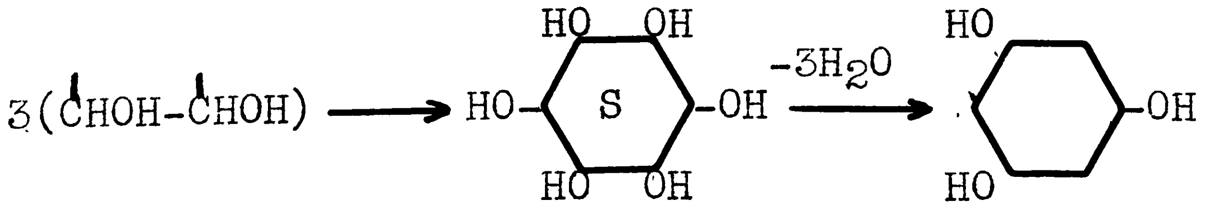
$CH_2OH.CHO \rightleftharpoons \overset{|}{C}HOH.\overset{|}{C}HOH$

(XVIII)

$CH_3.CHO \rightleftharpoons \overset{|}{C}H_2.\overset{|}{C}HOH$

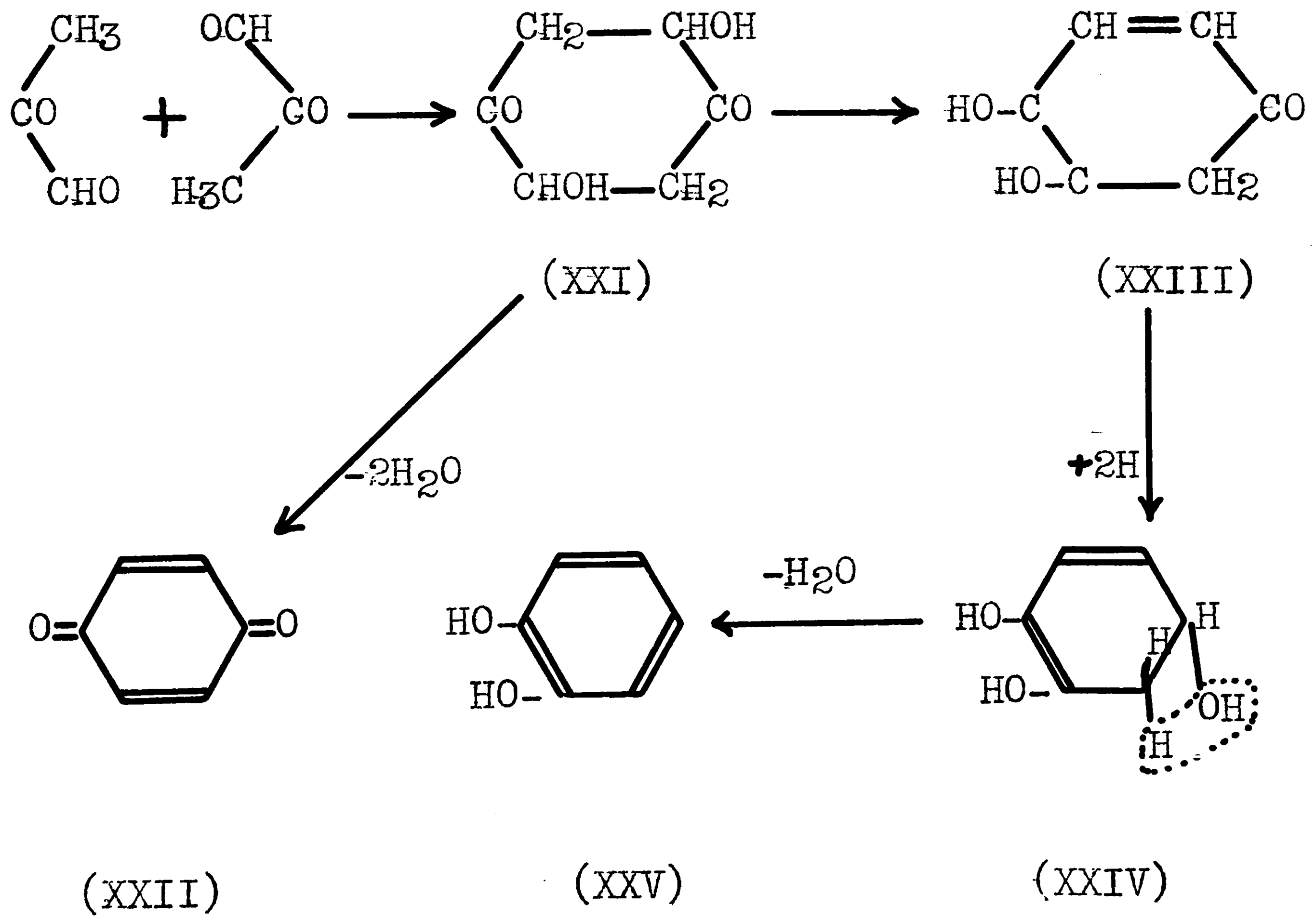
(XIX)

Union of the free radicals may give rise to hydroaromatic derivatives which, by loss of water, could yield phenols; for example, phloroglucinol (XX) from (XVIII):



(XVIII) Inositol (XX)

(ii) <u>Methyl Glyoxal Theory of Phenol Formation (51)</u> - Methyl glyoxal, which is a well-recognized intermediate in animal cell respiratory processes (52, page 244), presumably occupies a somewhat analogous position in plant carbohydrate metabolism (53, page 264) and has actually been isolated from a number of higher plants (54). Hibbert suggests the possibility of two molecules of methyl glyoxal polymerizing to yield a cyclic dihydroxydiketone (XXI) capable of undergoing the indicated reactions to give quinone (XXII) and 1,2-dihydroxy-4-ketocyclohexadiene (XXIII). This ketohexadiene,(XXIII)

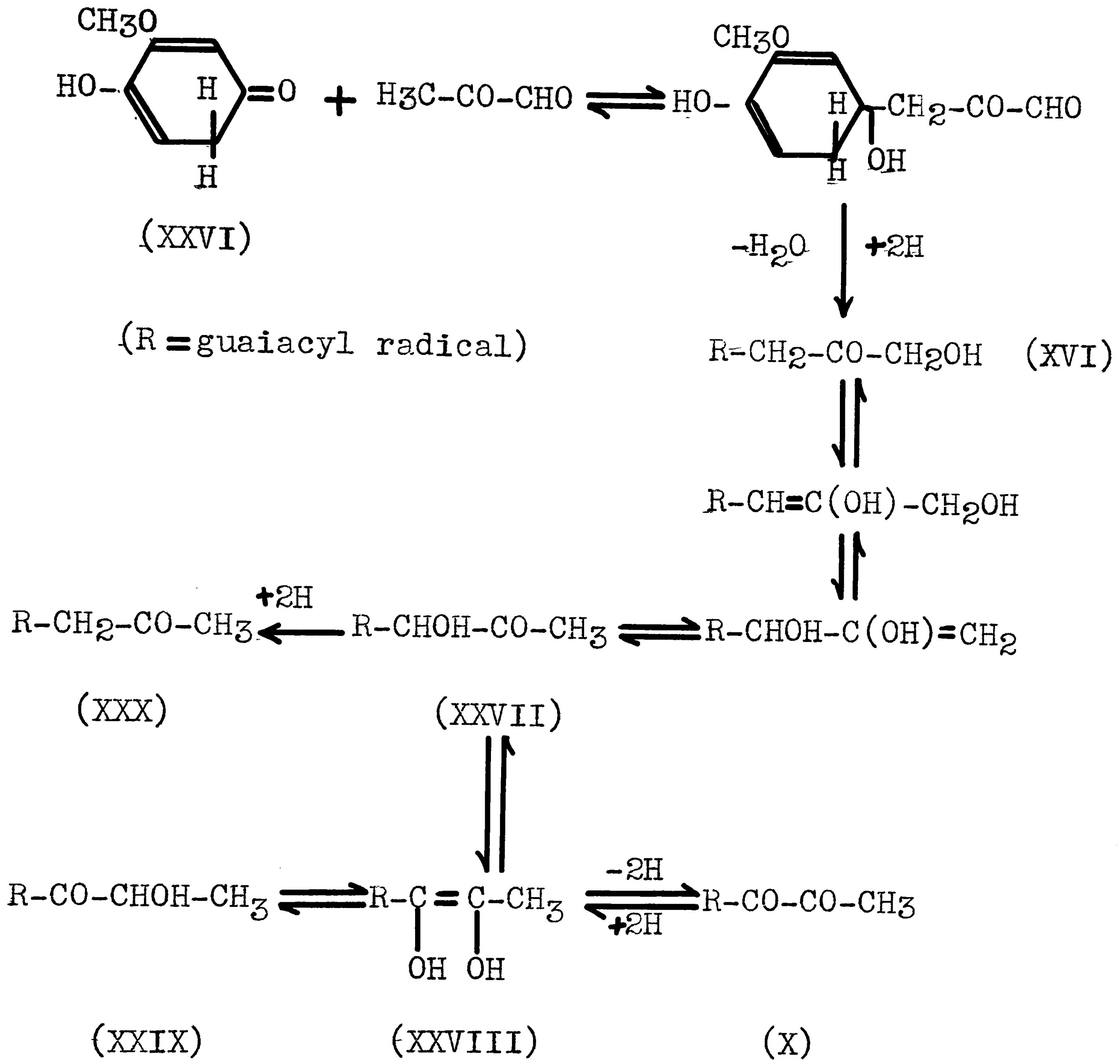


on reduction could give rise to a hydroxy-enediol, (XXIV) which could yield catechol (XXV) upon the loss of a mole of water.

Pyrogallol (the precursor of the syringyl nucleus) could be formed by enzymatic oxidation of catechol (XXV) just as the latter is formed from phenol (55).

(2) Suggested Plant Synthesis of Propylphenol Derivatives -

Condensation of the "methoxylated" ketocyclohexadiene, (XXVI), with a third mole of methyl glyoxal, followed by the loss of a mole of water and reduction would yield (XVI). An intramolecular change involving an allyl shift in (XVI) would give the primary dismutation isomer, (XXVII), (46), which could then yield the ene-diol (XXVIII), this in turn giving the benzoin derivative (XXIX). The benzoin derivative (XXVII) on reduction could yield the desoxybenzoin (XXX). Moreover the ene-diol, (XXVIII) is a dihydro derivative of the 1,2-diketone (X).



The only reaction of this series which conceivably could be open to question is concerned with the rearrangement of (XVI) to (XXVII). Apparently there are no analogous reactions described in the literature, although, if it is assumed that (XVI) is in equilibrium with its aldehydo form ($R\text{-}CH_2\text{-}CO\text{-}CH_2OH \rightleftharpoons R\text{-}CH_2\text{-}CHOH\text{-}CHO$), then the reaction undergone by its analog, benzyl glycollic aldehyde, (XXXI), in the presence of ethanol and sulfuric acid is highly significant (56), in view of its conversion, by this means, into a mixture of phenyl acetyl carbinol and benzoyl acetone. Furthermore, since it has been

$$\underset{\text{(XXXI)}}{2\ C_6H_5\text{-}CH_2\text{-}CHOH\text{-}CHO} \longrightarrow C_6H_5\text{-}CHOH\text{-}CO\text{-}CH_3 + C_6H_5\text{-}CO\text{-}CO\text{-}CH_3$$

shown experimentally (57) that the veratryl derivative of (XVI) is converted into the ethyl ether of (XXIX) by ethanolic hydrogen chloride, the postulation of (XXVII) and (XXVIII) as intermediates would appear to be justified. Added confirmation of the postulated allyl shift in the above series of changes is to be found in the recent isolation (46) of the ethoxy derivative (XIV) (pages 10, 11) of (XXVII) from the water soluble oils of spruce ethanolysis.

There is ample support in the literature for the postulated equilibrim (XXVII) $\rightleftharpoons$ (XXIX). The simplest, and best known examples of such dismutation reactions, in the case of 1,2-hydroxy ketones and aldehydes, are to be found in the field of carbohydrate chemistry, as for example, the well-known Lobry de Bruyn equilibrium transformation of glucose $\rightleftharpoons$ mannose $\rightleftharpoons$ fructose, and of glyceric aldehyde $\rightleftharpoons$ dihydroxyacetone, etc. (58). It has been pointed out (44, page 52) that in the equilibrium system $R\text{-}CHOH\text{-}CO\text{-}CH_3 \rightleftharpoons R\text{-}C(OH) = C(OH)\text{-}CH_3 \rightleftharpoons R\text{-}CO\text{-}CHOH\text{-}CH_3$ where R is a para substituted benzene radical, $R\text{-}CO\text{-}CHOH\text{-}CH_3$ is more stable than its dismutation isomer. This is in agreement with the results obtained in the ethanolysis of wood in which the products isolated are the ethyl ethers of the stabilized form $R-CO-CHOH-CH_3$, namely, α-ethoxypropiovanillone (VIII) and -syringone (IX). In the light of the above literature references (56,57), it is probable that these substances, (VIII) and (IX), represent only stabilized end products originating from the assumed lignin progenitors, 1-vanillo .-3-hydroxypropanone-2 (XIII) and its syringyl analogue respectively; (see also page 28) in other words, the first members of the proposed new aromatic system of plant respiratory catalysts (4).

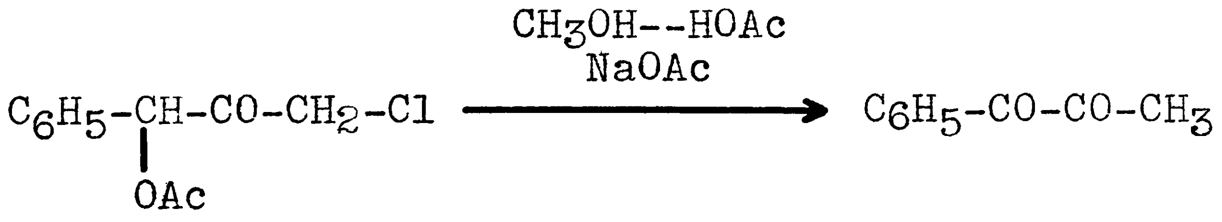
It is therefore of great importance to consider to what extent members of the second type of ethanolysis products isolated, namely, vanilloyl- (X) and syringoyl methyl ketones (XI), represent also stabilized end ethanolysis products derived from more reactive lignin progenitors. A consideration of a series of products, namely coniferyl alcohol (XXXII) ($R-CH{=}CH-CH_2OH$), oxyconiferyl alcohol (XXXIII) ($R-CH_2-CO-CH_2OH \rightleftharpoons R-CH{=}C(OH)-CH_2OH$) and dioxyconiferyl alcohol (XXXIV) ($R-CO-CHOH-CH_2OH \rightleftharpoons R-C(OH){=}C(OH)-CH_2OH$), points to the possibility of the existence of a similar dismutation equilibrium involving the dioxy-ketone (XXXIV) as one constituent:

$$R-CO-CHOH-CH_2OH \rightleftharpoons R-C(OH){=}C(OH)-CH_2OH \rightleftharpoons R-CHOH-CO-CH_2OH$$

Examination of the enediol (XXXIV), shows it differs only from that present in the dismutation system $R-CO-CHOH-CH_3 \rightleftharpoons R-C(OH){=}C(OH)-CH_3 \rightleftharpoons R-CHOH-CO-CH_3$ in that the methyl group is replaced by a terminal $-CH_2OH$, and by analogy this dioxyconiferyl alcohol type of compound might be expected to yield vanilloyl methyl ketone in the presence of dilute acids:

$$R\text{-}C(OH){=}C(OH)\text{-}CH_2OH \longrightarrow R\text{-}C(OH)_2\text{-}C(OH){=}CH_2 \longrightarrow R\text{-}CO\text{-}CO\text{-}CH_3$$

Substantial experimental support for this theory is to be found in the behavior of analogously constituted chain and cyclic derivatives. Thus Bradley and Eaton (59) observed that chloromethyl α-acetoxybenzyl ketone (XXXV.), when heated with a solution of sodium acetate in glacial acetic acid and methanol, was converted in almost quantitative yield into benzoyl methyl ketone (XXXVI). The same chloroketone (XXXV) when left standing at room temperature for one year decomposed

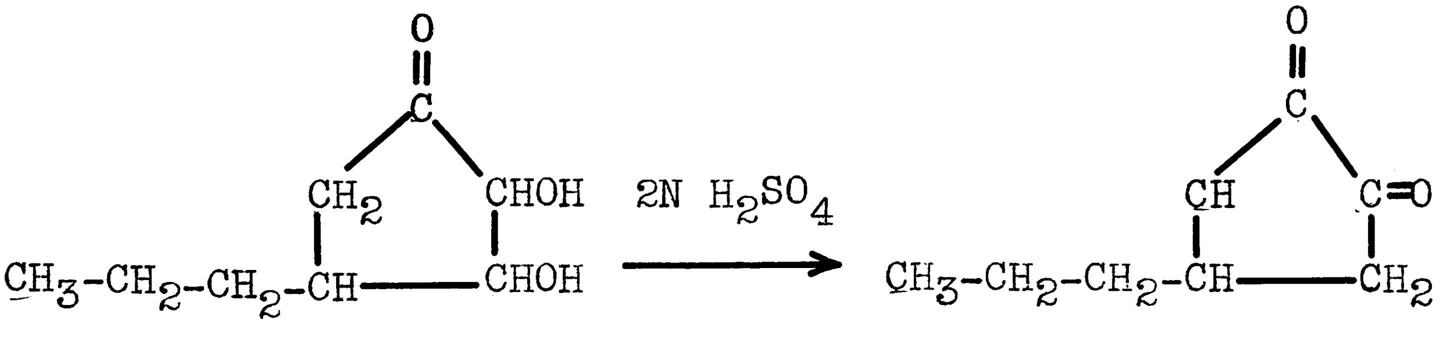


$$\underset{\displaystyle OAc}{C_6H_5\text{-}CH}\text{-}CO\text{-}CH_2\text{-}Cl \xrightarrow{\substack{CH_3OH\text{--}HOAc \\ NaOAc}} C_6H_5\text{-}CO\text{-}CO\text{-}CH_3$$

(XXXV) (XXXVI)

spontaneously into (XXXVI). It seems justifiable to conclude that during this period, (XXXV) underwent slow hydrolysis to $C_6H_5\text{-}CHOH\text{-}CO\text{-}CH_2OH$, followed by a molecular rearrangement to the diketone as indicated above.

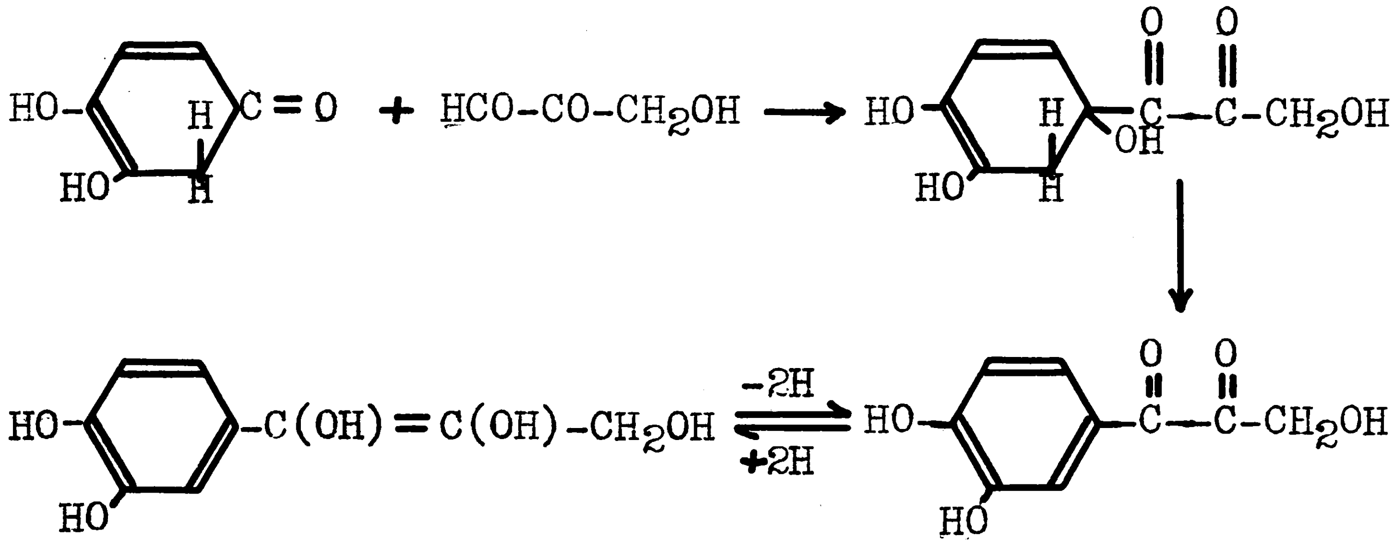
Further evidence for these speculations is to be found in the action of dilute sulfuric acid on the hydrogenated metabolic product terrein isolated by Raistrick and coworkers (60) by the action of several strains of <u>Aspergillus terreus Thom</u> on glucose as the sole organic substrate. It was found that terrein could be hydrogenated readily to yield tetrahydroterrein (XXXVII), and this in the presence of acid underwent rearrangement to a cyclic diketone (XXXVIII). It is evident that the molecule of tetrahydroterrein contains a grouping analogous to that in dioxyconiferyl alcohol (XXXIV) so that the diketone formation is not surprising.



(XXXVII) (XXXVIII)

It therefore seems highly probable that the 1,2-diketones isolated in the ethanolysis of wood represent stabilized end products derived from one or other of the dioxyconiferyl alcohol members of that dismutation system.

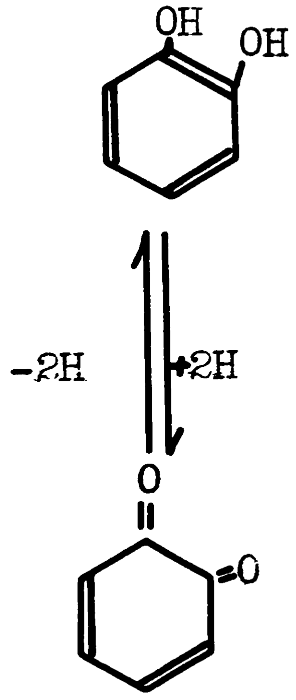
The plant origin of these dioxyconiferyl alcohol derivatives is, as yet, unknown, but it is interesting to note that their plant synthesis can be visualized as consisting of a primary condensation of two moles of methyl glyoxal, with the loss of a mole of water, followed by a further condensation with a third molecule, in this case hydroxymethyl glyoxal (instead of methyl glyoxal as in the case of the end methyl group derivatives)-(page 15).



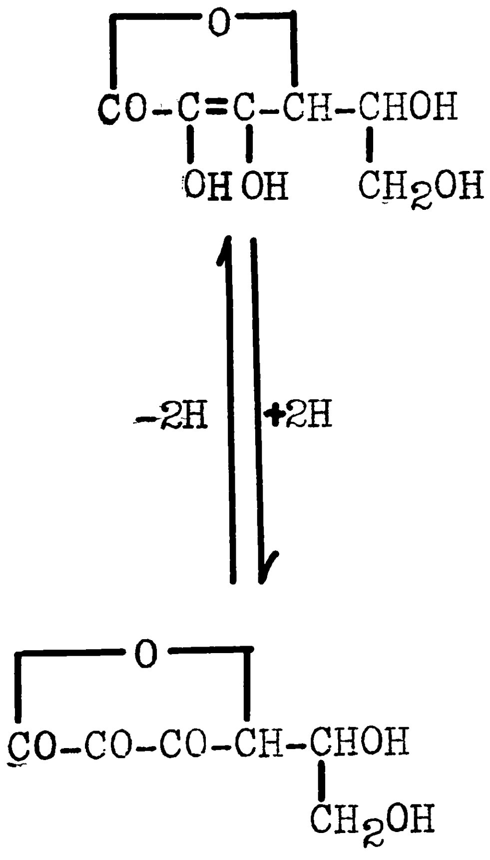
E. Possible Significance of Lignin Progenitors in Plant Oxidase Systems

The mechanism of animal respiration has engaged the attention of a large number of workers in biochemistry for some time. At present most workers in this field (52) believe that the energy necessary for the animal cell is liberated by the transformation of carbohydrates into carbon dioxide and water. This transformation consists of decarboxylation and dehydrogenation reactions. The greater part of the energy is derived from the reaction of hydrogen with oxygen. In the cell, carbohydrates undergo degradation and from the simpler fragments hydrogen in split off under the influence of enzymes known as dehydrogenases. This hydrogen is transported by what is known as a "carrier" or "hydrogen transporter". Thus hydrogen is transferred from one substance to another; this resulting in a chain of reactions which serve to transport hydrogen from negative to less negative oxidation-reduction systems until finally the stage of union with oxygen is reached. Thus during the course of a series of dehydrogenation reactions energy is liberated stepwise, in small amounts, and this provides the required energy for the living organism.

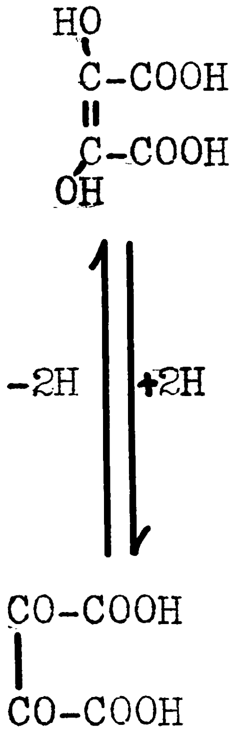
Szent-Györgyi has demonstrated the presence of a number of dehydrogenase-catalyst systems in various forms of plants; such as those of catechol (XXXIX) (61), ascorbic acid (XL) (62), and dioxymaleic acid (XLI) (63).



(XXXIX)



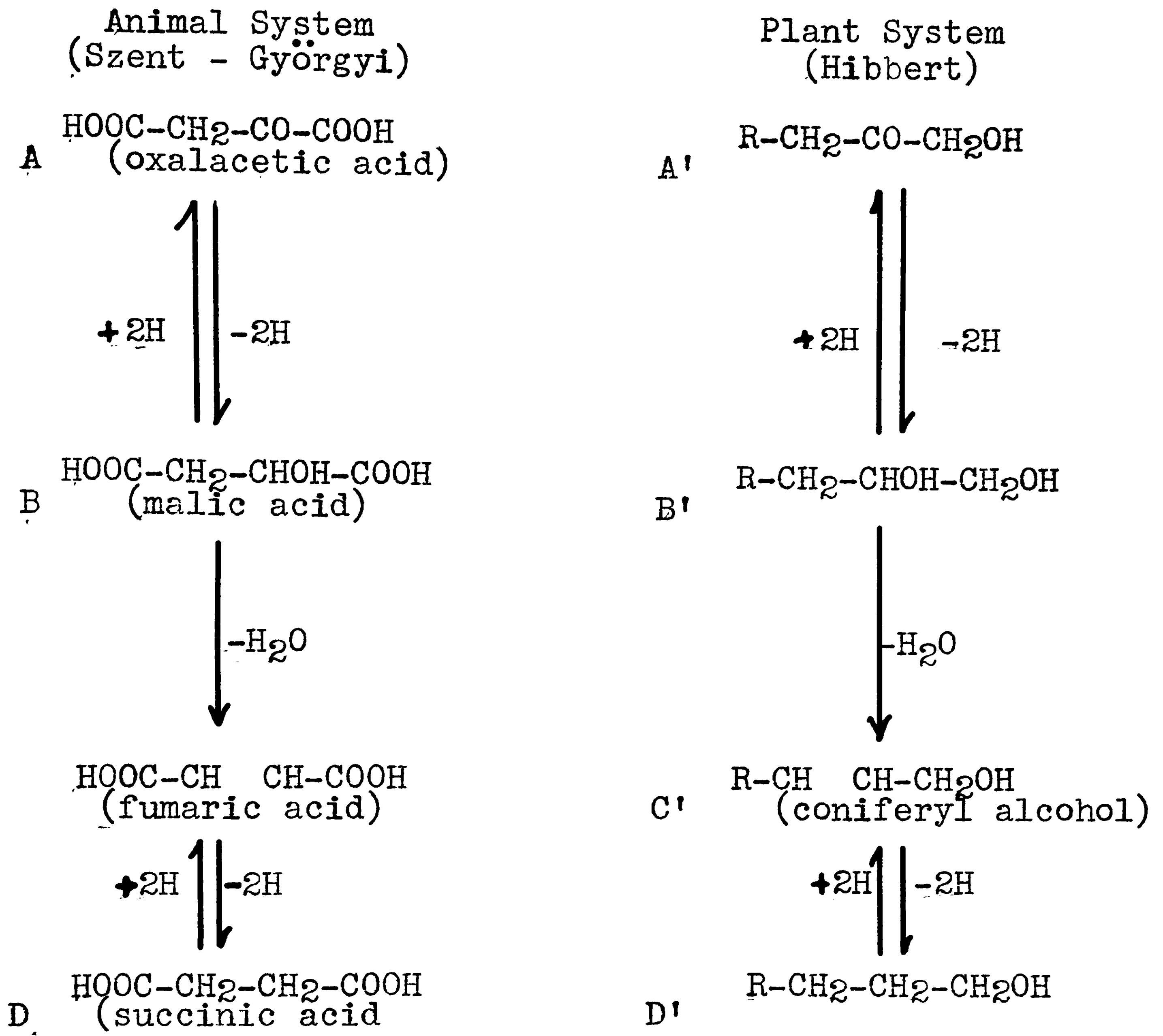
(XL)



(XLI)

Each of these can function as an oxidation-reduction system, the oxidized molecule being a 1,2-diketone and the reduced molecule an enediol.

Hibbert (4) has pointed out that the principal water-soluble ethanolysis products from spruce and maple represent enediol-1,2-diketone oxidation-reduction systems (XXIX) and (X). As discussed above (page 15), these presumably represent stabilized end products, their forerunners being lignin progenitors present in the plant cell as a series of monomolecular, hydrogen transporting catalysts, which later undergo conversion into more complex condensation polymeric products.
The presence of coniferin in the cambial sap of practically all plants, and other considerations, have led him (4) to propose a plant respiratory catalyst system similar to the C_4-dicarboxylic acid system of Szent-Györgyi (64).



R- syringyl or guaiacyl radical

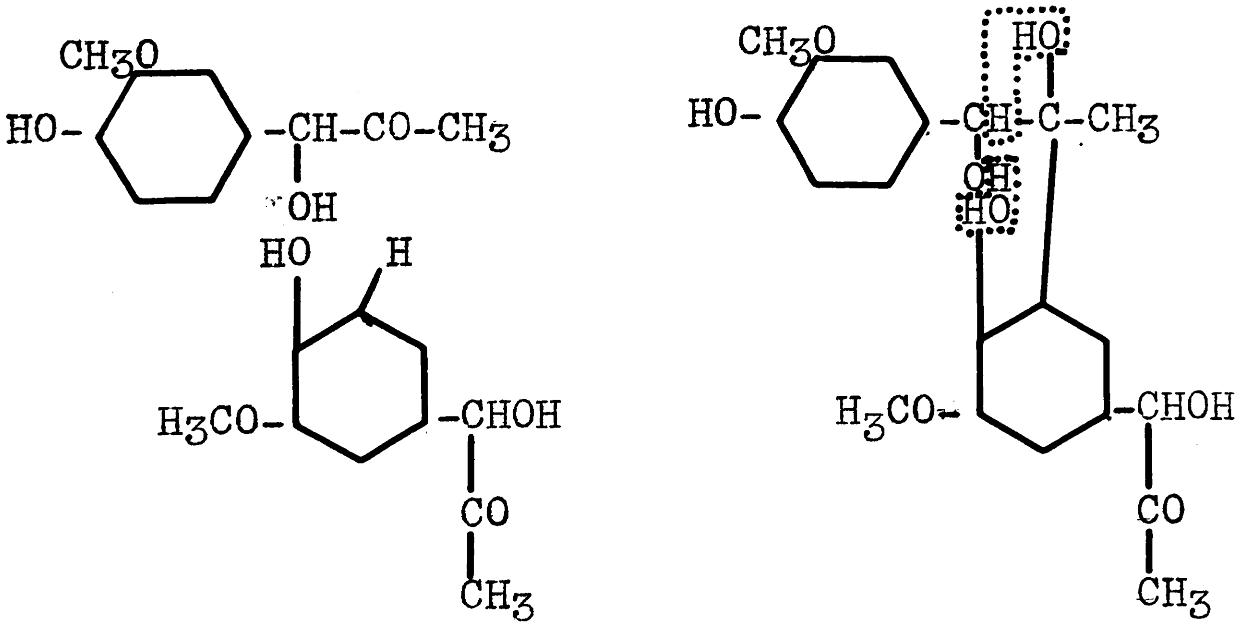
The first member (A') of the plant system, corresponding to oxalacetic acid (A), is the keto-alcohol believed to be obtained from the condensation of three mols of methyl glyoxal (page 15). It is seen that the third member of the new system is coniferyl alcohol corresponding to fumaric acid in the C_4 system. The isomeric form of (A'), $R-CO-CH_2-CH_2OH$, may also function similarly to (A') in the new system, while (B') and its isomeric form would provide analogs of the citric and isocitric acids which are the components of the Krebs animal cell oxidation system (65). The passage from Hibbert's new system to the ene-diol-1,2-diketone system can take place by an allylic rearrangement of the oxyconiferyl or oxysyringyl alcohol isomer, as represented on page 15. This has been confirmed, as indicated on page 16, by the isolation of $R-CO-CHOH-CH_3$ and $R-CHOH-CO-CH_3$ in the form of their ethyl ethers present in the alkali extracted ethanolysis products of spruce wood (46), as well as by the now established ease of conversion of $R-CH_2-CO-CH_2OH$ into $R-CO-CHOEt-CH_3$ (with probable simultaneous formation of $R-CHOEt-CO-CH_3$) in the ethanolysis treatment (56). Hydrogenation results (see later) have also demonstrated the presence of terminal ($-CH_2O-$) groupings in protolignin, which provides additional proof for the above suggested allylic rearrangement.

F. Formation of Protolignin from Propylphenol Units

(1) Polymerization Mechanisms of Guaiacyl Units

Prominent workers in the field of lignin chemistry believe that lignin originates from propylphenol units of the type isolated from wood by Hibbert and coworkers, or from closely related compounds, and Freudenberg, Erdtmann, Holmberg, and Hibbert have made significant contributions to the elucidation of the mechanism of lignin formation. Freudenberg (2) considers the union of the monomers to be of a carbon-carbon type involving oxygen-ring formation between side chains and aromatic nuclei.

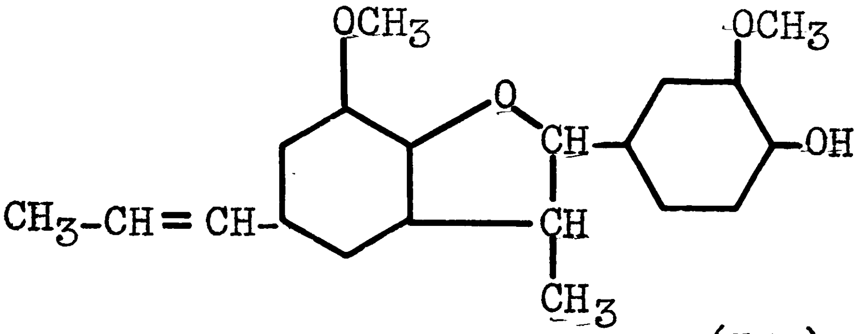
Hibbert (4) points out that the "lignin building units" containing a phenol group together with a carbonyl or an unsaturated linkage in the side chain would have a strong tendency to undergo para- and ortho -nuclear condensations both individually and collectively, under mild conditions, with formation of condensation polymers. This phenol-carbonyl type of reaction is well known, and was first suggested by Freudenberg solely on theoretical grounds, inasmuch as he has never succeeded in isolating any C_6H_5-C-C-C units.



(XLII)

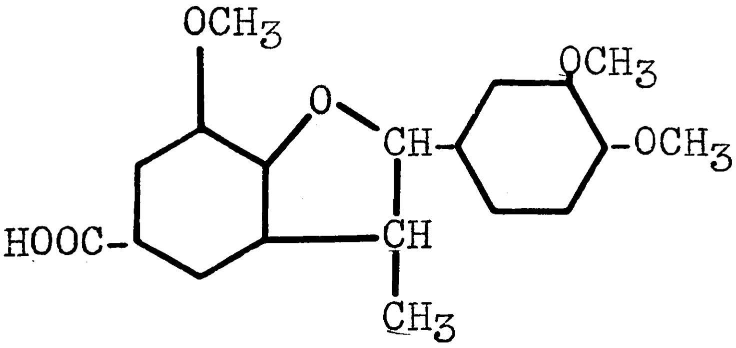
The condensation of the ortho-hydrogen atom of one unit with the carbonyl of another, followed by the elimination of two molecules of water as indicated would result in formation of a benzofurane derivative. Condensation with a third molecule would yield a trimer and so on. It is seen that this mechanism differs from Freudenberg's only in the order in which the first two steps are assumed to occur.

Under the action of bacterial enzymes or ferric chloride (66) isoeugenol forms a dehydrogenated dimer, dehydrodiisoeugenol, considered by Erdtmann (3) to have the formula (III).



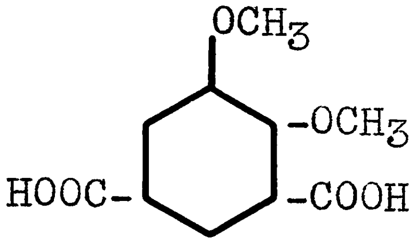
(III)

By the oxidation of the methyl ether of this dimer with cold potassium permanganate, Erdtmann prepared the acid (XLIII), which is regarded by Freudenberg as a model substance for the lignin polymer.

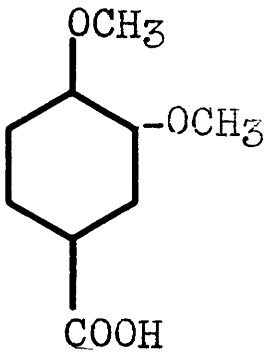


(XLIII)

Freudenberg found that (XLIII), after degradation with alkali, methylation, and permanganate oxidation, yielded isohemipinic acid (XLIV) and veratric acid (XLV). By the same treatment of spruce lignin Freudenberg obtained 2% of isohemipinic acid and 12% veratric acid, and traces of trimethyl gallic acid, and



(XLIV)

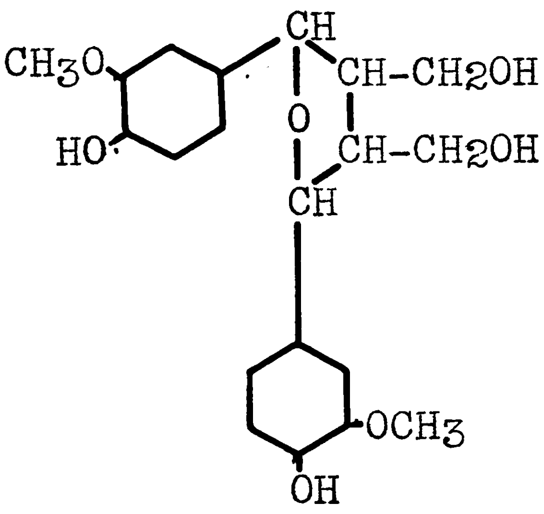


(XLV)

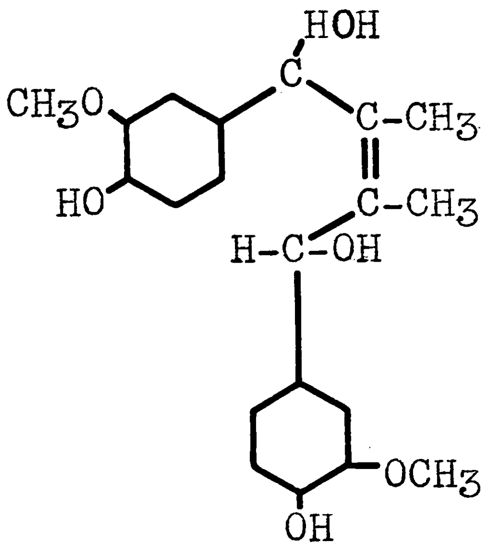
concluded (67) that some of the lignin molecules are of a type capable of yielding isohemipinic acid on alkali degradation, followed by methylation and oxidation. It is apparent that this observation supports the theory of Erdtmann (3) and of Hibbert (68) that protolignin is made up of dimers of the dehydrodiisoeugenol type (III).

Erdtmann in his recent review (3) points out that the structure of a wide variety of plant resins, e.g. olivil (XLVI), lariciresinol (XLVII), conidendrin (XLVIII) and others conform to a general dimer type, the monomer being a propylphenol derivative closely related to coniferyl alcohol, and that the dimer formation apparently always involves the β—carbon atom of the side chain.

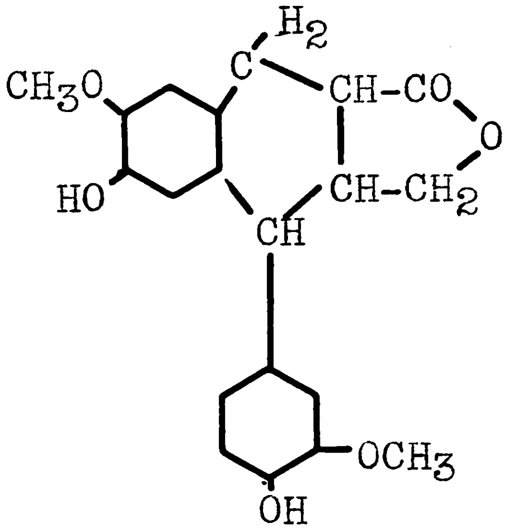
The similarity between these simple natural products and dehydrodiisoeugenol, and the analogies between lignin and dehydrodiisoeugenol have led Erdtmann to the belief that the phenomenon of dehydrogenative coupling of molecules probably plays a great role in the biogenesis of plant products.



(XLVI)



(XLVII)

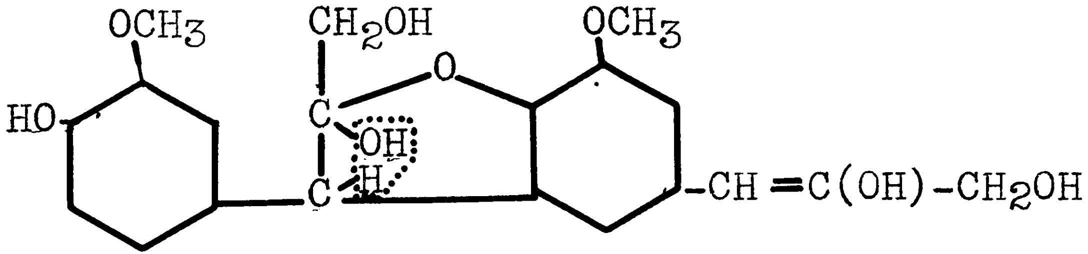


(XLVIII)

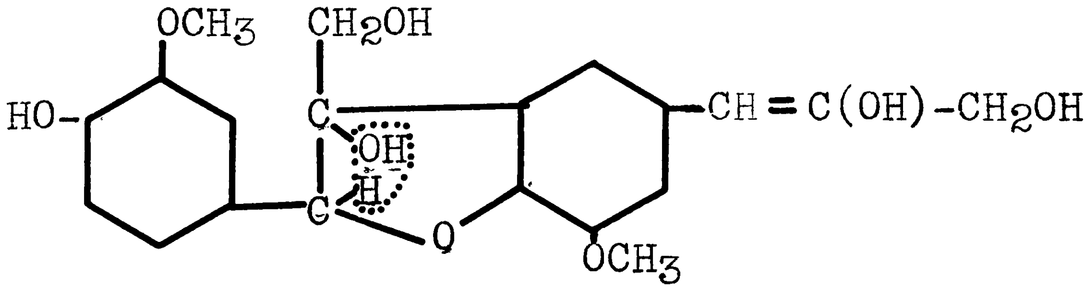
He states that the ethanolysis products α-hydroxypropiovanillone, (XXIX) and vanilloyl methyl ketone (X) and their syringyl analogues are not necessarily true lignin building units, since they may represent stabilized end products originating from dimeric types similar to dehydrodiisoeugenol. That such may well be the case has been recognized by Hibbert (68). (see also page 17)

There is a close relationship between the enolic forms of the side chains of certain propylphenol derivatives $R\text{-}C(OH)\text{=}C(OH)\cdot$ (XXVIII); $R\text{-}CH\text{=}C(OH)\text{-}CH_3$ (XXX); $R\text{-}CH\text{=}C(OH)\text{-}CH_2OH$ (XXXIII); and the side chains of isoeugenol $R\text{-}CH\text{=}CH\text{-}CH_3$ and coniferyl alcohol $R\text{-}CH\text{=}CH\text{-}CH_2OH$. This fact strongly suggests that protolignin may be present in the plant as a series of polymers of the dehydrodiisoeugenol type (III) derived from monomers of the oxyconiferyl alcohol type (XXXIII). These reactive dimers during the course of the ethanolysis could partially polymerize and partially undergo transformation to the stabilized ethanolysis units, as shown below.

Application of the dehydrodiisoeugenol type of polymerization of the enolic forms of certain propylphenol units, for example oxyconiferyl alcohol (XXXIII), as pointed out by Hibbert (68), could give rise to two general types of lignin polymers: (XLIX) and (L).

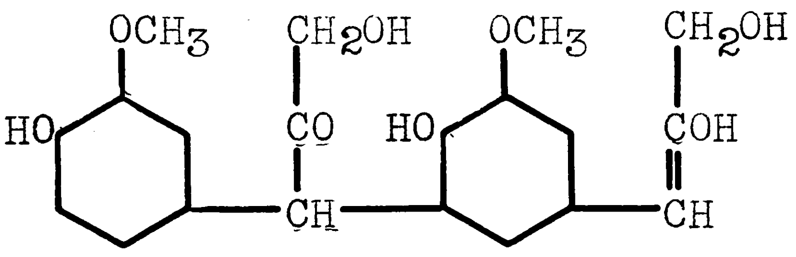


(XLIX)

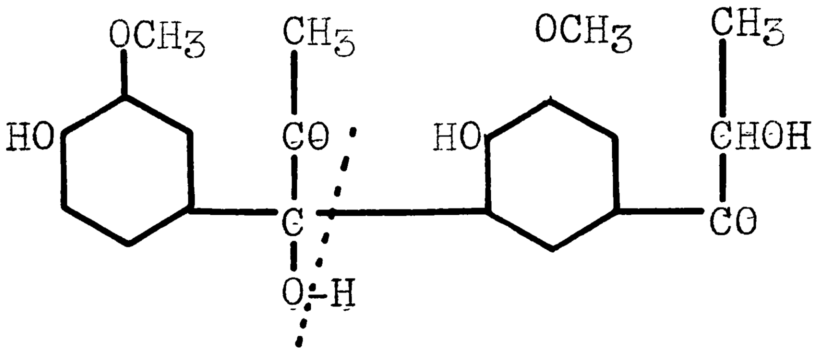


(L)

Each of these could condense further to give a trimer, a tetramer, etc., while the elimination of a mole of water from each dimer would yield benzofurane derivatives. Ring opening of (XLIX) could give rise to the (LI) form, from which, by a double allylic shift, and by cleavage, one mole each of the diketone (X) and of the ketol (XXIX) could be obtained. Such a cleavage would only be possible with a reversible type polymer and not with the benzofurane irreversible type. The



(LI)



(LII)

same dehydrogenative-coupling type of polymerization and depolymerization can be applied also to two moles of the enediol of α-hydroxypropiovanillone (XXVIII), or to two moles of the enol of (4-hydroxy-3-methoxyphenyl)-propanone-2 (XXX).

(2) Polymerization Mechanism of Syringyl Units

It is apparent that the syringyl analogs, due to the blocking of the ortho positions of the phenol could not undergo the same dehydrogenative coupling. Hibbert (4) points out that since the "lignin building units" (XXIX), (XXX) and (XVI) in their enediol forms are derivatives of styrene, they could possibly undergo the styrene type of polymerization, although this is regarded as much less probable.

Inasmuch as coniferyl, oxyconiferyl, syringyl, and oxysyringyl alcohols may be regarded as substituted cinnamyl alcohols, and in view of the ease with which cinnamyl derivatives, in the presence of dilute acids, not only undergo the allyl shift but also form dicinnamyl ethers (69) in high yield, it is possible that the syringyl units may exist in the woody tissue as ethers, thus accounting for their much readier extraction by ethanolysis and other methods.

In any event the type of polymerization of gymnosperms appears to be much more complex than in the case of the angiosperms, the reversible type being present in the latter to a much greater extent (4). Recent work (70) has shown that both the ether-soluble and -insoluble ethanol maple lignins undergo depolymerization on further treatment with ethanol-hydrochloric acid to give the 1,2-diketone (X) and the keto-alcohol (XXIX) a result in harmony with the above theoretical speculations.

The reactions of lignin with mercaptans, particularly with thioglycollic acid, have been investigated over a period of years by Holmberg (71) and are of particular importance in any appraisal of the various suggested polymerization mechanisms. The mercaptans, R-SH, are thio-alcohols, and in the presence of acids, react in the same way (namely through the -SH-group) as alcohol with lignin in the wood. This is emphasized by the fact that treatment of ethanol lignin with thioglycollic acid results in the replacement of the ethoxyl groups by the $-S-CH_2-COOH$ radical (72). By treating wood with thioglycollic acid in the presence of hydrochloric acid, Holmberg obtained products containing even more thioglycollic acid than the treated ethanol lignin.

Holmberg's experiments dealing with the reactions of model substances (presumably related to lignin) with thioglycollic acid (71) as well as the related experiments carried out by Freudenberg (73), by Häggland (74) and by Richtzenhain (75) were all designed to throw light upon the question of the actual groupings present in proto- and isolated lignins. Thus thioglycollic acid condenses with cinnamyl alcohol (76) with the loss of water to give cinnamyl thioglycollic acid.

$C_6H_5\text{-}CH{=}CH\text{-}CH_2OH + HS\text{-}CH_2\text{-}COOH \longrightarrow C_6H_5\text{-}CH{=}CH\text{-}CH_2\text{-}S\text{-}CH_2\text{-}COOH + H_2O$.

A similar reaction occurs with butyl alcohol, α-phenylethyl alcohol, and, more significantly with benzyl alcohol (77), its derivatives and the ethers of it and its derivatives, e.g. phenyl methyl carbinol (LIII), benzohydrol (LIV), α-ethoxyphenylethane (LV) and benzyl ethyl ether (LVI).

$$\underset{\text{(LIII)}}{C_6H_5\text{-}CH(CH_3)\text{-}OH} + HS\text{-}CH_2\text{-}COOH \longrightarrow C_6H_5\text{-}CH(CH_3)\text{-}S\text{-}CH_2\text{-}COOH + H_2O$$

$$\underset{\text{(LV)}}{C_6H_5\text{-}CH(CH_3)OEt} + HS\text{-}CH_2\text{-}COOH \longrightarrow C_6H_5\text{-}CH(CH_3)\text{-}S\text{-}CH_2\text{-}COOH + EtOH$$

$$\underset{\text{(LIV)}}{(C_6H_5)_2\text{-}CHOH} \qquad \underset{\text{(LVI)}}{C_6H_5\text{-}CH_2\text{-}OEt}$$

(LIV) and (LVI) react in the same way as (LIII) and (LV).

Thioglycollic acid does not condense with such alcohols as phenylpropanol (C_6H_5-CH_2-CH_2-CH_2OH), and phenyl ethanol (C_6H_5-CH_2-CH_2-OH) (72).

From the foregoing results, the following conclusion is drawn: Holmberg's experiments on the reaction of thioglycollic acid with model substances have shown that this reagent condenses with derivatives of benzyl alcohol and only with a limited number of other types of alcohols. The fact that lignin condenses with thioglycollic acid very readily, would suggest that the former is a derivative of benzyl alcohol. Examination of the various structures proposed for lignin (II), (L) and (LII) shows that they are such derivatives, hence Holmberg's work lends support to the proposed theories of lignin structure.

II. THE HIGH-PRESSURE HYDROGENATION OF ORGANIC COMPOUNDS IN THE PRESENCE OF COPPER-CHROMIUM OXIDE AND RANEY NICKEL CATALYSTS

Hydrogenation processes have been steadily increasing in size, variety and importance, and the unit process of hydrogenation is becoming one of the most useful and widespread in organic synthesis. A discussion of even a few of the many important industrial hydrogenation processes is out of place in this thesis, instead the discussion in this section is limited to hydrogenation reactions adaptable to laboratory investigations. Even more specifically, this discussion is concerned with those phases of high-pressure catalytic hydrogenation reactions and technique which bear directly on its utilization as a tool in the investigation of the structure of lignin.

Hydrogenation is correctly defined as reduction by means of molecular hydrogen; actually, however, the term has grown to include the reduction by means of molecular hydrogen *in the presence of a catalyst*. In addition, catalytic hydrogenation or, more commonly, hydrogenation may be divided into two classes; namely, high-pressure (above 50 atmospheres) and low-pressure hydrogenation.

A. Variables (Physical Factors) Affecting Hydrogenation

The most difficult problem involved in the application of hydrogenation technique to industrial or laboratory problems has been the determination of the optimum conditions for the production of a desired product. In the study and application of hydrogenation reactions it is essential to realize that the reactions are reversible. Thus Raney nickel, (78) which is one of the best catalysts for the reaction:

$$\text{Benzene} + 3H_2 \longrightarrow \text{Cyclohexane}$$

is also one of the best dehydrogenation catalysts for the production of aromatics from hydroaromatics (79). Similarily, catalysts containing copper and copper oxide which are especially useful in the reduction of aldehydes to alcohols (80, p. 50) are used commercially for the production of aldehydes from alcohols (81, p. 431). It is for this reason that changes in any given variable are so important in hydrogenation.

Of the many variables involved, the most important (exclusive of choice of catalyst) are temperature, pressure, time, solvent, concentration and quantity of catalyst.

(1) Temperature - For the most part, the temperatures used for hydrogenation reactions are below 400°C, except in cases where

pyrolytic decomposition occurs concurrently with hydrogenation as in the hydrogenation of coal at 500°C (82). It may be mentioned at this point that hydrogenolysis, which, like hydrolysis, is a cleavage of a molecule by hydrogen in the presence of a catalyst is not to be confused with pyrolysis, or cleavage due to heat energy.

Practically every hydrogenation reaction can be reversed by increasing the temperature sufficiently (81, p.411); obviously, then, it is desirable to work at as low a temperature as possible. On the other hand, a rise in the temperature increases the speed of the reaction. It therefore becomes necessary to balance the less favorable equilibrium position with the faster rate of reaction. Fortunately, in recent years, knowledge of catalysis has been so extended that satisfactory reaction rates are possible at lower temperatures where a more favorable equilibrium condition prevails.

Concerning the temperature coefficient of hydrogenation reactions, almost none fit the generalized statement that the speed of a reaction may be doubled every 10-15° rise in temperature, a change of 50° or more being usually necessary.

In general, the noble metal catalysts, such as Pt or Pd are used from room temperature to 150°; catalysts of the Ni and Cu type, from 150 to 250°; and various combinations of metals and metal oxides, from 250-400°.

(2) Pressure - Pressure, like temperature, can affect both the rate of reaction and the equilibrium position. The equilibrium, however, is noticeably affected only when there is a decrease in the reaction volume as it proceeds (Le Chatelier's principle). Increased rate with a rise in pressure is generally observed as a concentration effect. If the reaction is in the gas phase the concentration of one of the reactants has been increased; if in the liquid phase, the solubility of hydrogen in the liquid is increased, thereby increasing the effective hydrogen concentration. Several other factors are also involved, for there appears to be considerable difference between compounds with respect to the effectiveness of increased pressure in accelerating the reaction rate. The following figures for the hydrogenation of aniline, phenol and acetoacetic ester (AAE) over Ni(K) (Ni on Kieselguhr) illustrate this condition (83):

TABLE I

	Extent of Reaction (%) in Specified Time		
Pressure (Atm.)	Benzene (0.5 hr.)	Aniline (6 hrs.)	AAE (0.5 hr.)
30	40	29	40
200	68	65	72
350	75	75	100

Of major importance, however, is that increase in pressure is almost always desirable.

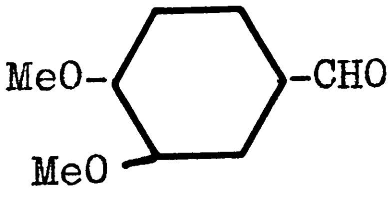
(3) Time - The importance of the time factor lies chiefly in the fact that all other variables remaining constant, the time necessary for a hydrogenation may vary from a few seconds to several hours depending upon the material being hydrogenated. In the laboratory this factor is useful as an additional means of promoting a selective hydrogenation.

(4) Solvent - When a solid material is to be hydrogenated, the choice of solvent becomes an important one. Obviously, a given solvent must be stable to hydrogenation conditions and be used below its critical temperature. That the solvent can and does affect the rate of hydrogenation was shown by Adkins in the case of ethyl nicotinate at 165° over RaNi (Raney Nickel) where the solvents were ethanol, methylcyclohexane, ethyl ether and dioxane. The hydrogenation times were 3, 1.5, 5, and 1 hour and the yields of product were 58, 80, 80 and 77%, respectively (84). With CuCrO and RaNi, ethanol, dioxane, ethyl ether and methylcyclohexane have been found quite satisfactory as solvents (80, p. 25).

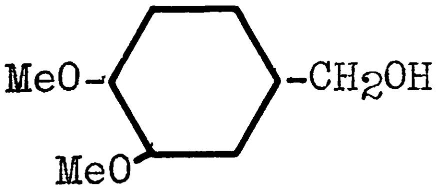
(5) Concentration - Changes in concentration of a solid in solution effect the hydrogenation to a marked extent only if the material is complex and side reactions are possible. It is of interest to note, however, that whereas a 10% solution of ethanol lignin in dioxane hydrogenated readily at 250°C, an 18%

solution underwent a slight change only (85).

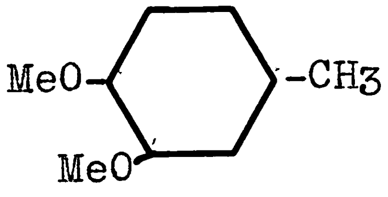
Of considerable interest in this respect are the results obtained by Cooke, McCarthy and Hibbert (85) in the hydrogenation of veratraldehyde, (LVII), at 180°C at 1100 lbs. / sq.in. hydrogen pressure. When this reaction was run with a solution containing 43.2 g. of veratraldehyde in 150 cc. of dioxane (350 cc. void), three products were obtained; namely, veratryl alcohol (LVIII), (55%), homoveratrol (LIX), (40%), and a trace of a crystalline compound (2%), melting at 74-75°C, of the probable structure represented by (LX) (86). When the concentration of veratraldehyde (from the same preparation) was increased to 66 g., however, only two products were obtained; namely, veratraldehyde (55%) and the crystalline compound (40%).



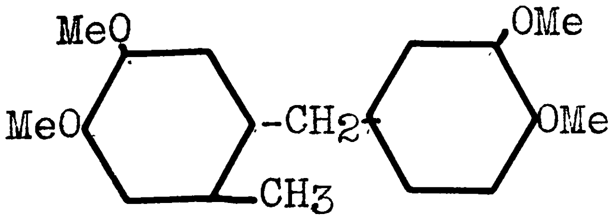
(LVII)



(LVIII)



(LIX)



(LX)

(6) Ratio of Catalyst to Acceptor - Although one might expect the concentration of catalyst to play a minor role in hydrogenation this is not found to be the case. This condition is due to the fact that all hydrogenation catalysis is based upon surface activation and is therefore dependent upon the amount of surface. Adkins makes the following statement "500 g. of compound with 25 g. of a catalyst will be hydrogenated very much more rapidly than would 50 g. of a compound with the same ratio of catalyst (2.5 g.)" (80, p.22). It has been observed frequently in these laboratories that an increase in quantity of catalyst will appreciably increase the rate of a hydrogenation reaction (85, 87). It may be of interest to note that in a typical lignin hydrogenation the ratio of lignin to CuCrO is 15/8 (85). For simple compounds such as acetone or benzene, however, the amount of catalyst generally ranges from 2-8% of the weight of acceptor. The following table shows the change in hydrogenation rate of benzaldehyde over Pt; 21.2 g. of benzaldehyde was used and the time to 100% reduction determined (88).

TABLE II

The Effect of Catalyst Concentration on Duration of Hydrogenation

Weight of Catalyst g.	Time
0.0288	5.5 hrs.
0.0575	60.0 min.
0.115	34.0 "
0.23	23.0 "

B. Hydrogenation Catalysts

(1) Principles Concerning Hydrogenation Catalysts

(a). Surface - Hydrogenation catalysts are solids consisting of metals, metal oxides, or metal sulfides which are prepared in such a manner that a highly extended surface is obtained. A consideration of the nature of surface catalysis is out of place in this thesis*; but it is of importance to note that this extensive surface is only effective when obtained by chemical and not mechanical means. In other words the phenomenon

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*An excellent review on the subject of hydrogenation catalysis is presented in the "Twelth Catalysis Report", Wiley (1940), of the (U. S.) National Research Council (1-131).

of adsorption plays a very important role and a porous material whose particles are of atomic size is essential. A good example of a catalyst preparation is that for Raney nickel (89). In this procedure the catalyst is prepared by alloying equal parts of nickel and aluminum and then dissolving out the latter with aqueous sodium hydroxide. The principle is quite clear; firstly, the aluminum atoms are removed from a solid "solution" of nickel-aluminum, leaving an atomic latticework composed of nickel, secondly, this very reactive form of nickel is protected from oxidation by the presence of the hydrogen formed during the dissolution of the aluminum. This catalyst is stored in a liquid (water, ethanol, etc.) to prevent reaction with the air, for as soon as it becomes dry in the presence of oxygen it oxidizes with explosive rapidity (87).

(b). <u>Mixed Metal Catalysts</u> - - Catalysts are easily poisoned and must be prepared very pure, although it has been found that when completely pure, some catalysts have a reduced activity. Careful study of this problem by many investigators has shown that certain metals have a definite promoting effect upon the catalyst. For example a small amount of chlorine or sulfur will render a copper catalyst used for the dehydrogenation of methanol completely inactive (90), while the addition of about 3% of zinc oxide to a pure copper catalyst will increase the activity threefold (91). The use of mixed metal catalysts, or promoted catalysts, has been extended rapidly in recent years. More commom mixtures of the well-known types of catalysts are Ni-Cu (92), $NiAl_2O_3$ (93), Cu-ZnO (94), Cu-CrO (95), and ZnO-CrO (96). However, the recent chemical and patent literature describes the use of practically every metal and metallic oxide in the periodic table.

(2) General Classification of Hydrogenation Catalysts - The number of catalysts capable of effecting hydrogenations is large, and in addition many types of hydrogenation are possible. Practically any type of unsaturated material can be hydrogenated catalytically. It will be pointed out that hydrogenation may involve the saturation of $C=C$, $C\equiv C$ or $C=O$ linkages; the reduction of carbalkoxyl, hydroxyl, nitro and cyano groups; and also the cleavage of C-C and C-O bonds. In general, however, hydrogenation catalysts may be classified as follows:

(a) Violent Hydrogenation Catalysts - These catalysts are usually characterized by the fact that they carry the hydrogenation to the fullest possible extent so that the maximum addition of hydrogen to a compound occurs under the particular operating conditions. Thus, in the case of the simple aldehydes the reduction will pass beyond the alcohol stage and end at the saturated hydrocarbon. Even here, the tendency to saturate the carbon atoms may be sufficiently great to cause cracking, or to break the C-C bond so that still more hydrogen can be added, the final result being CH_4. Cracking tendencies are usually associated with these violent hydrogenation catalysts, although, through control of the variables of temperature and pressure, the cracking reactions can usually be suppressed. Common catalysts belonging to this class consist of the iron, cobalt and nickel compounds (97, p.107) and oftimes of molybdenum and tungsten sulfides and oxides (97, p.111).

(b) Mild Hydrogenation Catalysts - The term mild should not be confused with activity. These catalysts will effect hydrogenations just as rapidly as the violent hydrogenation types but they are able to effect only one step at a time in a hydrogenation, or at least they do not permit the reaction to proceed to the hydrocarbon stage. A great many catalysts belong to this class, and more are being developed rapidly. These catalysts will easily reduce an aldehyde or ketone to the corresponding alcohol, or an acid or ester to an alcohol. The large number of catalysts developed for the direct synthesis of methanol from carbon monoxide belong to this class; they usually contain Cu, ZnO, CrO and MnO (98) and may include some of the rarer elements as promoters. In addition, the noble metal catalysts platinum and palladium, or their oxides are placed in this category.

(c). Catalysts with Properties other than those Associated with Hydrogenation - The synthesis of higher alcohols from carbon monoxide involves a condensation as well as hydrogenation. These so-called "higher alcohol" catalysts are usually of the mild hydrogenating type but contain some more alkaline materials such as sodium, calcium or barium carbonates or aluminum and magnesium oxides (99). Other types of catalysts are capable of splitting out water from a molecule along with the hydrogenation but do not possess any appreciable cracking tendencies. These are usually of the violent type but contain considerable, and sometimes even preponderant, quantities of dehydrating catalysts such as alumina, thoria, tungstic oxide, or chromic oxide (97, p. 127). They serve to effect such reductions as phenol to benzene, cresols to aromatic hydrocarbons, and convert various hydroxylic compounds to hydrocarbons with little or no other changes in the molecular structure.

C. Types of Reaction with Hydrogen

In laboratory high-pressure hydrogenation technique (specifically in these laboratories) two catalysts are generally employed - one from the "violent" category, RaNi; the other from the "mild" division, CuCrO. This section will be devoted essentially to the behavior of various type compounds over these two catalysts.

1. Hydrogenation (Reduction)

(a). Hydrogenation of Ethylenic (C=C) Linkage - - The hydrogenation of an ethylenic to a paraffinic linkage can be accomplished readily, usually in the presence of a Ni or Ni-containing catalyst. In general, the hydrogen pressure need not be high, except when the hydrogenation is slow, and then increased pressure usually speeds up the reaction. With RaNi it is safe to say that relatively few alkenes would resist hydrogenation at 100°C. and 100 atmospheres pressure (80). CuCrO is also an active catalyst for the hydrogenation of alkene linkages, but since higher temperatures (100-175°) are required, there appears to be little advantage in its use for hydrocarbons except where some other group such as carbonyl or carbethoxyl is to be hydrogenated. It is often advantageous to combine the two hydrogenations and use CuCrO to bring about both effects.

Examples:

TABLE III

Substance	Press. Atm.	Temp. oC.	Time Min.	Catalyst	Product
Styrene	3	20	75	Ni(K)	Ethylbenzene (100)
Styrene	34	20	25	Ni(K)	Ethylbenzene (100)
Styrene	34	125	7	CuCrO	Ethylbenzene (100)
Cinnamyl Ethyl Ester	200	250	180	CuCrO	3-Phenyl-propanol-1 (101)

In general, the alkene linkage is saturated at so low a temperature, and so rapidly, that other unsaturated groups such as benzenoid, furanoid, pyridinoid and carbethoxyl are not acted upon by hydrogen under conditions necessary for reduction of the C=C bond.(80). Care must be exercised in hydrogenating unsaturated aldehydes, ketones, cyanides, oximes, etc. or both functional groups will be hydrogenated.

(b). Hydrogenation of Carbonyl (C=O) Linkage - - The carbonyl group in aldehydes and ketones is readily hydrogenated (80). This group can be reduced either partially, to give an alcohol, or entirely to give a hydrocarbon. The partial reduction is obviously characterized as a "mild" hydrogenation and CuCrO is the appropriate catalyst. Acetone may be converted to isopropyl alcohol over RaNi at room temperature and 2-3 atmospheres pressure, but much more rapid reaction is obtained at higher temperatures and pressures. Apparently the great majority of aldehydes and ketones may be hydrogenated to the corresponding carbinols over either catalyst at temperatures not greater than 150°C and pressures not greater than 100 atmospheres, the yields of alcohols being practically quantitative. Keto- and aldo-alcohols and esters are hydrogenated almost as readily and they give yields of the same order as those from unsubstituted ketones and aldehydes. If a phenyl or pyrryl group is adjacent to the carbonyl group then the hydroxyl group first formed may undergo a secondary hydrogenolysis to a methylene group (see page 53). Since the alkene linkage is hydrogenated under conditions similar to those used for the hydrogenation of carbonyls, both reactions can be carried out in a single operation.

Examples: TABLE IV

Substance	Press. Atm.	Temp. oC	Time Min.	Catalyst	Product
Acetophenone	100	110	10	RaNi	91% Ø*-Me-carbinol (102)
Acetophenone	100	150	30	CuCrO	95% Ø-Me-carbinol (102)
Heptaldehyde	-	150	240	RaNi	92% heptanol-1 (102)
Glucose	-	160	240	CuCrO	97% sorbitol (92)
Benzalacetone	-	175	12	CuCrO	97% 4-Ø-butanol-2 (103)
Acetoacetic ester	100	150	180	CuCrO	97% ethyl-β-OH-butyrate (103)

* Ø = Phenyl.

(c). <u>Hydrogenation of the Benzenoid Nucleus</u> - - The benzenoid nucleus requires distinctly more drastic conditions for its complete hydrogenation than do the alkene, carbonyl, cyano or imino groups (80). CuCrO is seldom used for these reactions since high temperatures and pressures over a prolonged period are required. Over RaNi, however, benzene can be rather rapidly hydrogenated in the vicinity of 125°C at 100 atmospheres pressure. The phenols are more rapidly hydrogenated than other derivatives of benzene; the amino, carbethoxyl, ether and hydrocarbon groups definitely retard hydrogenation. In the case of the amino and carbethoxyl derivatives of benzene the yields of the corresponding cyclohexyl derivative are above 90%, but with ethers, hydrogenolysis occurs resulting in only 50-70% yields of the cyclohexyl ethers.

Examples: <u>TABLE V</u>

Substance	Temp. °C	Time Hrs.	Catalyst		Product
Benzene	150	1.0	RaNi	100%	Cyclohexane (78)
Toluene	175	0.12	RaNi	100%	Me-cyclohexane (78)
Benzene	125	0.25	Ni(K)	100%	Cyclohexane (78)
Di-Ø-methane	150	7.0	Ni(K)	100%	Dicyclohexylmethane (100)
Phenol	150	3.0	Ni(K)		Cyclohexanol (104)
Anisol	200	4.4	RaNi	66%	Methylcyclohexyl ether (105)
Aniline	175	9.0	Ni (K)	80%	cyclohexylamine (104)
Methyl Salicylate	200	9.0	Ni(K)	96%	Methylhexahydro-Salicylate (106)

(d). Hydrogenation of the Furanoid Nucleus - - The hydrogenation of the furanoid nucleus occurs under somewhat milder conditions than those used for the benzenoid ring, and also differs in that the former is an unsaturated cyclic ether, hence is subject to hydrogenolysis (80). Over RaNi, however, the furyl derivatives have been hydrogenated in yields of 80-97% to the corresponding tetrahydro compounds (107). (For reactions over CuCrO see page 54).

2. Hydrogenolysis (Cleavage)

(a). Hydrogenolysis of the C-C Bond

(1). C-C Cleavage in Hydrocarbons - - Hydrocarbon cleavage occurs most commonly at very high temperatures over the "violent type" catalyst (RaNi) although with certain groupings C-C cleavage may occur over CuCrO.

Some examples are:

$$\text{Pentaphenylethane} \xrightarrow[125^{\circ}\text{C}]{\text{RaNi}} \text{Tricylohexylmethane} + \text{Dicyclohexylmethane (100)}$$

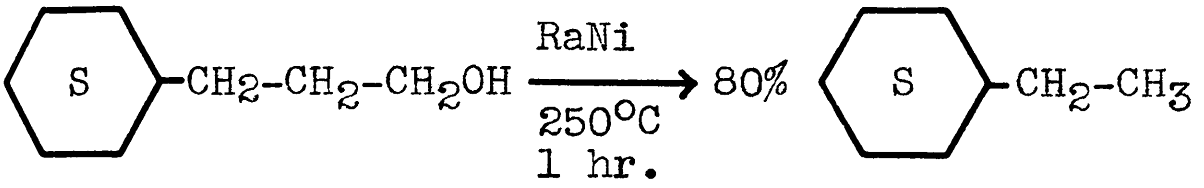
$$\text{Pentaphenylethane} \xrightarrow[200^{\circ}\text{C}]{\text{CuCrO}} \text{Triphenylmethane} + \text{Diphenylmethane (100)}$$

On the other hand the hydrogenated phenylethanes are completely stable toward hydrogen at 200°C; it is thus evident that the phenyl group is very much more effective than the cyclohexyl group in facilitating C-C cleavage (80).

(2). <u>C-C Cleavage in Alcohols</u> - - Primary alcohols react with hydrogen over RaNi at 250°C;

$$RCH_2OH + 2H_2 \longrightarrow RH + CH_4 + H_2O$$

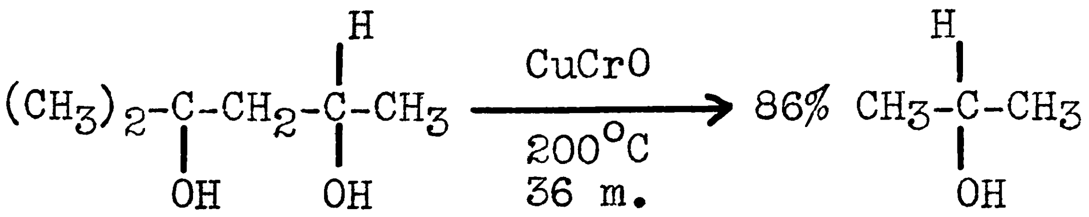
Thus:



(108)

Secondary alcohols undergo hydrogenolysis preferentially at the C-O bond rather than the C-C bond (108).

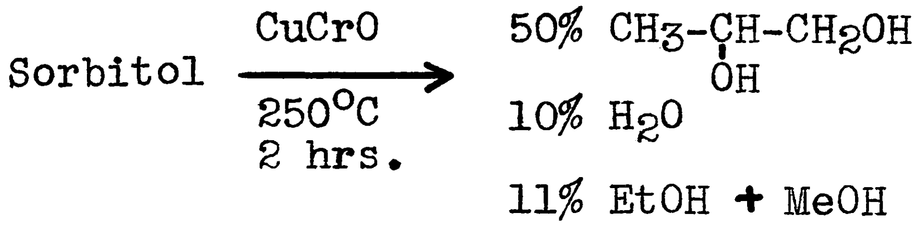
(3). <u>C-C Cleavage in Glycols</u> - - The hydrogenolysis of C-C linkages in alcohols, referred to above, takes place slowly even over RaNi at 250°C. However, if the hydroxyl groups in a glycol are in the 1,3- positions, and, in addition, if there are alkyl substituents in the 1,2 or 3 position, then hydrogenolysis at the C-C becomes a very important factor and occurs readily even over CuCrO (200-250°C).



$$(CH_3)_2\text{-}\underset{OH}{C}\text{-}CH_2\text{-}\overset{H}{\underset{OH}{C}}\text{-}CH_3 \xrightarrow[200^{\circ}C\ \ 36\ m.]{CuCrO} 86\%\ CH_3\text{-}\overset{H}{\underset{OH}{C}}\text{-}CH_3$$

(109)

A sufficient accumulation of hydroxyl groups, even without alkyl substitution, makes hydrogenolysis of C-C linkage possible.



$$\text{Sorbitol} \xrightarrow[\substack{250^{\circ}C \\ 2\ hrs.}]{CuCrO} \begin{array}{l} 50\%\ CH_3\text{-}\underset{\displaystyle OH}{CH}\text{-}CH_2OH \\ 10\%\ H_2O \\ 11\%\ EtOH + MeOH \end{array} \qquad (110)$$

(4). <u>C-C Cleavage in Diketones</u> - - These compounds behave similarly to 1,3 glycols in being labile toward hydrogenolysis (111).

(b). <u>Hydrogenolysis of the C-O Bond</u>

(1). <u>C-O Cleavage in Alcohols</u> - - The hydroxyl group in primary and secondary alcohols and in phenols is extremely resistant to hydrogenolysis below 250°C except where R contains a phenyl, furyl, pyrryl, hydroxyl, carbonyl, or carbethoxyl group. Thus, if there is an ethylenic bond or carbonyl group (80), in the β-position with respect to the C-O linkage, the latter is readily broken. This tendency is found in a lesser extent in the γ-position.

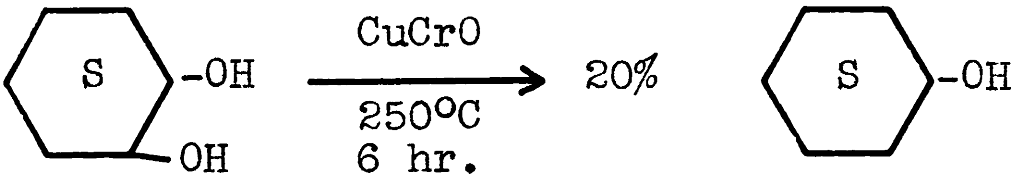
Examples:

$$\phi\text{-}CH_2OH \xrightarrow[\substack{125^{\circ}C \\ 10\ min.}]{RaNi} 88\%\quad \phi\text{-}CH_3 \qquad (92)$$

$$\text{Ø-CH}_2\text{-CH}_2\text{OH} \xrightarrow[\substack{250^{o}\text{C} \\ \text{5 hr.}}]{\text{CuCrO}} 95\% \quad \text{Ø-CH}_2\text{-CH}_3 \qquad (92)$$

$$\text{Ø-CO-Ø} \xrightarrow[\substack{175^{o}\text{C} \\ \text{1 hr.}}]{\text{CuCrO}} 97\% \quad \text{Ø-CH}_2\text{-Ø} \qquad (103)$$

$$\text{Ø-CO-CH}_2\text{-CH}_2\text{-CO}_2\text{Et} \xrightarrow[\substack{250^{o}\text{C} \\ \text{1 hr.}}]{\text{CuCrO}} 94\% \quad \text{Ø-(CH}_2)_3\text{-CH}_2\text{OH} \qquad (112)$$



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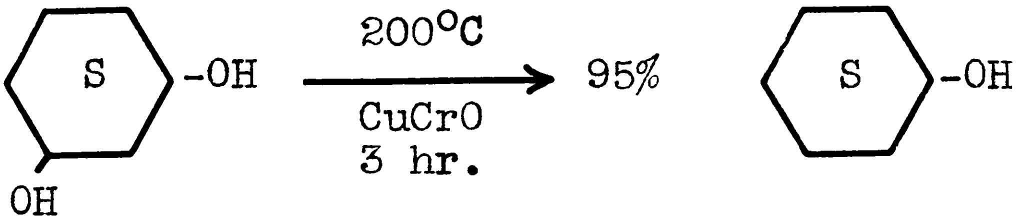
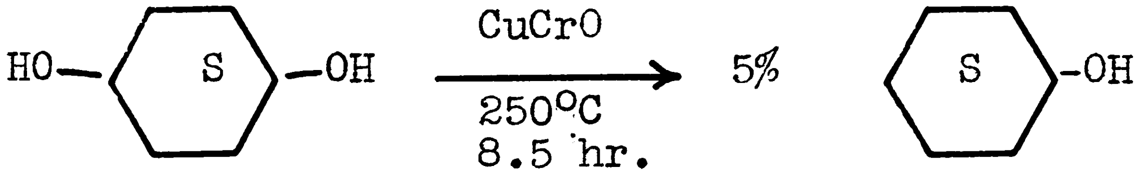


(109)



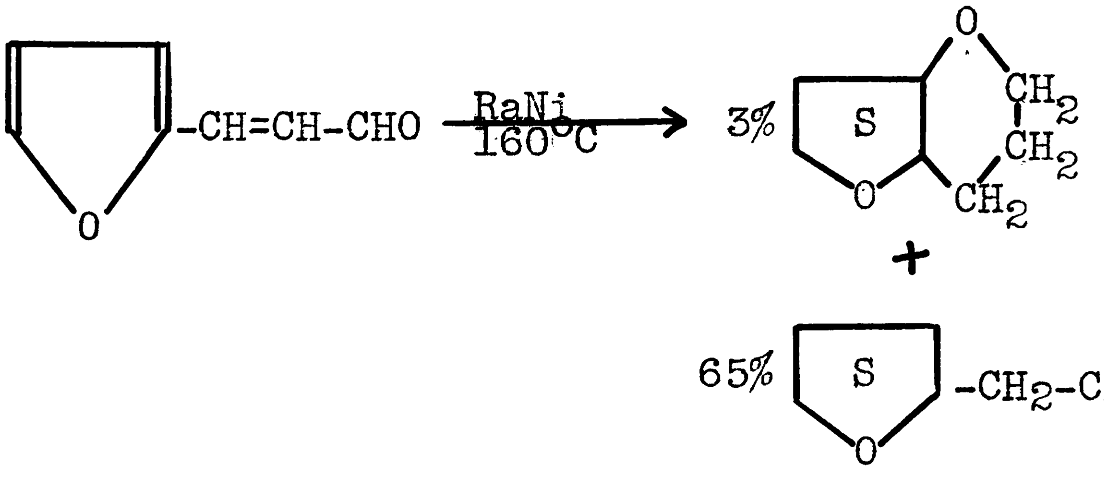
(109)

(2) <u>C-O Cleavage in Ethers</u> - - Over RaNi(80) the benzyl ethers undergo hydrogenolysis at lower temperatures than do others (effect of C=C-C•••O) and benzyl-aryl ethers cleave at lower temperatures than do benzyl-alkyl ethers. Di-aryl ethers are somewhat more stable to hydrogenolysis than benzyl-alkyl ethers

since the former cleave around 150-200°C. Aryl-alkyl ethers are more stable toward hydrogenolysis than other ethers. Where the alkyl group is large, hydrogenation occurs, otherwise the principal change is one of hydrogenolysis at 200°C. Di-Alkyl ethers are quite stable toward hydrogenolysis at 200°C; at temperatures sufficiently high to cleave dialkyl ethers over RaNi a C-C cleavage would also occur.

The situation is probably very much the same over CuCrO, although only little work has been reported in this field. Interestingly enough, especially in regard to proposed lignin structures, most of the work on CuCrO on ether cleavage has been done on furane and benzofurane compounds.

Examples:



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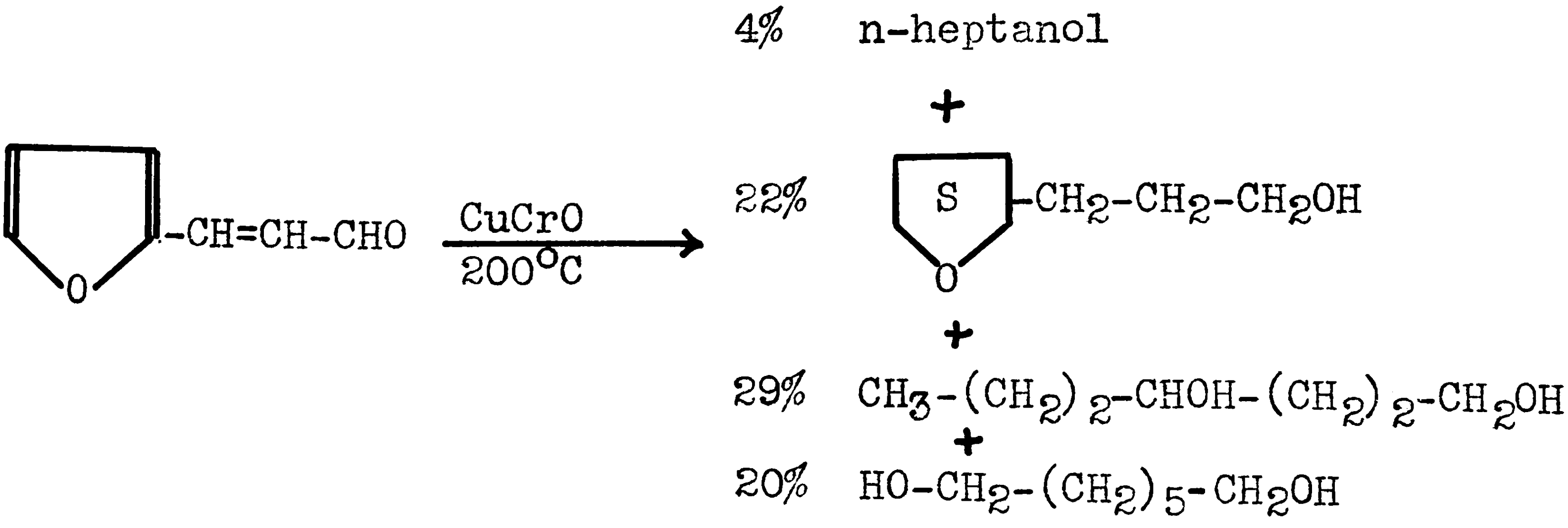
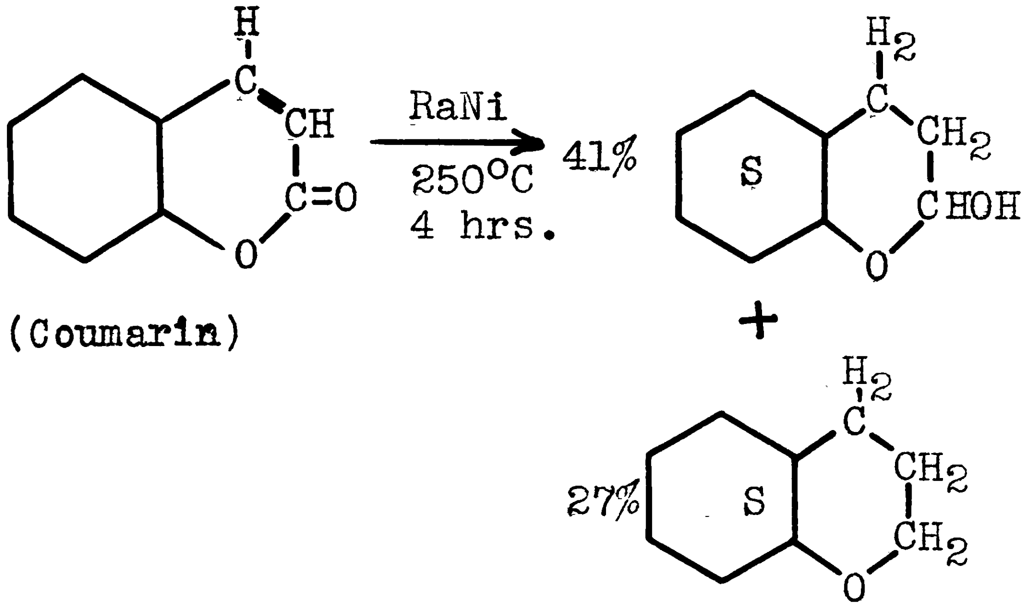
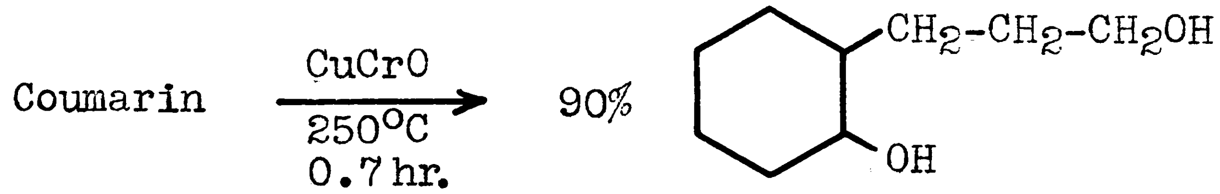


(107)



(113)



(113)

It is important to note, however, that tetrahydrofurane, prepared by RaNi hydrogenation of furane, is extremely resistant to hydrogenolysis over CuCrO (113). Thus again, the influence of a conjugated system in labilizing a C-O bond to hydrogenolysis is apparent.

3. Hydrogenation accompanied by Hydrogenolysis - - The most important reaction of this type is that of the preparation of alcohols and glycols from esters, a process which is becoming

very valuable in the laboratory for the synthesis of alcohols from acids (109, 114). As might be expected the yields decrease as the ideal situations for C-O hydrogenolysis are approached (e.g. proximity of phenyl, carbonyl, furyl or hydroxyl groups) (114). However, even though hydrogenolysis of the resulting C-OH group does occur, the yields, with only a few exceptions, are large enough to make the transformation of preparational value.

4. Selective Hydrogenation - - The problem of catalyzing the reaction of hydrogen with various functional groups has been in large part solved during the past forty years (80). The critical problem today is not that of finding better but more selective catalysts, and of obtaining more complete knowledge of the influence of one functional group on the hydrogenation of another.

By selective hydrogenation is meant the hydrogenation of one functional group in the presence of another which remains unreduced. Selective hydrogenation, at least at present, depends primarily upon the selection of catalyst, temperature and duration of reaction, and secondarily upon the medium of reaction. For example, CuCrO is relatively inactive toward the benzenoid nucleus, hence aldehydes, ketones and esters containing an aryl group may be hydrogenated to the corresponding alcohols containing the unchanged benzene ring. RaNi permits the hydrogenation of aryl groups in the presence of carbalkoxyl groups to give esters containing cyclohexyl groups.

An example of careful selection of catalyst to induce selective hydrogenation is shown by the remarkable hydrogenation of an unsaturated ester to give the unsaturated alcohol (96). It has been noted (page 46) that the C=C bond is hydrogenated under as mild conditions as any other group, even at room temperature and atmospheric pressure over RaNi or Pt-Pd catalysts. In contrast, the ester group requires a temperature of over 200° and pressures of over 100 atmospheres to be converted to a carbinol group over CuCrO, the most active catalyst for this type of transformation. From these facts it would appear that the preparation of an unsaturated alcohol from an unsaturated ester is one of the most hopeless of selective hydrogenation, yet this synthesis is accomplished in 35% yield over zinc-chromium oxide at 300° (96).

Selective hydrogenation is most commonly attained, however, through careful control of temperature and reaction time. This is possible because of a peculiar (and fortuitous) feature of hydrogenation reactions, namely, the pronounced tendency for hydrogenation to proceed stepwise; that is, for one functional group to be completely hydrogenated before action with another commences. Generally the most reactive group will hydrogenate at a somewhat lower temperature, and the reaction is controlled by cautious heating until the reaction just begins, then maintaining this, or a lower temperature until the reaction is complete. If the two react at about the same temperature the technique is to slowly raise the temperature until the reaction just begins and then rapidly cool the bomb by immersion in cold water. An example of this method is the preparation of β-phenylethyl alcohol from phenylethyl acetate:

$$\phi\text{-}CH_2\text{-}CO_2Et + 2H_2 \xrightarrow[250^\circ C]{CuCrO} \phi\text{-}CH_2\text{-}CH_2OH + EtOH$$

$$\phi\text{-}CH_2\text{-}CH_2OH + H_2 \xrightarrow[250^\circ C]{CuCrO} \phi\text{-}CH_2\text{-}CH_3 + H_2O$$

The optimum yield (about 60%) is obtained only by interrupting the hydrogenation before all of the ester has undergone the first reaction. (112)

An excellent example of the relative hydrogenations of various groups in one molecule was found in the hydrogenation of α-ethoxypropiovanillone (VIII) over CuCrO by Cooke, McCarthy and Hibbert (85). Fifteen grams of α-ethoxypropiovanillone were treated with hydrogen at 220 atmospheres pressure over CuCrO (8.0 g.) at 250°C. The products of this reaction were water, ethanol, methanol and 4-N-propylcyclohexanol. The hydrogen absorption curve indicated that: first, the carbonyl group was reduced to the methylene group with the absorption of two moles of hydrogen; second, the ethoxyl group was cleaved with the absorption of one mole of hydrogen; and third, the benzene ring was saturated and the methoxyl group cleaved with the absorption of four moles of hydrogen.

In considering a selective hydrogenation it is important to note, however, that the relative rates of reaction of two compounds with different functional groups taken separately is not always a safe basis for prediction as to the relative rates of hydrogenation of the two compounds in a mixture, or of the two groups when both are in the same molecule. For example, d-α-pinene is much more rapidly hydrogenated than is cinnamic acid, yet in a mixture of the two, cinnamic acid is completely hydrogenated before the former takes up any hydrogen (115). A reducible substance not undergoing hydrogenation may greatly accelerate the hydrogenation of another compound. Thus, pure pinene, which is much more rapidly hydrogenated than pure allyl alcohol was found to increase the rate of hydrogenation of allyl alcohol almost sevenfold, without itself being hydrogenated to any considerable extent.

III. Hydrogenation of Lignin

The first truly successful hydrogenation of an isolated lignin was reported by Harris, D'Ianni and Adkins (36) in 1938. Although lignin had been treated with hydrogen under various conditions prior to this time, no compounds were isolated and identified. Consequently, these earlier investigations will not be described in detail here. The following workers have attempted to gain knowledge of the structure of lignin by means of its hydrogenation: Fischer and Schrader (116); Fierz-David (117); Fierz-David and Hannig (118); Bowen and Nash (119); von Wacek (120); Lindblad (121); Ipatieff and Petrov (122); Trefliev and Filaterov (123); Moldavsky and Vainshtein (124); Freudenberg (125); and Hibbert and Moore (126).

Harris, D'Ianni and Adkins (36) hydrogenated methanol lignin (aspen) over CuCrO at 255° (5000 lb./sq.in. pressure). The hydrogenation products isolated and identified were methanol (28%); 4-n-propylcyclohexanol, _I_* (11.5%); 4-n-propylcyclohexanediol-1,2,_II_* (3.8%); 3-(4- hydroxycyclohexyl)-propanol-1, _III_* (25%); and a high boiling resinous residue (32%).

This process has been extended to other lignins by Harris and Adkins (37). The results obtained by these investigators are shown in Table VI. At a later date Harris (127) reported 9 to 11% water as an additional product from these hydrogenations.

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*The underlined numerals refer to Table VI, page 61.

TABLE VI

THE HYDROGENATION OF VARIOUS LIGNINS OVER COPPER-CHROMIUM OXIDE

(37)

Lignin	Proportion of Total Lignin in Wood %	Methoxyl Content of Lignin %	Products Isolated					
			MeOH %	I %	II %	III %	Residue %	Total Return %(a)
Methanol (aspen)	60	27.0	26.5	11.0	3.2	24.0	22.0	86.7
Klason (spruce)	30	20.6	19.0	6.0	2.0	15.0	48.0	90.0
Alkali (aspen)	60	11.6	10.5	4.0	1.4	9.0	66.0	90.9
Methanol (spruce)	25	23.0	15.0	7.0	2.0	12.0	52.0	88.0
Alkali (black gum)	60	11.8	11.0	5.0	1.0	14.0	60.0	91.1
(The following results were reported by Harris, D'Ianni and Adkins (36))								
Methanol (aspen)	90	----	28.0	11.5	3.8	25.0	32.0	100.3

%(a) = Percentage of original weight of lignin

Apparently the yields reported by Harris and Adkins (37) for 3-(4-hydroxycyclohexyl)-propanol-1 are decidedly open to question. This is particularly true with regard to those reported in the case of soda lignin (aspen and black gum); namely 9 and 14% respectively. Adkins has found recently (38) that soda lignins from hardwoods yield only traces of this glycol, and this investigator exphasizes the fact that Harris "has given no substantial evidence that he has isolated or characterized the glycol among the products of their hydrogenation of soda lignin", in referring to a previous paper by Harris (128) and co-workers.

The resins obtained in the hydrogenation of lignin have been studied by Harris, D'Ianni and Adkins (36) who found that the resinous residue obtained in the hydrogenation of methanol lignin (aspen) contained 73% carbon and 10.8% hydrogen. This residue was dehydrated with alumina and the unsaturated hydrocarbons thus obtained were rehydrogenated over Raney nickel yielding saturated hydrocarbons containing 86.6% carbon and 12.5% hydrogen. From the physical properties of these hydrocarbons (particularly boiling-point) Adkins concluded that, since the minimum number of carbon atoms present in the simplest hydrocarbon was fifteen, the original lignin was composed, at least in part, of units containing more than fifteen carbon atoms.

A more detailed investigation of the resins was made by Adkins, Frank and Bloom (38). The high-boiling residue obtained in the hydrogenation of alkali lignin (hardwoods), which contained 79.9% carbon and 11.4% hydrogen, was dehydrated with oxalic acid and then re-hydrogenated. The hydrocarbons thus obtained were carefully fractionated and analyzed. The results indicated that: (a) The soda lignin was converted to alcohols and glycols related to polycyclic hydrocarbons having 20 to 70 (or more) carbon atoms in the molecule; (b) although high molecular weight compounds were also obtained from methanol lignin (36), they were present in smaller amounts and were more highly oxygenated than the products of similar physical properties obtained from soda lignin; (c) the products from methanol lignin contained one oxygen atom per six carbon atoms, while the products from soda lignin had one oxygen atom per average of 13.5 carbon atoms.

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

Cooke, McCarthy and Hibbert (31) subjected maple ethanol lignin to hydrogenation (250°, 3400 lb./sq.in. initial pressure, 18 hours) over CuCrO and obtained water, methanol, ethanol, 4-n-propylcyclohexanol, 4-n-propylcyclohexanediol-1,2, 3-(4-hydroxycyclohexyl)-propanol-1, an apparently new, unidentified substance and high boiling resins in yields of 13.6, 5.0, 8.7, 8.1, 1.9, 3.2, 2.1 and 29.5% respectively. The variations in yield, especially of 3-(4-hydroxycyclohexyl)-propanol-1 as compared with the results of Harris, D'Ianni and Adkins (36) using aspen methanol lignin suggest that a difference may exist in the chemical structure of the two types of lignin. Similar products (31) were obtained for various ethanolysis lignin products.

Recently Freudenberg (33) and co-workers have hydrogenated (at 250-340° and 80-140 atmospheres pressure) Willstätter and cuproxam lignins in alkaline media (up to 5% NaOH) with the purpose of cracking the side chain while hindering the saturation of the nucleus. With a Cu-Ni-Al_2O_3 catalyst (low activity) 45 to 50% (lignin basis) of phenolic components were obtained together with small amounts of cyclohexyl lignin degradation products. Monocyclic phenolics (15% of lignin) included guaiacol, creosol and pyrocatechol. Ni catalysts precipitated on the lignin as the hydroxide or the carbonate gave similar results. With a highly-active catalyst (Ni-Al_2O_3, Raney Ni) under the same conditions (33), cyclohexyl derivatives (36-40%) were obtained, 15% (lignin basis) being monocyclic cyclohexanols.

In another paper Freudenberg and Adam (35) describe an experiment in which the lignin, impregnated with a Ni catalyst, is heated (in a revolving tube) while a stream of hydrogen is passed over it. At 220° a yellowish-brown oil begins to distill over and the distillation continues as the temperature is raised to 350°. Up to 50% of the weight of the lignin (spruce HCl lignin) is obtained as an ether-soluble oil of which 65 to 70% consists of distillable phenols. The over-all yields (average) are given as: phenols up to 35% (lignin basis); neutral up to 7%; acids, 0.2 to 0.3%. In these fractions the identified substances, all of which may be readily related to the phenylpropane structure for lignin, include the following (with the quoted percentage): phenol (5.5); p-Et phenol (1.1); guaiacol (3.9); p-cresol (7.1); p-Et guaiacol (1.6); o-Et guaiacol (0.5); isoeugenol (1.3); pryocatechol (2.9); p-Pr pyrocatechol (0.1); homopyrocatechol (1.1); toluene (0.7); o-Et-anisole (0.5); p-homoveratrole (2.0); methanol and ethanol (0.5); methylcyclopentanol (0.5) and higher boiling components (12).

IV. Hydrogenation of Wood, Cellulose and Related Materials

A survey of the earliest work (prior to 1935) on the hydrogenation of cellulose and wood will not be given here, but reference will merely be made to a survey by Boomer and co-workers (129). Most of the earlier experiments have been associated either with attempted production of liquid fuels or with the destructive distillation of wood or cellulose in the presence of hydrogen, and no attempt was made to separate and identify individual reaction products.

The only wood hydrogenation investigations relating to the lignin problem are those of Godard, McCarthy and Hibbert (30) and of Harris (127). The former (30) treated maple wood meal with hydrogen at 400 atmospheres pressure in the presence of CuCrO at 280° for 19 hours, and isolated 4-n-propylcyclohexanol (19.5%) and 3-(4-hydroxycyclohexyl)-propanol-1 (5.8%). (The yields are based upon the Klason lignin content of the wood.)

Harris (127) recently claimed to have isolated a high yield of protolignin hydrogenation products by hydrogenation of wood (maple, aspen and spruce) over Raney nickel catalyst in an aqueous alkaline medium. Thirty grams of aspen wood suspended in 300° cc. of 1% aqueous sodium hydroxide were treated with hydrogen (300 atmosphere pressure) at 175° for 4 hours. The yield of products (percentage of original wood) claimed were: pulp, 40%; methanol, 5.1%; propanol, 16%; propylcyclohexane derivatives, 20%; resin, 14%; unidentified residue, 2% total recovery, 97%. Since aspen wood contains 20-22% lignin (130), it would appear that the quantity of propylcyclohexane derivatives isolated by Harris accounts for nearly 100% of the Klason lignin content of the wood.

According to the results obtained by Zartman and Adkins (110), carbohydrate materials yield considerable quantities of water upon hydrogenation so that it is difficult to conceive of a 97% recovery of hydrogenation products which do not include water. No evidence was given to indicate that the propylcyclohexane derivatives were identified through the formation of derivatives. Brewer, Cooke, and Hibbert (87) have been unable to duplicate the work of Harris (127).

Recently Henze (131) and co-workers hydrogenated cotton cellulose (250°, 325-380 atmospheres pressure) in a 7% aqueous sodium hydroxide solution over Raney nickel and obtained semi-solid, liquid and gaseous products. The acidic liquid products (extracted from the reaction mixture with ether) were found to contain: lower fatty acids, including acetic and possibly propionic and one of the butyric acids; lactic acid; γ-or δ-hydroxycaproic acid and the corresponding lactone; and a dihydroxyvaleric acid and the corresponding lactone, with one hydroxyl of the acid in the α-position and the other probably in the δ-position.

Hydrogenation of simple carbohydrate materials has also been studied under various conditions. In a German patent (132), liquid and solid carbohydrate materials were treated with hydrogen (pressure not given) at 190-300° in the presence of Fe or Pt catalysts. Glycerol gave propanediol-1,2; glucose yielded, successively, hexitol, glycerol, and propanediol-1,2; cellulose gave glycerol, propanediol-1,2, and unidentified products. In a later patent (133) glycerol was obtained(under the same conditions) from cane sugar, starch, cellulose and sawdust. Adkins and Zartman (110) hydrogenated glucose, sorbitol, mannitol, sucrose, lactose, maltose, pentaacetylglucose, and gluconic lactone in ethanol solution (300 atmospheres, 250°) over CuCrO catalyst and obtained, in each case, methanol, ethanol, propanediol-1,2 (60% of the product), and three additional compounds tentatively identified as hexanetriol, hexanetetrol, and 2-(4-hydroxytetrahydrofuryl)-methyl carbinol. More recently (134) it has been reported that the hydrogenation of glucose (at 70-120°) and of sucrose and starch (160-180°) at 80-300 atmospheres pressure with Ni or Fe-Ni catalysts yields mixtures of hexitols. At 190-240°, propylene glycol and glycerol are formed in good yields together with ethylene glycol, methanol and ethanol.

V. Fractional Distillation

Fractional distillation has become one of the most important laboratory operations and in recent years very efficient apparatus has been developed for handling quantities of liquid varying from 100-1000 cc. Techniques for handling less than 1 cc. of liquid have also been developed (135). The present survey was undertaken to ascertain the apparatus and techniques already adapted or adaptable to the efficient fractionation of 5 to 15 cc. of complex liquid mixtures, such quantities being characteristic of the reaction mixture obtained in the hydrogenation of wood and lignin.

Fractional distillation is effected by two methods, namely, (a) "continuous" and (b) "batch" fractionation. The former employs a continuous feed, of constant composition, and permits simultaneous withdrawal of several fractions from different sections of the column, while the latter makes use of a design employing a single initial charge and giving a progessive series of fractions, each having a different composition. Due to the small quantities of material under investigation in lignin hydrogenation studies only the "batch" method is applicable.

A brief discussion of the theory of fractional distillation, or better "rectification", is necessary in order to disclose the more important variables which must be considered in the design of an efficient column. Essentially, fractional distillation columns accomplish the equivalent of a large number of repeated progressive simple distillations. In simple distillation the vapor above the liquid mixtures is somewhat richer in the more volatile component (usually the lower boiling one) and if removed and condensed gives a liquid correspondingly richer in the more volatile component. Obviously such a distillation is only suitable for a crude separation of materials with widely divergent boiling points, and the continued repetition of such a process to effect good separations would be costly both in terms of time and material.

In rectification all the vapor is condensed at the top of a column, and part of the condensate is returned to the top of the column as "reflux". Reflux flowing down the column is brought into contact with the ascending vapors and exchanges of heat and material occur. A portion of the less volatile components in the vapor is condensed through abstraction of heat by the reflux. The heat absorbed by the reflux causes vaporization of its more volatile components, thereby causing enrichment of the vapor in the volatile components. Thus the overall efficiency of a column may be expressed in terms of "theoretical plates", a theoretical plate being defined (136) as a column section that will effect equilibrium between vapor and liquid.

While the total number of theoretical plates is an important feature of a column, equally important are the amount of liquid hold-up and the height equivalent of each theoretical plate (H.E.T.P.). For analytical fractionation it is desirable that the amount of liquid used to wet the packing (the "hold-up") be as small as possible, compared with distilling capacity of the column, so that the cuts between true fractions will be sharp and not consist of large portions of intermediate mixtures. Actually, in this respect, it is the hold-up per theoretical plate that is the important function. This factor is quite often associated with H.E.T.P. although if the hold-up is low the importance of H.E.T.P. is more closely related to ease and economy of construction, ease of mounting, ruggedness of the whole assembly, and general simplicity of operation. In connection with the latter point, insulation of the column to secure approximate adiabatic operating conditions is important. Insulation, temperature control and limiting temperature range decrease in importance if the column is short and still has a high theoretical plate rating (low H.E.T.P.). Throughput or distilling capacity must be considered in the case of large installations but it is only of minor significance in the present investigation.

A. Column Packings

A fractionating column consists of a tube containing a "packing" the purpose of which is the promotion of thorough contact between ascending vapor and descending liquid. The efficiency of a given packing may be expressed most easily by the H.E.T.P. rating, although the other variables mentioned previously must be kept in mind.

Included among the numerous materials employed for this purpose are (136): glass beads and balls, particles of glass and stoneware, tacks, rivets, metal shot, Lessing rings, Raschig rings, carding teeth, chains, single-and multiple-turn glass and metal helices, and various wire forms. In general the solid type packings (136), the earliest used, present a rather small surface/volume ratio and, as a result, columns packed with such material are liable to flood at a low rate of distillation. Ring type packings (136), thin walled cylinders of approximately equal height and diameter, make a fairly uniform packing with a reasonably large surface and form no pockets to hold up liquid. Chain packing is used extensively owing to its availability, large surface area, and ease of packing and removal. Schiktanz (137) found that efficiency is increased as one progresses from a single-link chain through double-link chains to jeweler's brass-locket chains. Probably the most widely used packings are single-and double-turn helices as developed by Fenske (138) and co-workers. A comparison of the latter type packing is given in Table VII (138).

TABLE VII

H.E.T.P. VALUES OF VARIOUS PACKINGS

Packing	H.E.T.P.
Glass tubes 0.22" x 0.22"	8.3 cm.
Jack chain	8.8 "
1-turn Helices	4.6 "
2-turn "	7.0 "
6-turn "	13.5 "

Wilson (139) and co-workers have verified the two to one effectiveness of single-turn helices over glass cylinders. More recently Whitmore, Fenske, et al. (140) report that a packing of 1/16" I.D. single-turn helices of No. 34 stainless wire in an 8 mm. I.D. column has an H.E.T.P. of 1.3 cm. with a holdup of 0.16 cc. per plate. Bailey (141) has described a glass helices-packed column with an H.E.T.P. of 5 cm. and a holdup of less than 0.1 cc. per plate. However the holdup in the latter column increases rapidly with increased rates of distillation.

A simple type packing developed by Podbielniak (142) has been widely used in the petroleum industry for a number of years. It consists of a spiral coil of wire (6-7 turns per inch) fitted snugly into the fractionating tube, the center of the column being left empty. Podbielniak has failed to report

H.E.T.P. values for this column but Whitmore, et al. (140) mention a similar column (4.5 mm. I.D., No. 20 wire spiral) having an H.E.T.P. of 10.7 cm. and a holdup of 0.17 cc per plate. Rose (143) found that spiral packing gave a poorer separation than single-turn wire helices.

Selker (144) and co-workers describe a column packed with several concentric glass tubes and a solid core. This column has an H.E.T.P. of 1.8 cm. with a holdup of 0.059 cc. per plate. However, not only is this column difficult to construct but an elaborate and expensive system of controls is necessary, and for liquids boiling above 100°, a twenty-four hour reflux is required to attain optimum equilibrium condition. Rose (148) has realized efficiency up to 17 plates per foot with unpacked 6 mm. diameter columns; however, such columns operate efficiently only at extremely small throughput rates. Thus, the reflux rate for 17 plates is only 0.17 cc. per minute, and at 0.9 cc. per minute only a two-plate efficiency is observed.

An extremely efficient packing recently developed by Stedman (145) consists of flat truncated cones of stainless wire gauze, welded base to base and top to top to form a series of closed conical chambers when fitted snugly (with grinding) into the column. Small openings are provided on alternate faces to provide a long vapor path. Under optimum conditions (145) an

H.E.T.P. of 1.08 cm. and a holdup of 0.125 cc. per plate is obtained. The only disadvantages of the Stedman column are the high cost of construction and limitation in minimum size to a column diameter of approximately 1.5 cm.

An excellent spiral screen packing with an efficiency quite close to that of Stedman's has been developed by Lecky and Ewell (146). Washers of stainless wire screen are stamped out, split, and spot-welded to form a long continuous spiral which is fitted around a solid core and slipped into a closely fitting outer jacket. Such a column has an H.E.T.P. of 1.7 cm. and a holdup of 0.25-0.40 cc. per plate. If the outer tube is heated to softness and collapsed on to the screen spiral to give a perfect fit, the H.E.T.P. is decreased to approximately 1 cm. but the resultant column is too fragile for normal usage. Stallcup (147) and co-workers, in building a similar column having an H.E.T.P. of 1.8 cm. and a holdup of 0.14 cc. per plate, had to modify the construction by cupping the spiral and grinding or filing the packing to permit a snug fit within the glass tube.

The best column reported in the literature seems to be Podbielniak's "heli-grid" column (148) which has an H.E.T.P. of 0.5 cm. and a holdup of 0.02 to 0.2 cc. per plate (reflux 60 to 250 cc./hr.). This column, however, could not be build without special tools and a complete assembly costs several hundred dollars.

A novel column designed by Lesesne and Lochte (149) employs a 4 mm. wide nichrome ribbon suspended in the center of a 6 mm. distilling tube and rotated at 1000 r.p.m. during the distillation. Although an H.E.T.P. of 2.5 cm. at 0.12 cc./plate holdup has been reported, mechanical difficulties would limit its use under reduced pressure. Baker (150) and co-workers built a similar column having 70 plates in 18 feet.

An efficient glass bubble cap column with an H.E.T.P. of 2 cm. has been built by Brunn (151) but it has an extremely high holdup of 0.7 cc. per plate and is rather complicated and delicate.

B. Column Insulation

On theoretical grounds (135), if a fractionation is to be efficient it should occur under adiabatic conditions. It is obvious that the necessary equilibrium conditions between down-flowing liquid and upward-moving vapors cannot be established if too much cooling is taking place on the walls of the column. The most common methods of insulating a column are with asbestos, magnesia, air jacket, or vacuum jacket. Podbielniak (142,148) places his columns inside silvered or reflector-equipped vacuum jackets. According to Podbielniak, it is necessary to construct the vacuum jacket of quartz or bellowed-pyrex in order to compensate for thermal expansion. Insulation of this type is particularly valuable if the compound boils below room temperature. Above

100^o, however, it is necessary to resort to other methods (135) if the column is to give satisfactory performance. Some workers (144,152) have sealed the vacuum jacket directly on the column, making the inner wall of the jacket the outer wall of the column.

A common method for operating at higher temperatures (153) is to surround the column with a glass jacket, wind this with electrical resistance wire, and insulate the whole with an outer glass tube. The resistance wire may be wound in separately controlled sections if desired, and the heat input regulated to compensate for losses from the column. If visibility is not important the column may be insulated with commerical pipe covering (asbestos, magnesia, etc. (135))in which resistance wires are imbedded. A double-walled insulating jacket (135) through which hot or cold liquids may be circulated can also be used to maintain semi-adiabatic condition. A novel column in which the packed section is jacketed by the hot vapors from the distilling pot has been designed by Fenske and co-workers (154).

C. Still Head

The still head or condensing section may be of two types, namely, (a) "partial condensation" or (b) "total condensation". In the former a portion of the vapors are condensed and returned to the column as reflux and the remainder of the vapor is condensed separately and collected in the fraction receiver; in the latter, all of the vapor is condensed and a portion of the condensate is withdrawn as product, the remainder being returned to the column as reflux. Ward (136) points out that there is considerable controversy as to which type is most desirable, but in general, as emphasized by Podbielniak (142), the partial condensation type is to be desired where the charge is small or the amounts of individual components are small, since the total condensation type, having 1-2 cc. head holdup, causes considerable reblending. The total condensation type is more suitable for larger columns as it requires less attention and the reflux ratio can be held practically constant by any of several liquid partitioning devices.

D. Operation

One of the most important precautions to be observed in the operation of a packed column seems to be the thorough wetting of the packing before starting the distillation. Tongberg (155) and co-workers recommend the wetting of the packing by deliberate flooding of the column by the application of an excess of heat at the start of the distillation. This is superior to merely pouring the liquid over the packing as illustrated by the following results:

	H.E.T.P.
Column started with packing dry	4.3 - 5.1 cm.
Column flooded by rapid distillation	2.7 - 3.3 cm.
Column wet by pouring liquid through packing	3.4 - 3.7 cm.

This principle has been confirmed by Bragg (145) and Podbielniak (148).

Podbielniak (148) also states that intermittent take-off of samples, with time to establish equilibrium between sampling, has proven superior (with his heli-grid column) to the commonly accepted method of a constant, slow rate of take-off.

Rate of vaporization, reflux, and take-off will vary with different columns so that the column should be tested at several different rates with standard binary test mixtures in order to establish optimum operating conditions prior to using the column on unknown mixtures (136).

E. Column Testing

The testing of columns to determine theoretical plate and H.E.T.P. efficiences is a well-established procedure which is discussed thoroughly by Ward (136), Morton (135), and in various chemical engineering texts (156).

The determination of hold-up is discussed by Tongberg, Quiggle and Fenske (154) and Ward (136).

VI. Discussion of Experimental Results

A. Design of Fractionating Column

In connection with the hydrogenation studies on lignin and wood being carried out in these laboratories an urgent necessity was that of a highly efficient, low-holdup, laboratory fractionating column. In the previous work of Godard (30), for example, it was found that only a crude separation of the complex hydrogenation products obtained from maple wood by high-pressure hydrogenation technique, was obtainable with the Podbielniak single-wire spiral type column then in use. Even on refractionation of his supposed 4-n-propylcyclohexanol fraction he could only obtain an approximate "flat" (30) in the distillation curve. Moreover, the ideal column should not only be more efficient from the point of view of fractionation ability but must also have a very low holdup since the quantities involved in the customary hydrogenation mixtures in these laboratories usually amounted to only 5 to 15 cc.

For this investigation a new design, showing definite advantages for the use intended (small volumes, high temperature and vacuum fractionation) over existing columns, was developed. The column in question has the outstanding advantage of ease and cheapness of construction as compared to the highly efficient columns of Lecky and Ewell (146), Stedman (145) and Podbielniak

(148). It can be constructed by the average amateur glass blower and no special tools or dies are required for making the packing as in the other cases. The finished column has an H.E.T.P. equal to that of Lecky and Ewell (146) and approximately double that of Stedman (145) but has only 1/3 the operating hold-up of these columns. This important combination of low-holdup, and low-H.E.T.P. (height of each theoretical plate) is surpassed only by that of the Podbielniak Heli-grid column, the cost of which, however, is prohibitive for the ordinary laboratory in which the present column should prove invaluable. It has proven its worth in the present investigation and has also played an important role in solving problems in the separation of complex lignin ethanolysis products (44, 46).

Comparison with the known most efficient columns is given in the following table:

TABLE VIII

OPERATING EFFICIENCIES OF FRACTIONATING COLUMNS

Column Type	H.E.T.P. cm.	Holdup cc./plate
Podbielniak (Heli-grid)(148)	0.5	0.02-0.2
Stedman (145)	1.08	0.125
Lecky and Ewell (Spiral screen type)(146)	1.7	0.25
" (by Stallcup et al.)(147)	1.8	0.15
Podbielniak (Single-wire spiral)(140)	10.7	0.17
Present Column	1.88	0.045

From the above table it can be seen that the present column is superior to all, with the exception of the Podbielniak Heli-grid, in the important low-holdup-low-H.E.T.P. combination. While it is surpassed by the Stedman in low H.E.T.P., the lower holdup of the present column makes it fully as effective in fractionating ability per cc. of liquid in the column and, moreover, the H.E.T.P. is still sufficiently small to give a very compact unit.

Tests were made (with methylcyclohexane-n-heptane test mixtures) at various rates to determine the optimum operating conditions results of which are given in Table IX.

TABLE IX

EFFICIENCY TESTS ON NEW FRACTIONATING COLUMN

17 inch column

Reflux Rate (cc/hour)	Reflux Rate (drops/min.)	Theoretical Plates	H.E.T.P. cm.	Operating Holdup (cc/plate)
38.5	32	23	1.88	0.045
63.0	52	19	2.28	-----
84.0	70	17	2.54	-----
110.0	92	15.5	2.79	0.066
20.5 inch column				
38.5	32	27	1.92	0.045

The results clearly indicate that the column should be operated at a reflux rate of 32 drops per minute (or slower) for maximum efficiency. This rate was employed in all of the subsequent fractionations described in this thesis.

Details of construction of the two most used columns are given in the accompanying diagrams. The larger column was used ordinarily for separating mixtures having a volume of 5 to 30 cc. and the semi-micro model for mixtures with a volume of 0.5 to 1.5 cc. The electrical heating circuits for the columns and heating baths are shown diagramatically in Figure III. Ordinary

FIGURE I

FRACTIONATING COLUMN, CONDENSER AND RECEIVER

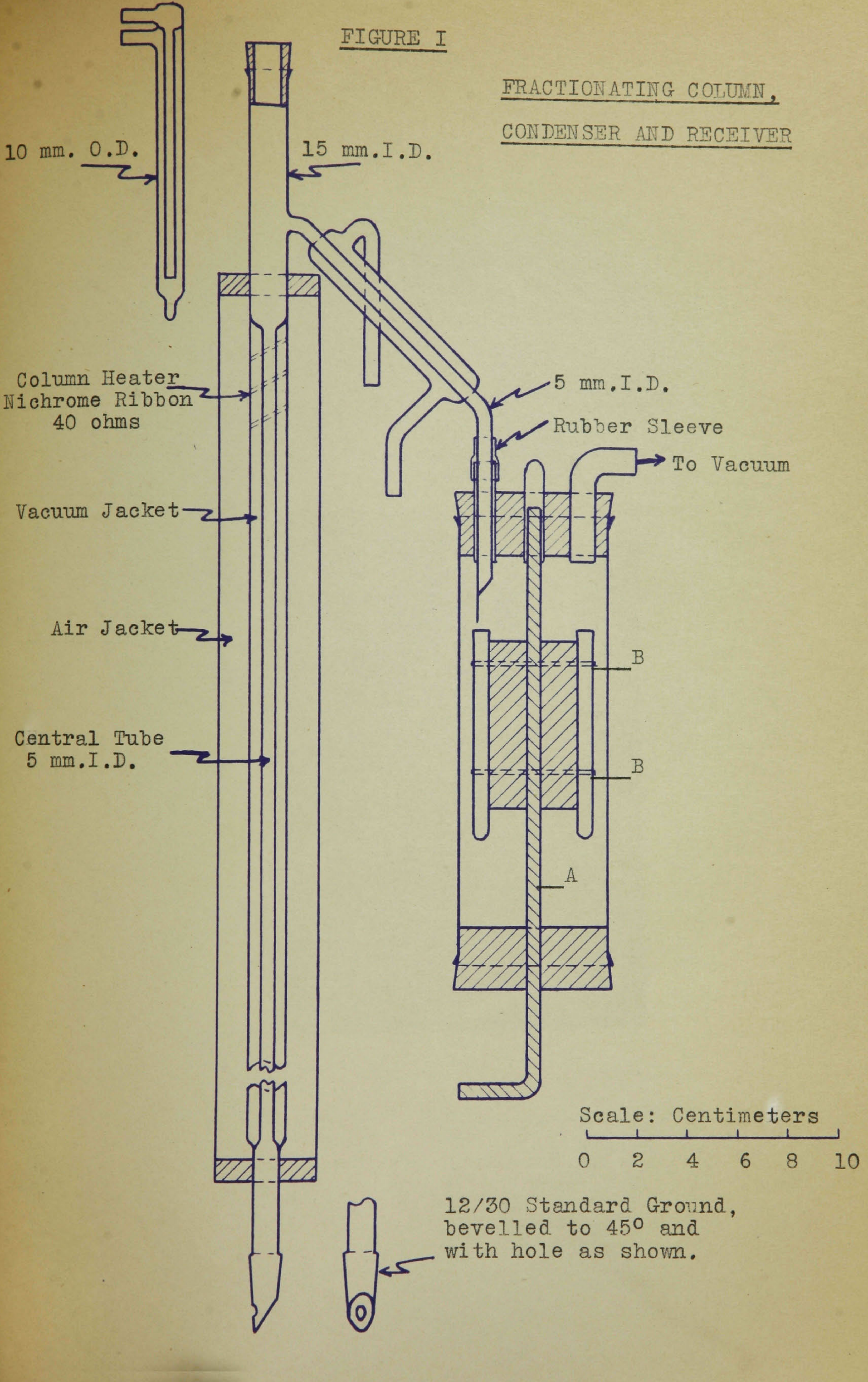


FIGURE I-A

PACKING IN PLACE

FIGURE II

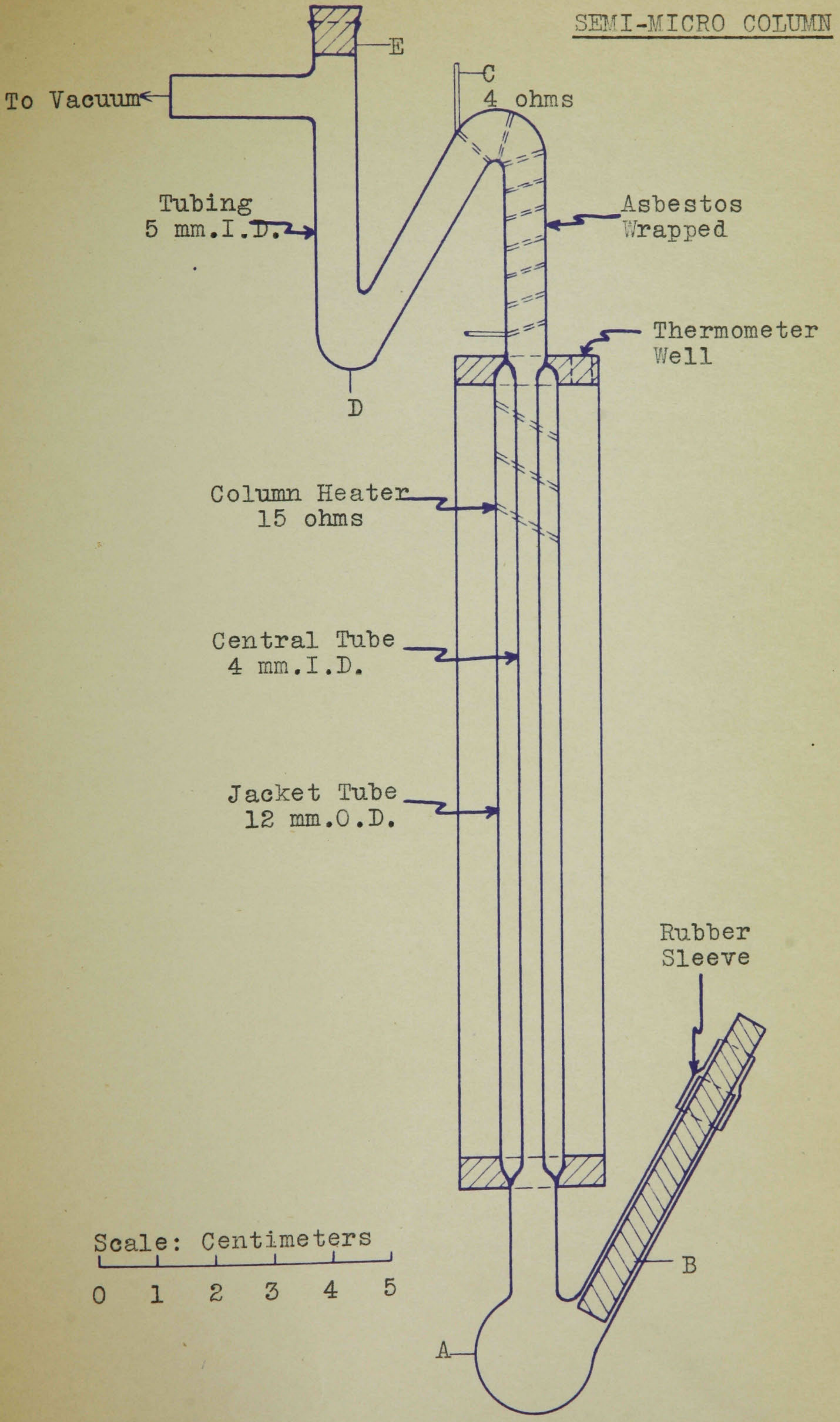
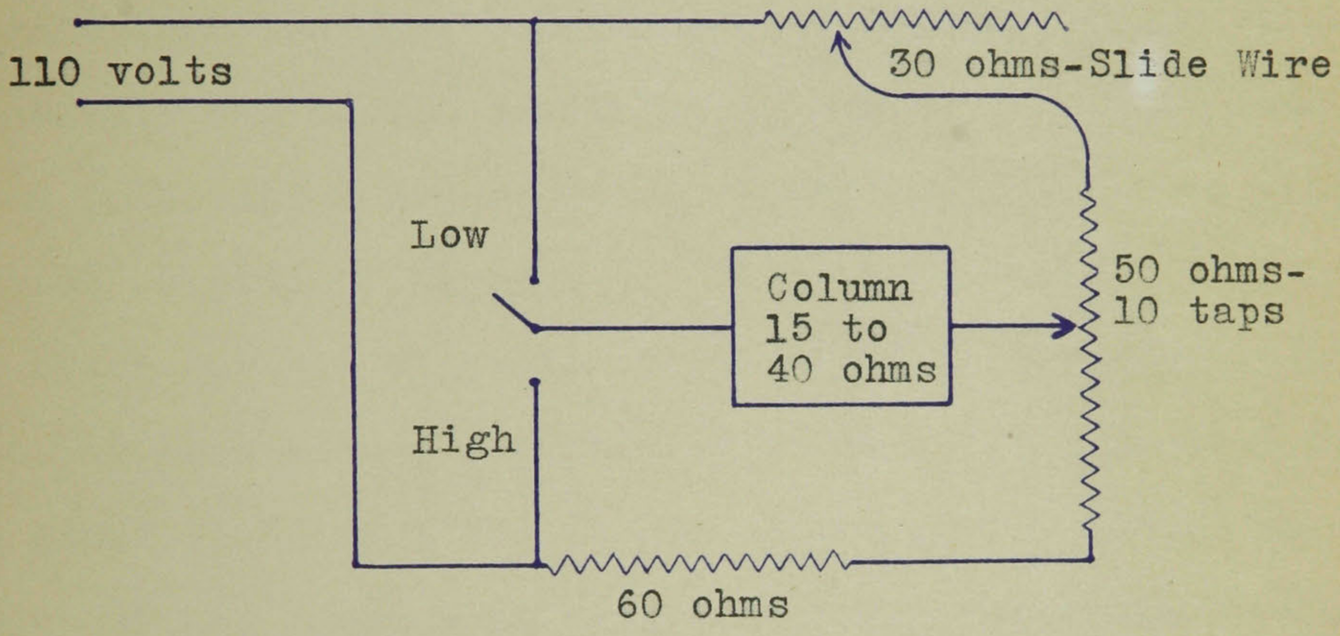

SEMI-MICRO COLUMN
E
To Vacuum
C
4 ohms
Tubing
5 mm.I.D.
Asbestos
Wrapped
Thermometer
Well
D
Column Heater
15 ohms
Central Tube
4 mm.I.D.
Jacket Tube
12 mm.O.D.
Rubber
Sleeve
Scale: Centimeters
0 1 2 3 4 5
B
A

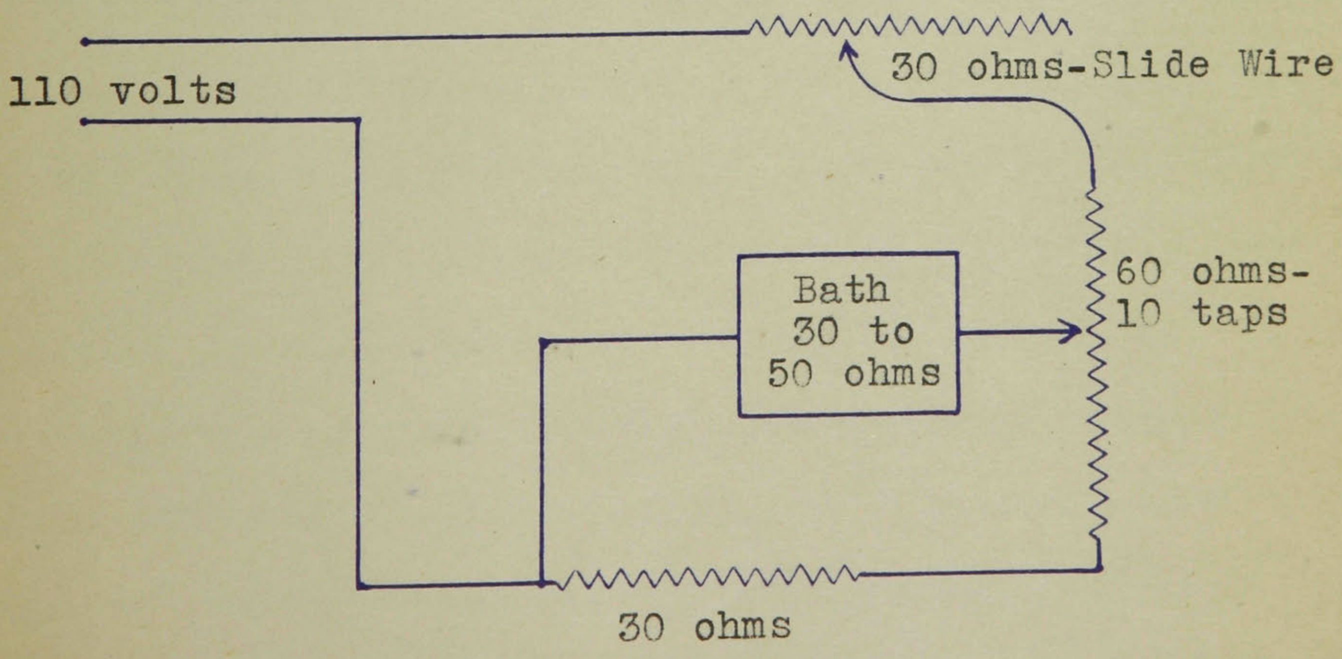
FIGURE III

HEATING CIRCUITS

COLUMN CIRCUIT



BATH CIRCUIT



B. & S. No. 24 nichrome wire was used in the construction of the fixed and variable resistances.

1. Construction of Columns

The construction of the glass portions of the columns is apparent from the diagrams. The wire packing, however, is of an entirely new design developed in these laboratories by the writer following a suggestion by D. F. Stedman of the National Research Council of Canada.

After several attempts to prepare a satisfactory packing the following method was adopted: A strip of 40 x 60 mesh Monel meta wire gauze (1.5 times the length of the glass column) was cut from a sheet of the gauze with heavy scissors, the width of the strip being two wire strands greater than the internal diameter of the column. The two outside (longitudinal) strands were then removed and the projecting (lateral) strands were bent back in one directi until the strip fitted tightly in the glass column. The gauze strip was then ready for twisting; this was accomplished with two pairs of round nosed pliers, the nose of one pair of which had been ground to a thickness of about 1/16 inch. The top of the gauze strip was gripped tightly with the thin nosed pliers and 1/8 in. away with the standard pliers, and the strip then twisted through 90°, with a simultaneous compression force, so that when the two pliers were at an angle of 90° they were touching each other. The result of such a procedure was the formation of two flat vertical planes at 90° to each other separated by two horizontal, opposite quadrants. The further twisting of the gauze strip was accomplished by gripping it just below the first bend with the thin nosed pliers and 1/8 in. below that point with the standard pliers. The twisting (in the same direction as the first turn) and compression motions were then carried out as described above. This process was repeated until the whole strip had been converted into a series of about 1/8 in. platelets separated by horizontal quadrants (see Figure I-A). It was found essential that the vertical axis of each platelet coincide with the line of axes of the adjoining platelets if a perfect fit was to be obtained.

When the entire strip had been so treated it was found that the previously flattened horizontal strands had spread somewhat and the strip was then too wide to fit the glass column. This was remedied by placing the twisted strip on a hard flat surface and tapping gently, while rolling, until the packing just fit the column snugly. The packing was inserted by lubricating with oleic acid and pulling it through the tube with a strand of copper wire which was later removed by the action of a drop of acid on the joint.

If the packing had been properly fitted, a continuous film of liquid was formed at the two lines of contact between the glass and the twisted wire strip when alcohol was poured down the column. If breaks occurred in this film the packing was discarded as being too loose and improperly fitted.

2. Operation of Columns

(a) Normal Column (See Figure I) - The material to be fractionated (5-30cc.) was placed in a small pear-shaped distilling pot equipped with a standard-taper 12/18 ground, a packing of glass wool being used to prevent "bumping" of the contents at reduced pressures. The contents of the pot were slowly heated by an electrically controlled oil bath until distillate appeared in the packed section of the column. The bath temperature at which this occurred was noted since it represented the minimum bath temperature at which the fractionation could be carried out. Current was then passed through the column heater until the lower portion of the packed secion began to dry. In this manner, the maximum column temperature was determined. The heating unit for the column was adjusted so as to decrease the temperature from 3 to 5° and the heat used for the bath rapidly increased until the column was flooded (cold water flowing meanwhile through the cold-finger condenser). The bath temperature was then decreased to a point approximately 5° greater than the minimum temperature observed above, and the bath lowered in order to allow the packed section to drain.

As soon as all of the excess liquid had drained from the wire gauze the bath was replaced and the two heating units so regulated as to produce a reflux rate of approximately 30 drops per minute. This adjustment of reflux rate was controlled mainly by the bath temperature, although as the fractionation proceeded, especially when the mixture boiled over a wide range, it was necessary to raise the column temperature slowly. After the column had run at total reflux for at least thirty minutes (in order to reach equilibrium) the sampling was carried out in one of two ways, either (a) continuously, or (b) in batches. In the continuous method, which required careful control of the cold-finger temperature, the distillate was collected steadily at a rate of 100-200 mg./hour. In the batch method 100mg. samples of distillate were collected every 45 minutes by rapidly increasing the temperature of the cold finger. As soon as the sample appeared in the side-arm, the cold-finger was cooled to total reflux temperature again and the system permitted to attain equilibrium.

The column was found to operate satisfactorily either at atmospheric or reduced pressure, and quite efficiently with materials boiling as high as 200^{o} at 1 mm.

(b) Semi-micro Column (See Figure II) - The operation of this column, although relatively simple, called for greater care than that of the larger one. The liquid sample (0.5-1.5 cc.), dissolved in a low boiling solvent, was placed in the bulb (A) together with a wad of glass wool. The side arm was closed with a glass rod plug (B) as shown in Figure II and the solvent removed at atmospheric pressure. Following this, the procedure, until equilibrium was attained, was the same as that described in part (a), namely, flooding, draining, then slow, controlled reflux for 30 minutes. The vapor was condensed for reflux by means of an air jet directed on the top of the column. The "sample-collecting" step was similar to that used in the batch method described in part (a). In order to collect a given fraction, the head was heated by means of an electric current in the heating unit (C). As soon as the distillate appeared in the side-arm the current through (C) was shut off, the bath removed, and the bath temperature raised. While the bath temperature was again being raised to the flood point, the fraction just collected was removed from the receiver (D) as follows:

Air (or better, nitrogen) was admitted to the system and the sample in (D) removed through the side-arm (E) (with the aid of a clean medicine dropper) to a tared test-tube. The residual material in (D), in addition to that remaining in the medicine dropper, was washed into a second tared test-tube with a pure low-boiling solvent. (In washing (D) it is important that some solvent be forced back into the system in order to remove all traces of the first fraction from the condensing area.) After the washing operation, the system was closed, re-evacuated, the bath replaced, and the procedure of flooding, draining and refluxing repeated.

The cuts obtained by this prodedure, using the apparatus shown in Figure II, weighed approximately 50 mg. If larger samples were desired the procedure was modified as follows: After the first fraction had been forced over, the current in (C) was shut off but the liquid in the pot was allowed to reflux at the same bath and column temperatures as used prior to the collection of the first fraction. After refluxing had been continued for about thirty minutes, a second fraction was collected and the total contents of the receiver (D) removed as described above.

B. Hydrogenation of Maple Holocellulose by Use of Copper Chromite in Dioxane Solution

It has been shown (30) that maple wood can be completely liquified by high pressure hydrogenation over copper chromite catalyst, to yield a mixture of dioxane soluble oils (and gases) containing (a) 4-n-propylcyclohexanol and 3-(4-hydroxycyclohexyl)-propanol-1, both of which undoubtedly originate from protolignin (since they have been obtained by direct hydrogenation of isolated lignins (36,31)); and (b) unidentified distillable oils, originating from either lignin or carbohydrates, not readily separable by fractional distillation.

This phase of the present investigation was undertaken, therefore, in an attempt to isolate woodmeal hydrogenation products of non-lignin origin by comparison of the fractionation results from maple holocellulose (the total carbohydrate content of the wood) hydrogenation products with those previously obtained from maple wood (30).

Maple holocellulose, prepared according to the method of Van Beckum and Ritter (157), was hydrogenated over copper chromite catalyst under the conditions prescribed for maple wood (30) (initial hydrogen pressure 3500 lb./sq. in., 280°C., 20 hours). Complete conversion to liquid and gaseous products resulted, following a hydrogen absorption of 2 moles/100 grams holocellulose (as compared to 3.1 moles/100 grams for maple wood). Due to the dark color of the liquid products (in contrast to the colorless hydrogenation products from maple wood), they were rehydrogenated under the same conditions with fresh catalyst. The total hydrogen absorption was then 2.5 moles/100 grams of maple holocellulose and the liquid products were water white. The hydrogenation products were worked up according to the same scheme used for maple wood (30), and illustrated in the accompanying skeleton flow sheet (Flow Sheet I)(a detailed flow sheet is given in the experimental section).

The results of the maple holocellulose fractionations as compared to those of maple wood (30) are presented in both graphical (Figures IV,V)and tabular (Table X) form (page 97).

The first noticeable feature in the maple holocellulose hydrogenation products is the complete absence of products in the 4-n-propylcyclohexanol range (n_D^{25}1.4610-1.4675, Figure IV) as well as in the 3-(4-hydroxycyclohexyl)-propanol-1 range (n_D^{25}1.4865, Figure V) as reported by Godard (30) for the products from maple wood hydrogenation. This is definite confirmation of the lignin origin of these propylcyclohexyl derivatives obtained from maple wood hydrogenation products since the holocellulose, which gave none of these derivatives, represents the total carbohydrate portion of the wood.

FLOW SHEET I

FRACTIONATION PROCEDURE FOR MAPLE HOLOCELLULOSE HYDROGENATION PRODUCTS

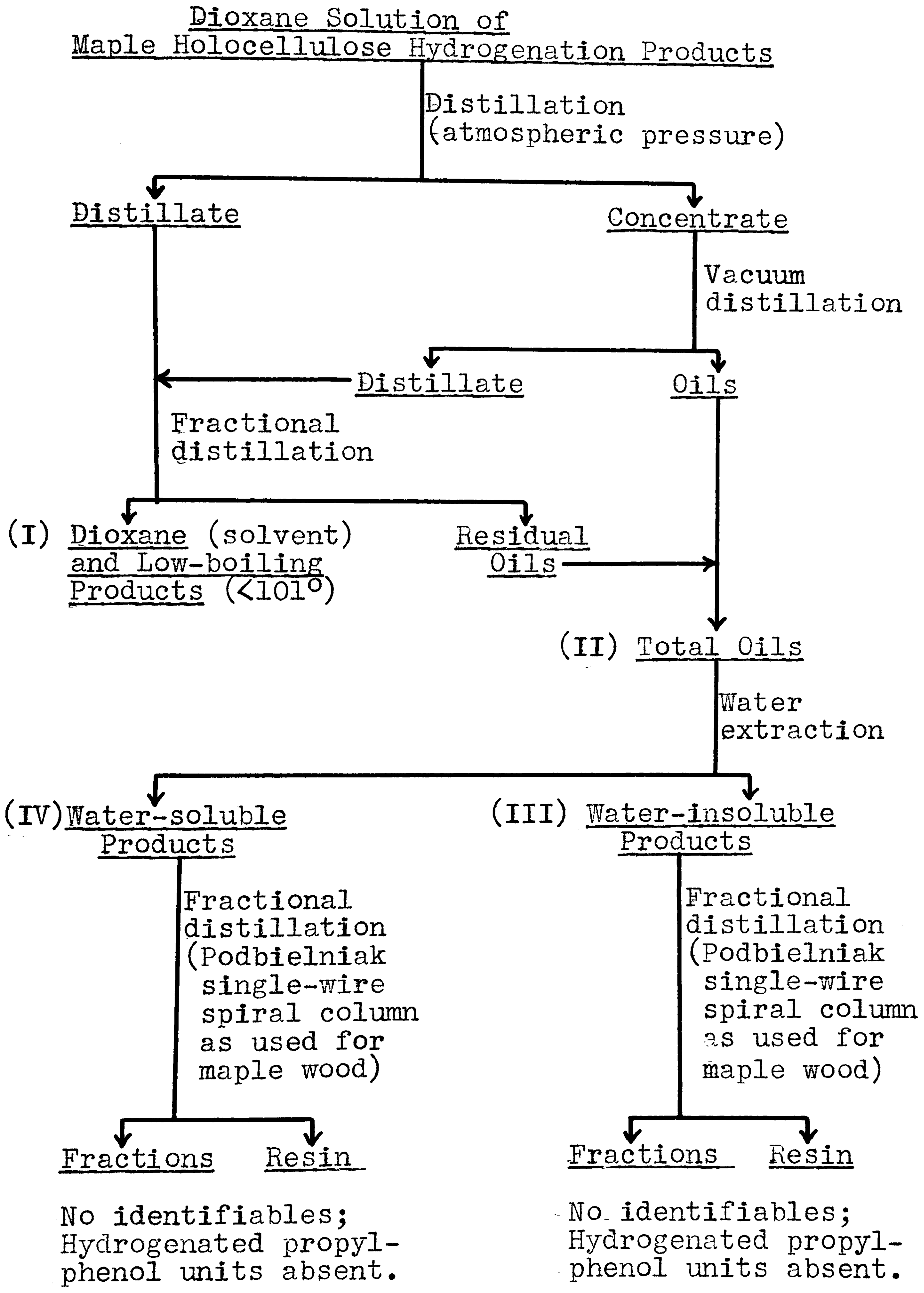


TABLE X

COMPARISON OF HYDROGENATION PRODUCTS FROM MAPLE HOLOCELLULOSE AND MAPLE WOODS

Fraction	Holocellulose			Wood(30)		
	Temp. °C.	Press. mm.	Yield %[a]	Temp. °C.	Press. mm.	Yield %[a]
I, b.p.<101° (760mm.)						
(a) Methanol	60-66	760	1	65-67	760	6-7
(b) Ethanol	75-79	760	5	79	760	14
(c) Water[b]	88-88.4	760	24	88-88.4	760	17
II, b.p. >101° (760mm.) (Separated into water-insoluble Fraction III and water-soluble Fraction IV)						
III, b.p. >101°(760mm.), water-insoluble						
(a) n_D^{25} 1.4100-.4275	----	--	None	to 95	100	3.5
(b) 1.4275-.4625	70-125	20	1.7	to 76	20	3.6
(c) 1.4625-.4680 4-n-propyl-cyclohexanol[c]	----	--	None	80	20	4.4
(d) n_D^{25} 1.4680-.5100	70-190	1	3.3	65-190	1	3.0
(e) Resin	190	1	1.4	190	1	3.6
(f) Cold Trap			0.3			1.2
IV, b.p.>101° (760mm.), water-soluble						
(a) Water-immiscible[d]	100	760	2.0	100	760	2.1
(b) n_D^{25} 1.4375-.4525	40-80	1	1.3	50-80	1	1.2
(c) 1.4525-.4860	80-125	1	1.2	80-127	1	1.2
(d) 1.4865 3-(4-hydroxycyclohexyl)-propanol-1	----	--	None	129-130	1	1.6
(e) Resin	125	1	0.5	130	1	
(f) Cold Trap			0.2			2.4

[a] Grams per 100 grams wood.
[b] Water in dioxane-water azeotrope.
[c] Product identity corrected in Section C.
[d] Steam distilled during water removal.

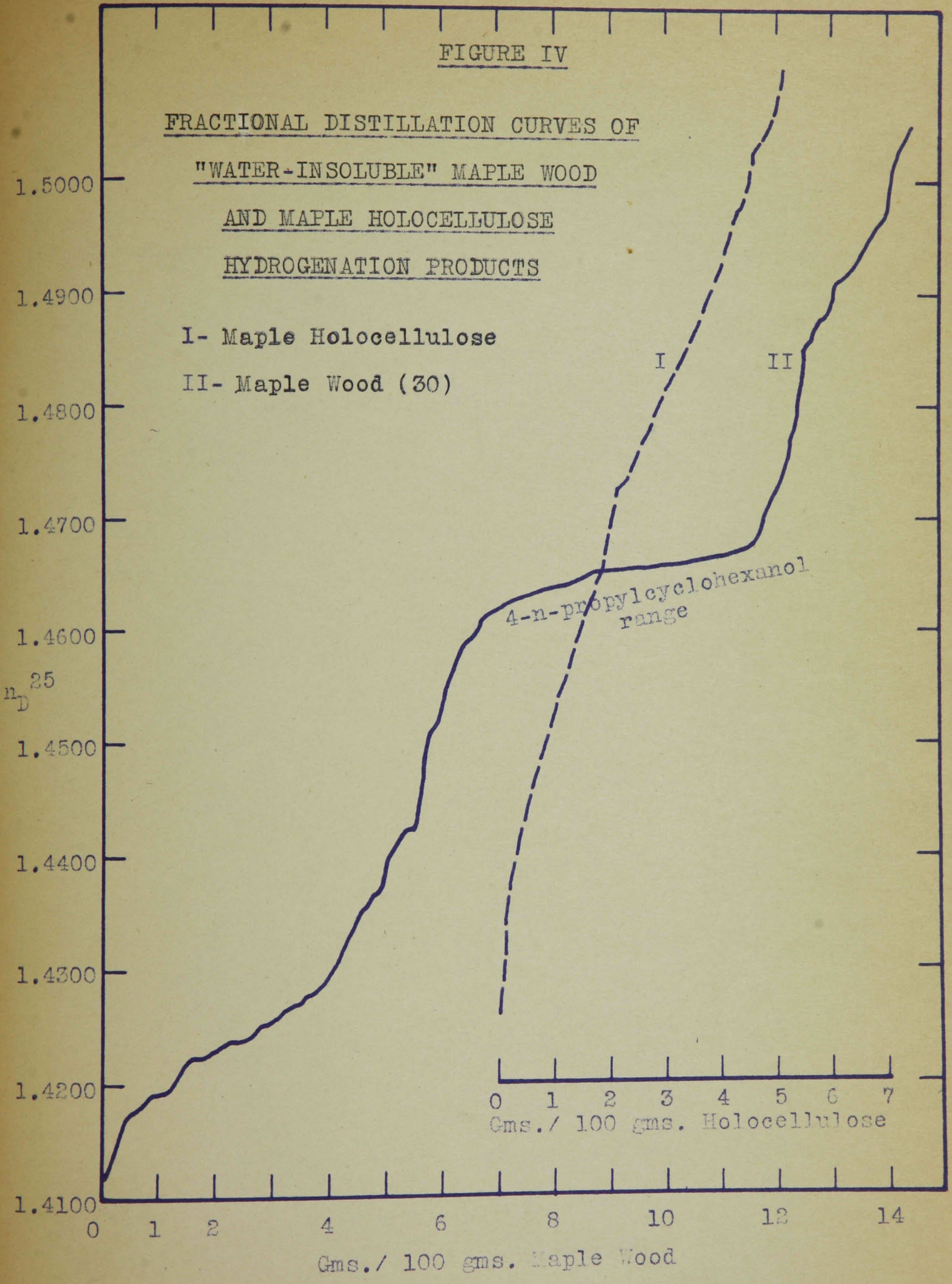


FIGURE IV

FRACTIONAL DISTILLATION CURVES OF "WATER-INSOLUBLE" MAPLE WOOD AND MAPLE HOLOCELLULOSE HYDROGENATION PRODUCTS

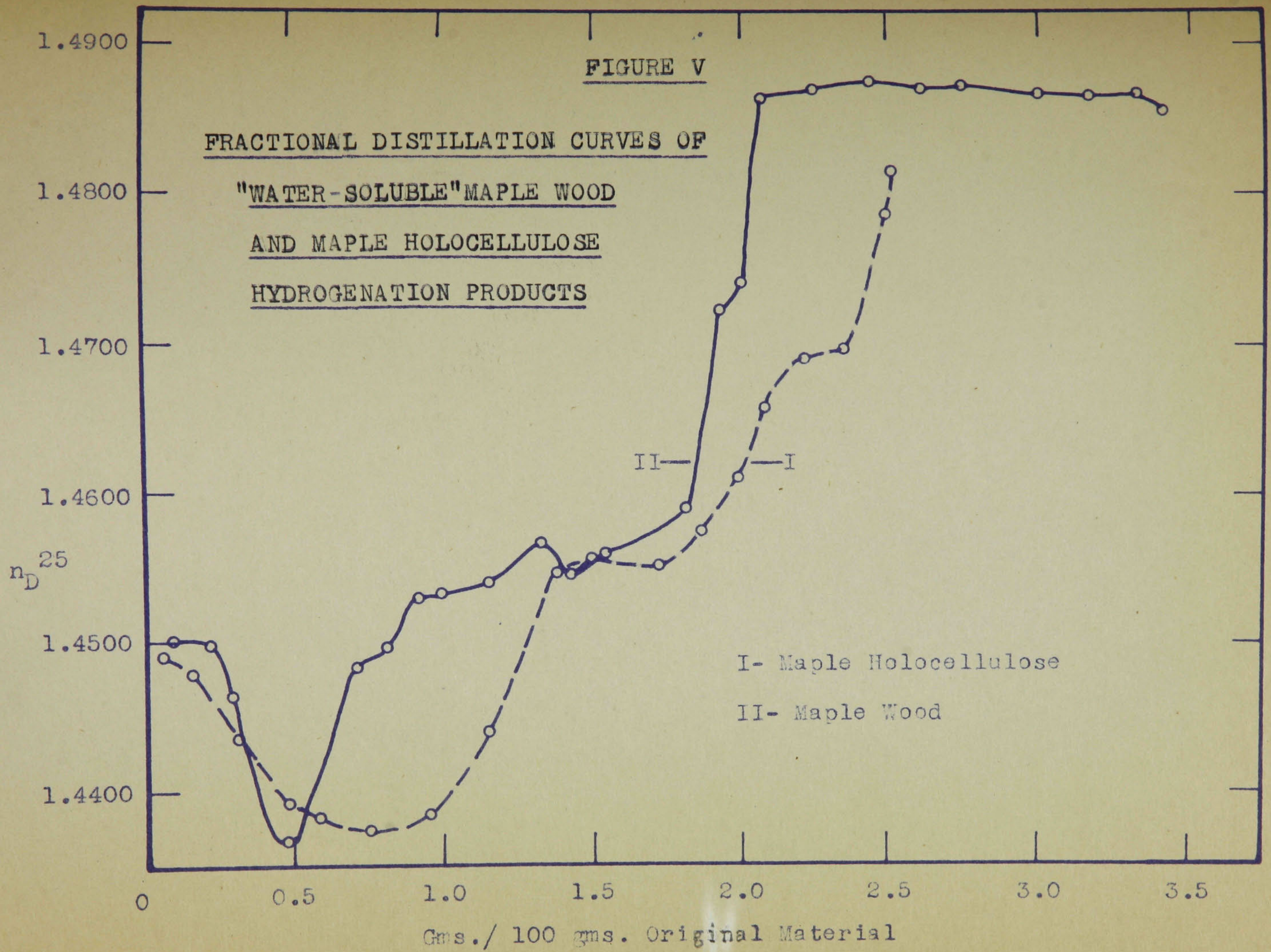


FIGURE V

FRACTIONAL DISTILLATION CURVES OF "WATER-SOLUBLE" MAPLE WOOD AND MAPLE HOLOCELLULOSE HYDROGENATION PRODUCTS

The second important point is the evidence showing that the major part of the unidentified products from maple wood hydrogenation (30) are probably of carbohydrate origin. This is indicated by the very close parallelism of the fractionation curves of the products from maple wood and maple holocellulose hydrogenations in quantity, refractive index and boiling point range (Figures IV and V, Table X). Thus the necessity for studying large quantities of difficultly separable oils to isolate materials of possible lignin origin has been eliminated.

An exception to this parallelism existed in the lowest-boiling ranges of the water-insoluble oils from maple wood hydrogenation where considerable material, with no counterpart in the holocellulose products (n_D^{25}1.4100-1.4400), was found. In order to obtain, for purposes of a more extensive study, additional material boiling in this range (n_D^{25}1.4100-1.4400) (such product not having been separable into even approximate fractions by the single-wire spiral Podbielniak type column used by the previous worker (30)), dried, solvent-extracted maple wood meal was hydrogenated under the same conditions used previously (30) and the oils recovered in the manner prescribed (30).

The lowest-boiling oils were then fractionated through the new fractionation set-up whereby more clean-cut separations (Figure VI) were obtained as compared with the previous indeterminate fractionation (Figure IV).

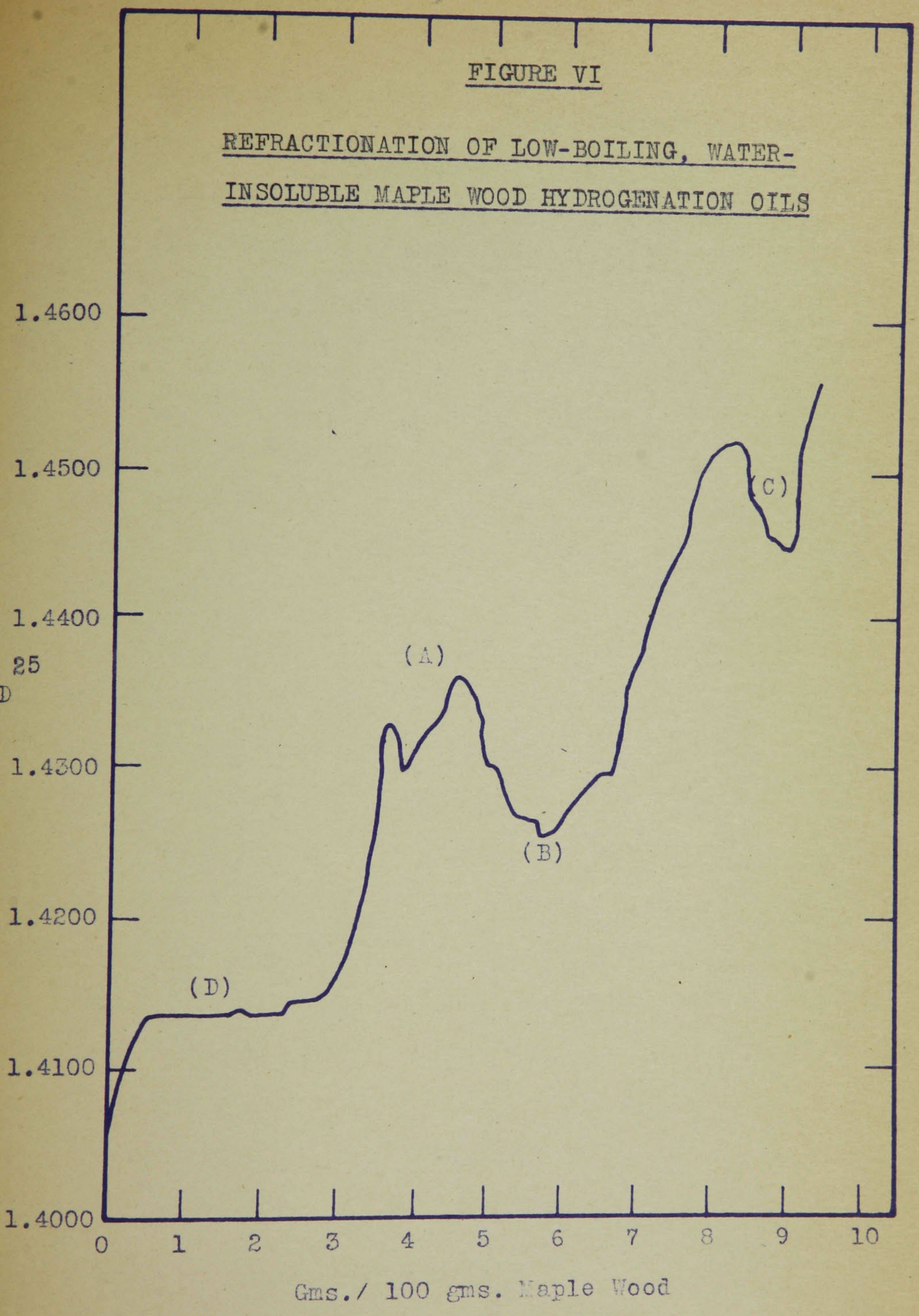


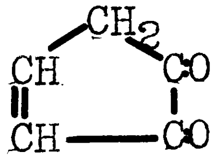
FIGURE VI

REFRACTIONATION OF LOW-BOILING, WATER-INSOLUBLE MAPLE WOOD HYDROGENATION OILS

The oils in the ranges of the maxima and minima (A, B, C, Figure VI) were refractionated but no further indication of any "flattening" obtained, indicating that somewhat complex mixtures, inseparable by fractional distillation with a 28 plate column, existed in these ranges. However, one definite "flat" (D, Figure VI) (n_D^{25}1.4133, b.p. 134-5°) was found in the lowest boiling range. This material (considered to be of constant composition since 10 fractions of constant boiling point and refractive index were secured) was analyzed and gave: C, 68.2% H, 13.2%; Molecular weight, 86-89 (Vapor density method (158)). The phenyl urethane of this material melted at 46-46.5°C.

The above properties agreed with those of n-amyl alcohol (n-pentanol) recorded in the literature and a sample of Eastman synthetic n-amyl alcohol was found to give a phenyl urethane melting at the same point (46-46.5°). A mixed melting point of the phenyl urethanes of the synthetic compound and of the product from maple wood hydrogenation melted at the same point (46-46.5°) confirming the identity of the material.

While this material (n-pentanol) seems unrelated to the lignin structure as known today (Section I-A) it does seem to be related to the "neutral" fraction obtained by the ethanolysis of maple (166). This material was tentatively identified as cyclopentenedione, by analysis of the material and its derivatives(166).



Such a structure could, presumably, give rise to n-pentanol by hydrogenolysis. Pentosans of the wood also seem to be a possible source of n-pentanol although this compound was not obtained by the hydrogenation of maple holocellulose which, theoretically, contains the total carbohydrate portion of the wood.

C. Isolation of 3-cyclohexylpropanol-1 As A Hydrogenation Product of Wood and Lignin

1. Isolation from Maple Wood

As stated in the preceding section, the writer hydrogenated maple wood under the conditions used previously by Godard, McCarthy and Hibbert (30) in order to refractionate the oils and check the preceding workers' results. The fractionation results for the water-soluble oils confirmed those already reported (30) in which 3-(4-hydroxycyclohexyl)-propanol-1 was apparently the only product of lignin origin.

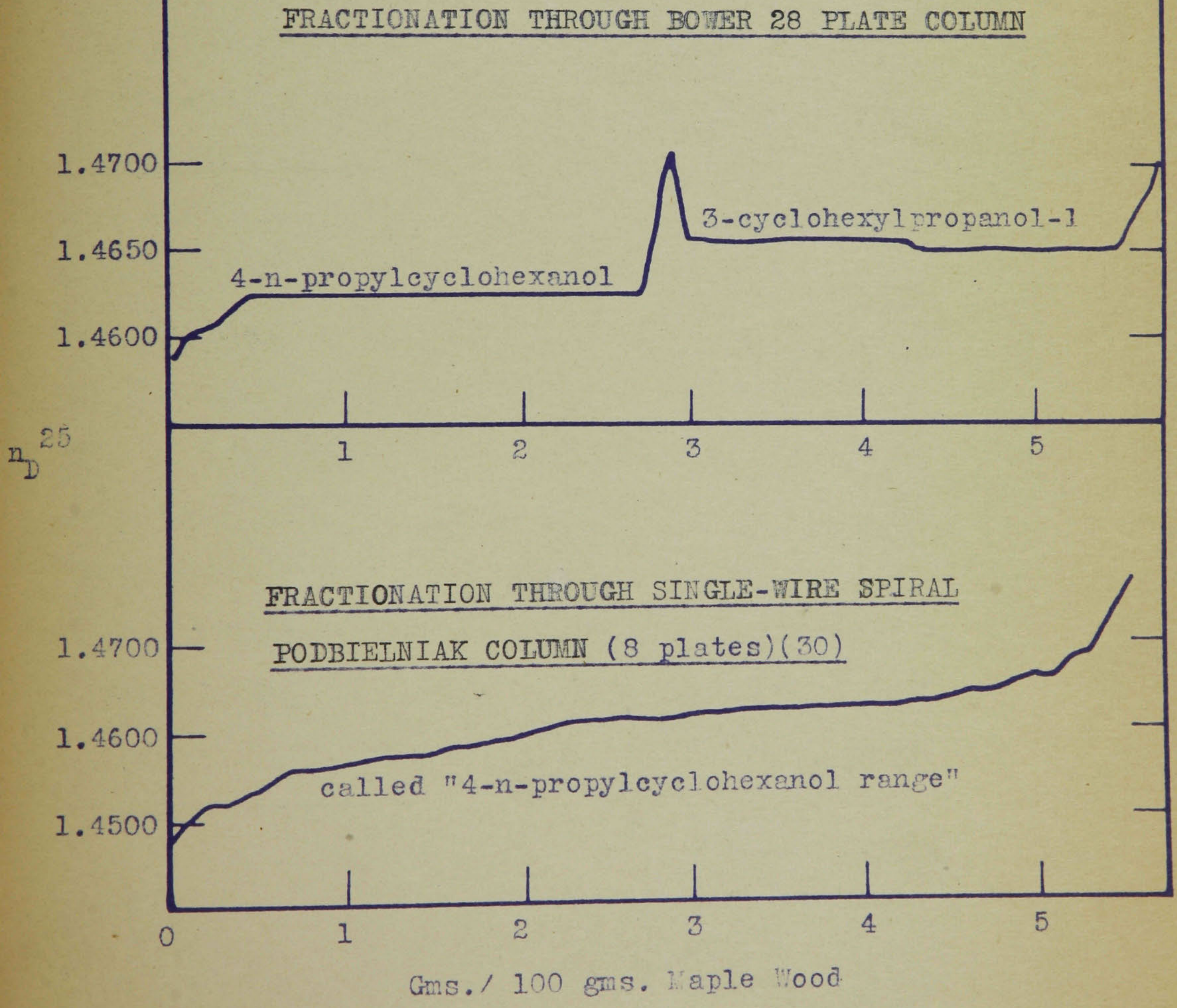
Using the author's new and much more efficient fractionating column, a different form of fractionation curve was found for the 4-n-propyl-cyclohexanol range (n_D^{25}1.4610-1.4675) in the fractionation of the water-insoluble oils (Figure VII). It can be seen that two well defined "flats" are present in the new fractionation curve as compared with the gradual sloping rise of the curve found previously (30). In order to check the identity of the material within this range, phenyl urethanes were prepared from a number of samples on each "flat" of the new curve.

The phenyl urethanes of the samples from material on the lower "flat" (n_D^{25}1.4625, Figure VII) all melted at 126-127° and gave a mixed melting point of 126-127° with the urethane from an authentic sample of 4-n-propylcyclohexanol (synthesized by

FIGURE VII

COMPARATIVE FRACTIONATION RESULTS OF WATER-INSOLUBLE MAPLE HYDROGENATION PRODUCTS

n_D^{25} 1.4600-1.4700 Range


FRACTIONATION THROUGH BOWER 28 PLATE COLUMN

FRACTIONATION THROUGH SINGLE-WIRE SPIRAL PODBIELNIAK COLUMN (8 plates)(30) hydrogenation of α-ethoxypropiovanillone), thus proving its identity as 4-n-propylcyclohexanol.

The urethanes from samples of the material on the upper "flat" (n_D^{25}1.4655, Figure VII), however, melted at 84-85°, a value not previously reported for any of the hydrogenation products from wood or lignin. A search of the literature revealed that the phenyl urethane of 3-cyclohexylpropanol-1 (obtained by the hydrogenation of cinnamyl alcohol (159)) melted at 88° and, moreover, that this material boiled within the same range (b.p.218-220°, 730mm.; 4-n-propylcyclohexanol, b.p. 208-210°, 760mm.) as 4-n-propylcyclohexanol. Cinnamyl alcohol was therefore hydrogenated over CuCrO (initial pressure 3000 lb./sq.in.; 6 hours; total absorption of hydrogen, 4 equivalents) to give 3-cyclohexylpropanol-1 (82% yield, n_D^{25}1.4655). The phenyl urethane of this material melted at 84-85° while a mixture of this and the unknown derivative from maple wood melted at 84-85° also, thus proving the identity of the new maple wood hydrogenation product. Table XI shows the revised figures for the yields of propylcyclohexyl derivatives from the hydrogenation products of maple wood.

TABLE XI

PREVIOUS (30) AND REVISED YIELDS OF PROPYLCYCLOHEXYL DERIVATIVES OBTAINED FROM HYDROGENATION OF MAPLE WOOD

Product	Yields per 100 grams Maple Wood		
	Godard, McCarthy and Hibbert (30) gms.	Bower gms.	
3-(4-hydroxycyclohexyl)-propanol-1	1.29	1.29	
4-n-propylcyclohexanol	4.4	2.2	5.0
3-cyclohexylpropanol-1	---	2.8	

It will be noted that a slight increase in the total amount of water-insoluble propylcyclohexyl derivatives (4-n-propylcyclohexanol and 3-cyclohexylpropanol-1) was obtained during this re-investigation (from 4.4 gms. to 5.0 gms. per 100 gms. maple wood). This raises the total yield of water-insoluble propylcyclohexyl derivatives to 22.2% of the Klason lignin (as compared to 19.5% by the previous workers (30)). This is equivalent to 32.3% of the methoxyl-free lignin carbon as compared to the 28.5% obtained previously. The total yield of methoxyl-free lignin carbon obtained from the identifiable products in the form of propylcyclohexyl derivatives (and including both water-soluble and water-insoluble products) has thus been increased to 39.8% as compared with the value of 36% reported previously (30).

The new product (3-cyclohexylpropanol-1) was also isolated from the hydrogenation products of spruce wood as will be discussed later (Section D, page 115).

2. Isolation From Various Lignin Fractions

A study of the above results led to a re-examination of the similar fractionation curves obtained by Cooke, McCarthy and Hibbert (31, Fig. 1, Page 3058) in their examination of the hydrogenation products from various lignin fractions (Figure VIII, page 109, is a copy of the original). The step-wise form of their curves was attributed by them to the presence of cis-trans isomers of 4-n-propylcyclohexanol.

Samples of their products, still on hand, were secured by the author, treated with phenyl isocyanate and melting points and mixed melting points of the phenyl urethanes determined. These proved that, in each case, the products present in the two flat portions of the curves (Figure VIII, page 109) were the two propylcyclohexyl derivatives found by the author in the case of maple wood. Their so-called 4-n-propylcyclohexanol obtained by hydrogenation of "ethanol lignin", "benzene-soluble lignins", and "lignin tars" thus, in reality, consisted of 30 to 50% (depending on the material) of the author's newly identified 3-cyclohexylpropanol-1, the remainder being 4-n-propylcyclohexanol. The

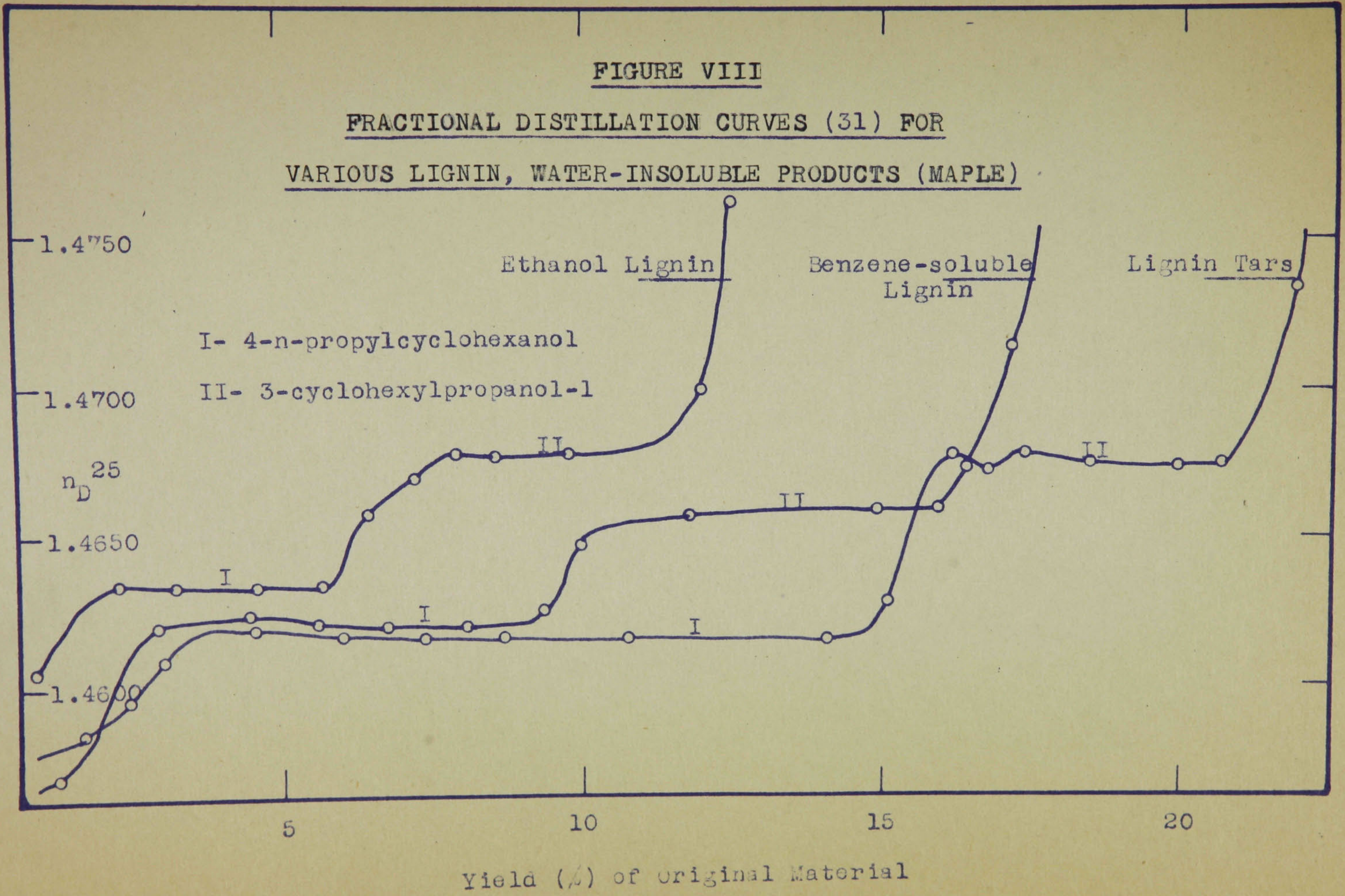


FIGURE VIII

FRACTIONAL DISTILLATION CURVES (31) FOR VARIOUS LIGNIN, WATER-INSOLUBLE PRODUCTS (MAPLE) results of this re-investigation are recorded in Table XII.

TABLE XII

PREVIOUS (31) AND REVISED YIELDS OF PROPYLCYCLOHEXYL DERIVATIVES OBTAINED FROM HYDROGENATION OF MAPLE ETHANOL LIGNIN FRACTIONS (Water-insoluble Products)

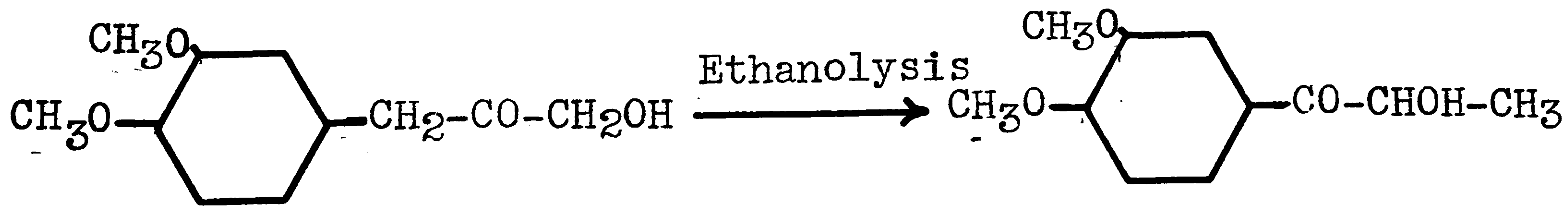
	Cooke, McCarthy and Hibbert(31)	Bower	
	4-n-propyl-cyclohexanol %	4-n-propyl-cyclohexanol %	3-cyclohexyl-propanol-1 %
Ethanol Lignin	9.9	5.0	4.9
Benzene-soluble Lignin	13.5	7.0	6.5
Lignin Tars	17.5	12.0	5.5

This phase of the investigation has proven definitely the value of the author's fractionating column since it was not until this was put into use that the previously reported 4-n-propylcyclohexanol range of wood hydrogenation products could be broken down into its two pure components. It also seems highly probable that, in the light of the above results, the material reported by Harris, et al. (36), obtained by the hydrogenation of various lignins and reported by them as 4-n-propylcyclohexanol, contains this new derivative (3-cyclohexylpropanol-1) since Harris used the much less efficient Widmer type fractionating column in his investigations.

3. Significance of the Isolation of 3-cyclohexylpropanol-1

Up to the present the only evidence for the presence of a terminal -CH_2O- group on the propyl phenol side chain of the assumed lignin fragments has been the small amount of 3-(4-hydroxycyclohexyl)-propanol-1 (20% of isolated propylcyclohexyl derivatives) isolated from hydrogenation products of wood and lignin. Isolation of the newly discovered 3-cyclohexylpropanol-1 proves that, in the case of maple wood, a minimum of 65% of the isolated propylcyclohexyl derivatives (Table XI) have the terminal -CH_2O- grouping on the side chain. The definite possibility exists that in the proto-lignin an even higher percentage of the side chains have this end grouping since, as will be discussed later, the writer has shown that β-hydroxypropiovanillone (XV), under the conditions used for the hydrogenation of wood and lignins, loses a considerable percentage of its terminal oxygen to give 4-n-propylcyclohexanol in addition to the principal product, namely 3-cyclohexylpropanol-1 (page 124).

Eastham (57) has shown quite recently that 1-veratryl-3-hydroxypropanone-2 (LXI) rearranges to give α-hydroxypropioveratrone (XXIX)



(LXI) (XXIX)

under acidic conditions. While the actual initial phase of hydrogenation of wood takes place in a neutral solvent, it is completed at a relatively high temperature in a slightly acidic medium resulting from the formation of formic and acetic acids, and this fact, together with the recent observations of MacGregor (167) that there are apparently no terminal $-CH_3$ groups in the unchanged protolignin of the wood, both provide strong evidence that the native lignin propyl phenol building units are probably united by R-C-C-C-O- terminal linkages.

D. Plant Synthesis of Propylphenol Units in Spruce Wood

1. Stage of Development

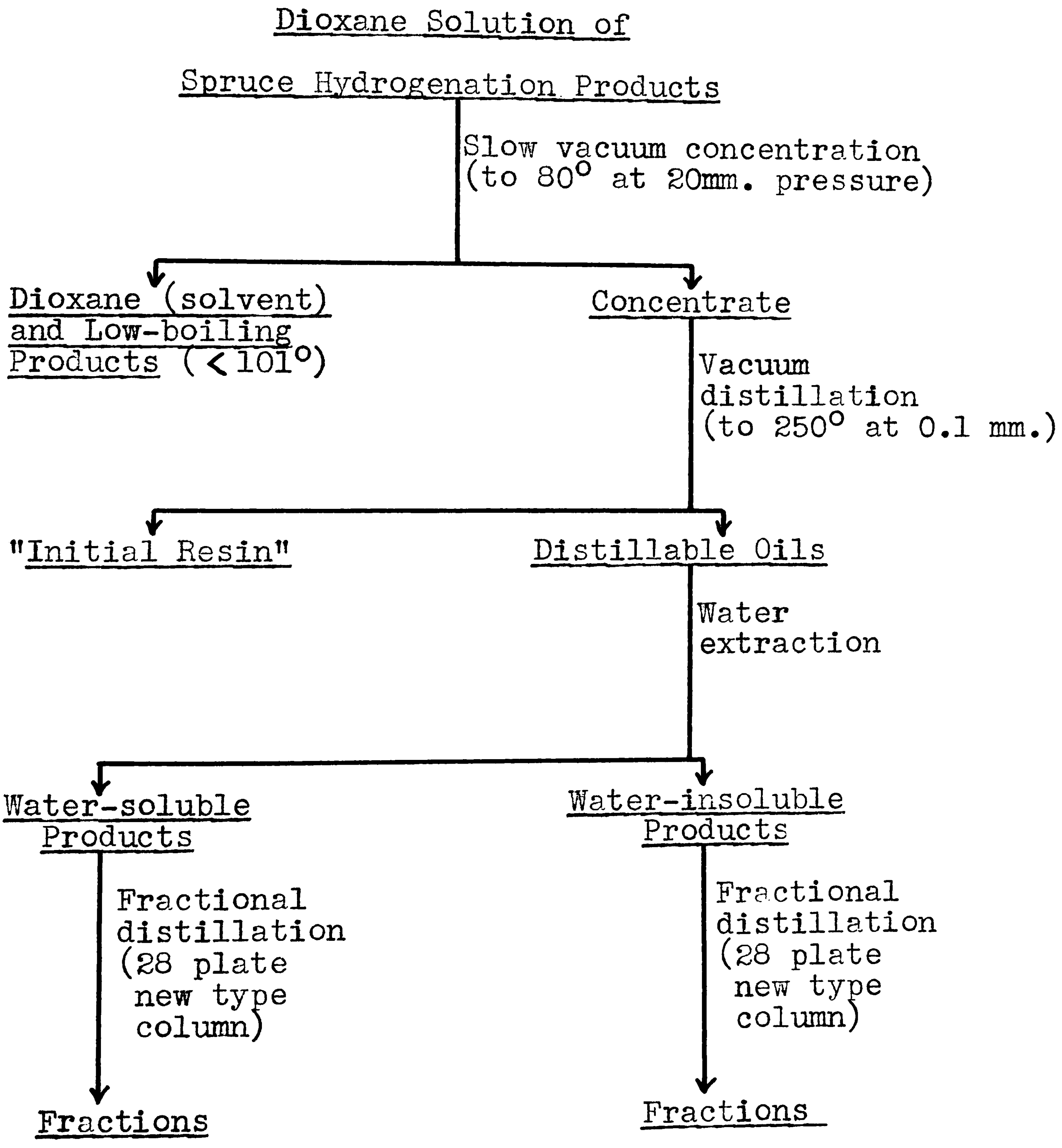
After having established the lignin origin of the propylphenol units of maple wood (Section B) and ascertained definitely the identity of all these derivatives occurring in the hydrogenation products of maple wood(Section C) there remained a final phase of this research, namely, an attempt to establish by means of the hydrogenation technique, the period, in early plant growth, characterized by the initial appearance of propylphenol units. Spruce wood was chosen for this study because of the availability of plant material of the species at various stages of new plant growth.

Three stages of growth were investigated and these comprised spruce tips, two to three weeks old (Stage I), spruce tips, $3\frac{1}{2}$ to 4 months old (Stage II), and mature spruce wood, 35 to 40 years old.

(a) Mature Spruce Wood - In order to establish a reference basis, mature spruce wood, ethanol-benzene extracted, was hydrogenated over CuCrO catalyst under the identical conditions used for maple wood (30, and section B) and the hydrogenation products worked up and fractionated in a similar manner to that used for maple wood and maple holocellulose products. (Flow Sheet II is a skeleton outline of the recovery procedure used for all of the

FLOW SHEET II

FRACTIONATION PROCEDURE FOR SPRUCE HYDROGENATION PRODUCTS

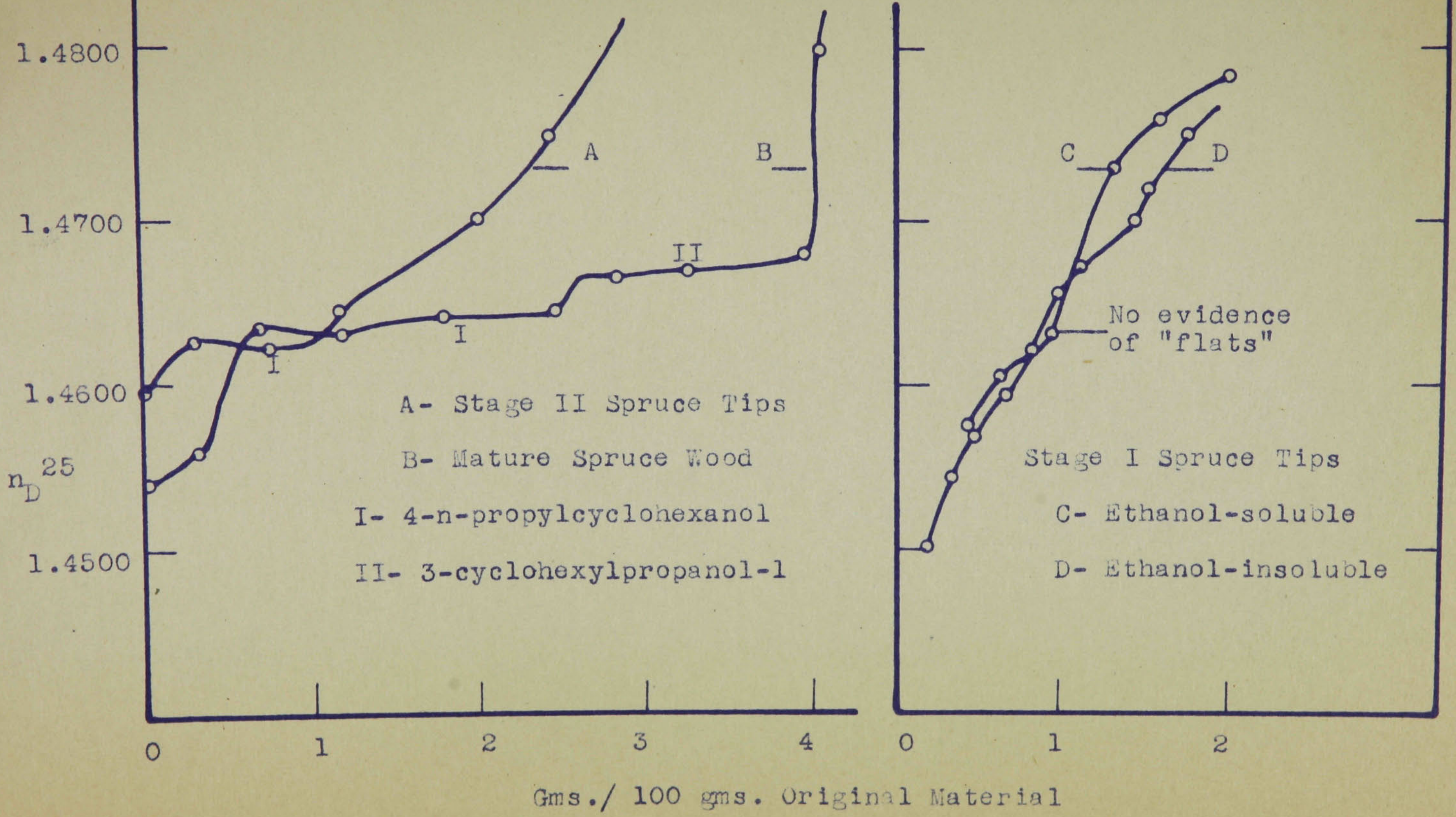


hydrogenation products in the present series. Detailed flow sheets will be found in the experimental section.) The only important difference in this procedure and that used for the maple wood products was the vacuum distillation serving to remove the distillable oils from "initial resins". It was considered this procedure would minimize further resin formation during the course of the long fractionations (often 40 to 60 hours).

The fractionation curves for the hydrogenation products of mature spruce wood (Figures IX-B and X-C) show the same general form as those for maple wood (Figures V- II and VII) and differ only in the amounts of the propylcyclohexyl derivatives present. Only the ranges of the curves containing the propylcyclohexyl derivatives are shown, the complicated and indeterminate carbohydrate portions of the curves being omitted (complete fractionation data for all parts of the curves are given in the experimental section). The yields of propylcyclohexyl derivatives (identities proven through formation and melting points of appropriate derivatives) for both spruce and maple woods are given in Table XIII (page 118).

FIGURE IX

FRACTIONATION CURVES OF SPRUCE "WATER-INSOLUBLE" PRODUCTS IN PROPYLCYCLOHEXYL DERIVATIVE RANGE



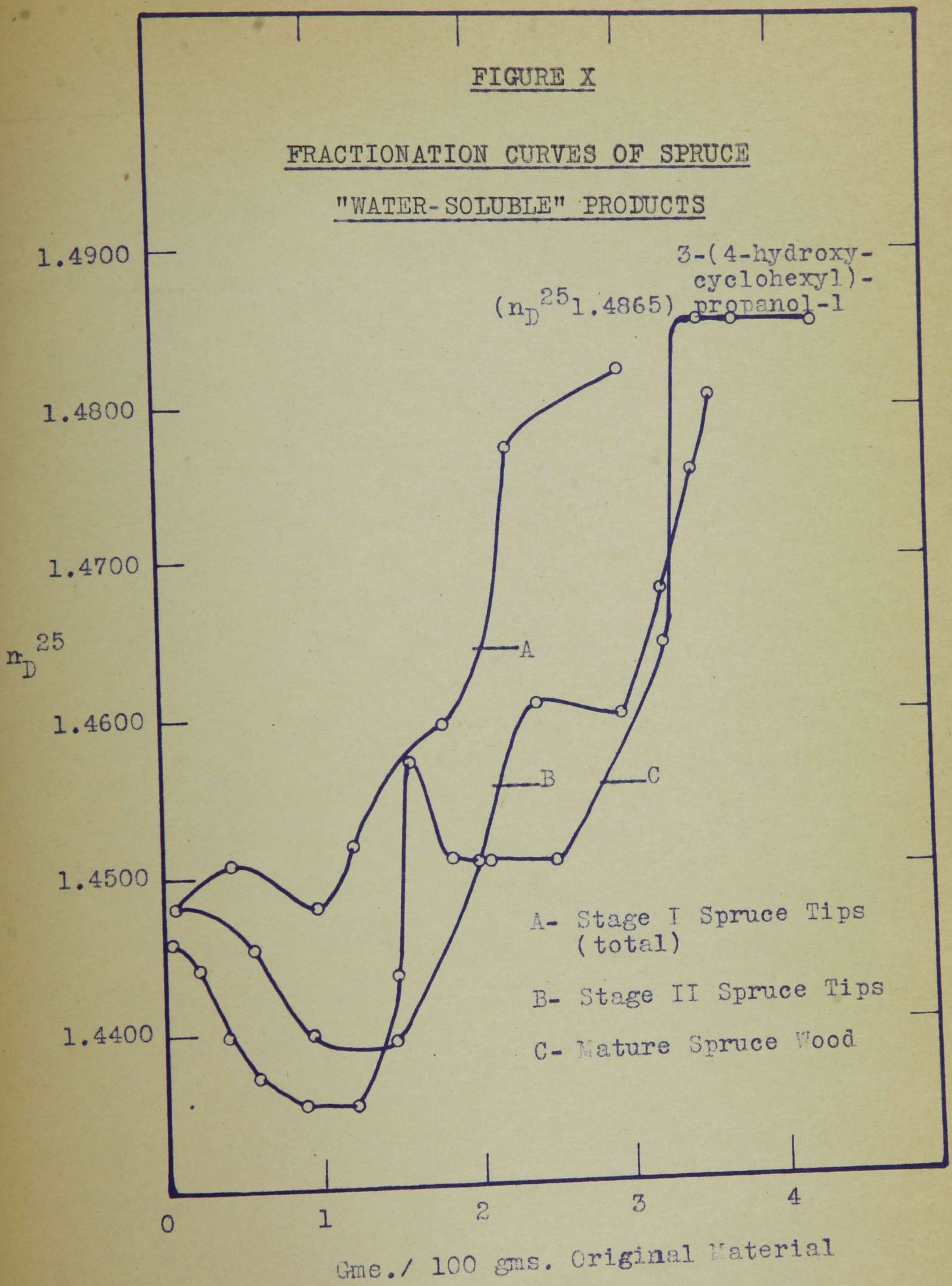


FIGURE X

FRACTIONATION CURVES OF SPRUCE "WATER-SOLUBLE" PRODUCTS

TABLE XIII

YIELDS OF PROPYLCYCLOHEXYL DERIVATIVES FROM HYDROGENATION OF MAPLE AND SPRUCE MATERIALS

Material Hydrogenated	Yields (% of Original Dry Materials)		
	4-n-propyl-cyclohexanol	3-cyclohexyl-propanol-1	3-(4-hydroxy-cyclohexyl)-propanol-1
Mature Maple Wood	2.2	2.8	1.29
Mature Spruce Wood	1.9	1.4	0.9
Spruce Tips (Stage I)	0.0	0.0	0.0
Spruce Tips (Stage II)	0.8	0.0	0.0

It will be noted that all three of the propylcyclohexyl derivatives isolated from maple wood hydrogenation oils, were also isolated from mature spruce wood, the sole difference being that only 3/5 the quantity of such derivatives were isolated from spruce as compared with maple. This yield is in general agreement with the yields of ethanolysis products from these two sources found in these laboratories.

With the establishment of this basis of yields of propylcyclohexyl derivatives from mature spruce wood, the next step was the hydrogenation of spruce tips (Stage I, 2-3 weeks old). Ethanol-benzene extractions of wood meals have been customary, in these laboratories, for removal of fats and waxes prior to use of the woods for lignin investigations. However, it was found that 50% of the Stage I spruce tips was dissolved in this process and therefore both the dried extracted bud meal and the dried alcoholic extract were hydrogenated, separately, in order to avoid any possible loss of lignin materials.

(b) Alcohol Extracted Bud Meal (Stage I) - This was hydrogenated in the usual manner in dioxane solution over CuCrO (initial pressure 3000 lb./sq.in., 280°., 22 hours) but since the solution recovered was dark green in color, it was rehydrogenated over fresh catalyst for a further period of 5 hours. The final dioxane solution of the hydrogenation products was colorless.

(c) Alcoholic Extract of Bud Meal (Stage I) - This was concentrated to a thick syrup, dioxane added, and the concentration continued until all traces of ethanol and water had been removed, leaving pure dioxane. This solution was then hydrogenated in the usual manner and after one treatment was water white in appearance.

Each of the solutions(from (b) and (c) respectively) was separated and fractionated in the usual manner (Flow Sheet II) but no trace of propylcyclohexyl derivatives was found in either material (Table XIII). The fractionation curves for (b) and (c) in the regions previously established for propylcyclohexyl derivatives are shown in Figures IX-C-D and X-A and confirm the absence of the latter.

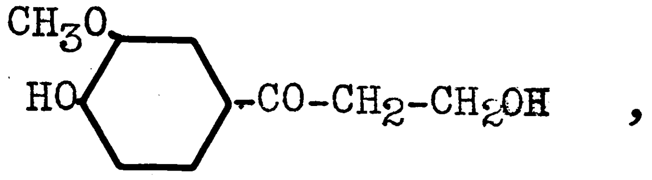
(d) Spruce Tips, Stage II - Because of the high alcohol solubility found in the case of Stage I tips, the Stage II material was hydrogenated as such (that is, without a previous alcohol extraction) after vacuum oven drying at 50°C. The hydrogenation was carried out under the usual conditions and gave a dark colored solution as in the case of Stage I spruce tips. The material was therefore retreated for 5 hours with fresh catalyst and gave the usual water-white dioxane solution.

Fractionation of this Stage II spruce tip material in the usual manner (Flow Sheet II) gave a yield of 0.8% of 4-n-propylcyclohexanol but no evidence of any of the other propylcyclohexyl derivatives (Table XIII). The fractionation curves in the ranges of such products are included in Figures IX-A and X-B.

The results of the above series of experiments indicate that the formation of lignin, if isolation of propylphenol derivatives is accepted as evidence of its presence, takes place only slowly during the early process of plant growth (spruce). Lignin seems to be completely absent in the early growing tip (2-3 week old), while near the end of the first growing season (4 months) it is present to the extent of approximately 20% of that found in mature wood (Table XIII) (page 118).

2. Reliability of Experimental Procedure

To prove that the hydrogenation conditions used were not resulting in an actual destruction of the propylphenol nucleus, it was decided to hydrogenate, under identical conditions, a second batch of Stage II spruce tips in a dioxane medium to which had been added β-hydroxypropiovanillone,



a product that offered the possibility of yielding all three of the previously identified propylcyclohexyl derivatives. The percentage recovery of the added β-hydroxypropiovanillone in the form of propylcyclohexyl derivatives would provide evidence regarding the possible effect of the hydrogenation conditions on propylphenol derivatives in the wood.

Therefore a mixture of Stage II spruce tips and β-hydroxypropiovanillone (5%) in dioxane was hydrogenated under the identical conditions used for Stage II spruce tips alone. The hydrogenation products were recovered in the same manner as before, and the results are shown in Table XIV and Figure XI.

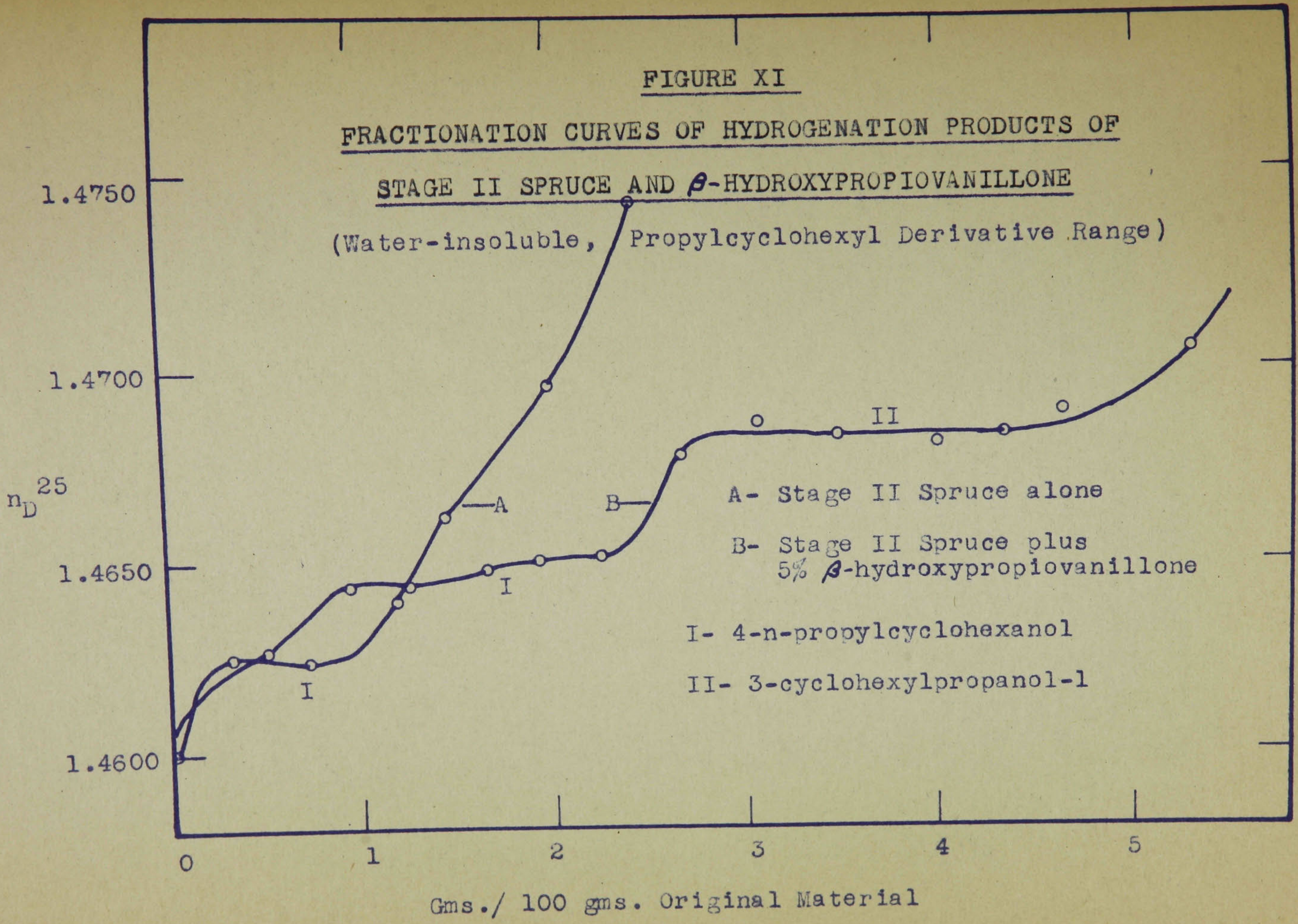


FIGURE XI

FRACTIONATION CURVES OF HYDROGENATION PRODUCTS OF STAGE II SPRUCE AND β-HYDROXYPROPIOVANILLONE

(Water-insoluble, Propylcyclohexyl Derivative Range)

TABLE XIV

YIELDS OF PROPYLCYCLOHEXYL DERIVATIVES FROM HYDROGENATION OF STAGE II SPRUCE TIPS AND β-HYDROXYPROPIOVANILLONE

Material Hydrogenated	Yields (% of Original Dry Materials) 4-n-propyl-cyclohexanol	3-cyclohexyl-propanol-1	3-(4-hydroxy-cyclohexyl)-propanol-1
Stage II Spruce Tips	0.8	0.0	0.0
Stage II Spruce Tips plus β-hydroxy-propiovanillone (5%)	2.3	2.1	0.0
Pure β-hydroxy-propiovanillone	19.5	61.5	0.0

Examination of the yields of propylcyclohexyl derivatives from the hydrogenation products of the mixture of Stage II spruce tips and β-hydroxypropiovanillone (5%) reveals that a total of 4.4% of such derivatives was isolated. Allowing for the amount of 4-n-propylcyclohexanol previously isolated from Stage II spruce tips alone (0.8%), it follows that the remaining amount of propylcyclohexyl derivatives (3.6%) is that formed from the hydrogenation of the added β-hydroxypropiovanillone. When allowance is made for the loss of oxygen and carbon atoms, and gain of hydrogen atoms, during the hydrogenation of β-hydroxypropiovanillone to 4-n-propylcyclohexanol (or to 3-cyclohexylpropanol-1) the maximum theoretical yield of such products would be 3.6 grams from 5.0 grams of the starting material. Thus 100% of the theoretically possible yield of propylcyclohexyl derivatives has been recovered, and, if the assumed similarity in behavior on hydrogenation between β-hydroxypropiovanillone and of the propylphenol units present in wood is true, it follows that no decomposition of such derivatives has taken place during the hydrogenation, thus providing support for the conclusions drawn at the end of part 1 (page 120).

To prove that 4-n-propylcyclohexanol and 3-cyclohexylpropanol-1 are actually hydrogenation products from β-hydroxypropiovanillone, five grams of this were hydrogenated over CuCrO in dioxane. The results are given in Table XIV and Figure XII. It is seen that the yield of propylcyclohexyl derivatives amounted to 81%, of which 24% was 4-n-propylcyclohexanol and 76%, 3-cyclohexylpropanol-1. The loss of material (19%) probably occured in the recovery during concentration of 150cc. of dioxane solution containing a theoretical 3.6 grams of these propylcyclohexyl derivatives. However, even if this amount were an actual hydrogenation loss (through decomposition) it is relatively so small that it would in no way invalidate the general conclusions drawn above.

All products mentioned in the preceding discussion were definitely identified through formation of solid derivatives (phenyl

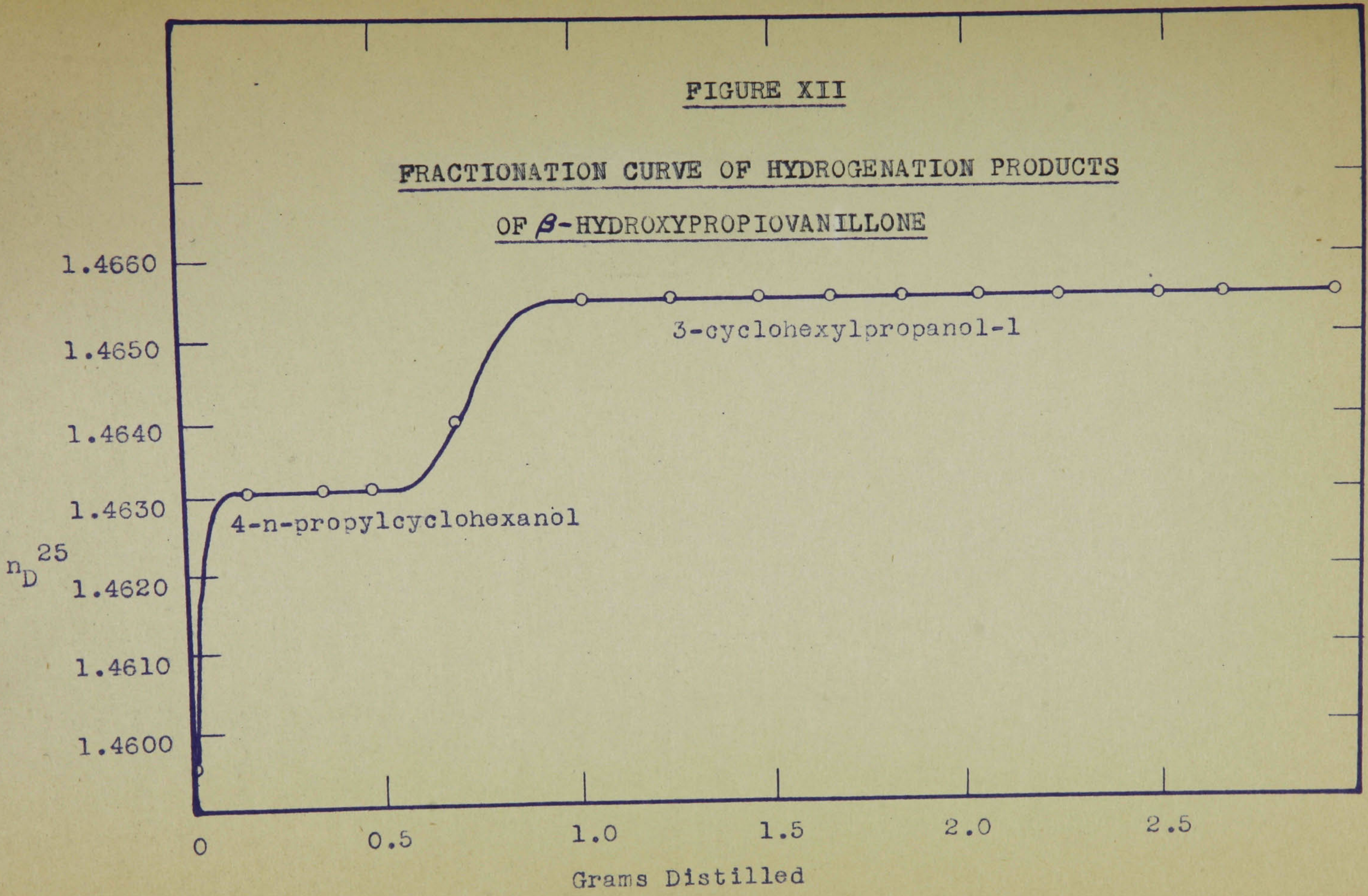


FIGURE XII

FRACTIONATION CURVE OF HYDROGENATION PRODUCTS OF β-HYDROXYPROPIOVANILLONE urethanes in the case of 4-n-propylcyclohexanol and 3-cyclohexylpropanol-1, and the semicarbazone of the keto-acid oxidation product in the case of 3-(4-hydroxycyclohexyl)-propanol-1); determination of melting points; and comparison with synthetic derivatives by means of mixed melting points. Physical properties (refractive indices and boiling points) proved valuable in indicating suspected derivatives but, as was illustrated in section C, could not be accepted as final proof of identity.

3. Isolation of n-octadecanol

An additional product, n-octadecanol, was isolated from both Stage I and Stage II spruce tips in a yield of approximately five percent (calculated on the weight of original material). It was found in the highest-boiling distillate, obtained from the water-insoluble fractions, as a viscous, colorless oil which crystallized very rapidly on standing. After recrystallization to a constant melting point (57-57.5^o) from petroleum ether or ethanol, analysis for carbon and hydrogen indicated its empirical formula as $C_{18}H_{38}O$. A mixed melting point with a sample of Eastman n-octadecanol (m.p. 56-57^o) showed no depression, thus proving the identity of the material.

While this n-octadecanol has probably little or no significance to the lignin problem, and is probably formed from the fats or waxes present in the growing tip, the large amount of it present seems worthy of note. Related to its presence is the fact that oleic and linoleic acids (160) and stearates (161) (18 carbon atom derivatives) have been found among the ether-soluble extracts of pine needles.

VII. Experimental Results

A. Design of Fractionating Column

1. Construction

The glass portion of the column was made of pyrex tubing to the scale illustrated in Figure I (Figure II for the semi-micro column)(page 84). The construction of the receiver, likewise, should be obvious from the diagram, the sample tubes being supported about a central metal rod which could be rotated to bring successive ones under the delivery tube. A short nichrome wire was sealed into the delivery tip to provide a flexible, easily-adjusted guide to direct the sample into the center of the sample tube.

The column packing was made from 40 x 60 mesh Monel metal wire screen (40 mesh horizontally, 60 mesh vertically), cut and twisted as described in the discussion section (page 88).

The vacuum system contained a dry ice trap and a 5 liter surge bottle connected in series between the column and the Cenco Hy-vac pump and could be evacuated to 0.002mm. of Hg. Ten mm. tubing was used for all connections (sealed glass to glass). Pressure was read from a barometric column or, for higher vacuums, from a McLeod gauge and was controlled by means of a filed-stopcock, bleeder valve leading into the surge bottle.

The electrical circuits used to control the column and bath heaters are shown in Figure III (page 87), the resistances being constructed of No. 24 B. & S. nichrome wire, mounted on a transite base. Control was maintained through use of a voltmeter wired across the heater resistance.

2. Testing

The theoretical plate values for the columns were determined by use of methylcyclohexane-n-heptane mixtures according to the standard method described by Ward (136). A mixture of pure n-heptane (n_D^{20}1.3885) and methylcyclohexane (n_D^{20}1.4236) was placed in a 100 cc. pyrex glass distilling pot fitted with a side arm, and placed on the bottom of the column. The column was then brought to equilibrium operating conditions at total reflux (as described on page 90) and samples withdrawn simultaneously from the top of the column and from the pot by means of medicine droppers. Analysis of the samples was by means of refractive indices and the plate values were determined by both algebraic and graphic methods as suggested by Ward (136).

The results obtained by operating the new type 17 inch column (packed with 50 mesh Cu gauze) at various reflux rates are recorded in the following table.

TABLE XV

FRACTIONATION COLUMN TEST DATA

Reflux Rate drops/min.	Refractive Index (25°) Pot Liquid	Distillate	Operating Holdup Total ccs.
32	1.4133	1.3994	1.03
52	1.4132	1.4010	--
70	1.4135	1.4031	--
92	1.4132	1.4034	1.03
Results for 20.5 inch column (Monel packed)			
30	1.4134	1.3990	1.21

Theoretical plate values were computed from the above data and are recorded in Table IX in part VI - A (page 83).

The operating holdup was determined by Fenske's method (138) in which a definite weight of a nonvolatile solute (stearic acid) is added to a known volume of solvent (benzene) in the still pot and, after equilibrium has been established, a sample of the pot liquor withdrawn and analyzed for stearic acid content (by evaporation of the solvent). From the original known concentration, and the final experimentally determined concentration of stearic acid in the pot liquors, the amount of benzene held in the column, while operating, was computed.

The observed reflux rate in drops per minute was translated to ccs. per hour by counting the drops formed when a known volume of liquid was allowed to flow over the cold finger and drip from the point.

B. Hydrogenation of Maple Holocellulose and Maple Wood by use of Copper Chromite in Dioxane Solution

1. Preparation of Maple Holocellulose

The holocellulose analytical method of Van Beckum and Ritter (157) was adapted to the large scale preparation of holocellulose. Maple wood (200 g., 7% H_2O) was placed in an 8-in. Büchner funnel, moistened with water and then, with a moderate vacuum applied, chlorine was led on to the wood through an inverted glass funnel. The treatment (with occasional stirring) was continued for five to ten minutes until no further color change of the wood was apparent, and the reaction product washed on the funnel successively with 95% ethanol (400 cc.), hot ethanolamine (75°, two 500-cc. portions of a 3% solution in 95% ethanol to remove the chlorinated lignin), 95% ethanol (two 500-cc. portions), and cold water, and then the woodmeal transferred to a fresh filter. This cycle of operations was repeated seven times until the residual product remained white after chlorination and washing with ethanolamine. The maple holocellulose was finally washed with ethanol and vacuum-dried; yield, 120g.; Klason lignin, 0.0%

2. Hydrogenation of Maple Holocellulose

This material was hydrogenated under the same conditions used for maple wood by Godard, McCarthy and Hibbert (30).

Bomb charge (500 cc. Parr Hydrogenation Bomb):

35 grams maple holocellulose
20 grams CuCrO catalyst (80, page 13) or (95)
240 cc. dry dioxane
270 cc. total volume

Conditions:

Initial hydrogen pressure 3300 lb./sq.in.
Average temperature 280°C.
Total time 20 hours

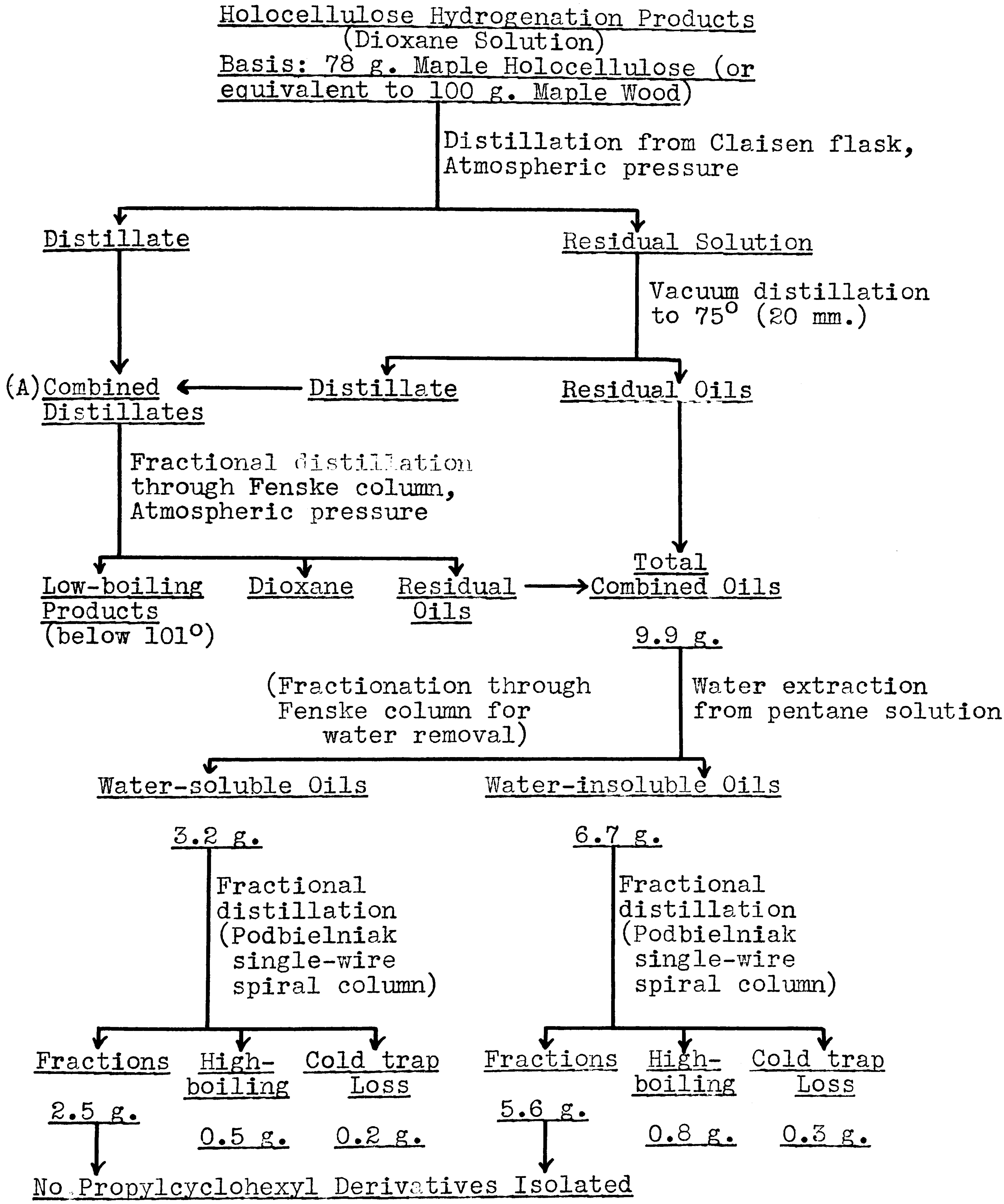
At the end of 20 hours hydrogen absorption had ceased, with a total hydrogen uptake of 2.0 mols per 100 grams of holocellulose. Upon cooling the bomb, removing the reaction mixture, and centrifuging off the catalyst, the solution was found to be dark brown in color. It was replaced in the bomb with 20 grams fresh CuCrO catalyst and rehydrogenated, as before, for an additional 15 hours, at the end of which time an additional 0.5 mols of hydrogen (per 100 grams holocellulose) had been absorbed; the reaction mixture was now water-white in appearance.

A second batch of holocellulose was treated in exactly the same manner and the two products combined to give sufficient material for investigation.

3. Separation and Fractionation of Holocellulose Hydrogenation Products

The hydrogenation products (in dioxane solution) of maple holocellulose were worked up in a similar manner to that used previously (30) for maple wood hydrogenation products, and as

FLOW SHEET III



outlined in Flow Sheet III. This, in general, is self-explanatory. The Fenske column used in the separation of the residual oils from the dioxane solution was constructed in these laboratories and was an exact copy of that described by Fenske and co-workers (154). The Podbielniak single-wire spiral column used for final fractionations of the oils was of the type described by Podbielniak (141) and had a plate efficiency of 7 theoretical plates as determined by Cooke (85).

The division of the total oils into water-soluble and -insoluble fractions was accomplished by successive extractions of a pentane solution of the oils with water (using a motor stirrer in a separatory funnel) until the refractive index of the last two extractions was identical with that of water saturated with pentane (n_D^{25}1.3356).

TABLE XVI

WATER-EXTRACTION OF MAPLE HOLOCELLULOSE HYDROGENATION OILS

(9.9 gms. oils in 35 cc. pentane)

Extraction	Amount of Water Used cc.	Time of Extraction min.	n_D^{25} Water Solution
1	100	5	1.3485
2	50	5	1.3419
3	30	5	1.3380
4	25	5	1.3357
5	20	5	1.3356

The water-soluble oils (3.2 grams) obtained by this separation were recovered from the water solution by concentration through the Fenske column (page 135) and then fractionated through the Podbielniak column to give the following results (also plotted in Figure V):

Fraction No.	Weight Gms.	Distillate per 100 g. of original Material (%)	Refractive Index n_D^{25}
1	0.001	-	-
2	0.026	0.034	1.4487
3	0.097	0.155	1.4475
4	0.105	0.286	1.4431
5	0.110	0.423	1.4393
6	0.123	0.577	1.4380
7	0.142	0.753	1.4373
8	0.134	0.921	1.4379
9	0.169	1.133	1.4438
10	0.167	1.340	1.4546
11	0.128	1.500	1.4556
12	0.155	1.691	1.4546
13	0.121	1.844	1.4575
14	0.101	1.970	1.4615
15	0.067	2.054	1.4660
16	0.109	2.191	1.4690
17	0.113	2.331	1.4695
18	0.090	2.444	1.4785

The water-insoluble maple holocellulose hydrogenation oils (6.7 grams) were fractionated through the Podbielniak column to give the following results (also plotted in Figure IV):

Fraction No.	Weight Gms.	Distillate per 100 g. of original Material (%)	Refractive Index n_D^{25}
1	0.039	0.041	1.4265
2	0.105	0.150	1.4350
3	0.183	0.340	1.4405
4	0.157	0.503	1.4440
5	0.179	0.690	1.4473
6	0.165	0.862	1.4503
7	0.146	1.013	1.4530
8	0.152	1.170	1.4550
9	0.174	1.352	1.4582
10	0.174	1.533	1.4609
11	0.134	1.672	1.4632
12	0.218	1.900	1.4651
13	0.102	2.005	1.4679
14	0.097	2.105	1.4730
15	0.148	2.26	1.4732
16	0.214	2.49	1.4749
17	0.110	2.59	1.4770
18	0.167	2.77	1.4793
19	0.163	2.94	1.4812
20	0.189	3.14	1.4828
21	0.157	3.30	1.4847
22	0.208	3.52	1.4864
23	0.123	3.64	1.4882
24	0.159	3.81	1.4910
25	0.182	4.00	1.4932
26	0.094	4.09	1.4945
27	0.047	4.15	1.4949
28	0.094	4.24	1.4975
29	0.167	4.42	1.4990
30	0.052	4.47	1.4991
31	0.113	4.59	1.5030
32	0.138	4.73	1.5035
33	0.278	5.03	1.5067
34	0.153	5.18	1.5120
35	0.165	5.35	1.5148
36	0.248	5.61	1.5180

The original combined distillates ((A), Flow Sheet III), obtained in the recovery of the oils by concentration of the dioxane reaction solution, were analyzed for methanol and ethanol according to the method of Cooke (162), and as applied to the maple wood products by Godard (30). The values are recorded and compared in Table X (page 97). The amount of water was also determined, by fractional distillation (Fenske column) to determine the amount of dioxane-water azeotrope (b.p. 88°, n_D^{25}1.4079, 18.1% water by weight, (162)), and the comparative results are shown in the same table (X, page 97).

4. Hydrogenation of Maple Wood

This was carried out in the manner described by Godard (30).

Bomb charge (2500 cc. Aminco Hydrogenation Bomb):

175	grams extracted maple wood
100	grams CuCrO catalyst
1030	cc. dry dioxane
1214	cc. total volume

Conditions:

Initial hydrogen pressure 3300 lb./sq.in.
Average temperature 280°
Total time 20 hours

At the end of 20 hours hydrogen absorption had ceased, the total hydrogen uptake being 3.1 mols per 100 grams of wood. Upon removing the mixture from the bomb and centrifuging off the catalyst, the reaction mixture was found to be water-white in appearance.

5. Separation and Fractionation of Maple Wood Hydrogenation Products

(next page)

The dioxane solution was treated in an exactly analogous manner to that used for maple holocellulose and outlined in Flow Sheet III. Fractionation results are shown graphically in Figures VI and VII and the quantitative aspects of the curves are discussed in sections VI-B and VI-C. Complete fractionation results (obtained by use of the newly developed spiral screen column) for the water-insoluble oils follow:

Fraction No.	Weight Gms.	Distillate per 100 g. of original Material (%)	Refractive Index n_D^{25}
1	0.150	0.064	1.4050
2	0.190	0.147	1.4093
3	0.199	0.233	1.4104
4	0.212	0.324	1.4120
5	0.224	0.422	1.4125
6	0.215	0.514	1.4133
7	0.303	0.645	1.4133
8	0.314	0.781	1.4133
9	0.220	0.876	1.4133
10	0.327	1.013	1.4133
11	0.240	1.12	1.4133
12	0.249	1.23	1.4133
13	0.178	1.31	1.4133
14	0.202	1.39	1.4133
15	0.310	1.55	1.4135
16	0.315	1.71	1.4140
17	0.233	1.82	1.4135
18	0.250	1.95	1.4135
19	0.307	2.11	1.4137
20	0.252	2.23	1.4137
21	0.293	2.38	1.4143
22	0.267	2.52	1.4145
23	0.265	2.65	1.4145
24	0.257	2.78	1.4145
25	0.200	2.88	1.4155
26	0.315	3.04	1.4165
27	0.248	3.17	1.4200
28	0.255	3.29	1.4245

- continued -

29	0.169	3.39	1.4229
30	0.183	3.46	1.4257
31	0.198	3.55	1.4310
32	0.208	3.64	1.4325
33	0.173	3.71	1.4320
34	0.190	3.79	1.4292
35	0.239	3.90	1.4300
36	0.210	3.99	1.4305
37	0.172	4.07	1.4320
38	0.194	4.15	1.4320
39	0.240	4.25	1.4326
40	0.244	4.36	1.4335
41	0.201	4.44	1.4350
42	0.188	4.53	1.4360
43	0.275	4.65	1.4356
44	0.269	4.76	1.4348
45	0.256	4.87	1.4333
46	0.245	4.99	1.4320
47	0.223	5.09	1.4300
48	0.325	5.25	1.4275
49	0.324	5.41	1.4248
50	0.225	5.52	1.4236
51	0.284	5.65	1.4236
52	0.267	5.78	1.4236
53	0.315	5.93	1.4236
54	0.221	6.03	1.4237
55	0.341	6.20	1.4245
56	0.192	6.29	1.4255
57	0.253	6.41	1.4285
58	0.254	6.54	1.4290
59	0.212	6.63	1.4290
60	0.148	6.70	1.4290
61	0.186	6.79	1.4325
62	0.119	6.85	1.4345
63	0.211	6.95	1.4355
64	0.239	7.05	1.4360
65	0.184	7.13	1.4365
66	0.308	7.27	1.4375
67	0.207	7.36	1.4390
68	0.224	7.46	1.4410
69	0.196	7.54	1.4420
70	0.228	7.64	1.4440
71	0.289	7.76	1.4465
72	0.222	7.86	1.4485
73	0.225	7.92	1.4493
74	0.185	8.01	1.4501
75	0.180	8.10	1.4506
76	0.241	8.21	1.4513
77	0.248	8.32	1.4513

- continued -

78	0.404	8.49	1.4486
79	0.147	8.55	1.4470
80	0.288	8.68	1.4460
81	0.223	8.78	1.4450
82	0.316	8.91	1.4444
83	0.214	9.00	1.4442
84	0.154	9.07	1.4445
85	0.157	9.13	1.4495
86	0.206	9.22	1.4520
87	0.143	9.28	1.4535
88	0.328	9.42	1.4560
89	0.151	9.49	1.4560
90	0.346	9.64	1.4561
91	0.167	9.71	1.4560
92	0.185	9.79	1.4561
93	0.136	9.85	1.4560
94	0.245	9.95	1.4560
95	0.135	10.01	1.4560
96	0.231	10.11	1.4560
97	0.228	10.20	1.4582
98	0.191	10.29	1.4602
99	0.215	10.38	1.4580
100	0.172	10.45	1.4600
101	0.200	10.54	1.4600
102	0.232	10.64	1.4620
103	0.348	10.79	1.4626
104	0.321	10.92	1.4625
105	0.215	11.02	1.4625
106	0.319	11.15	1.4625
107	0.205	11.24	1.4625
108	0.238	11.34	1.4626
109	0.555	11.58	1.4625
110	0.219	11.60	1.4625
111	0.228	11.77	1.4626
112	0.457	11.96	1.4625
113	0.455	12.15	1.4625
114	0.440	12.35	1.4625
115	0.272	12.47	1.4625
116	0.233	12.56	1.4625
117	0.510	12.77	1.4700
118	0.682	13.07	1.4660
119	0.542	13.30	1.4666
120	0.890	13.68	1.4662
121	0.602	13.94	1.4670
122	0.520	14.17	1.4653
123	0.432	14.35	1.4647
124	0.577	14.60	1.4652
125	0.488	14.80	1.4646
126	0.795	15.15	1.4644

- continued -

127	0.575	15.39	1.4650
128	0.287	15.52	1.4693
129	0.377	15.67	1.4692
130	0.314	15.81	1.4692
131	0.550	16.01	1.4700
132	0.197	16.13	1.4700
133	0.273	16.25	1.4740
134	0.734	16.82	1.4790
135	2.619	18.10	1.4865
136	1.819	18.80	1.4915
137	2.298	19.70	1.4915
138	1.576	20.30	1.4980
139	1.155	20.70	1.5020
140	0.923	21.10	1.5020

6. Identification of Pentanol-1 Among The Hydrogenation Products of Maple Wood

The material in the low-boiling "flat" (n_D^{25}1.4133-1.4137) (D) of the new water-insoluble fractionation curve (Figure VI) was analyzed and gave the following results:

Boiling Point, 134-136° (Emich micro method (163))
Molecular Weight, 88 (Vapor pressure micro method (158))
Carbon and Hydrogen, 68.1% and 13.2% respectively

The phenyl urethane of this material, crystallized from 100-110 petroleum ether, melted at 46-47°C.

The phenyl urethane of Eastman synthetic n-amyl alcohol was prepared and crystallized from 100-110 petroleum ether; m.p. 46-47°C. A mixed melting point of the unknown with the synthetic derivative showed no depression, thus confirming the identity of the pentanol-1.

C. Identification and Synthesis of 3-cyclohexylpropanol-1, 4-n-propylcyclohexanol and 3-(4-hydroxycyclohexyl)-propanol-1 Isolated by Hydrogenation of Maple Wood and Various Maple Lignin Fractions

1. Maple Wood Hydrogenation

This has been described and the results listed in the preceding section. Fractionation of the n_D^{25}1.4600-1.4700 range was carried out in the newly developed wire spiral column, using the technique described in section VI-A, and comparison of the results obtained with those of the previous workers (30) are shown diagramatically in Figure VII (page 105).

2. Preparation of Derivatives from The Fractions Comprising The n_D^{25}1.4600-1.4700 Range.

The phenyl urethanes of these fractions were prepared by adding approximately 150% the weight of phenyl isocyanate to the dry sample in a dry test tube and permitting the reaction mixture to stand over night in a desiccator. In about half the cases scratching had to be resorted to, to initiate crystallization. The crystalline product was transferred to a nail filter and washed with cold pet ether (30-50°). It was then transferred to a small test tube, dissolved in boiling pet ether (100-110°), and quickly filtered through the nail filter to remove any by-product diphenyl urea present. The filtrate was then cooled in a dry-ice bath and the resulting crystalline product filtered off, washed with pet ether (30-50°), and dried in a vacuum desiccator. The following urethanes (with corresponding yields) were obtained:

TABLE XVII

PHENYL URETHANES OF MAPLE WOOD n_D^{25}1.4600-1.4700 RANGE

Product No.	Material Tested n_D^{25}	Yield of Urethane %	M.P. of Urethane °C
I	1.4625	35	126-127
II	1.4670	37	84-85
III	1.4652	28	84-85

Note:
M.p. phenyl urethane of 4-n-propylcyclohexanol, 126-127°
M.p. phenyl urethane of 3-cyclohexylpropanol-1, 84-85°

3. Synthesis of 3-cyclohexylpropanol-1

Stock cinnamyl alcohol was distilled at 0.5 mm. and 120-160° bath temperature, and a center cut of 20 grams (out of a total of 40 grams distilled) taken for hydrogenation. This was placed in the 500 cc. Parr bomb with 10 grams CuCrO catalyst and 150 cc. dry dioxane. Hydrogen was introduced to an initial pressure of 3000 lb./sq.in. and the temperature slowly increased. Within one-half hour (between 80 and 150°) the ethylenic bond was saturated as indicated by the hydrogen absorption but not until 270-280°

(6 hours) had been reached was the saturation of the benzene nucleus completed. After centrifuging off the catalyst the solution was transferred to a Claisen flask and concentrated (20 mm. pressure) over a steam bath for 5 hours to remove the solvent.

Yield, 16.6 grams product; n_D^{25}1.4635.

The phenyl urethane of the product (3-cyclohexylpropanol-1) was easily prepared in 36% yield; m.p. 84-85°C.

Mixed melting points of the phenyl urethane from this synthetic 3-cyclohexylpropanol-1 with those from products II and III (Table XVII) having the same melting points showed no depression, thus confirming the identity of the two unknown products. The latter amounted to 2.8% by weight of the original maple wood taken.

4. Identification of 4-n-propylcyclohexanol

This cyclohexanol was prepared in a yield of 78% by Cooke (162) who hydrogenated α-ethoxypropiovanillone under similar conditions (15 g. in 155 cc. dioxane with 8 g. CuCrO catalyst, 3000 lb./sq.in., 280°, 8 hours) to those used above. Product, n_D^{25}1.4618.

The phenyl urethane from this material, after one crystallization from 100-110 pet ether, melted at 126-127°C. A mixed melting point with that of sample I (Table XVII) (n_D^{25}1.4626) showed no depression, thus proving its identity. The yield of this product was 2.2% of the original maple wood weight.

5. Phenyl Urethanes of 3-cyclohexylpropanol-1 and 4-n-propylcyclohexanol Obtained in The Hydrogenation of Various Lignin Fractions

Hydrogenation of ethanol lignin, benzene-soluble ethanol lignin and ethanolysis tars by Cooke (31) gave two products distilling within the 4-n-propylcyclohexanol range (n_D^{25}1.4610-1.4680) and assumed by him to be cis-trans isomers of this product. Samples of each pair of products, kindly supplied by this author (Cooke), were converted, by the present writer, into their respective phenyl urethanes, having the respective melting points shown in Table XVIII.

TABLE XVIII

PHENYL URETHANES OF LIGNIN FRACTIONS

Lignin Type		Material Tested n_D^{25}	Yield of Urethane %	M.P. of Urethane °C
Ethanol Lignin	I	1.4635	32	126-127
	II	1.4678	24	84-85
Benzene-soluble Ethanol Lignin	I	1.4618	27	126-127
	II	1.4660	28	84-85
Ethanolysis Tars	I	1.4615	30	126-127
	II	1.4675	29	84-85

Comparison of mixed melting points with the urethanes from the corresponding pure synthetic derivatives proved that each of the above products melting at 84-85° (II) was the phenyl urethane of 3-cyclohexylpropanol-1, while those melting at 126-127° (I) were shown to be the phenyl urethanes of 4-n-propylcyclohexanol.

6. Identification of 3-(4-hydroxycyclohexyl)-propanol-1

This material was also synthesized by Cooke (162) who had obtained it by the method of Bowden and Adkins (164). It was characterized by formation of the semicarbazone (m.p. 203-204°) of 3-(4-ketocyclohexyl)-propionic acid, this acid being obtained by the chromic acid oxidation of Cooke's synthetic product.

A portion of the author's material of the water-soluble maple wood hydrogenation product embraced in the "flat" at n_D^{25}1.4865 (Figure V, page 99) was oxidized with chromic acid and the keto-acid oxidation product identified as 3-(4-keto-cyclohexyl)-propionic acid by conversion into its semicarbazone (m.p. 203-204°); a mixed melting point of this with the authentic derivative showed no lowering of the melting point, thus confirming the identity.

D. Hydrogenation of Spruce Wood and Spruce Tips

1. Mature Spruce Wood

(a) Hydrogenation - The material was hydrogenated under the same conditions used previously for maple wood (page 138) and for maple holocellulose (page 132).

Bomb charge (2500 cc. Aminco Hydrogenation Bomb):

175 grams extracted spruce wood
100 grams CuCrO catalyst
1030 cc. dry dioxane

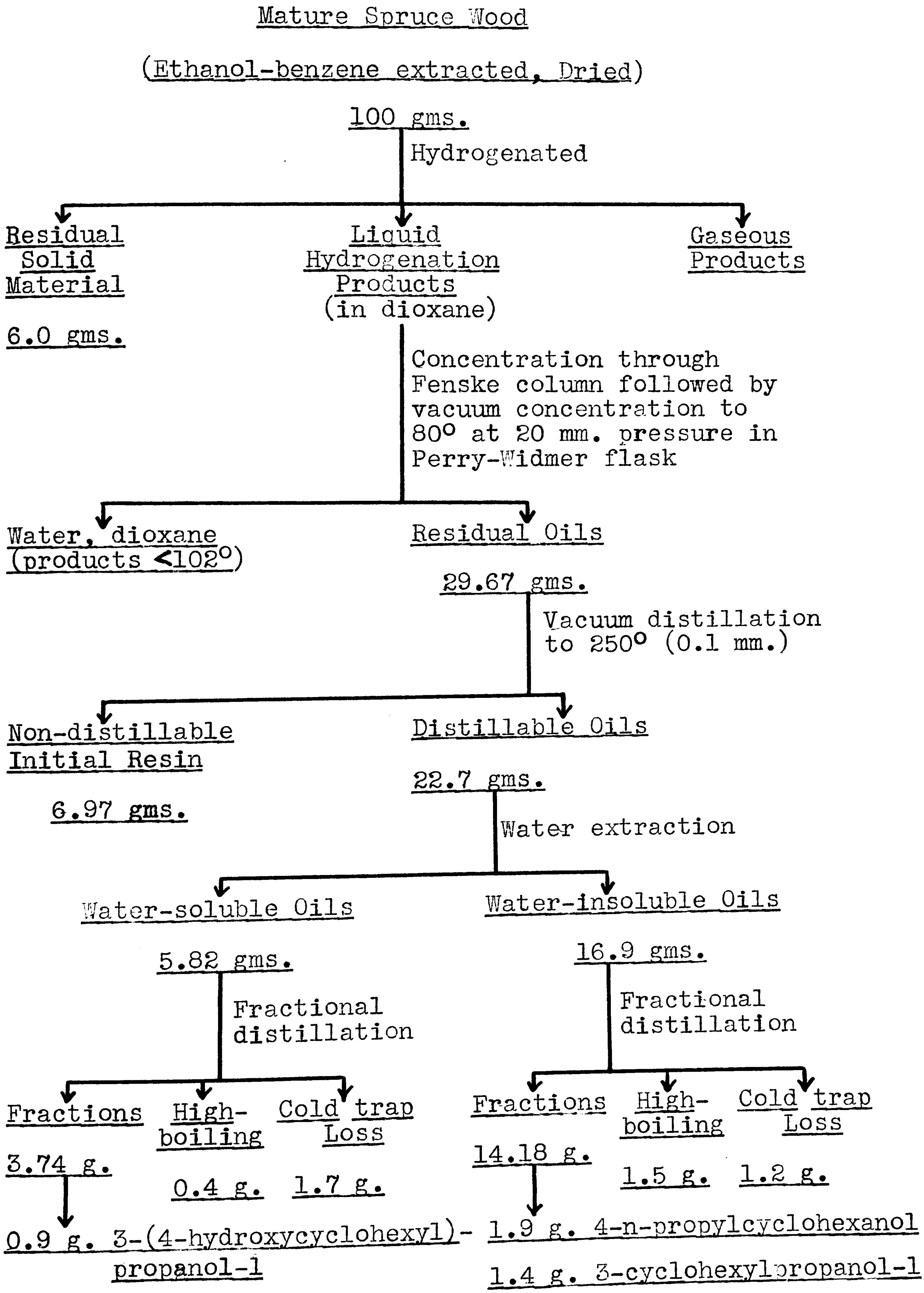
Conditions:

Initial hydrogen pressure 3300 lb./sq.in.
Average temperature 280°C.
Total time 22 hours

At the end of this time hydrogen absorption had ceased, with a total uptake of 3.2 mols per 100 grams of wood. The products were water-white in appearance as was the case for maple wood.

(b) Separation and Fractionation of Hydrogenation Products - The hydrogenation products were worked up in the standard manner as outlined in Flow Sheet IV. Final fractionations of the oils were carried out in the new fractionating column and the following results obtained for the spruce wood water-insoluble oils (page 150):

FLOW SHEET IV



Fraction No.	Weight Gms.	Distillate per 100 g. of original Material (%)	Refractive Index n_D^{25}
1	0.224	0.473	1.4086
2	0.187	0.866	1.4150
3	0.198	1.29	1.4179
4	0.188	1.68	1.4210
5	0.230	2.17	1.4260
6	0.221	2.63	1.4325
7	0.220	3.09	1.4320
8	0.211	3.54	1.4295
9	0.180	3.92	1.4282
10	0.155	4.25	1.4292
11	0.522	5.35	1.4400
12	0.197	5.76	1.4453
13	0.247	6.28	1.4470
14	0.178	6.66	1.4470
15	0.179	7.04	1.4515
16	0.205	7.48	1.4540
17	0.171	7.83	1.4553
18	0.167	8.18	1.4635
19	0.244	8.70	1.4630
20	0.199	9.12	1.4636
21	0.333	9.82	1.4647
22	0.248	10.36	1.4667
23	0.212	10.80	1.4670
24	0.244	11.31	1.4680
25	0.112	11.54	1.4775
26	0.226	12.03	1.4840
27	0.266	12.60	1.4860
28	0.408	13.45	1.4910
29	0.221	13.92	1.4925
30	0.125	14.18	1.4930

The following results were obtained for the fractionation of the spruce wood water-soluble oils:

Fraction No.	Weight Gms.	Distillate per 100 g. of original Material (%)	Refractive Index n_D^{25}
1	0.096	0.096	1.4463

- continued -

2	0.141	0.237	1.4440
3	0.130	0.367	1.4440
4	0.206	0.573	1.4370
5	0.304	0.877	1.4356
6	0.353	1.230	1.4352
7	0.231	1.461	1.4434
8	0.134	1.595	1.4570
9	0.213	1.808	1.4510
10	0.268	2.076	1.4504
11	0.481	2.557	1.4505
12	0.695	3.252	1.4645
13	0.402	3.654	1.485
14	0.083	3.737	1.4865
15	0.400	4.137	1.4865

(c) Identification of The Propylcyclohexyl Derivatives

The product represented by the flat in the water-insoluble distillation curve at n_D^{25}1.4630-1.4640 (Figure IX-B, page **116**) was proven to be 4-n-propylcyclohexanol (1.9% of wood weight) by formation of its phenyl urethane (m.p. 126-127°) and mixed melting point with the authentic derivative as described in Sections C-2 and C-4.

The material represented by the flat in the water-insoluble distillation curve at n_D^{25}1.4670-1.4675 (Figure IX-B, page 116) was proven to be 3-cyclohexylpropanol-1 (1.4% of wood weight) by formation of its phenyl urethane (m.p. 84-85°) and mixed melting point with the authentic derivative as described in Sections C-2 and C-3.

In the water-soluble curve (Figure X -C, page 117) at n_D^{25}1.4865, the flat was found to be due to the presence of 3-(4-hydroxycyclohexyl)-propanol-1 (0.9% of wood weight), proven by formation of the semicarbazone of the keto-acid oxidation product (m.p. 203-204°) and mixed melting point with the authentic derivative as described in Section C-6.

2. Stage I Spruce Tips

(a) Preparation - The spruce tips were ground under absolute ethanol and the meal (100 grams dry basis) transferred to a flask and refluxed with ethanol (4 liters) for 24 hours. After filtration, the bud meal was dried in a vacuum oven (50°C.) to 2.3% moisture content. This extraction resulted in the removal of 50 grams of the spruce tip as ethanol-soluble material and left 50 grams of extracted residue.

The ethanol extract was concentrated to approximately 200 cc. during which a white, gummy product separated out. Dioxane (1000 cc.) was added and distillation continued until all water and ethanol had been removed, as was evidenced by the collection of pure dioxane (b.p. 101.5°C.). The volume had again been reduced to approximately 200 cc.

(b) Stage I Spruce "Ethanol-soluble" Material

(1) Hydrogenation - The material, in dioxane, was partly in solution and partly in the form of a white gummy residue which separated out during concentration. The total material was hydrogenated in two separate portions (25 grams each) under the following conditions, the two products being united for subsequent treatment.

Bomb charge (500 cc. Parr Hydrogenation Bomb)

25	grams stage I ethanol-soluble spruce material
15	grams CuCrO catalyst
235	cc. dry dioxane
250	cc. total volume

Conditions:

Initial hydrogen pressure 3300 lb./sq.in.
Average temperature 280°C
Total time 21 hours

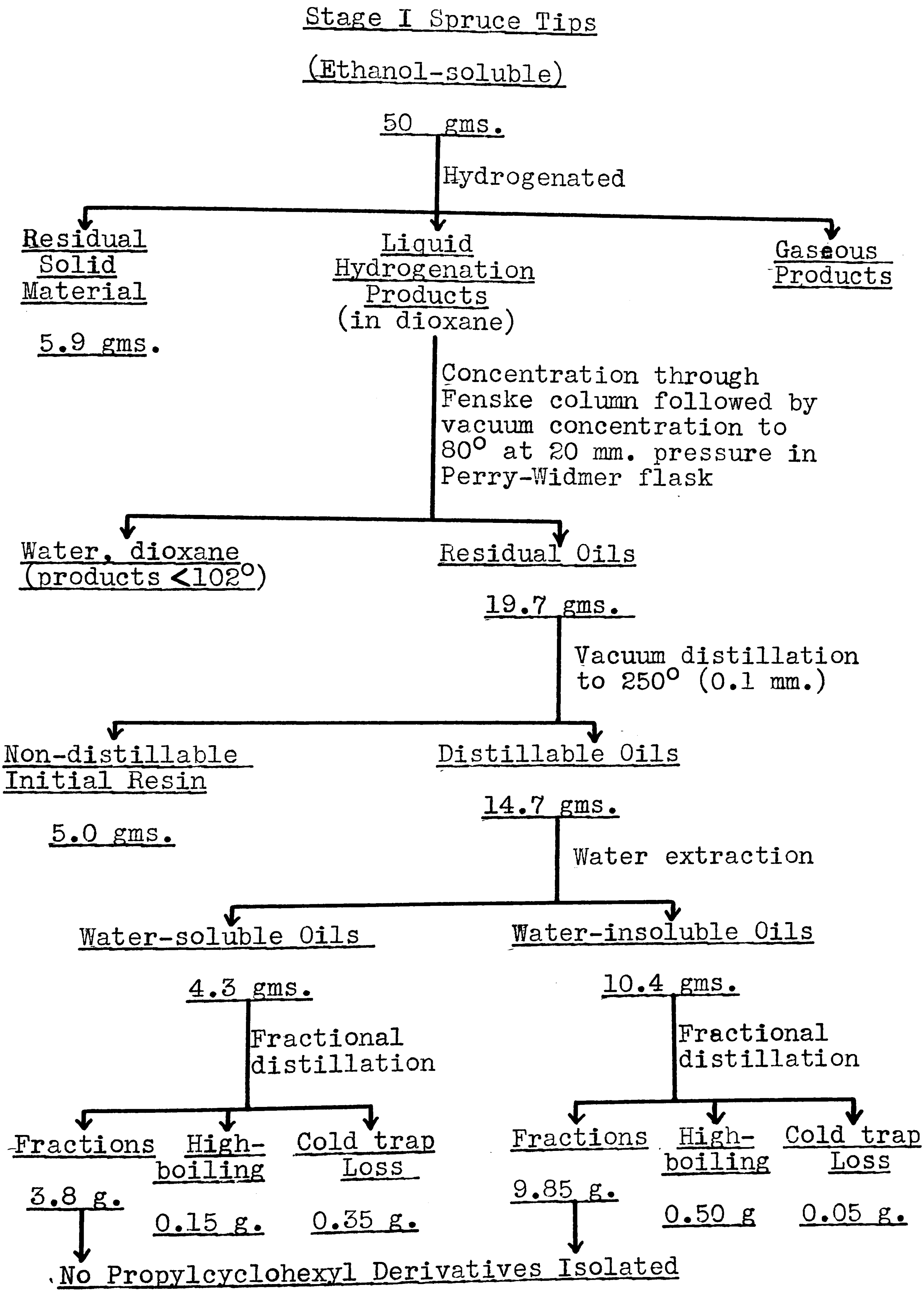
At the end of this time hydrogen absorption had ceased with a total uptake of 4.5 mols per 100 grams of material. The products were water-white in appearance.

(2) Separation and Fractionation of Hydrogenation Products - The hydrogenation products were worked up in the standard manner as outlined in Flow Sheet V. The following results were obtained by the fractionation of the water-insoluble products (Stage I Spruce, ethanol-soluble):

Fraction No.	Weight Gms.	Distillate per 100 g. of Original Material (%)	Refractive Index n_D^{25}
1	0.406	0.63	1.4470
2	0.157	0.87	1.4570
3	0.203	1.19	1.4610
4	0.165	1.44	1.4630
5	0.239	1.81	1.4735
6	0.193	2.11	1.4758
7	0.242	2.49	1.4780
8	0.203	2.80	1.4800
9	0.172	3.09	1.4820
10	0.207	3.39	1.4833

-continued (page 155)-

FLOW SHEET V


Stage I Spruce Tips
(Ethanol-soluble)
50 gms.
Hydrogenated
Residual Solid Material
5.9 gms.
Liquid Hydrogenation Products (in dioxane)
Gaseous Products
Concentration through Fenske column followed by vacuum concentration to 80° at 20 mm. pressure in Perry-Widmer flask
Water, dioxane (products <102°)
Residual Oils
19.7 gms.
Vacuum distillation to 250° (0.1 mm.)
Non-distillable Initial Resin
5.0 gms.
Distillable Oils
14.7 gms.
Water extraction
Water-soluble Oils
4.3 gms.
Fractional distillation
Fractions
3.8 g.
High-boiling
0.15 g.
Cold trap Loss
0.35 g.
Water-insoluble Oils
10.4 gms.
Fractional distillation
Fractions
9.85 g.
High-boiling
0.50 g
Cold trap Loss
0.05 g.
No Propylcyclohexyl Derivatives Isolated

11	0.249	3.77	1.4810	
12	0.193	4.07	1.4750	
13	0.151	4.31		Small amounts of oils containing solid material shown to be n-octadecanol
14	0.145	4.53		
15	0.179	4.81		
16	0.237	5.18		
17	0.538	6.01		
18	0.537	6.85		
19	0.315	7.33		
20	0.111	7.50		
21	0.421	8.15		
22	0.456	8.86	1.4920	
23	0.618	9.83	1.5030	

The following results were obtained by the fractionation of the water-soluble oils:

Fraction No.	Weight Gms.	Distillate per 100 g. of Original Material(%)	Refractive Index n_D^{25}
1	0.108	0.150	1.4375
2	0.228	0.467	1.4435
3	0.178	0.714	1.4700
4	0.267	1.09	----
5	0.676	2.07	1.4790
6	0.597	2.87	1.4830
7	0.406	3.42	1.4880

(3) Identification of Fractionation Products - No materials were found in the refractive index ranges of the previously isolated propylcyclohexyl derivatives (n_D^{25}1.4620-1.4680, water-insoluble; 1.4685, water-soluble) (Figures IX and X, pages 116 and 117).

Water-insoluble fractions 13 to 21 (above) crystallized almost solidly upon standing. Crystallization from petroleum ether (100-110°) or from ethanol gave a solid material melting at 57-57.5°C. Carbon and hydrogen analysis gave the following results: C, 80.1%; H, 13.6%.

This crystalline material was proven to be n-octadecanol by determination of the mixed melting point (57-57.5°) with Eastman n-octadecanol (m.p. 56.5-57°).

(c) Stage I Spruce "Ethanol-insoluble" Material

(1) Hydrogenation - This dried, extracted bud meal was hydrogenated in the usual manner in two identical runs, the resulting hydrogenation products being united prior to fractionation.

Bomb charge (500 cc. Parr Hydrogenation Bomb):

35	grams dried Stage I bud meal
20	grams CuCrO catalyst
200	cc. dry dioxane
230	cc. total volume

Conditions:

Initial hydrogen pressure 3300 lb./sq.in.
Average temperature 280°
Total time 21 hours

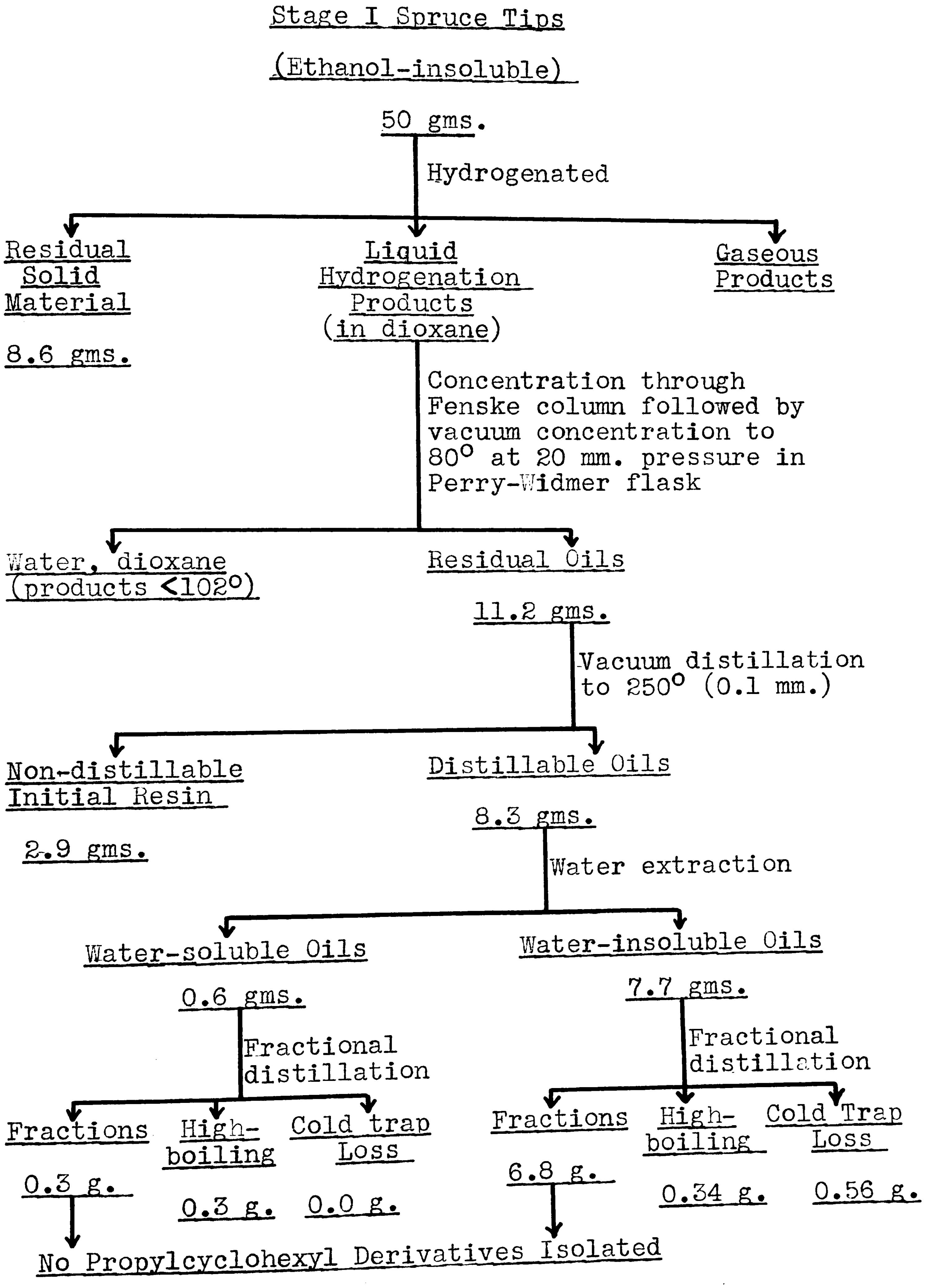
At the end of this time hydrogen absorption had ceased with a total uptake of 1.1 mols of hydrogen per 100 grams of material. Upon opening the bomb and centrifuging off the catalyst, the latter was found to be pink in color, indicating poisoning had taken place. The greenish-brown liquors were replaced in the bomb with 20 grams fresh catalyst and the hydrogenation continued under the usual conditions for 18 hours. At the end of this time 0.7 mols additional hydrogen (per 100 grams of material) had been absorbed and the reaction mixture was nearly water-white in appearance.

(2) Separation and Fractionation of Hydrogenation Products - The hydrogenation products were worked up in the standard manner as outlined in Flow Sheet VI. The following results were obtained by fractionation of the water-insoluble products (Stage I Spruce, ethanol-insoluble):

Fraction No.	Weight Gms.	Distillate per 100 g. of Original Material (%)	Refractive Index n_D^{25}
1	0.034	0.031	
2	0.139	0.157	1.4372
3	0.158	0.299	1.4435
4	0.104	0.394	1.4480
5	0.275	0.642	1.4500
6	0.200	0.823	1.4540
7	0.171	0.978	1.4570
8	0.113	1.08	1.4590
9	0.120	1.19	1.4598
10	0.165	1.34	1.4625
11	0.155	1.48	1.4660
12	0.189	1.65	1.4675
13	0.244	1.87	1.4700
14	0.145	1.91	1.4725
15	0.270	2.16	1.4750
16	0.276	2.50	1.4757
17	0.247	2.72	1.4785
18	0.314	3.00	1.4795
19	0.394	3.36	1.4840
20	0.136	3.48	1.4863
21	0.113	3.58	1.4880
22	0.177	3.74	1.4870

- continued -

FLOW SHEET VI



23	0.119	3.85	1.4880
24	0.092	3.94	1.4870
25	0.298	4.20	1.4905
26	0.223	4.41	1.4905
27	0.127	4.52	1.4905
28	0.126	4.64	1.4905
29	0.149	4.77	1.4912
30	0.297	5.04	1.4910
31	0.192	5.21	---
32	0.337	5.51	1.4940
33	0.369	5.85	---
34	0.498	6.30	1.4980
35	0.224	6.50	---
36	0.323	6.80	1.5020

Only a trace of water-soluble material (0.6 g./100 g. original material) was found and of this only 0.3 g. (n_D^{25}1.4400) was distillable under the usual conditions.

No materials were found in the refractive index ranges of known propylcyclohexyl derivatives (Figure IX, page 116).

3. Stage II Spruce Tips

(a) Hydrogenation - Stage II spruce tips (3½-4 months old) were ground to 40-60 mesh size after drying (vacuum oven, 50°C.) and hydrogenated under the usual conditions for wood products.

Bomb charge (500 cc. Parr Hydrogenation Bomb):

35	grams dried Stage II bud meal
20	grams CuCrO catalyst
200	cc. dry dioxane
230	cc. total volume

Conditions:

Initial hydrogen pressure 3300 lb./sq.in.
Average temperature 280°C
Total time 20 hours

At the end of this time hydrogen absorption had ceased with a total uptake of 2.6 mols of hydrogen per 100 grams of original material. The catalyst was found to have been poisoned, as in the case of Stage I bud material, and the solution was dark brown in color. After removing the old catalyst the brown solution was replaced in the bomb with 20 grams fresh catalyst and hydrogenated under the usual conditions for a further 5 hours. No additional hydrogen absorption was apparent from the pressure readings but the reaction mixture was found to be almost water-white in appearance. A second identical run was carried out and the hydrogenation products united for fractionation study.

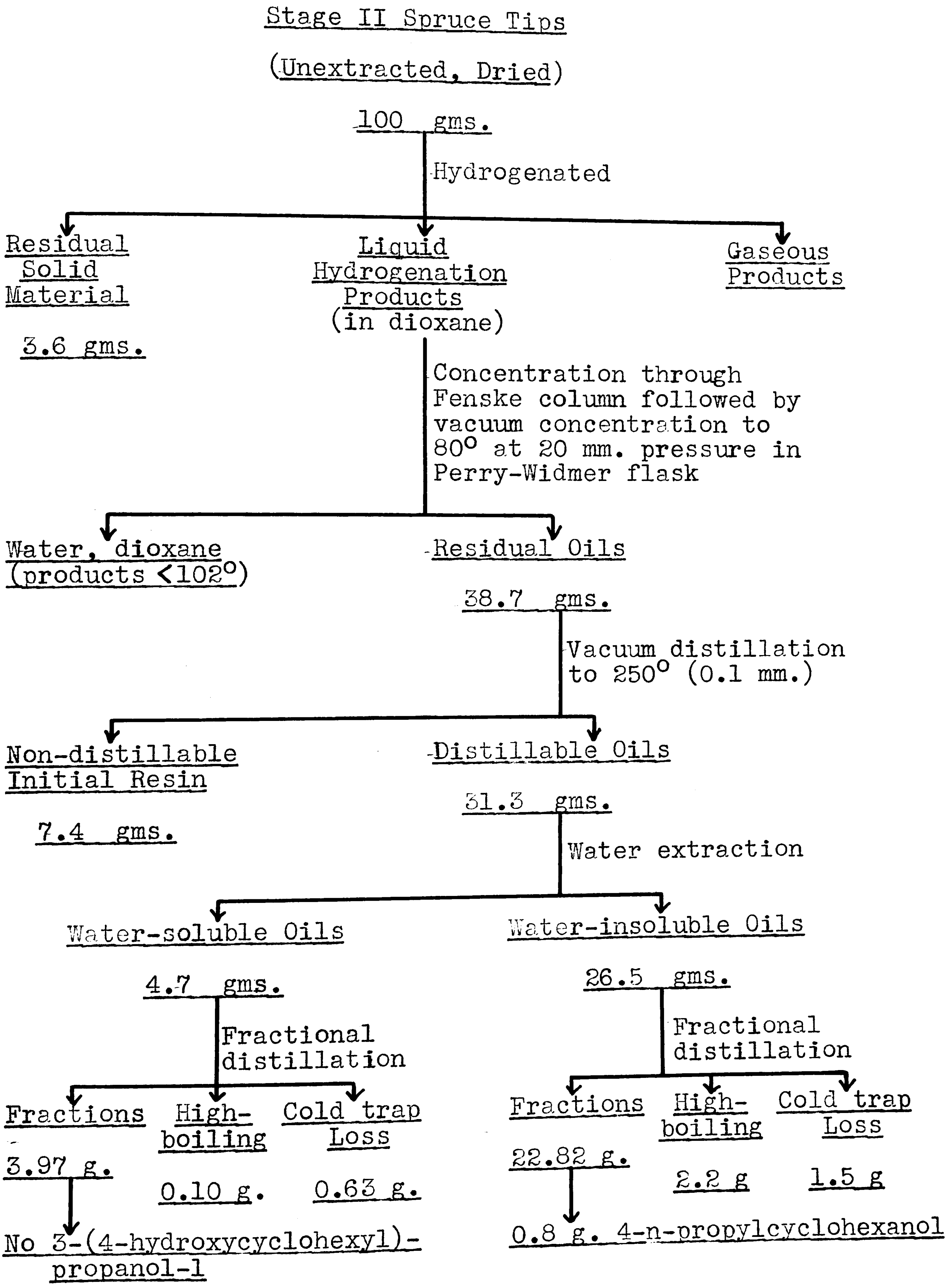
(b) Separation and Fractionation of Hydrogenation Products

The hydrogenation products were worked up in the standard manner as outlined in Flow Sheet VII. The following results were obtained by fractionation of the water-insoluble products (Stage II Spruce tips):

Fraction No.	Weight Gms.	Distillate per 100 g. of Original Material (%)	Refractive Index n_D^{25}
1	0.100	0.17	1.4130
2	0.118	0.37	1.4165
3	0.136	0.60	1.4187
4	0.151	0.86	1.4200
5	0.151	1.13	1.4250

- continued -

FLOW SHEET VII



6	0.150	1.38	1.4300
7	0.181	1.69	1.4310
8	0.162	1.96	1.4325
9	0.194	2.29	1.4353
10	0.153	2.55	1.4375
11	0.142	2.79	1.4410
12	0.588	3.79	1.4467
13	0.112	3.98	1.4469
14	0.298	4.49	1.4465
15	0.125	4.70	1.4495
16	0.156	4.97	1.4496
17	0.177	5.26	1.4529
18	0.169	5.55	1.4550
19	0.286	6.03	1.4565
20	0.261	6.48	1.4570
21	0.144	6.72	1.4565
22	0.240	7.12	1.4575
23	0.279	7.60	1.4580
24	0.261	8.05	1.4598
25	0.182	8.36	1.4625
26	0.230	8.74	1.4625
27	0.259	9.20	1.4640
28	0.242	9.58	1.4664
29	0.257	10.01	1.4698
30	0.091	10.19	1.4708
31	0.138	10.43	1.4744
32	0.183	10.73	1.4776
33	0.111	10.92	1.4792
34	0.206	11.28	1.4794
35	0.549	12.21	1.4780
36	0.217	12.58	1.4772
37	0.287	13.07	1.4778
38	0.244	13.49	1.4806
39	0.309	14.00	1.4788
40	0.267	14.47	1.4800
41	0.211	14.82	1.4827
42	0.228	15.20	1.4873
43	0.256	15.64	1.4881
44	0.183	15.96	1.4840
45	0.317	16.50	1.4830
46	0.224	16.88	Small amounts of oils containing solid material shown to be n-octadecanol
47	0.127	17.19	
48	0.128	17.31	
49	0.142	17.55	
50	0.255	17.99	
51	0.234	18.39	
52	0.320	18.91	
53	0.452	19.70	

- continued -

54	0.247	20.12	Small amounts of oils containing solid material shown to be n-octadecanol
55	0.253	20.54	
56	0.325	21.10	
57	1.016	22.82	

The following results were obtained by fractionation of the water-soluble hydrogenation products (Stage II Spruce):

Fraction No.	Weight Gms.	Distillate per 100 g. or Original Material (%)	Refractive Index n_D^{25}
1	0.139	0.22	1.4475
2	0.246	0.61	1.4454
3	0.185	0.90	1.4400
4	0.172	1.17	1.4390
5	0.123	1.37	1.4400
6	0.176	1.65	1.4485
7	0.257	2.05	1.4513
8	0.218	2.39	1.4608
9	0.181	2.68	1.4593
10	0.198	2.98	1.4600
11	0.144	3.21	1.4685
12	0.144	3.43	1.4763
13	0.145	3.66	1.4805
14	0.196	3.97	1.4800

(c) Identification of Fractionation Products - In the water-insoluble portion the phenyl urethane of the material in the flat at n_D^{25}1.4625 (Figure XI, page 122) (0.8% of the original material) was found to melt at 126-127° and to give the same mixed melting point with that from synthetic 4-n-propylcyclohexanol, thus establishing its identity.

No flat was found in the range of 3-cyclohexylpropanol-1 (n_D^{25} 1.4675) (page 122).

Likewise there was no indication of any material in the range of 3-(4-hydroxycyclohexyl)-propanol-1 (water-soluble, n_D^{25} 1.4865) (Figure X, page 117).

The solid crystalline material found in fractions 46 to 57 of the water insoluble oils (page 162) was crystallized from petroleum ether (100-110°) and melted at 57-57.5°. A mixed melting point with Eastman n-octadecanol showed no depression, thus confirming the identity of the solid (approximately 5%) as n-octadecanol.

E. Hydrogenations of β-hydroxypropiovanillone

1. Preparation of β-hydroxypropiovanillone

This was synthesized by the method of West (165) and involved three steps: (a) The synthesis of β-chloropropiovanillone by the condensation of β-chloropropionyl chloride with veratrole, with simultaneous demethoxylation in the para position, using 3 mols of anhydrous aluminum chloride; (b) The conversion of the β-chloropropiovanillone into β-acetoxypropiovanillone by acetylation with potassium acetate-glacial acetic acid; (c) The hydrolysis of the β-acetoxypropiovanillone to β-hydroxypropiovanillone in the presence of $BaCO_3$. A similar yield was obtained to that found by West (165).

2. Stage II Spruce Tips plus β-hydroxypropiovanillone

(a) Hydrogenation - A mixture of dried, non-extracted Stage II spruce tip meal with 5% added β-hydroxypropiovanillone was hydrogenated under the identical conditions used for Stage II meal alone (page 159).

Bomb charge (500 cc. Parr Hydrogenation Bomb):

35 grams Stage II bud meal
1.75 grams β- hydroxypropiovanillone
20 grams CuCrO catalyst
200 cc. dry dioxane
230 cc. total volume

Conditions:

Initial hydrogen pressure 3300 lb./sq.in.
Average temperature 280°C
Total time 21 hours

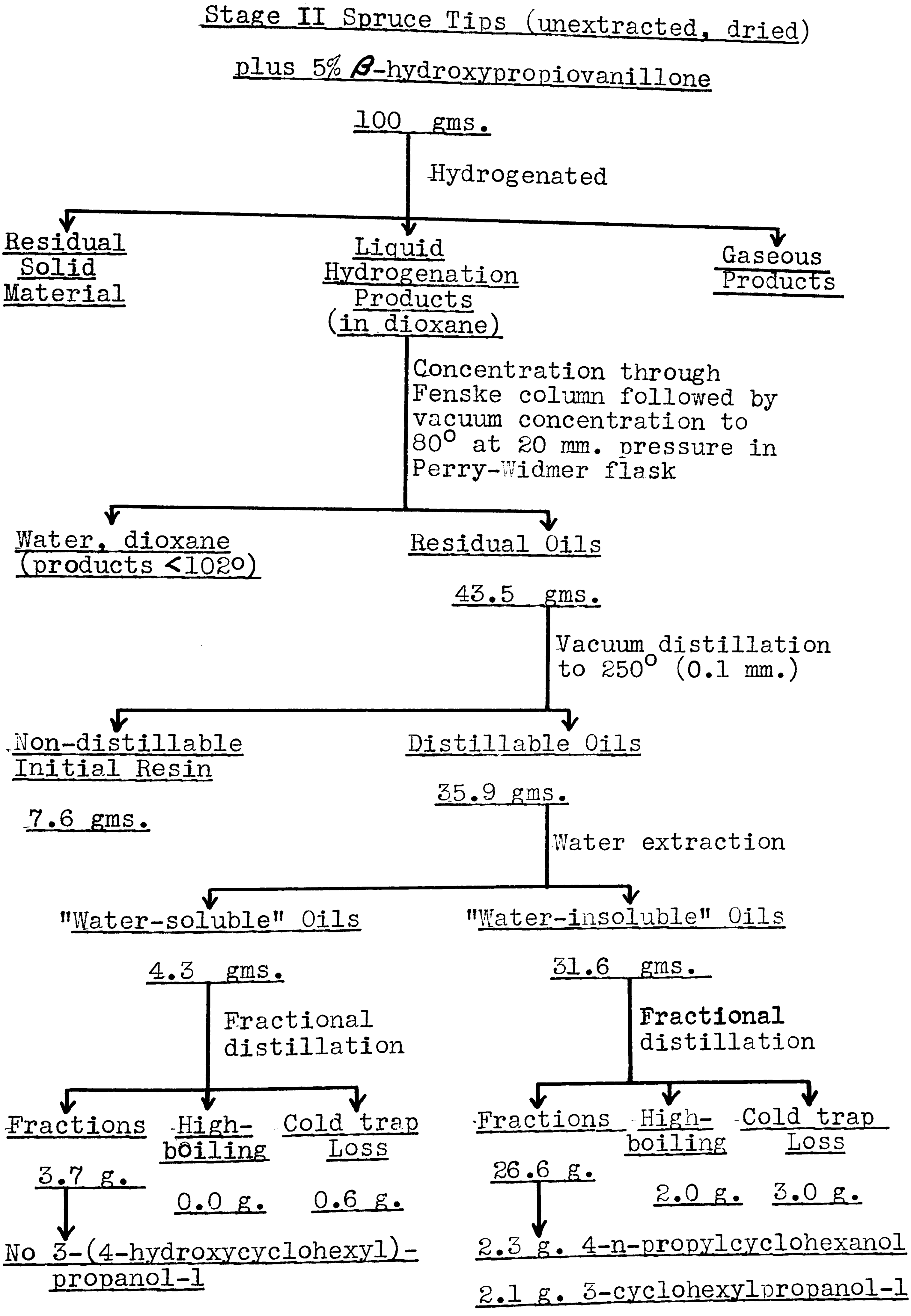
At the end of this time hydrogen absorption had ceased with a total uptake of 3.0 mols per hundred grams of bud meal (0.18 mols required for the β-hydroxypropiovanillone). As was the case with the Stage II bud meal alone, the solution of reaction products was replaced in the bomb with 20 grams fresh CuCrO catalyst for a further period of 5 hours under the usual conditions. No further hydrogen absorption was noted from the gauge readings and the reaction mixture was found to be water-white. A duplicate run was made to provide sufficient material for separation and fractionation.

(b) <u>Separation and Fractionation of Hydrogenation Products</u> - The hydrogenation products were worked up in the standard manner as outlined in Flow Sheet VIII. The following results were obtained by fractionation of the <u>water-insoluble</u> products (Stage II Spruce + β-hydroxypropiovanillone):

Fraction No.	Weight Gms.	Distillate per 100 g. of Original Material (%)	Refractive Index n_D^{25}
1	0.058	0.162	1.4170
2	0.149	0.580	1.4180
3	0.118	0.910	1.4235
4	0.123	1.25	1.4295
5	0.170	1.73	1.4325
6	0.188	2.26	1.4340

- continued -

FLOW SHEET VIII



7	0.173	2.74	1.4385
8	0.154	3.15	1.4425
9	0.141	3.57	1.4470
10	0.092	3.91	1.4471
11	0.140	4.30	1.4496
12	0.182	4.81	1.4501
13	0.136	5.19	1.4510
14	0.141	5.58	1.4542
15	0.192	6.12	1.4560
16	0.094	6.39	1.4595
17	0.142	6.79	1.4595
18	0.154	7.21	1.4590
19	0.159	7.65	1.4594
20	0.160	8.10	1.4610
21	0.155	8.54	1.4625
22	0.160	8.99	1.4645
23	0.114	9.31	1.4645
24	0.141	9.70	1.4650
25	0.107	10.00	1.4655
26	0.121	10.34	1.4655
27	0.125	10.69	1.4678
28	0.136	11.07	1.4690
29	0.140	11.47	1.4685
30	0.192	12.00	1.4680
31	0.114	12.33	1.4685
32	0.108	12.62	1.4694
33	0.229	13.27	1.4706
34	0.130	13.63	1.4706
35	0.134	14.00	1.4725
36	0.081	14.23	1.4725
37	0.131	14.61	1.4725
38	0.350	15.59	1.4748
39	0.410	16.72	1.4820
40	0.258	17.45	1.4800
41	0.174	17.95	1.4760
42	0.105	18.23	1.4770
43	0.269	18.99	Small amounts of Oils containing solid material shown to be n-octadecanol
44	0.225	19.60	
45	0.236	20.30	
46	0.090	20.55	
47	0.601	22.20	
48	0.425	23.40	
49	1.151	26.60	

The <u>water-soluble</u> oils were fractionated to give the following results (Stage II Spruce + β-hydroxypropiovanillone):

Fraction No.	Weight Gms.	Distillate per 100 g. of Original Material (%)	Refractive Index n_D^{25}
1	0.024	0.100	1.4477
2	0.061	0.357	1.4528
3	0.093	0.748	1.4505
4	0.117	1.24	1.4483
5	0.132	1.79	1.4523
6	0.194	2.62	1.4773
7	0.126	3.01	1.4815
8	0.136	3.60	1.4827

(c) Identification of Fractionation Products - In the water-insoluble oils, the phenyl urethane of the material in the flat at n_D^{25}1.4650 (Figure XI, page 122) (2.3% of the original material) was found to melt at 126-127° and to give the same mixed melting point as that obtained from synthetic 4-n-propylcyclohexanol, thus establishing its identity.

The phenyl urethane of the material in the flat at n_D^{25}1.4685 (Figure XI, page 122)(2.1% of the original material) was found to melt at 84-85° and to give the same mixed melting point with that from synthetic 3-cyclohexylpropanol-1, thus establishing its identity.

There was no indication of any material within the range of 3-(4-hydroxycyclohexyl)-propanol-1 (water-soluble, n_D^{25}1.4865, see above).

The solid crystalline material found in fractions 42 to 49 (page 169) of the water-insoluble oils was again identified as n-octadecanol by crystallization from petroleum ether (100-110°) and comparison of melting point (57-57.5°) and mixed melting point with Eastman n-octadecanol.

3. Pure β-hydroxypropiovanillone

(a) Hydrogenation - This material was hydrogenated in the usual manner over copper chromite catalyst.

Bomb Charge (500 cc. Parr Hydrogenation Bomb):

5.0 grams β-hydroxypropiovanillone (m.p. 110-111°C.)
3.0 grams CuCrO catalyst
150 cc. dry dioxane

Conditions:

Initial hydrogen pressure 3000 lb./sq.in.
Average temperature 280°C
Total time 9 hours

At the end of this time hydrogen absorption had ceased (0.25 mols absorbed) and the product was water-white in color.

(b) Recovery and Identification of Products - The bulk of the dioxane solvent was removed by concentration in a Perry-Widmer flask. Twenty cc. of residual oils and dioxane were transferred to the pot of the newly developed fractionating column and the remainder of the solvent removed by maintaining a pot temperature of 150° for 4 hours.

The material remaining was then fractionated to give the following results:

Fraction No.	Weight Gms.	Cumulative Weight Gms.	Refractive Index n_D^{25}
1	0.184	0.184	1.4595
2	0.177	0.361	1.4631
3	0.127	0.488	1.4631
4	0.208	0.696	1.4640
5	0.324	1.020	1.4655
6	0.229	1.249	1.4655
7	0.211	1.460	1.4655
8	0.189	1.649	1.4655
9	0.194	1.843	1.4655
10	0.192	2.035	1.4655
11	0.183	2.218	1.4655
12	0.274	2.492	1.4655
13	0.154	2.646	1.4655
14	0.277	2.923	1.4655
15	0.06	2.983	Residue

These data are presented graphically in Figure XII (page 125).

The phenyl urethane of the material in the first flat (n_D^{25} 1.4631), approximately 0.7 grams, was found to melt at 126-127° and to give the same mixed melting point as that from synthetic 4-n-propylcyclohexanol, thus confirming its identity.

The phenyl urethane of the material in the upper flat (n_D^{25} 1.4655), approximately 2.22 grams, was found to melt at 84-85° and to give the same mixed melting point as that from synthetic 3-cyclohexylpropanol-1, thus establishing its identity. The combined yield represents a recovery of 81% caculated on the weight of the original β-hydroxypropiovanillone taken.

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