THE HIGH PRESSURE CATALYTIC HYDROGENATION OF THE TANNIN OF BLACK WATTLE.

(Acacia mollissima Willd.).

by

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THE HIGH PRESSURE CATALYTIC HYDROGENATION OF THE TANNIN OF BLACK WATTLE(*Acacia mollissima* Willd.).

PART I.

CHAPTER 1.

INTRODUCTION.

The Wattle Industry in South Africa has, from its commencement in the middle of the last century, gradually assumed a position of increasing importance in the economic structure of the country. Apart from the provision of a valuable tanning extract for home use and for export, the tree itself has proved of considerable importance to the Union's mining industries. In addition there would appear to be possibilities for the utilisation in the near future, of the raw ground bark and the wattle extract for the manufacture of a number of by-products, including certain types of plastics.

The realisation that data must be available concerning the chemical nature of South Africa's main tanning agent, wattle tannin, if the tanning process is to be fully understood and controlled, has led to the initiation of a number of researches at this Institute, with the aim of producing evidence concerning the chemical structure of wattle tannin and its practical application. The dissertation presented in the following pages is a further contribution towards an understanding of the chemical constitution of wattle tannin.

As will be shown in the following chapter, information concerning the nature of wattle tannin is not abundant, with the result that work was commenced with but little knowledge as to its fundamental nature and properties.

Most of the methods of investigating the nature of wattle tannin have been suggested by the general techniques employed during the last twenty years for the elucidation of the structures of naturally occurring macro-molecular compounds. In the main these have been degradative treatments such as oxidation, alkali fusion, and hydrogenation.

The oxidation and alkali fusion of wattle tannin and its derivatives, have recently been investigated at this Institute by A.M. Stephen (1), with the result that a number of identifiable end products were isolated. The results of this work have indicated that wattle tannin may well be a complex condensation product of polyhydric phenols, linked together partly through aromatic side chains and partly through ether linkages.

The low yields of products obtained, and the fact that the methods employed caused not only breakdown of the molecule, but condensation to further complex substances, have made it necessary to seek information from some further degradative reaction. The considerable degree of success met with in the elucidation of the structure of lignin by high pressure catalytic hydrogenation, where other techniques had failed (2,3,4, 5,6,7,8), indicated that in all probability wattle tannin might yield to similar treatment. Certain preliminary experiments along these lines were conducted by Stephen (1), but it has been left to the author to pursue the study in greater detail.

Chemical reduction of substances considered likely to be related in structure to the natural phlobatannins was carried out twelve years ago by Russell and Todd (9), who measured the hydrogen absorbed by known amounts of their synthetic catechin-like polymers. However, since the recent researches conducted on wattle tannin have produced no evidence as to its structure being related to the catechin model, the results obtained by these workers have been of little value in the present investigation. Catalytic hydrogenation of the natural tannins has as yet not been reported.

CHAPTER 2.

THE CHEMICAL CONSTITUTION OF WATTLE TANNIN.

Information concerning the chemical structure of wattle tannin,and indeed of any naturally occurring tannin of similar type,is extremely scarce.

A review of the classification of natural tanning materials has been compiled by Corbett(16), while others are available in the literature; particularly in a dissertation by Russell(17).

For the sake of completeness, therefore, only the briefest of summaries of previous work on tannins, including wattle, will be given.

The natural tannins possess many properties in common; first and foremost being their ability to precipitate gelatin and other proteins from solution, and to convert raw hide to imputrescible leather. They are in general slightly acidic, high molecular weight substances with colloidal properties. By virtue of their phenolic nature they are coloured blue or green by aqueous ferric chloride,and they precipitate with alkaloids and certain metallic ions.

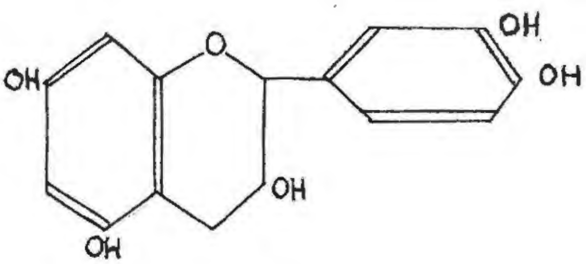
The classification of tannins is based on their reaction with hydrochloric acid and with neutral ferric chloride. Those called "Hydrolysable Tannins" yield on treatment with dilute acid,gallic or ellagic acids together with glucose. These were at one time termed pyrogallol tannins on account of their blue colour reaction with ferric chloride, and largely owing to the work of Fischer during the early part of this century, their structure is now fairly definitely established.

Wattle tannin belongs to another class known as catechol tannins or phlobatannins. These are converted by hydrochloric acid into dark coloured, amorphous, insoluble compounds and give green colours with ferric chloride. The chemical constitution of this type of tannin has been the subject of much speculation, and as yet nothing definite has been established.

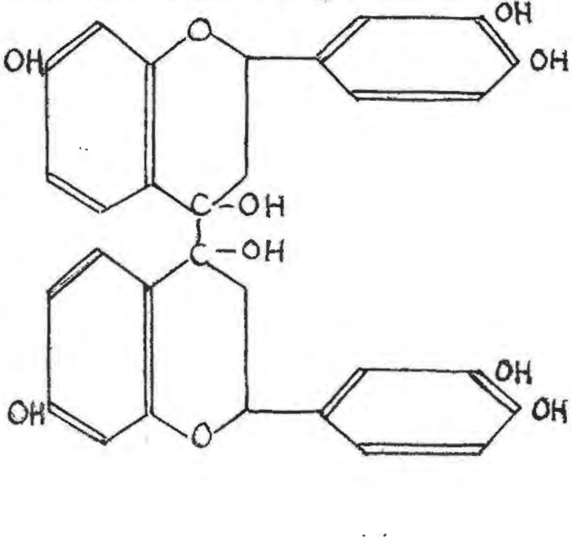
The similarity of wattle tannin to quebracho, hemlock, redwood and others of the phlobatannin class is indicated by its ability to produce a heavy brown precipitate with gelatin,,and a dark violet colour with ferric chloride. It is non hydrolysable, readily absorbed on hide powder, and is also precipitated with lead acetate, calcium hydroxide and bromine water. In solution it behaves as a negatively charged colloid, while molecular weight determinations show it to consist of large particles of approximately 1800 molecular weight units. Its solution shows a pH of 4.5-5 and is astringent.

Most of the chemical literature concerning the phlobatannins is to be found between the years 1935-1937 (17,19,20,21). Since that time the only recorded work of note is that of Russell and his co-workers in the U.S.A. (18,22), who have recently undertaken a constitutional study of a series of compounds related to their earliest synthetic product, bis (7,3',4' trihydroxy) flavpinacol, which they consider to be the structural unit of the phlobatannins.

Russell considers the phlobatannins to be related to the catechin (3,5,7,3',4' pentahydroxyflavan) model i.e.



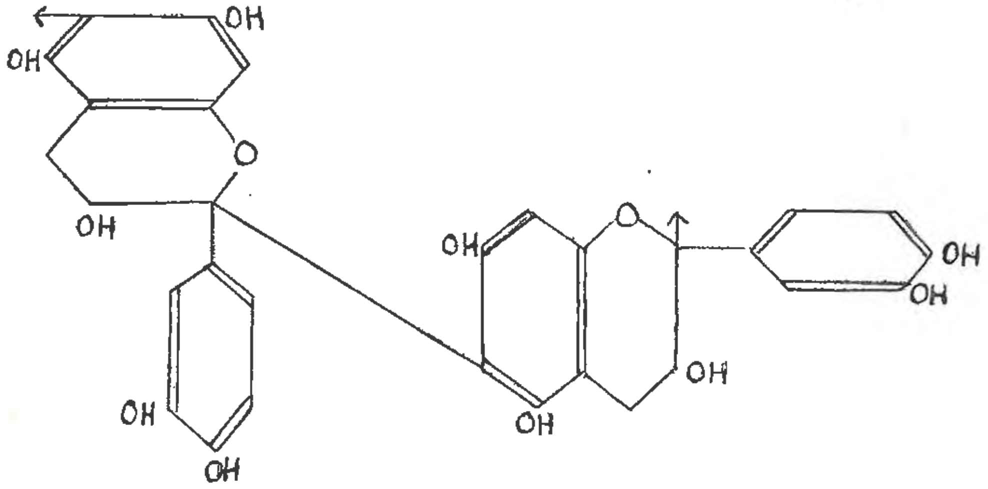
His reasoning was based on the grounds that he had synthesised from such units, compounds qualitatively indistinguishable from the natural product. The raw material used was mimosa tannin (whether from the species Acacia mollissima or not, is unknown). This gave on alkali fusion, phloroglucinol, pyrocatechol and protocatechuic acid. Working on the supposition that the tannins resulted from condensation of these units through the 4-carbon atoms in a pinacol fashion Russell prepared the following:-



This substance was amorphous and qualitatively indistinguishable from mimosa and hemlock tannins, especially in regard to its absorption spectra, and was hence regarded as the basic structure allowing for variations in the positions of the OH groups.

Freudenberg in 1934 argued that owing to the complexity of the reaction by which Russell had prepared the above, it was unlikely that a single product such as this flavpinacol could have resulted. In addition he did not accept the evidence on spectroscopic grounds as sufficient in view of the fact that the hydrolysable tannins behave similarly, and in any case there was no reason to suppose that the pinacol nucleus should occur exclusively in the natural tannins.

Freudenberg's work was aimed at the constitution of quebracho tannin, and his theory postulated that the phlobatannins were catechol polymers joined from the C-2 atom in one unit to the C-6 in the other i.e.



Russell's and Freudenberg's views although differing greatly, may both be essentially correct since they apply to different tannins, but no attempt to draw an analogy with the constitution of wattle tannin can be made.

In 1935 Chater(23) experimented on the oxidation of numerous tannins to discover if any anthocyanidins resulted. If the tannins were catechin polymers they should, according to the work of Appel and Robinson(24), yield anthocyanidins. Chater obtained solutions of substances whose colour reactions resembled those of the required products, but did not definitely prove that these were actually produced.

Later work on the constitution of wattle tannin is almost entirely due to Stephen(1), who obtained on oxidation of methylated tannin, veratric and trimethyl gallic acids. On hydrogen peroxide oxidation, methylated tannin shows no similarity in behaviour to a methylated anthocyanidin, nor indeed on treatment with periodic acid, lead tetra-acetate or lead tetroxide, does it give any indication of conforming to a structure such as that proposed by Russell, since no ketonic acids are produced.

The alkali fusion of wattle tannin produces resorcinol in fiar quantity while no other phenols can be isolated. The action of nitric acid results in oxalic and styphnic acids, and oxidation by bromine in dioxan produces no anthocyanidins, which it would do if wattle tannin were a catechin polymer.

The conclusion arrived at by Stephen(1) is as follows:-

> "We know that the tanning material in wattle is built up predominantly of resorcinol, catechol and pyrogallol nuclei, and in addition of aliphatic chains or rings which are fairly highly oxygenated. The mode of linkage of the aromatic rings is such that carboxylic acids related to catechol and pyrogallol, but not to resorcinol, may be liberated by oxidation after suitable stabilisation by conversion of the more reactive OH groups to methoxyl, but that the low yields indicate a great complexity of structure. The stability of resorcinol as compared with the other polyhydric phenols leads to its recovery in high proportion after vigorous acid or alkaline treatment where catechol and pyrogallol are unable to survive. The points of attachment of resorcinol to the rest of the structure are as yet unknown but should be capable of determination by degradation of suitable derivatives of the tannin".

CHAPTER 3.

PRINCIPLES UNDERLYING THE HIGH PRESSURE CATALYTIC HYDROGENATION METHOD.

Numerous reviews concerning the hydrogenation reaction, are in existence (10,11,12,13,14), and in so far as the results of these studies have acted as a guide during the work, they may be briefly summarised as follows:-

Factors Other Than Choice of Catalyst Governing the Reaction.

1) The Reaction Must be Possible.

Since catalysts do not affect the inherent tendency of a reaction to proceed, it is advisable that the chemical affinity of the reactants under the particular conditions chosen, should be calculated from free energy data.

2) Temperature.

In general, temperatures employed are less than 400°C. Practically every hydrogenation reaction can be reversed by increase of temperature, so that it becomes necessary to work at as low a temperature as possible, and to strike a balance between increasing the reaction rate, and so altering the equilibrium position in order to obtain the required product in reasonable yield. In certain cases increase of temperature may de-activate a catalyst and perhaps necessitate the addition of a promotor. The reaction speed is, in very general terms, doubled for every 50°C rise in temperature.

3) Pressure.

Pressure will affect the hydrogenation reaction according to Le Chatelier's principle, and since in most hydrogenation reactions a gas phase is present and decrease in volume occurs , increase of pressure will cause increased reaction speed . The effect of pressure is however not governed by any quantitative laws.

4) Time.

This factor is entirely an arbitrary one, and is contolled by the choice of other variables and the product required , especially in reactions where selective hydrogenation is desired.

5) Ratio of Hydrogen to Substance Being Hydrogenated.

Up to a certain limit, the yield of product is controlled by the amount of active catalyst present. For the hydrogenation of liquids, the speed of reaction and the product,are determined by the ratio of the partial pressures of the reactants.

6). Solvent.

A necessary condition governing the choice of solvent in liquid phase reactions , is that it must dissolve the substance to be hydrogenated , the product and the hydrogen. Intimate contact between the reactants and catalyst , is generally accomplished by some form of shaking . The ratio of substance to hydrogen is governed by the solubility of hydrogen in the solvent, and hence the latter must be chosen with due regard to this factor. Moreover, the nature of the solvent appears not only to affect the rate or extent of formation, but also the kind of product obtained.

<u>The Choice and Properties of the Catalyst.</u>

For high temperature-pressure liquid phase reactions the two catalysts in general use, are Raney Nickel (25,26,27,28) and Copper Chromite (29). An excellent paper has been published (29), on the effect of adding various mixed oxides as promotors to the latter, and in the course of the work one of these activated catalysts, No.39 KAF, has been used.

As regards compounds containing only carbon and oxygen, the action of COPPER CHROMITE may be summarised as follows:-

1) An oxygen to carbon link is very labile towards hydrogenolysis over copper chromium oxide at 250°C or above, if it is:

   a) In the 1-2 position with respect to a double bond in the 3-4 position i.e. $\overset{4}{C}=\overset{3}{C}-\overset{2}{C}\cdots\overset{1}{O}$

   b) In the 1-2 position with respect to an oxygen to carbon link in the 4-5 position i.e. $\overset{5}{O}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}\cdots\overset{1}{O}$

   An oxygen to carbon linkage is labile although not so markedly as in a) or b) if it is in the 1-2 position.

   c) With respect to a 3-4 carbon to oxygen link i.e. $\overset{4}{O}-\overset{3}{C}-\overset{2}{C}\cdots\overset{1}{O}$ or

d) with respect to a double bond in the 4-5 position i.e. $\overset{5}{C}=\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\cdot\cdot\overset{1}{O}$

2) 1-2 or 1-3 aliphatic glycols are labile towards hydrogenolysis.

3) The effectiveness of copper chromite towards saturation of double bonds where hydrogenolysis (the splitting of structures and groups into fragments under vigorous reduction with hydrogen), does not occur, is somewhat less than Raney Nickel under comparable conditions.

RANEY NICKEL.

1) This catalyst always contains a certain amount of aluminum which acts as a promoter.

2) As under 3 above the catalyst is more specific towards the saturation of double bonds than towards hydrogenolysis. It is particularly useful in the saturation of aromatic rings, where copper chromite fails.

For a more detailed comparison of the two catalysts and their effect on various types of compounds under hydrogenation, Ref.28 may be consulted. Further, an excellent monograph by H. Adkins, entitled "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts" (Wisconsin 1937) is available. This latter makes a systematic study of the somewhat chaotic literature concerning this subject.

Discussion.

A review of the available literature suggests two main avenues of approach towards the planning of experiments, which might prove profitable when applied to wattle tannin.

1) Hydrogenation under mild conditions to give a stable product, which would probably still be a fairly large molecule and whose properties could be investigated by further mild degradative reactions, and by the preparation of derivatives.
2) A drastic hydrogenation designed to cause hydrogenolysis, and the recovery of certain elementary building units of the tannin molecule.

By analogy with the work on lignin the author has pursued the latter course, but a discussion as to the advisability of this, will be deferred until the concluding remarks are made.

CHAPTER 4.

THE HYDROGENATION OF LIGNIN.

The work presented in this thesis has been based to a great extent on the method used for the elucidation of the structure of lignin, by means of high pressure catalytic hydrogenation. It has therefore been deemed advantageous to include in the introductory section, something of the general plan used and the results obtained in America.

Discussion.

In many respects tannin resembles lignin (30,31, 32,33) . Both are insoluble, high molecular weight polymers which occur together in wide distribution throughout the vegetable kingdom, and in close association with substances intermediate between lignin, cellulose and hemicellulose. This latter fact makes the isolation of both in a pure state, almost an impossibility.

Although the extraction of tannin from bark is a matter of comparative ease, its separation from the water soluble substances occurring with it, cannot be accomplished without severe chemical treatment, which may well modify its structure. With lignin, the best that can be achieved is a preparation termed "acid" or "alkali" lignin, according to the method of extraction used. Owing to the considerable modification of the structure likely to occur on extraction by acid or alkali treatment, all later work on the hydrogenation of lignin has been concerned with the hydrogenation of wood, without isolation of the lignin present.

Chemically, tannin and lignin do not appear to be directly related, in that lignin contains a certain percentage of methoxyl groups and a carbonyl group whereas tannin has none. Unlike tannin it produces carbonyl compounds on boiling sulphited and methylated derivatives with strong alkali for long periods, while on methylation it shows two reactive OH groups per molecule, as against four for tannin.

In view of the general similarity of the type of compound to tannin, it was considered profitable to survey the work on the hydrogenation of lignin and where possible to adapt the technique to wattle tannin.

Hydrogenation of Lignin (2,3,4,5,6,7,8).

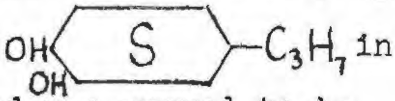
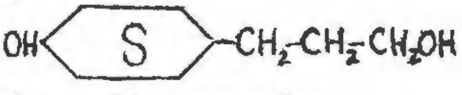
The raw product used was extracted from alcohol treated aspen wood, by refluxing with methanol containing 3% hydrochloric acid. It was re-precipitated from methanol solution and dried.

The resulting lignin was found to react with hydrogen over copper chromite in dioxan solution, at 250-260°C under 200-300 atmospheres, during eighteen hours, producing a colourless or faintly yellow solution and absorbing 1 mole of hydrogen for every 25 grams of lignin.

There was obtained from the hydrogenation of 80 grams lignin, 22 grams methanol, 9 grams of an alcohol of Boiling Point 92-95°C (7mm), about 3 grams of a glycol Boiling Point 107-110°C(1mm), 20 grams of a glycol Boiling Point 125-127°C(1mm), 18 grams of a mixture of compounds Boiling Point 130-260°C(1mm), 4 grams of intermediate fractions and 5 grams of compounds boiling above 260°C(1mm).

The separation of the above products was achieved by repeated re-fractionation through a specially designed modified Widmer column (34), and later through a more efficient series of columns (5). The authors themselves state that the identification of the products is a direct tribute to the efficiency of the fractionating columns used (5).

The products after isolation were re-hydrogenated over copper chromite in dioxan at 290°C(3). The alcohol was characterised as 4-n propyl cyclohexanol-1 i.e.  by isolation of its phenyl and α-naphthyl urethans, and comparison of its properties and those of its derivatives with a sample of artificially synthesised compound.

The first glycol was identified as 4-n propyl cyclohexanediol 1-2 i.e.  in the same manner, while the second was proved to be 3(4-hydroxycyclohexyl)-propanol-1,  by two separate oxidations to a keto acid - one by chromic acid, and the other using chromium oxide with acetic acid, in a mixture of water and benzene. The resulting keto acid was identified by means of its 2-4 dinitro phenylhydrazone, while a 3-5 dinitro benzoate of the glycol was also prepared.

The high Boiling Point fraction 150-260°C(1mm), was dehydrated over alumina at 400°C and re-hydrogenated over Raney Nickel, producing a series of hydrocarbons whose analyses showed that there are in lignin, units containing more than nine carbon atoms.

The hydrogenation of meade "soda" lignin in a similar manner (3) produced the above alcohols, and in addition, cyclohexanol, 4-methyl cyclohexanol, 4-ethyl cyclohexanol and a series of high boiling point resins of the same nature as the 150-260°C(1mm) fraction already noted. From maple ethanol lignin there was obtained another product, 3-cyclohexyl 1-propanol (6), identified by synthesis and comparison as before.

In addition, a study was made of the volatile hydrogenation derivatives of lignin, which occur in the solvent (5), and amongst these were identified 2-3 dimethyl butane, methanol, tetrahydrofurfuryl alcohol, ethanol, 2-2 dimethyl butanol, secondary butanol and methyl isopropyl carbinol. The optimum yield of these substances was obtained using Raney Nickel in butanol as solvent, at temperatures just below the critical temperature of butanol, and at as high a pressure as was consistent with safety.

The conclusions drawn from the above data as to the structure of lignin, will be omitted for the present purpose, but a general observation may be quoted viz:

"The proportion and nature of products obtained in separate hydrogenations of the same substance, may be a function of the relative rates of hydrogenation and hydrogenolysis, and not of any difference in structure of the material used. For if hydrogenation of unsaturated linkages precedes hydrogenolysis of carbon to carbon, or oxygen to carbon links, then cleavage (hydrogenolysis) may not ensue, because the unsaturated groups which facilitate cleavage are no longer present. If hydrogenolysis takes place first, then hydrogenation will ensue. The relative rates of hydrogenation and hydrogenolysis are often extremely sensitive to small changes in conditions".

It will be seen from the work described in the following pages that, in general, the hydrogenation of tannin produces a similar series of products to those of lignin, under comparable experimental conditions.

Reference concerning the nature of the saturated cyclic products expected, is indeed scanty in the reported literature. Apart from the above quoted papers, Beilstein's "Handbuch der Organischen Chemie" and particularly a dissertation entitled "Cyclohexanols from Phenols" by Ungnade and McLaren(15) may be consulted.

CHAPTER 5.

A - THE PURIFICATION OF WATTLE TANNIN.

The raw material for the study of the chemistry of wattle tannin, may be derived from either of two convenient sources, 1) the bark of the tree itself or 2) the commercially marketed wattle extract containing approximately 62% tannins, 20% non-tannins and 18% moisture, according to the standard method of analysis by absorption on hide powder. The material resulting from either source is similar in moisture, tannin and non-tannin content. Up to the present, no process, not involving chemical change in the tannin, has been evolved to produce a product with more than 86% tannin content, or one with more than 76% non-tans.

The results of investigations conducted at this Institute (1), have shown that the extraction of commercial wattle extract with cold acetone, results in a material with a tannin content of approximately 82%; this value being higher than that obtained by any other means. This "acetone extract", which for the sake of convenience will in future be termed "tannin", has been the raw product for all investigations described in the following pages.

The electrodialysis of a 5% aqueous solution of acetone extract through a cellophane membrane at 300 volts (35), has resulted in the separating out of a certain proportion of the smaller non-tan particles, leaving a material of molecular weight approximately 1800 and consisting after concentration and drying of 8% moisture, 8% non-tans and 84% tannin. This represents a slight increase in the ratio of tans to non-tans, but the time taken and the small yield, have made impracticable the use of electrodialysed tannin as a starting product.

B - THE NON-TAN CONSTITUENTS OF ACETONE EXTRACT.

In the use of the term "non-tans", it must be borne in mind that, owing to the method of acetone extraction used, the so called non-tans are contaminated to the extent of about 25%, with material still capable of tanning hide.

A valuable survey of the non tanning compounds in wattle bark extract, has been presented by G. S. Tarboton(36), while further data has been accumulated by Stephen(1). The results of these investigations have shown that, as a whole, the non-tan constituents contain 2.1% nitrogen, of which .55% is in the form of ammonium ion or amide, 22.2% "sugar" content, of which 9.0% is present as reducing sugar, 1% of inorganic matter and 7.6% of ash.

The chief elementary units from which the non-tans are evidently formed, are HEXOSES, PENTOSES, METHYL PENTOSES and URONIC ACIDS. These are found in the combined state in a series of related compounds, which can be divided into the following groups:

HEMICELLULOSES e.g. pentosans (xylan etc.), found in abundance in ligninified tissues.

PECTINS produced by the de-esterification of pectinogen, the chief encrusting substance of unlignified tissue. The parent compound is composed of four molecules of a uronic acid, one molecule of a pentose, and one molecule of a hexose.

GUMS are polymerides of hexoses and pentoses, and usually contain an acid characteristic of each gum. Gum arabic for example contains arabinose, a uronic acid and an acid of unknown constitution, called arabic acid.

LIGNINOCELLULOSE is a combination of lignin, a pentosan and cellulose. Lignin is produced at the expense of cellulose in the cell walls of woody tissue, and may exist free or in the above combination.

C - NON-TANS UNDER HYDROGENATION.

Data concerning the behaviour of the various constituents of the non-tans, under the conditions of hydrogenation likely to be used for tannin, is not directly available in the literature. A number of helpful reviews have however been consulted, amongst which are described:

1) The hydrogenation of a variety of sugars over copper chromite at 300 atmospheres and 250°C (37); the chief products obtained being methanol, ethanol, propanediol 1-2, 2-(4 hydroxytetrahydrofuryl)-methyl carbinol, hexanetriol and hexanetetrol.

2) The hydrogenation of a number of derivatives of furane over Raney Nickel and Copper Chromite (38,39,40),

The products being chiefly low boiling point alcohols, and substances such as tetrahydrofurfuralcohol. In view of the close relationship between the behaviour of pentoses and furane derivatives, the foregoing was considered helpful.

The hydrogenation of cellulose and lignocellulose over Raney Nickel and Copper Chromite has not been reported, but data concerning the hydrogenation of these substances under other conditions is available (41,42).

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PART II.

EXPERIMENTAL.

CHAPTER 6.

THE APPARATUS AND PROCEDURE OF HYDROGENATION.

The hydrogenation bomb used, was constructed according to the general design advocated by Adkins(43) and was intended to withstand pressures up to 400 atmospheres and temperatures up to 400°C.

The material used was nickel steel and the bomb itself was constructed in four portions.

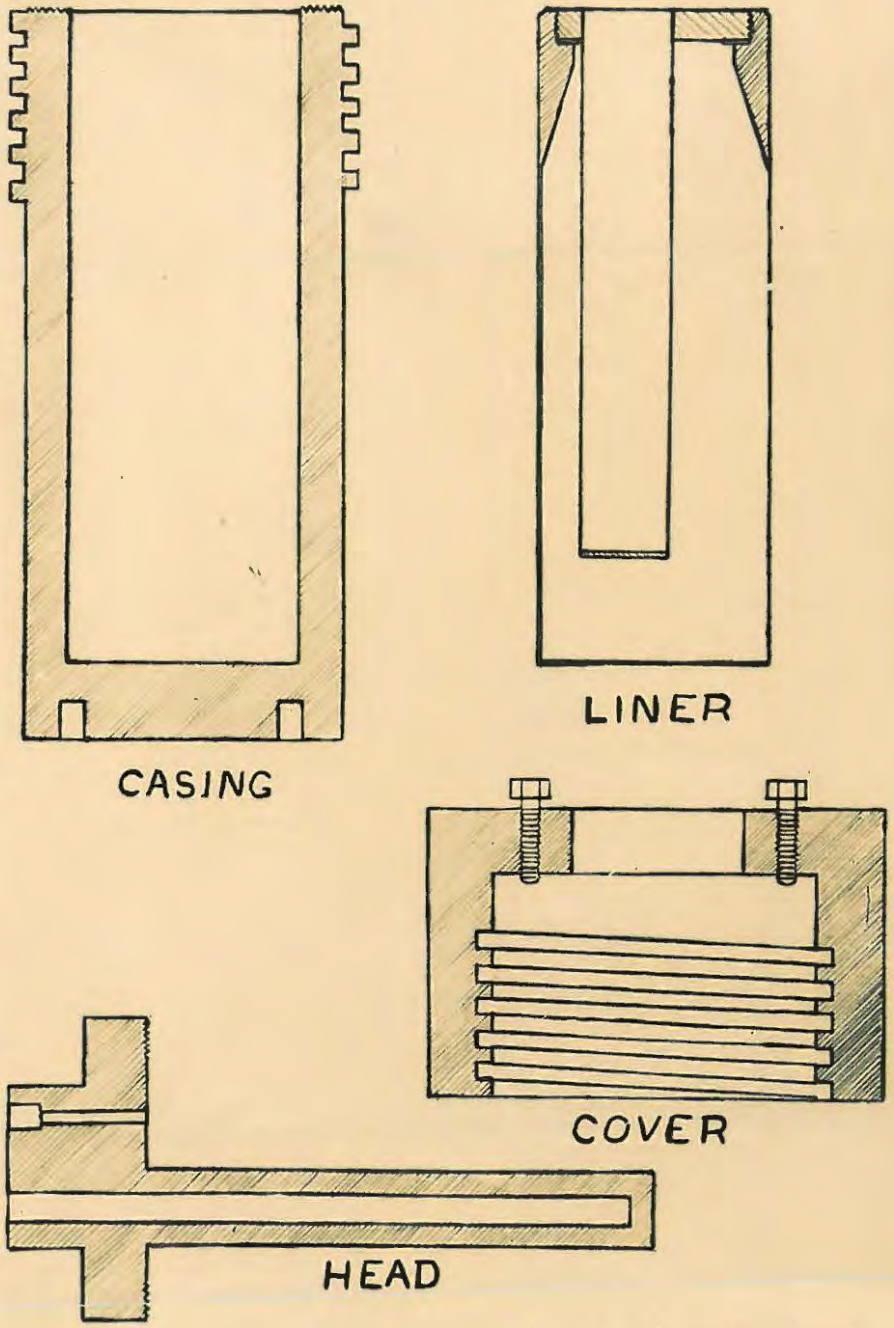
1) An outer cylinder one foot long, $5\frac{1}{8}$ inches in external diameter and $3\frac{5}{8}$ inches internal diameter, with threads turned on the top, for the screwing on of the cover.

2) The bomb head consisting of a steel plate one inch thick with a long thermocouple well attached slightly off centre.

3) The bomb cover, in the form of a screw cap with six bolts, for producing the necessary pressure on a, square cross section, circular gasket between the outer cylinder and the bomb head, in order to seal the bomb.

4) The reaction liner; a brass cylinder with a screw top, asbestos gasket, and hydrogen inlet, which contains the reactants and fits inside the thick steel casing.

After charging and assembly, a gauge and needle valve gas fitting were screwed into the hydrogen inlet, and the whole inserted into a cylindrical electric furnace, wound with 23 turns of 22 gauge nichrome wire. The furnace in turn was secured in a galvanised iron cradle suspended from a wooden frame, while rocking



HYDROGENATION BOMB PARTS

backwards and forwards at the rate of one cycle per second was accomplished by means of a continuous rated $\frac{1}{4}$HP motor. Heating and rocking were controlled independently from outside the hydrogenation room. The temperature was read by means of a thermocouple inserted into the bomb itself and attached to a direct reading millivoltmeter calibrated in ^{o}C. The gauge which was attached directly to the bomb was read through an aperture in the wall.

Procedure.

After charging the liner with substance to be hydrogenated, solvent and catalyst, an asbestos gasket was inserted. The lid portion, with a well for the thermocouple tube, was screwed into position in such a manner that the small gas inlet on the side of the liner was, as far as possible, remote from the thermocouple well. This was to ensure that during the hydrogenation the gas inlet should be uppermost to prevent oozing out of the contents, while the thermocouple well should be immersed in the reaction mixture.

The liner was then inserted into the outer casing noting the position of the gas inlet. The copper gasket was placed in position on the smooth upper surface of the outer container, and after positioning the bomb head, the cover was screwed on and the bolts tightened alternatively to secure even pressure on the gasket surface. After insertion of the gauge and needle valve, the assembly was secured into the furnace cradle, with the gas inlet uppermost.

The thermocouple was introduced and by means of soft copper tubing, a hydrogen cylinder of 100-130 atmospheres pressure was connected to the inlet valve. After filling, rocking and heating were commenced and continued for 20 minutes, during which time the temperature rose approximately 80°C. The temperature and pressure continued to rise for a further 10-15 minutes, after which interval the current was again switched on. By intermittent heating the temperature was maintained within desirable limits, while on each day during a hydrogenation, the bomb was re-charged with hydrogen from a cylinder kept at a fairly high pressure. The average hydrogenation was one lasting for three days of eight hours each.

On completion of the reaction, and after the residual gas had been allowed to escape slowly, the liner was removed. The contents were poured out while the residual sticky solids were scraped out, usually with some difficulty.

IMPROVEMENTS INTRODUCED INTO THE HYDROGENATION ASSEMBLY BY THE AUTHOR.

The apparatus and procedure described, were those employed by Stephen(1), during preliminary experiments. It was however obvious that, owing to the very sensitive nature of the hydrogenation reaction, the method used was too empiric and that more standardised conditions were required. Moreover, certain structural elements of the assembly were considered somewhat imperfect and these were either remedied or replaced by more efficient parts.

A - Temperature Control.

The arbitrary method of switching the heater successively on and off, was considered the greatest drawback in the procedure, especially as hydrogenations could not be run over night, thus making the whole process unnecessarily tedious. In addition the possibility of gas escaping, and of the temperature being allowed to rise sufficiently to burn out the heater unit, and also to cause possible unwanted modification of the reaction products inside the bomb, was considerably increased.

A thermoregulator of the bimetallic spiral type was therefore constructed and inserted directly into a well in the furnace jacket. In order to prevent movement of the regulator with respect to the furnace during shaking, it was firmly attached to a stout bracket which was welded onto the cradle.

The spiral was made of 1/32" spring steel, and 1/64" brass strips, 1/4" wide and welded together with silver solder. The diameter of the helix was 1/2" and its length 3". The bottom end was attached to an 1/8" brass rod which extended 14" inside a wider tube attached at one end to the spiral, and at the other to a small box which enclosed the contacts. The torsion produced in the spiral by heating, opened the tungsten contact points, which were in turn connected to the primary circuit of a "Sun-Vic" relay control. To the secondary circuit were connected the furnace leads and also the shaking motor. It was considered advisable also to make and break the shaking, in order to conserve the motor during long runs.

The above described arrangement was found to control the temperature between 199-200°C, and between 297-300°C for longer than 48 hours, on numerous trial runs. The lag period between successive shakings and heatings of eight minutes, was approximately nine minutes.

B - New Pressure Gauge and Device for Filling Bomb.

As a result of continued trouble encountered with faulty pressure gauges, and the inconvenience of reading small and very inacurate gauges through an aperture in the room wall, a new fixture calibrated up to 6 tons per square inch was attached to a wall bracket outside the room. This was connected to the bomb by steel fuel-feed tubing (.61cm OD and .3cm ID) through the wall. In order to absorb shock during shaking, the piping was coiled into three spirals of 17" diameter. This arrangement enabled filling with hydrogen to be done from outside the room, thus allowing greater ease of manipulation.

A new and specially constructed high pressure hydrogen cylinder was used for topping up the pressure before each hydrogenation. This provided a constant starting pressure of 2500 lbs. per square inch, or less if required.

C - Improved Heating Assembly.

Owing to consistent long delays encountered by the fusing of the nichrome heating wire, the furnace wiring was re-organised. Two spiral 1000 watt tungsten elements were wound in parallel onto a steel jacket with mica insulation, and set in a fire clay of composition: 1400 grams China Clay, 220 grams Magnesium Oxide, 750 ml of 50% Sodium Silicate, and 500 ml Water. The furnace was then slowly baked out and finally after strong heating, packed tightly with dried China Clay and hermetically sealed. The whole assembly was thickly lagged with asbestos cloth.

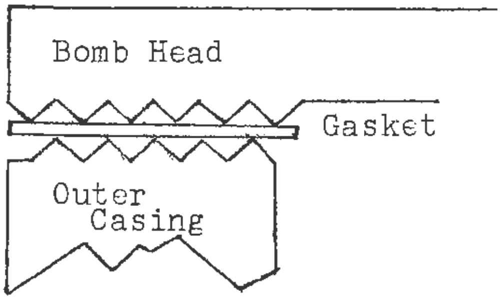
D - Insertion of a Temperature Fuse.

In order to guard against possible failure of the regulator, a temperature fuse was introduced in the form of a small strip of suitable metal welded in series with the heater element. This was placed inside a small Pyrex tube which could be inserted into the thermocouple well. A lead strip was used for temperature control at 200°C and zinc for 300°C. Too great a rise in temperature would thereby melt the metal and break the heater circuit.

E - Prevention of Leakage at High Pressures.

The form of smooth copper gasket employed in the preliminary experiments, was found to be inefficient at high pressure. The two gasket surfaces of the bomb were accordingly serrated, and new flat copper gaskets (1/16" thick, $5\frac{1}{8}$" OD, $3\frac{5}{8}$" ID) were procured.

These were annealed before each hydrogenation, and before sealing the bomb, were in each case thickly smeared with a linseed oil-graphite jointing compound. The serrations were 1/32" deep and 1/8" apart and designed so that the teeth of the upper surface, would fit into those of the lower, viz.

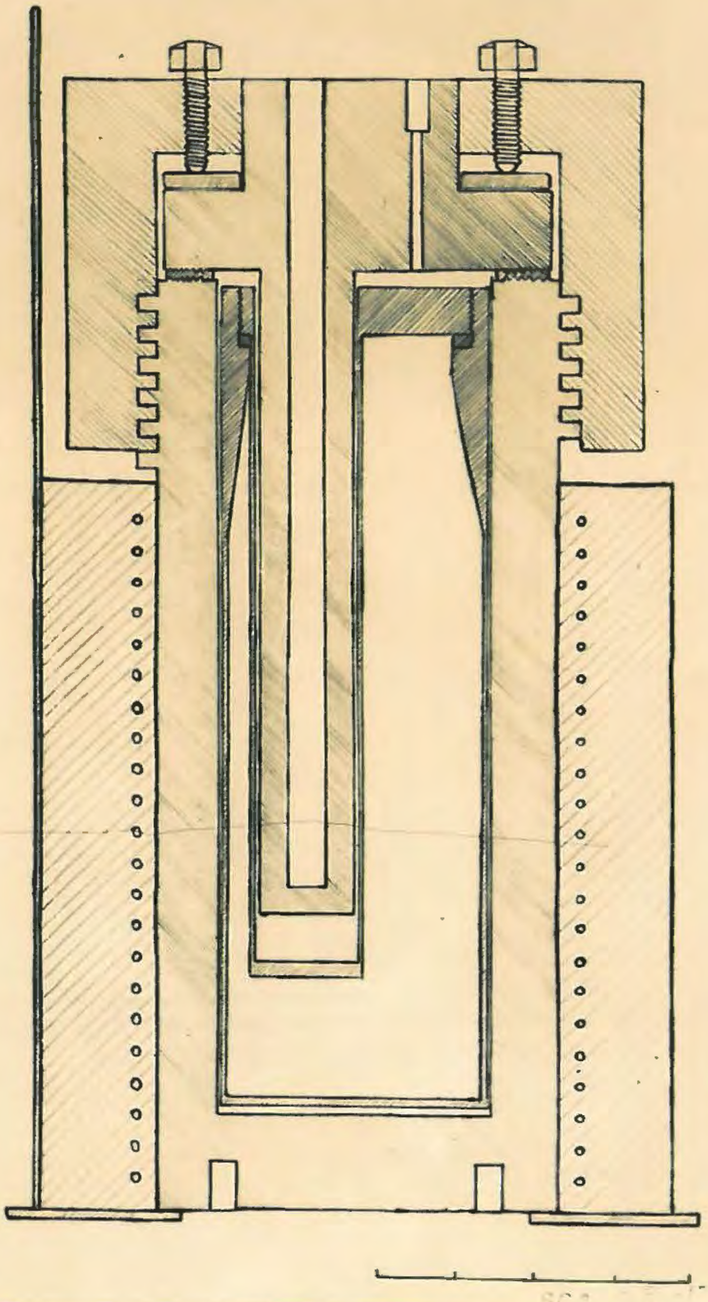


F - Miscellaneous.

Nichrome steel bolts were used to replace iron bolts in the bomb cover. A second reaction liner of heavier material, although similar in design to the original, was employed to allow of saving of time lost in cleaning out this part between successive hydrogenations.

The procedure adopted for charging the bomb and for the carrying out of the hydrogenation, was similar to that already described, and need not be repeated.

HYDROGENATION BOMB ASSEMBLY



CHAPTER 7.

DESCRIPTION OF APPARATUS AND TECHNIQUES OTHER THAN FOR HYDROGENATION.

A - Combustion Analyses.

All combustion analyses reported in the following pages, were done on .03 to .07 grams of substance, using an electric furnace with a three foot tube packed only with copper oxide. The absorbents were; for the CO_2, microanalytical 20 mesh AR soda lime, and for the water, calcium chloride which had been previously fused, re-ground and retained under an atmosphere of CO_2 for some time. These were placed in small sealed glass U-Tubes.

The initial combustion after introduction of the boat was accomplished using a slow stream of air. Oxygen which had been pre-heated over copper oxide, to remove traces of reducing substance, was then bubbled in, and finally air was aspirated through the system.

A certain amount of difficulty was encountered owing to the consistent breaking of tubes, due to local hot spots in the large furnace. This was accordingly re-wound with three separate 1000 watt spiral elements, set in fireclay, and attached to separate rheostats. With this arrangement even heating was secured throughout the whole furnace length.

B - Refractive Indices.

These were determined using a standardised refractometer of the Abbe type. Water from a thermostat at the required temperature, was circulated around the refracting surfaces by means of a small pump.

C - Molecular Weights.

The molecular weights recorded, were determined by measurement of the depression of freezing point observed, on introduction of a small quantity of substance into a known amount of DIOXAN as solvent.

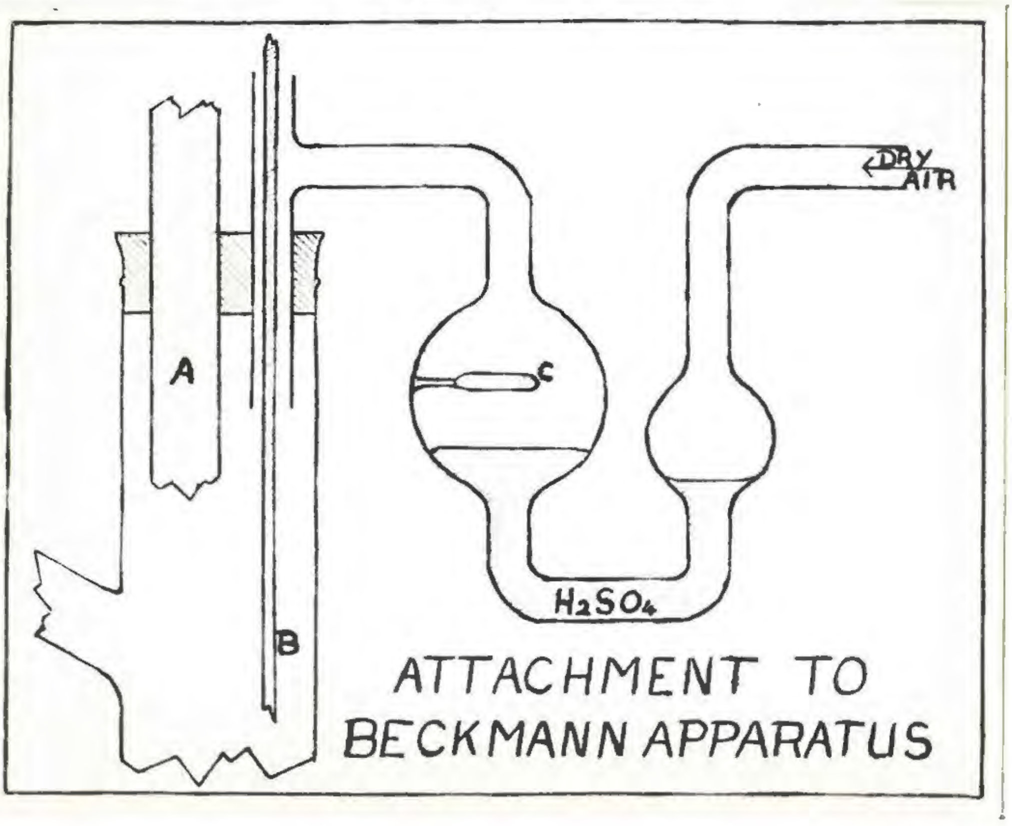
Dioxan was chosen owing to its ability to disolve all the hydrogenation products, water being entirely useless while benzene was only capable of disolving some of the lower boiling point products obtained.

Pure dioxan was prepared according to the method of Eisenberger(45) as follows:-

> One and a half litres of technical dioxan were boiled under gentle reflux with 150 ml of normal hydrochloric acid for seven hours, with a slow stream of air being passed through the stopper and into the flask, in order to remove the acetaldehyde literated. Solid potassium hydroxide was added to the cool liquid in a large separating funnel, and after shaking at intervals for a day and standing over night, the aqueous layer was run off. This process was repeated on the following day, after which the dioxan was transfered to a large flask and a quantity of wire-form sodium added. After standing for four hours, a twenty inch fractionating column packed with Berl porcelain saddles was attached, and the mixture distilled on an

oil bath. A boiling point of 99°C (714mm) was reached after the distillation of 300 ml, while one litre of dioxan was collected at 99°C. This latter was placed in a tightly stoppered bottle and cooled in the bottom of an ice chest at 10°C for a day. After crystallisation of the greater portion, the residual liquid was poured off and the crystals melted giving 950 ml of very pure dioxan, of freezing point 11.7°C, as quoted in the literature.

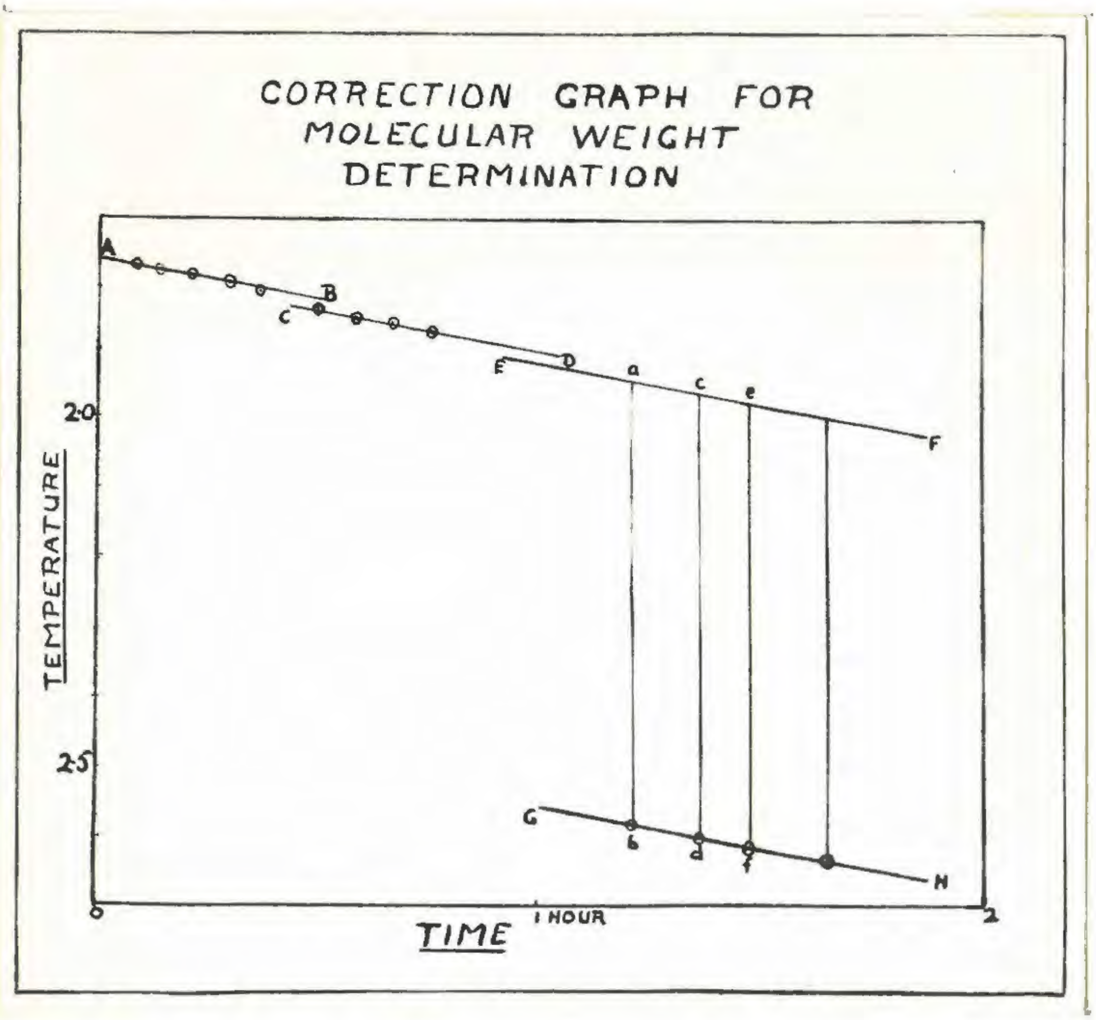
The ordinary Beckmann freezing point apparatus was used, but owing to the extremely hygroscopic nature of dioxan, a device for prevention of the entry of atmospheric moisture during stirring, was affixed as shown in the diagram.



A=Beckmann Thermometer B=Stirrer. C=Mica Spray Trap.

This attachment is in essential a sulphuric acid bubbler with a mica spray trap, through which dry air is forced at the rate of one bubble per second. However in spite of this precaution being taken, a small but steady drop of the dioxan freezing point was still observed. The procedure was therefore modified in order to make a simple extrapolation correction, viz.

Successive freezing points of the pure dioxan were observed and plotted vs time on a graph, giving the straight line AB see figure



The side arm of the solvent tube was then opened for a short while simulating the entry of solute, which was in each case contained in a small glass capsule i.e. , which could be broken by the stirrer after introduction.

A sudden small drop in freezing point was observed and further readings of the freezing point of pure solvent were observed and plotted vs time, giving a straight line CD parallel to and slightly below AB. The solute was then added, opening the side arm for the same time as previously, and dissolved while successive freezing points plotted vs time, gave the line GH approximately parallel to AB and CD.

In order to measure the depression of freezing point a theoretical line EF was drawn parallel to CD and at the same distance below it as that between AB and CD. EF therefore represents the drop in freezing point of pure solvent with time after the introduction of the actual solute, and the depression of freezing point is thus taken as the mean of the distances ab, cd and ef etc. between the freezing points observed for the solution and those extrapolated for the solvent.

Molecular weights were calculated using the formula:

$$M = \frac{1000 \times k \times w}{T \times W}$$

where M = Molecular weight of solute.
w = Weight of solute.
k = Cryoscopic constant for dioxan.
T = Observed freezing point depression.
W = Weight of solvent.

W was in each case obtained by pipetting 25 ml dioxan into the freezing point tube, and multiplying this volume by the density of dioxan at 20°C=1.0332. The accuracy of this was checked by actual weighing and the error involved found to be ± .01 grams, which is small in comparison to the accuracy of the method as a whole, which is claimed to be between 3% and 5%.

The Cryoscopic constant for the dioxan was determined using a variety of solutes.

1) CYCLOHEXANOL.

Pure cyclohexanol was re-distilled and weighed into a capsule.

.1566 gram caused a depression of .282°C (mean of .283, .282, .283, .281 from extrapolation graph)

Hence $$k = \frac{100.16 \times .282 \times 25 \times 1.0332}{.1566} = \underline{\underline{4.67}}$$

2) DIPHENYLAMINE. Pure re-crystallised AR.

a) .1956 gram in the form of a pellet gave a depression of .209°C (mean of .209, .210, .208, .209 from graph)

Hence $$k = \frac{169.22 \times .209 \times 25 \times 1.0332}{.1956} = \underline{\underline{4.67}}$$

b) .3751 gram gave a depression of .399°C (mean of .399, .399, .399, .398 from graph)

Hence $$k = \frac{169.22 \times .399 \times 25 \times 1.0332}{.3751} = \underline{\underline{4.66}}$$

3) β-NAPHTHOL. Pure white re-crystallised AR.

a) .1750 gram gave a depression of .220°C (mean of .220, .219, .220, .220 from graph)

Hence $$k = \frac{144.16 \times .220 \times 25 \times 1.0332}{.1750} = \underline{\underline{4.68}}$$

b) .3283 gram gave a depression of .409°C (mean of .409, .408, .409, .410 from graph)

Hence $$k = \frac{144.16 \times .409 \times 25 \times 1.0332}{.3283} = \underline{\underline{4.65}}$$

The mean depression constant was taken as 4.66 (as against 4.70 as quoted in the literature (45)) and this value was used for the determinations made.

CHAPTER 8.

PREPARATION OF RAW MATERIAL AND CATALYSTS.

A - TANNIN.

It will be noted from the previous discussion concerning the purification of tannin, that the material most easily prepared and having the highest tannin content, resulted from the extraction of commercial wattle extract with cold acetone.

Three kilograms of commercial extract were accordingly reduced to a fairly fine powder in a mill, and soaked in six portions with cold acetone for three days, with intermittent stirring. The resulting dark brown solution was decanted from the remaining solid, and concentrated by removal of the acetone in a large distilling flask. Extraction of the raw material was continued until the decanted liquid showed only a slight yellowish colouration.

The concentrates were then poured into eight inch evaporation dishes and after warming on a hot plate, were placed under suction in large desiccators. As the residual acetone was removed the whole puffed up into an easily powderable aerated mass. On fine crushing and further drying under suction on a water bath, there were obtained two and one quarter kilograms of a light fawn powder, which was used for the following investigations.

B - RANEY NICKEL.

This catalyst was prepared according to standard procedure (25), from a finely ground 50% nickel aluminum alloy.

A solution of 380 grams AR sodium hydroxide in 1½ litres of distilled water contained in the large beaker, equipped with a mechanical stirrer, was cooled in an ice bath to 10°C. 300 grams of nickel aluminum alloy was added to the solution over a period of about two hours, with stirring, and at such a rate that the temperature did not rise above 25°C. The beaker was allowed to remain in the ice bath during the operation. After addition of the alloy, stirring was stopped and the beaker and contents allowed to come to room temperature. After evolution of hydrogen became slow the reaction mixture was heated on a steam bath for about eight hours, keeping the volume constant by addition of distilled water. Hydrogen evolution again became slow, and after settling of the nickel, most of the liquid suspension of white sodium aluminate was decanted. Distilled water was added, the nickel stirred up and after settling, decanted again. The catalyst was then washed by decantation with a solution of 50 grams sodium hydroxide in 500 ml distilled water, and thereafter with water again, until the washings were **neutral** to litmus. Water washing was then repeated ten times more; then with three 200 ml portions of 95% alcohol and finally three times with absolute alcohol. There resulted from this process 150 grams of finely divided and highly pyrophoric nickel, which

in what form?

was stored under absolute alcohol in tightly closed and completely filled bottles.

Notes.

1) The catalyst may be stored under methylcyclohexanol or pure dioxan, but whatever liquid is used must be soluble in the solvent used for hydrogenation.

2) The stirrer motor must not be of a type which might ignite the liberated hydrogen. The stirrer blades should be of glass or stainless steel.

3) To prevent corrosion of the thermometer bulb, it should not be left in the alkaline solution.

4) Two ml of n-octyl alcohol may be added to prevent foaming, during addition of the alloy.

5) The settled material contains approximately .6 grams per ml of the catalyst, and is more conveniently measured out by volume, than weighed, for addition to the reaction mixture.

C - COPPER CHROMITE.

Connor, Folkers and Adkins in an excellent review (29), have examined the properties of copper-chromium oxide catalysts under three main headings:

1) The improvement of the method of preparation, through the decomposition of copper ammonium chromate.

2) The promotion and stabilisation of the activity of copper-chromium oxide catalysts, by the addition of various metal oxides.

3) The development of other methods of preparation.

The catalyst recommended by these authors as being the most generally active, was one containing calcium, No.39 KAF, which was accordingly prepared as follows.

900 ml of a solution (80°C), containing 261 grams hydrated copper nitrate ($Cu(NO_3)_2.3H_2O$) and 19.8 grams calcium nitrate, was added to 720 ml of a solution (25-30°C), containing 151.2 grams of ammonium dichromate and 150 ml of 28% ammonium hydroxide. The precipitate was filtered, the cake pressed and sucked as dry as possible. After drying in an oven at 75-80°C overnight and pulverising, the product was decomposed in three portions in a casserole over a free flame. During decomposition the powder was continuously stirred and the flame was removed after the decomposition was well started. After a little more stirring, a sudden evolution of gases occurred and the entire mass became black. The powder was then allowed to cool and the combined product leached for thirty minutes with 600 ml of 10% acetic acid solution, filtered and washed with 600 ml of water in six portions, dried overnight at 125°C and finally pulverised.

CHAPTER 9.

THE HYDROGENATION OF TANNIN.

A - Summary of Preliminary Results Obtained by Stephen (1).

After a series of trial experiments it was found by Stephen,that on the hydrogenation of tannin in aqueous solution over Raney Nickel catalyst at 180-250°C and 150-190 atmospheres pressure, during a period of three days of eight hours each, there was obtained from 30 grams of tannin, 12.5 grams of a brownish black powder and three or four drops of an oil (Boiling Point 93°C, micro), which floated on the surface of the solvent.

Of the powder which as a whole was insoluble in water, 7.5 grams was soluble in alcohol, the remainder being carbonised but slightly soluble in pyridine. The alcohol soluble portion on destructive distillation in vacuo yielded three fractions of dark viscous liquid and left a dark carbonised residue. These fractions were analysed by combustion and the results placed on a C_{15} basis as used for tannin, showed absorption of a maximum of 12 hydrogen atoms per molecule for the lowest boiling fraction. Acetyl derivatives were prepared, isolated and separately hydrolysed, showing a decrease in numbers of OH groups with rise in boiling point.

The hydrogenation of tannin over copper chromite in water solution and under comparable conditions produced similar results, but a greater proportion of carbonised product was obtained, and the oils from destructive distillation of the alcohol soluble portion showed a lower oxygen content, probably due to hydrogenolysis.

B - EXPERIMENTS USING RANEY NICKEL CATALYST.

With the foregoing background, the present work was commenced on the hydrogenation of tannin. The first experiments conducted were in order to establish the optimum conditions for obtaining a workable product using Raney Nickel catalyst. Since saturation of aromatic nuclei was desired, this catalyst was considered likely to be of more use than Copper Chromite (Chapter 3).

Experiment I.

Substance.	100 grams of Tannin, freed of acetone by drying at 100°C under suction.
Solvent.	200 ml hot water, since tannin is not readily soluble in the cold.
Pressure.	1900 lbs. per sq.in., rising to 3000 lbs. per sq.in. as the temperature rose. 1300 lbs. per sq.in. after reaction.
Catalyst.	6 grams Raney Nickel.
Temperature.	400°C.
Time.	8 hours.

From this reaction there was obtained 20 grams of a highly carbonised material, none of which was soluble in alcohol, ether, dioxan, benzene or pyridine. This residue glowed on heating and resisted concentrated nitric acid treatment, while the container smelt strongly of low boiling point hydrocarbons such as petrol.

It was concluded that the temperature employed was too high and consequently Experiment II was conducted under similar conditions, except that the temperature was reduced to 300°C. The product resulting from this hydrogenation exhibited similar properties to those already described, with the exception that this time a very small portion was found to be soluble in warm alcohol, giving a dark brown solution. The petrol smell was again observed.

As it was not considered profitable to examine the carbonised products of Experiments I and II in greater detail, Experiment III was conducted as follows.

Experiment III.

Substance.	100 grams of acetone-free Tannin.
Solvent.	200 ml of hot distilled water.
Pressure.	1900 lbs. per sq.in., rising to 3000 lbs. per sq.in. 1300 lbs. per sq.in. after reaction.
Catalyst.	7 grams of Raney Nickel.
Temperature.	200°C.
Time.	24 hours continuous.

On opening the reaction liner, a distinct smell of cyclohexanol was noticed. The solvent was poured off from the sticky black mass inside, and the bomb washed out with cold water.

The combined washings were fractionally distilled using a column 20 inches long and packed with porcelain saddles. With the first 20 ml of water distillate a few drops of pleasant smelling, faintly yellowish oil were obtained. An examination of these will be described in Chapter 12, under treatment of individual fractions. The remainder of the distillate consisted of pure water as proved by;

1) its Boiling Point of 98°C (714mm),
2) its Freezing Point of 0°C,
3) its reaction with anhydrous copper sulphate, producing a blue colouration,
4) its Refractive index n_D^{20}= 1.3330.

The sticky black mass inside the bomb was then scraped out and extracted three times with hot absolute alcohol. On filtration, a dark brown and viscous filtrate was obtained, while 34 grams of a highly carbonised material containing the used catalyst, was left on the filter. The viscous solution was then evapourated under reduced pressure in a stream of carbon dioxide to remove the ethanol, taken up in a small quantity of acetone, and warmed on a hot plate. On placing under suction in a large desiccator it puffed up and was obtained in an easily powderable form. Yield 40 grams of alcohol soluble black hydrogenated tannin, which is a definite product of the hydrogenation using the above conditions.

In order to obtain a suitable quantity of this substance, one and a half kilograms of tannin was hydrogenated in nine portions under the conditions described in Experiment III, yielding in all 832 grams of hydrogenated tannin.

During the course of the preparation, the effect on the percentage yield due to varying the ratio of catalyst to tannin, was investigated. The results may be tabulated as follows for 200 grams of tannin.

	Grams of Catalyst.	Yield (grams) of Hydrogenated Tannin.
1)	11.5	70
2)	15.0	118
3)	16.0	120
4)	25.0	120

Thus up to a certain limit (i.e. 16 grams of Raney Nickel), the percentage yield is increased, but beyond the maximum of 60% yield no increment is observed.

The water washings from the hydrogenations were all retained and the low boiling point oils extracted and treated as described in Chapter 12.

C - Examination of the Hydrogenated Tannin as Such.

1) The hydrogenated tannin was shaken with benzene, acetone, dioxan, ether and alcohol to discover whether it could be extracted fractionally. In each case all dissolved and nothing could be frozen out. It is therefore not a mechanical mixture of products, or if it is, then these have solubilities so closely related as not to allow of separation by differential extraction. Water does not dissolve the substance.

2) A portion was dried for five days in a modified Abderhalden drying apparatus (1, 44) at 112°C. On combustion analysis

.0873 gram gave .2216 gram CO_2 and .0643 gram H_2O, showing 69.2%C and 8.18%H.

On a C_{15} basis, this may be expressed as a formula $C_{15}H_{21.3}O_{3.68}$.
.0632 gram of the tannin on similar drying and combustion gave .1419 gram CO_2 and .0294 gram H_2O.
On a C_{15} basis, this corresponds to $C_{15}H_{15.1}O_{6.2}$.

The above product is thus produced from the hydrogenation of tannin over Raney Nickel and under the conditions of Experiment III, by the absorption of ± 1 mol. hydrogen for every 100 grams of tannin.

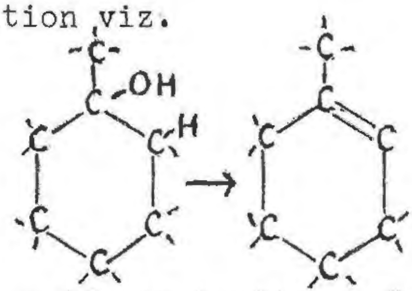
3) A further portion was placed after drying in a small Claisen flask, and heated for $\frac{3}{4}$ hour on a glycerol bath at 200°C with Hyvac applied. No change resulted, but on the application of direct heat destructive distillation commenced with the production of a 10% yield of thick viscous brown oil, the properties of which will be described in the following chapter. A black and highly carbonised residue remained, which on extraction with benzene produced a further small quantity of viscous brown oil. The remainder was similar in behavour to the carbonised residue from Experiment I.

4) An attempt was made to distil the hydrogenation product using naphthalene as solvent. On heating under vacuum, destructive distillation occurred after fusion to a viscous mass, and the oils plus naphthalene distilled over. After freezing out of the naphthalene from an ethanol solution of the distillate, it was found that the yield of oils was in no way increased above 10%.

5) 20 grams of hydrogenated tannin were distilled under vacuum, with an equal quantity of solid sodium hydroxide. The usual yield of oils was obtained , and on acidification and ether extraction of the residual mass, nothing resulted.

6) 10 grams of hydrogenated tannin were added to 100 ml of 10% caustic soda, whereupon immediate solution occurred, and a few drops of oil were liberated on the surface. This oil on extraction with ether , proved to be similar in nature to that isolated from the water solution of the hydrogenation, and was probably adsorped on the surface of the hydrogenated tannin, when the latter was extracted from the bomb as a sticky mass. The alkaline solution of hydrogenated tannin was then refluxed in an atmosphere of nitrogen for three hours, after which it was steam distilled. The distillate consisted of pure water. Nothing was obtained on salting out and ether extraction, or by careful evaporation of a portion. Acidification of the flask contents with hydrochloric acid , precipitated the hydrogenated tannin again ,but nothing resulted on steam distillation ; the distillate being neutral to litmus.

It may therefore be concluded from the foregoing, that the hydrogenation product obtained,is probably only partly hydrogenated, since it's dissolving in 10% caustic soda , would indicate some residual phenolic character. Moreover, as will be shown later, the oils resulting from its destructive distillation, absorb more hydrogen on re-hydrogenation. This may however be due to the formation of ethylenic linkages during distillation viz.



This would happen if any tertiary alcohols were produced during the cracking process.

CHAPTER 10.

PRELIMINARY EXAMINATION OF THE OILS FROM THE CRACKING OF HYDROGENATED TANNIN.

Since the results of the preliminary examination of the Raney Nickel hydrogenated tannin just described, provided no indication that a further and more detailed examination of it would produce useful evidence as to the structure of wattle tannin, it was decided to disrupt this substance by destructive distillation. By this means it was anticipated that certain of the more elementary building units of the molecule might be obtained. After possible identification of these products, a less drastic degradation could be applied to the re-hydrogenated tannin, designed to produce larger fragments, which on analysis might show the manner of bonding between the elementary units.

With this end in view, 40 grams of the hydrogenated product already obtained, was placed in a Claisen flask with side arm packed with glass wool and saddles for fractionation of the liberated oil. Vacuum was applied using a Cenco Hyvac pump, and on the application of direct heat the substance was observed to melt and decompose with the liberation of the previously noted oils. The following rough fractions were collected.

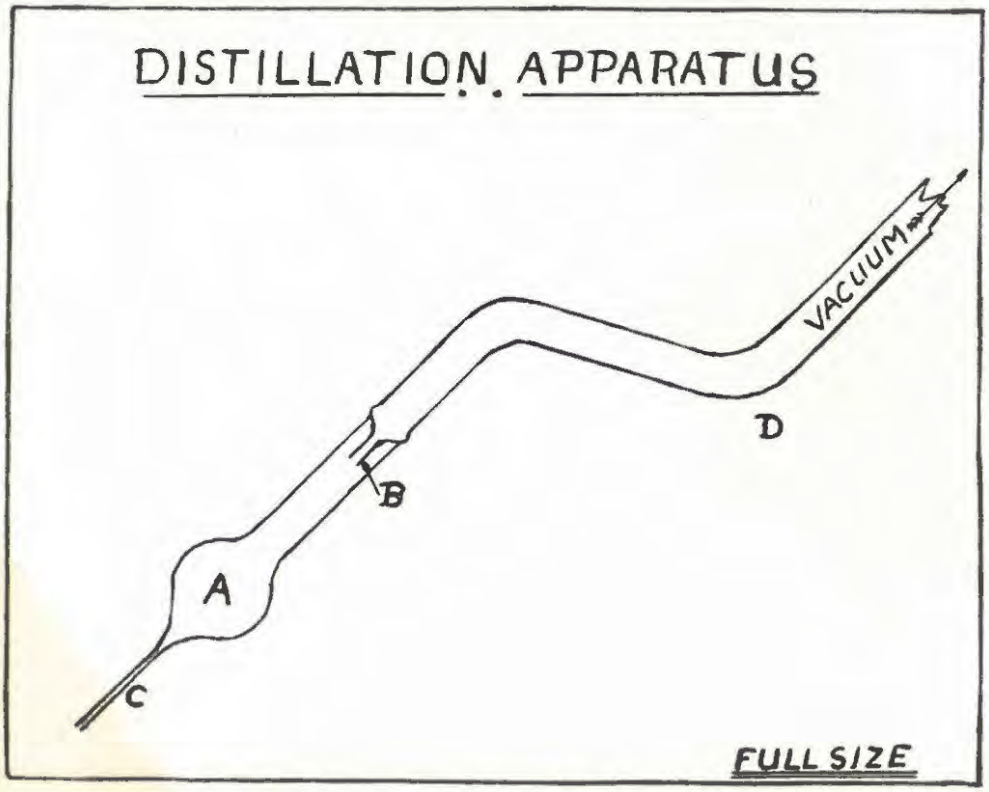
	Temperature.	Pressure.	Quantity.	Remarks.
1)	95-110°C	1 mm	1.4 ml	Colourless with main bulk at 110°C.
2)	128-145°C	2 mm	1.5 ml	Yellowish with sudden distillation at 128°C and fair quantity 140-145°C.
3)	175-190°C	2 mm	1.6 ml	Dark yellow-brown and resinous.

The highly carbonised residue was discarded.

These fractions all darkened considerably even when kept in sealed tubes in the dark. This may well be due to either, 1) polymerisation with the production of a dark resin or 2) absorption of oxygen by any partly saturated nuclei present. The probability of these nuclei being present is, as previously noted, fairly high.

The fractions were all found to be completely soluble in alcohol, ether, pyridine, dioxan and acetone, while benzene and petrol ether dissolved only the lowest boiling of the three.

Before examination, the fractions were all re-distilled in a semi-micro apparatus of the following design.



The fractions were drawn into bulb A of about 2 ml capacity through capillary C, which was then sealed. The apparatus was immersed up to neck B in a glycerol bath and Hyvac applied. On distillation, the oil collected at the bend D and was withdrawn with a capillary pipette.

By this means the same boiling point fractions were obtained, but this time each was colourless.

FRACTION I.

a) .0663 gram gave on combustion .1720 gram CO_2 and .0666 gram H_2O showing 70.8%C and 11.24%H.

b) The refractive index n^{25}_{D} was 1.489.

c) A micro - boiling point by the inverted capillary method, showed Boiling Point = 220°C (714 mm) with some darkening.

FRACTION II.

a) .0623 gram gave on combustion .1543 gram CO_2 and .0592 gram H_2O, showing 67.56%C and 10.62%H.

b) The refractive index n^{25}_{D} was 1.703.

FRACTION III.

a) .0639 gram gave on combustion .1740 gram CO_2 and .0564 gram H_2O , showing 74.4%C and 9.8%H.

b) The refractive index was too great to be measured on the scale of the instrument used.

The three fractions all decolourised bromine water, indicating the presence of unsaturated compounds. Since the boiling ranges were too wide to suggest the presence of any particular product, it was considered that any further treatment of the fractions as such would be valueless, without a preliminary re-hydrogenation.

On re-hydrogenation one might expect hydrogenolysis and complete saturation to occur, with the production of a number of definite compounds, and hence better definition of the boiling ranges of the fractions.

Re-Hydrogenation of Cracking Products of Raney Nickel Hydrogenated Tannin.

One hundred grams of hydrogenated tannin was decomposed in two portions as previously described, yielding 10 ml of a mixture of oils. By analogy with the work on lignin, these were re-hydrogenated over copper chromite in dioxan under the following conditions.

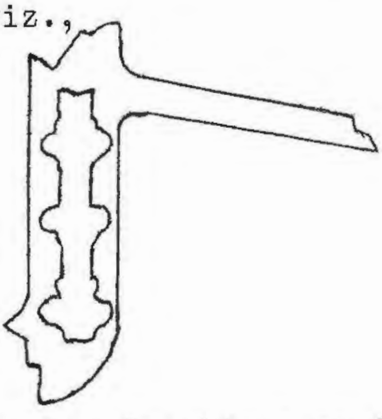
Experiment IV.

Substance.	10 ml of mixed oils.
Solvent.	100 ml of pure dry dioxan, prepared according to the method of Eisenberger, already described.
Pressure.	1700 lbs. per sq.in., rising to 2700 lbs. per sq.in. 1200 lbs. per sq.in. after reaction.
Catalyst.	7 grams Copper Chromite catalyst 39 KAF.
Temperature.	240°C.
Time.	7 hours.

The solution on removal from the bomb was very light yellow, whereas it was black and opaque when put in. It would thus appear that the oils became either de-polymerised or de-oxygenated, according to whichever alternative was the cause of their original darkening. Moreover, as is noted from the drop in pressure, a considerable additional amount of hydrogen was absorbed. After filtering off the catalyst, the solvent was removed under reduced pressure in a stream of CO_2, leaving about 10 ml of oils which gradually darkened again even when retained under vacuum and out of the light.

A certain amount of water was liberated during the reaction, as evidenced by the reaction of a few drops of solvent with anhydrous copper sulphate. An attempt was made to fractionate the solvent using a long column packed with porcelain saddles, but no sharp increases in boiling point were observed. The mixture started boiling at 80°C and the temperature rose steadily to 98.5°C (735 mm), as the azeotrope became richer in the second component.

Careful fractionation of the re-hydrogenated oils in a 25 ml Claisen flask fitted with small glass plates in the side arm viz.,



produced the following fractions on distillation using a glycerol bath.

	Boiling Point°C.	Pressure.	Quantity.	Combustion Analyses.		Remarks.
				%C	%H	
I.	55-80	1 mm	½ ml	71.15, 71.10,	10.12 10.11	Colourless, darkened, mobile.
II.	80-83	1 mm	1½ ml	69.98, 69.75,	9.38 9.29	Colourless, darkened, mobile.
III.	93-96	1 mm	1¼ ml	68.70, 68.55,	8.83 8.91	Viscous, darkened.
IV.	115-125	3 mm	2½ ml	68.71, 68.90,	8.15 8.26	Semi-solid, yellowish.
V.	140-150	3 mm	1½ ml	69.98, 69.97,	8.45 8.41	Solid, yellowish.
VI.	150-200	3 mm	2 ml	71.80, 72.10,	9.07 9.16	Solid, yellow-brown.

The boiling points recorded for fractions II and III, were on re-distillation in a semi-micro apparatus, while the remainder are those observed during fractionation.

Each of these portions was analysed by combustion to determine whether the percentages of carbon and hydrogen would correspond to those of various arbitrarily chosen empiric formulae. It was not expected that all the fractions would conform to a basis of the same number of carbon atoms, but rather that those of lower boiling points would contain less carbon atoms per molecular unit than the higher ones, as was found to be the case during the work on lignin.

The Combustion Analyses may be recorded in greater detail as follows:-

FRACTION I. 55-80°C (1 mm).

a) .0699 gram gave .1823 gram CO_2 and .0632 gram H_2O, showing 71.15%C and 10.12%H.

b) .0692 gram gave .1803 gram CO_2 and .0625 gram H_2O. showing 71.10%C and 10.11%H.

FRACTION II. 80-83°C (1 mm).

a) .0679 gram gave .1742 gram CO_2 and .0569 gram H_2O, showing 69.98%C and 9.38%H.

b) .0716 gram gave .1830 gram CO_2 and .0595 gram H_2O, showing 69.75%C and 9.29%H.

FRACTION III. 93-96°C (1 mm).

a) .0707 gram gave .1780 gram CO_2 and .0558 gram H_2O, showing 68.70%C and 8.83%H.

b) .0693 gram gave .1741 gram CO_2 and .0552 gram H_2O, showing 68.55%C and 8.91%H.

FRACTION IV. 115-125°C (3 mm).

a) .0717 gram gave .1806 gram CO_2 and .0552 gram H_2O, showing 68.71%C and 8.15%H.

b) .0694 gram gave .1753 gram CO_2 and .0501 gram H_2O, showing 68.9%C and 8.26%H.

FRACTION V. 140-150°C (3 mm).

a) .0717 gram gave .1839 gram CO_2 and .0542 gram H_2O, showing 69.98%C and 8.45%H.

b) .0725 gram gave .1859 gram CO_2 and .0545 gram H_2O, showing 69.97%C and 8.41%H.

FRACTION VI. 150-200°C (3 mm).

a) .0712 gram gave .1874 gram CO_2 and .0576 gram H_2O, showing 71.80%C and 9.07%H.

b) .0713 gram gave .1884 gram CO_2 and .0581 gram H_2O, showing 72.1%C and 9.16%H.

However not much success was encountered in trying to fit the data to empiric formulae, and as a result it must be concluded that the fractions obtained are in all probability azeotropes of closely related hydrogenation products.

The result of re-hydrogenation has therefore been to more clearly define the fractions obtained, probably owing to the production of a number of definite compounds, by further saturation of those only hydrogenated to intermediate stages. Darkening of the oils has been eliminated by re-hydrogenation, but on removal from the bomb this has again occurred.

CHAPTER 11.

FURTHER GENERAL PROPERTIES OF THE OILS OBTAINED FROM THE CRACKING OF HYDROGENATED TANNIN.

From the previous chapter it will be noted that an attempt to discover suitable empiric formulae for the various hydrogenation products obtained, did not meet with much success. It was thus considered that before possible characterisation of individual compounds could be attempted, further information as to the general properties of each fraction would have to be available.

To this end, therefore, it was decided that a knowledge of molecular weights in conjunction with combustion data would be particularly useful, and moreover that a study of the variation in hydroxyl content of the fractions, would serve to indicate the type of compound present i.e. whether a primary alcohol or a glycol etc. [illegible]?

Since the quantity of oils left over from the study of the effect of re-hydrogenation was insufficient for the above described purpose, most of the remaining bulk of the Raney Nickel hydrogenated tannin was accordingly disrupted in the manner previously noted, yielding 50 ml of brown viscous oils. These were re-hydrogenated in three separate portions under the conditions of Experiment IV. The catalyst and solvent were removed by filtration of the yellowish solution and distillation under reduced pressure in an atmosphere of carbon dioxide.

The combined yields from these three hydrogenations were then distilled on a glycerol bath under Hyvac, with the production of roughly the same fractions as recorded in the previous chapter. However since it is known that under vacuum fractionation, compounds may not exhibit the same boiling point on re-distillation, each fraction obtained was carefully re-distilled in a small Claisen flask.

The following table records the fractions obtained on re-distillation. The pressures were read from a small McLeod gauge.

	Boiling Point°C.	Pressure.	Quantity.	Remarks.
I.	25-49	4 mm	.5 ml	Colourless, mobile.
II.	52-57	1.4 mm	5.4 ml	Colourless, mobile.
III.	65-70	1 mm	6.4 ml	Colourless, mobile.
IV.	83-85	.6 mm	7.6 ml	Faint yellowish, semi-viscous.
V.	92-96	.6 mm	10.5 ml	Light yellow, viscous.
VI.	110-112	1 mm	5.5 ml	Orange, semi-solid.
VII.	150-200	3 mm	6.0 ml	Dark orange-brown resin.

In each case on re-distillation there was left as residue in the flask, a small amount of brown solid oil, very closely resembling Fraction VII above. Since the combustion analysis of this fraction is not very different from that of the others (Chapter 10), it is possible that it may not be a hydrogenation product at all, but a condensation polymer formed from the other fractions.

Attempted Freezing Out of the Fractions.

The fractions collected, were all kept in a refrigerator for over a month in an attempt to obtain crystals, but in no case was any change in nature observed.

Refractive Indices.

These were determined at 25.1°C for sodium light as described in Chapter 7. Measurements were made on two separate portions of each fraction.

	Fraction.	Portion 1.	Portion 2.	Mean $n_D^{25.1}$
I.	25-49°C(4mm)	1.4584 1.4584 1.4583	1.4585 1.4585 1.4583	1.4584
II.	52-57°C(1.4mm)	1.4738 1.4737 1.4737	1.4739 1.4741 1.4740	1.4738
III.	65-70°C(1mm)	1.4907 1.4907 1.4907	1.4906 1.4907 1.4907	1.4907
IV.	83-85°C(.6mm)	1.5072 1.5071 1.5071	1.5071 1.5071 1.5071	1.5071
V.	92-96°C(.6mm)	1.5267 1.5267 1.5267	1.5269 1.5269 1.5269	1.5268
VI.	110-112°C(1mm)	1.5365 1.5365 1.5365	1.5366 1.5365 1.5364	1.5365
VII.	150-200°C(3mm)	was too dark in colour for measurement.		

Molecular Weights.

The molecular weights of the fractions were determined by depression of freezing point in dioxan solution, using the method of graphical extrapolation described in Chapter 7.

The results obtained were as follows.

FRACTION II. 52-57°C (1.4 mm).

a) .1995 gram gave a depression of .317°C (mean of .317, .317, .317, .316, from graph).

Whence Molecular Weight = 113.5.

b) .3276 gram gave a depression of .512°C (mean of .512, .513, .512, .512, from graph).

Whence Molecular Weight = 115.0.

FRACTION III. 65-70°C (1 mm).

a) .1325 gram gave a depression of .181°C (mean of .181, .181, .182, .181, from graph).

Whence Molecular Weight = 131.8.

b) .2800 gram gave a depression of .390°C (mean of .390, .390, .390, .389, from graph).

Whence Molecular Weight = 129.2.

FRACTION IV. 83-85°C (.6 mm).

a) .1981 gram gave a depression of .257°C (mean of .258, .257, .257, .257, from graph).

Whence Molecular Weight = 139.0.

b) .4193 gram gave a depression of .539°C (mean of .539, .540, .539, .539, from graph).

Whence Molecular Weight = 140.0.

FRACTION V. 92-96°C (.6 mm).

a) .1861 gram gave a depression of .228°C (mean of .228, .229, .228, .228, from graph).

Whence Molecular Weight = 147.0.

b) .3425 gram gave a depression of .415°C (mean of .416, .416, .414, .414, from graph).

Whence Molecular Weight = <u>148.7.</u>

<u>FRACTION VI.</u> 110-112°C (1 mm).

a) .2552 gram gave a depression of .255°C (mean of .255, .256, .255, .255, from graph).

Whence Molecular Weight = <u>180.0.</u>

b) .4637 gram gave a depression of .465°C (mean of .466, .465, .464, .464, from graph).

Whence Molecular Weight = <u>179.0.</u>

<u>FRACTION VII.</u> 150-200°C (3 mm).

a) .2523 gram gave a depression of .215°C (mean of .215, .215, .215, .214, from graph).

Whence Molecular Weight = <u>218.5.</u>

b) .4870 gram gave a depression of .411°C (mean of .411, .410, .411, .412, from graph).

Whence Molecular Weight = <u>214.0.</u>

<u>Combustion Analyses.</u>

The fractions were each analysed by combustion in order to obtain data which could be used in conjunction with the above determined molecular weights, to ascertain the number of carbon atoms per molecular unit.

<u>FRACTION I.</u> 25-49°C (4 mm).

.0691 gram gave .1754 gram CO_2 and .0710 gram H_2O, showing 69.1%C and 11.4%H.

<u>FRACTION II.</u> 52-57°C (1.4 mm)

.0742 gram gave .1930 gram CO_2 and .0723 gram H_2O, showing 71.0%C and 10.8%H.

FRACTION III. 65-70°C (1 mm).

.0705 gram gave .1763 gram CO_2 and .0615 gram H_2O, showing 68.2%C and 9.69%H.

FRACTION IV. 83-85°C (.6 mm).

.0729 gram gave .1827 gram CO_2 and .0629 gram H_2O, showing 68.3%C and 9.59%H.

FRACTION V. 92-96°C (.6 mm).

.0704 gram gave .1783 gram CO_2 and .0574 gram H_2O, showing 69.1%C and 9.07%H.

FRACTION VI. 110-112°C (1 mm).

.0702 gram gave .1815 gram CO_2 and .0549 gram H_2O, showing 70.5%C and 8.68%H.

FRACTION VII. 150-200°C (3 mm).

.0694 gram gave .1828 gram CO_2 and .0569 gram H_2O, showing 71.9%C and 9.11%H.

Determination of the Percentage OH Groups of the Fractions Obtained.

The quantity of oils available did not permit of the preparation and isolation of an acetyl derivative of each, followed by a separate hydrolysis experiment. Moreover, the necessary distillation involved before hydrolysis of such a derivative might lead to unwanted complication in the formation of ethylenic linkages, thus causing inaccuracy in the determination.

Literature concerning the determination of percentage OH groups on a reduced scale was therefore consulted (46,47,48,49), and the method finally adopted was that of Adkins, Frank and Bloom (46) with a number of modifications introduced by the author.

Between .15 and .3 gram of the oil was weighed out into a glass phial with a long neck, made by drawing out a 1.5cm x 11cm test tube in a hot flame. Two grams of a mixture of one part of pure acetic anhydride and seven parts of pure anhydrous pyridine, was introduced from a weight burette inserted as far as possible into the neck of the phial, to prevent splashing and evaporation. The phial was then sealed by directing a point flame at the centre of the long neck and drawing it out, thus preventing condensation of moisture from the flame in the phial itself.

The sealed tube was then heated for nine hours or longer in boiling water. It was then opened and the contents washed out into a flask with cold distilled water. The mixture, on top of which the acetyl derivative floated, was titrated with .2N sodium hydroxide solution using phenolphthalein as indicator. The difference between this titre and that of a blank portion of the acetic anhydride - pyridine mixture, represents the equivalent of acetic acid used for acetylation, from which the percentage acetyl groups may be calculated.

The method described in the original paper, advocates the use of ground glass stoppered tubes for the acetylation and claims an accuracy of 1%, but it was found by the author that this procedure was inefficient owing to the oozing out of acetic anhydride during digestion on an oil bath. By using sealed ampules, an accuracy of .6% was consistently obtained for an alcohol such as cyclohexanol (i.e. a result of 29.85% acetyl groups as against 30.04% calculated).

Further, the original paper recommends addition of the acetylation mixture from a pipette, but it was considered more accurate to weigh out such a small quantity of substance from a weight burette. The digestion time of four hours advocated, was found to be insufficient for full acetylation; a minimum of nine hours being required for cyclohexanol. By a series of trial experiments it was found unnecessary to digest the blanks before titration.

Determination of the Blank Titres for the Acetylation Mixture.

The pyridine was made anhydrous by double distillation and standing over solid potassium hydroxide. A mixture of 105 grams of pyridine with 15 grams of acetic anhydride was then made and weighed out in six portions for titration with .2151 normal NaOH, previously standardised against Acid Potassium Phthalate and Hydrochloric Acid.

a) 2.0474 grams mixture required 23.7ml .2151N NaOH.
b) 2.0285 " " " 23.5ml " "
c) 2.1263 " " " 24.6ml " "
d) 1.9463 " " " 22.54ml " "
e) 1.9708 " " " 22.8ml " "
f) 2.0474 " " " 23.7ml " "

The ratio of Volume to Weight calculated for each was:-

a) 11.57
b) 11.58
c) 11.57
d) 11.58
e) 11.57
f) 11.57

The mean factor of 11.57 was thus used in all determinations, for calculation of the blank titre for any weight of the acetylation mixture.

Determination of the Percentage Acetyl Groups for Each Fraction.

Note. All fractions were digested with the acetylation mixture for sixteen hours at 98°C during a period of three days. This time was considered sufficient since a portion of the high boiling point Fraction V, showed no increase in %Ac on acetylation for thirty hours at 98°C.

FRACTION II. 52-57°C (1.4 mm).

.2224 gram substance were digested with 2.1348 gram Ac_2O-Py mixture. Volume .2151N NaOH required after acetylation = 16.87 ml.

Blank titre = 11.57 x 2.1348 = 24.70 ml.

Equivalent of .2151N acetic acid used = 24.7-16.87
= 7.83 ml.

$$\%Ac = \frac{7.83 \times .2151 \times 43.04}{1000 \times \left(.2224 + \frac{7.83 \times .2151 \times 42.03}{1000}\right)} = \underline{\underline{24.73\%.}}$$

FRACTION III. 65-70°C (1 mm).

.2087 gram substance were digested with 2.0616 gram Ac_2O-Py mixture. Volume .2151N NaOH required after acetylation = 16.25 ml.

Whence %Ac groups = 25.36%.

FRACTION IV. 83-85°C (.6 mm).

.2631 gram substance were digested with 2.1101 gram Ac_2O-Py mixture. Volume .2151N NaOH required after acetylation = 16.35 ml.

Whence %Ac groups = 23.38%.

FRACTION V. 92-96°C (.6 mm).

.2151 gram substance were digested with 2.0733 gram Ac_2O-Py mixture. Volume .2151N NaOH required after acetylation = 16.20 ml.

Whence %Ac groups = 25.24%.

FRACTION VI. 110-112°C (1 mm).

.2459 gram substance were digested with 2.1301 gram Ac_2O-Py mixture. Volume .2151N NaOH required after acetylation = 16.45 ml.

Whence %Ac groups = 23.70%.

FRACTION VII. 150-200°C (3 mm).

.2328 gram substance were digested with 2.3173 gram Ac_2O-Py mixture. Volume .2151N NaOH required after acetylation = 18.5 ml.

Whence %Ac groups = 24.97%.

Calculation of the Number of OH Groups per Molecular Unit of the Fractions Obtained.

In order to gain some further indication of the type of compound present, a calculation was made of the number of OH groups per molecular unit, on the basis of the molecular weights already determined.

In tabular form.

	Fraction.	%Ac Groups.	Mean Molecular Wt. Found.	No. of OH Groups per Molecule.
II.	52-57°C	24.73	114.25	.865
III.	65-70°C	25.36	130.5	1.02
IV.	83-85°C	23.38	139.5	.982
V.	92-96°C	25.24	147.8	1.15
VI.	110-112°C	23.70	179.5	1.29
VII.	150-200°C	24.97	216.25	1.66

For the sake of comparison, some actual figures determined for cyclohexanol are given:-

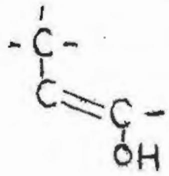
.2370 gram cyclohexanol were digested with 2.0734 gram Ac_2O-Py mixture of blank factor 11.68 for 9 hours. After acetylation 13.44 ml of .2151N NaOH were required to neutralise.

Whence %Ac groups = <u>29.85</u> (30.04 Calculated).

Molecular weight of cyclohexanol = 100.16.

Whence No. of OH groups per molecular unit = <u>.97.</u>

Discussion.

An examination of the results obtained for the variation in hydroxyl content is not particularly enlightening, and would indicate that owing to the formation of various unsaturated links through the elimination of water during distillation, the hydroxyl content of each fraction is largly distorted. Further, if such groupings as  were present, these would probably ketonise and not undergo acetylation.

It is moreover still not possible to assign empiric formulae to the compounds obtained, probably as a result of the presence of unsaturated groups.

The foregoing results may, for the sake of clarity, be presented in the following tabular form. (See overleaf).

TEMPERATURE.	PRESSURE.	MEAN REFRACTIVE INDEX $n_D^{25.1}$	MOLECULAR WEIGHT.	MEAN MOLECULAR WEIGHT.	QUANTITY.	REMARKS.	%AC.	NO. OF OH GRPS/MOL. USING M.WT. FOUND.	COMBUSTION ANALYSIS.
25-49°C	4mm	1.4504	--	--	.5ml	Colourless mobile oil.	--	--	69.1%C 11.4%H
52-57°C	.14cm	1.4730	1)113.5 2)115	114.25	5.4ml	Colourless mobile oil.	24.73%	.865	71.0%C 10.8%H
65-70°C	1mm	1.4907	1)131.8 2)129.2	130.5	6.4ml	Colourless, mobile.	25.36%	1.02	68.2%C 9.69%H
83-85°C	.06cm	1.5071	1)139 2)140	139.5	7.6ml	Very faint yellowish, semi-viscous.	23.38%	.982	68.3%C 9.59%H
92-96°C	.06cm	1.5260	1)147 2)148.7	147.8	10.5ml	Light yellow, viscous.	25.24%	1.15	69.1%C 9.07%H
110-112°C	1mm	1.5365	1)180 2)179	179.5	5.5ml	Orange, semi-solid.	25.70%	1.29	70.5%C 8.68%H
150-200°C	3mm	--	1)218.5 2)214.0	216.25	6.0ml	Dark orange-brown resin.	24.97%	1.66	71.9%C 9.11%H

CHAPTER 12.

TREATMENT OF THE INDIVIDUAL FRACTIONS.

A - The Low Boiling Point Oils Produced in the Raney Nickel Hydrogenation of Tannin.

It will be recalled from Chapter 9 that after hydrogenation of tannin over Raney Nickel, a few drops of pleasant smelling oil were observed floating on the surface of the water solvent. During the preparation of a quantity of Raney Nickel hydrogenated tannin, the water washings were therefore conserved after each hydrogenation. Two litres of a faintly yellowish solution were collected and saturated with common salt, whereupon the oil floated to the surface. On extraction of portions with ether and after drying of the extracts over freshly baked anhydrous sodium sulphate, there were obtained on evaporation of the ether, 5 ml of a pleasant smelling, yellowish, oily liquid, from the processing of 1½ kilograms of tannin.

On distillation this exhibited a boiling point of 92°C and became colourless. Litmus gave a strongly acidic reaction with the oil, and as a result an attempt was made to effect a separation of the acid present.

Two and a half grams were accordingly shaken with 100 ml water containing 9 grams sodium bicarbonate, for 2½ hours. After testing the solution for alkalinity, it was extracted three times with an equal volume of ether. The ether extracts were colourless and after drying over baked sodium sulphate, gave on evaporation 1 ml of a colourless oil which was neutral to litmus and smelt like an ester.

The aqueous solution was then taken to dryness on a water bath. The contents of the dish were then exactly neutralised with 5N H_2SO_4, 5% excess acid being added. After cooling and ether extraction there was obtained 1 ml of a faintly yellowish oil with a pungent odour and strongly acidic to litmus.

A separation into an acidic and a non-acidic portion was thus effected.

Acid Portion.

One drop of the acidic portion was shaken with ½ ml water, one drop of 6N NH_4OH and one drop of .2N $AgNO_3$ were added, and on warming the alkaline solution, black silver was deposited indicating the probable presence of FORMIC ACID, which was also evidenced by smell. The Boiling Point was 78°C (720 mm) as determined by the inverted capillary method.

Non-Acid Portion.

The Boiling Point was taken as above and found to be 73°C (720 mm). As this smelt like an ester, an attempt was made to hydrolyse it.

.2588 gram were boiled under reflux for 1 hour with 53.9 ml of .1001N alcoholic potash. After hydrolysis, 38.15 ml of .1216N HCl were required to neutralise, giving as a value for the Equivalent Weight 340. This figure is extraordinarily high considered in relation to the boiling point, but may be due to the presence of non ester-like impurities.

The solution from the hydrolysis was made alkaline and evaporated to dryness. On acidification and ether extraction, there was obtained $\frac{1}{2}$ ml of a yellowish and strongly acidic oil which smelt of Formic and some other higher acid.

In order to further examine the properties of these yellowish oils, an attempt was made to fractionally distil both the acid and non-acid portion, and also the remaining mixture. Unfortunately the last traces of each exploded violently, blowing the apparatus to pieces and destroying the oil. The cause of the explosion was later ascertained to be due to the presence of peroxides in the ether used for extraction purposes.

B - Examination of Fraction II. 52-57°C (1.4 mm).

The general properties of this fraction recorded in the foregoing chapter seemed to suggest the presence of cyclohexanol.

(Cyclohexanol. Boiling Point 53-54°C (1 mm), n_D^{25} = 1.4650, 71.9%C and 12.07%H, Molecular Wt. 100.16, Freezing Point 23°C).

(Fraction II. Boiling Point 52-57°C (1.4 mm), n_D^{25} = 1.4738 (note: Fraction I. n_D^{25} = 1.4584), 71.0%C and 10.8%H, Molecular Wt. 114).

The properties of cyclohexanol, it will be noted, are therefore vaguely intermediate between those of the very small Fraction I and those of Fraction II.

However it was realised that Fraction II was highly impure, and as a result an attempt was made to isolate its phenyl-urethan (50) for fractional crystallisation purposes.

A small quantity was dehydrated by dissolving in ether and standing over baked anhydrous sodium sulphate for 48 hours. On evaporation of the ether under suction, the oil crystallised but later melted. Concurrently with this process some distilled ligroin, containing one drop of triethylamine catalyst per ml, was dehydrated over anhydrous sodium sulphate.

About .2 gram of the dehydrated oil was then introduced into a glass phial with a long neck, made by drawing out the lower half of a test tube. 3 ml of the ligroin - catalyst mixture, and 6 drops of phenylisocyanate were then added, and the phial sealed by drawing out the long neck from the centre in order to prevent condensation of moisture from the flame in the tube.

The whole was then heated in the vapours of refluxing methanol for $\frac{1}{2}$ hour, after which it was cooled in ice. From the mixture an oily sludge and a quantity of crystals separated. The crystals were found to be diphenylurea, while vacuum distillation of the sludge in a small glass tube,failed to produce any crystals other than diphenylurea. Repeated attempts to isolate crystals failed even with the most stringent precautions taken against entry of water.

This behaviour with phenyl-isocyanate would appear to indicate the presence of a tertiary alcohol in Fraction II (50).

Since the isolation of a solid phenylurethan of this fraction was not possible, it was considered likely that on acetylation and fractionation of the product, there might be obtained an acetyl derivative of sufficient purity to permit of hydrolysis and subsequent preparation of a urethan from the oil so liberated.

.3 gram of Fraction II was therefore acetylated by heating at 98°C for nine hours in a sealed tube, with 2 ml of a mixture of 7 parts of anhydrous pyridine to 1 of acetic anhydride. The product resulting from this was removed from the reaction mixture by pouring the whole into water and extracting with ether. On evaporation of the ether there was obtained .25 ml of a yellow oil smelling strongly of cyclohexanol acetate. This was drawn into a glass tube with a small bulb blown at one end. After sealing, this was distilled under Hyvac by placing the bulb into a hole drilled in a brass block which was slowly heated with a small flame. The temperature was read by means of a thermometer inserted into another hole in the block.

On careful distillation, a colourless oil distilled at 93°C (3 mm) but no further fractions were observed. Thus no separation of acetyl derivatives has been accomplished, and further, the oil obtained decolourised

bromine water, indicating the presence of double bonds.
On combustion,

a) .0721 gram gave .1777 gram CO_2 and .0547 gram H_2O, showing 67.1%C and 8.43%H.

b) .0457 gram gave .1121 gram CO_2 and .0338 gram H_2O, showing 67.0%C and 8.20%H.

(Cyclohexanol Acetate - 67.5%C and 9.86%H).

Two possibilities are therefore indicated.

1) That the fraction is a mixture of cyclohexanol and various cyclohexenols.
2) That the fraction may contain cyclohexanol and a tertiary alcohol, as suggested by the attempted urethan preparation. A likely tertiary alcohol would be 1-Methyl Cyclohexanol whose properties also vaguely conform to those of Fraction II, and whose acetate boils at the same temperature as cyclohexanol acetate. In the event of a tertiary alcohol such as 1-Methyl Cyclohexanol being present, the presence of 1-Methyl Cyclohexene is also likely as a result of distillation processes.

If as suggested under 1), the only impurities are cyclohexenols, then a low temperature and low pressure hydrogenation over a platinum or palladium catalyst, might offer a solution to the problem.

C - Examination of Fraction 1V. 83-85°C (.6 mm).

1) Preparation of an Acetyl Derivative.

An acetate of this fraction was also prepared in an attempt to cause separation of the components by distillation of the product.

.3 gram of the acetate gave on distillation,
a) about 4 drops of colourless oil at 87-89°C (3 mm)and
b) about .2 gram of colourless oil at 93-94°C (3 mm).
Portion b) smelt like an ester and on combustion,
.0690 gram gave .1711 gram CO_2 and .0492 gram H_2O,
showing 67.66%C and 8.16%H.
.0722 gram gave .1793 gram CO_2 and .0530 gram H_2O,
showing 67.62%C and 8.22%H.

However both portions a) and b) decolourised bromine water, so that not much can be inferred from the above results.

2) Oxidation with Neutral Permanganate.

One gram of the fraction was added to 75 ml of 10% potassium permanganate solution, causing immediate reduction of the latter. The beaker was cooled in ice and mechanically stirred for 10 hours, after which stirring was continued for a further 5 hours at room temperature. After filtration, sodium bisulphite crystals were added until the permanganate colour was destroyed. The solution was warmed and again filtered. 1 ml of N NaOH was added to make alkaline. After evaporation to dryness, 20 ml of 6N H_2SO_4 were added and the mixture extracted twice with 20 ml of ether. The extracts, which were acid to litmus, were filtered and dried over baked anhydrous sodium sulphate. On evaporation of the ether, some solid whitish crystals were obtained, and also about .2 gram of yellowish oil.

The crystals were soluble in ethanol, water and methanol, but recrystallised best from water. A melting point determination showed 188°C for the crystals, which are therefore in all probability, SUCCINIC ACID.

The yellowish oil was removed from the remaining few crystals, by means of a small pipette, stuffed at one end with cotton wool. After sealing of the end, the oil was distilled by the usual method , using a brass block with thermometer inserted.

A colourless oil of Boiling Point 86-94°C (3 mm), was obtained and analysed by combustion.
.0344 gram gave .0700 gram CO_2 and .0252 gram H_2O, showing 55.5%C and 8.14%H.

3) Separation of Fraction IV into Two Components.

On the addition of 2 drops of 40% NaOH solution to 1 drop of Fraction IV, the latter darkened considerably , probably due to the oxidation of some phenolic substance still present in the oil.

2 grams of Fraction IV were therefore taken up in 25 ml of ether and shaken with 25 ml of 40% NaOH. The aqueous layer went black, while the ether layer remained only faintly coloured . On standing

overnight, three layers formed.

1) A light yellow ether layer on top.

2) A small black layer of oily sludge.

3) The dark brown 40% NaOH layer.

These three were separated and treated as follows.

Layer 1.

The ether layer was filtered, and on evaporation under suction, some crystals were obtained which later melted leaving 1 ml of a brownish oil.

On distillation this boiled at 90-93°C (3 mm).

The refractive index determined was $n_D^{25} = 1.4983$.

On combustion:-

a) .0716 gram gave .1896 gram CO_2 and .0678 gram H_2O, showing 72.1%C and 10.5%H.

b) .0686 gram gave .1807 gram CO_2 and .0636 gram H_2O, showing 71.8%C and 10.3%H.

Two drops of this portion however still decolourised bromine water.

Layer 2.

On distillation the whole set solid, probably due to some caustic soda being present, while about 4 drops of slightly yellowish oil distilled over between 95-110°C (3 mm). The mass then darkened and carbonised.

The refractive index determined was $n_D^{25} = 1.4833$.

On combustion:

.0647 gram gave .1558 gram CO_2 and .0611 gram H_2O, showing 65.6%C and 10.5%H.

One drop of this portion decolourised $\frac{1}{4}$ ml bromine water.

One drop of each of portions 1 and 2 was dissolved in a small quantity of ether on a watch glass, and $\frac{1}{2}$ ml 40% NaOH added. No further darkening was evidenced.

4) Oxygenation of Fraction IV.

One half gram of this fraction was continuously oxygenated for 30 hours by bubbling in oxygen from a cylinder. This was in order to ascertain whether the darkening noted in all fractions including IV, could be due to oxidation of partly saturated nuclei present. No darkening was evidenced from this procedure.

CHAPTER 13.

CRITICISM OF RESULTS OF THE HYDROGENATION OF TANNIN OVER RANEY NICKEL.

It is evident first and foremost, that the use of water as a solvent for the Raney Nickel hydrogenation of tannin is unsuitable, since the hydrogenated tannin obtained from the reaction is insoluble in it. It may be inferred from the fact that a large amount of carbonised material occurs together with the hydrogenated tannin, that as soon as the reaction has proceeded to a certain degree of saturation, the product precipitates out of solution and becomes carbonised on the side of the reaction liner. This latter, being made of brass, acts to a certain extent as a de-hydrogenator owing to the presence of copper, which is notable in this respect.

Although it is not to be expected that the product from the Raney Nickel - water hydrogenation would be fully saturated, nevertheless a study of its cracking products, especially after re-hydrogenation, might be expected to give some evidence as to the elementary building units present in the tannin molecule.

Further, the results have indicated that the cracking process employed has been somewhat too drastic, in that great difficulty has arisen owing to the formation of numerous degradation products which are so closely related as to form almost inseparable azeotropes. In addition, owing to the vigorous conditions used, these substances have formed ethylenic linkages, thus giving a mixture of saturated and partly saturated compounds. The whole investigation has moreover been hampered by the lack of specially designed and highly efficient fractionating columns employed in the work on lignin.

As improvements on the preliminary results obtained by Stephen (1) and summarised in Chapter 9, may be noted:

1) That owing to the sensitive nature of the hydrogenation reaction, the conditions of the process have been standardised.

2) That all fractions have been re-hydrogenated and re-distilled, before any attempt at the preparation of derivatives has been made.

3) That the preparation and isolation of acetyl derivatives with a subsequent hydrolysis to determine the percentage acetyl groups, has been deemed inadvisable owing to the increased possibility of the formation of double bonds on necessary distillation.

4) That whereas the combustion data obtained by Stephen were placed on a C_{15} basis used for tannin itself, determinations of the molecular weights of the fractions obtained, have shown this to be an erroneous procedure.

It is suggested that a low temperature and low pressure re-hydrogenation of the fractions over platinum or palladium, might prove profitable before attempted characterisation of the products. Further, that by analogy with the work on lignin, a dehydration of the highest boiling point resin (Fraction VII) with oxalic acid at 400°C, and subsequent re-hydrogenation over Raney Nickel, might lead to the production of hydrocarbons, whose analytical data might show the presence of certain larger fragment of the tannin molecule, containing perhaps 15 or more carbon atoms per molecular unit.

CHAPTER 14.

FURTHER HYDROGENATIONS OF TANNIN.

On consideration of the process involved in the cracking of the Raney Nickel hydrogenated tannin under the conditions previously described, it will be noted that when disruption of a single carbon to carbon bond occurs, the valencies become stabilised by the formation of a double bond. If full saturation is to be maintained then the two valency bonds must be satisfied by the addition of two hydrogen atoms. For this reason it was considered that if cracking of the hydrogenated tannin could be accomplished under an atmosphere of hydrogen in the bomb during an actual hydrogenation, then a series of fully saturated products might be obtained. Further, if the correct solvent were used, then the wasteful process involving enormous carbonisation with only a 10% yield of oils,would be obviated, since no opportunity for carbonisation by precipitation of the partly hydrogenated product out of solution, would occur.

Since the partly hydrogenated tannin already obtained was soluble in alcohol and also the oils, this solvent was considered likely to be suitable. In addition,since the effect of temperature and not only the type of catalyst chosen, seemed to influence the cracking process, it was decided to employ a temperature higher than the 200°C at which the partly hydrogenated tannin had been formed.

Experiment V was accordingly performed under the following conditions.

Experiment V.

Substance.	50 gram of the partly hydrogenated tannin already obtained, and previously dried.
Solvent.	400 ml absolute ethanol.
Pressure.	2400 lbs. per sq.in.,rising to 3½ Tons per sq.in.
Catalyst.	24 gram of Raney Nickel.
Temperature.	300°C.
Time.	24 hours continuous.

No water was thus present in the reaction mixture.

From this hydrogenation only pure carbon and pure water were obtained. It must therefore be concluded that the alcohol had been hydrogenated to ethane or some higher hydrocarbon and water, thus leaving the hydrogenated tannin without any solvent and free to carbonise on the walls of the liner. This was also evidenced by the enormous increase in pressure noted.

The following solvents may therefore be considered of no use in combination with Raney Nickel at 300°C.

Water. Since as soon as the tannin becomes partly hydrogenated,it precipitates out of solution and becomes carbonised.

Alcohol. Since this undergoes hydrogenolysis to hydrocarbons and water.

Dioxan. Since Raney Nickel and Dioxan explode above 200°C.

As a result of the foregoing conclusion, two alternatives appear to be indicated.

1) The use of a catalyst other than Raney Nickel to cause hydrogenation of the tannin and disruption into oils.

2) The use of Raney Nickel with a suitable solvent (such as absolute ethanol or dioxan) at a lower temperature than 300°C.

Of the two alternatives, the former was preferred. Since the ultimate aim was to cause hydrogenolysis and also complete saturation of the partly hydrogenated tannin, Copper Chromite was chosen as it is more specific towards hydrogenolysis than Raney Nickel.

A suitable solvent was considered to be pure dry Dioxan, as this dissolves both the hydrogenated tannin and the cracking oils.

Experiment VI.

Substance.	20 gram of dry, partly hydrogenated tannin.
Solvent.	200 ml of pure dry Dioxan.
Pressure.	2400 lbs. per sq.in., rising to 5300 lbs. per sq.in.
Catalyst.	10 gram Copper Chromite.
Temperature.	300°C.
Time.	12 hours continuous.

The solution after removal from the reaction liner and filtration to separate the catalyst, was light yellow in colour, whereas it was black when introduced into the bomb. Moreover, the appearance of the solution was similar to that of a solution of the cracking oils in dioxan. In addition the absence of carbonisation showed the solvent to be suitable.

The solvent was evaporated off under reduced pressure in a stream of carbon dioxide, and on examination by fractional distillation was found to contain only water (probably from hydrogenolysis) and dioxan.

There was left in the flask about 10 ml of a viscous golden brown oil which gradually darkened to black. On distillation at 2 mm pressure with a glycerol bath this gave a series of oils from 95-250°C, the first portions colourless and the latter golden brown exactly as before. A small charred residue was left in the flask. This may be some hydrogenated tannin not completely broken down, owing to the short reaction time.

Thus tannin which has previously been partly hydrogenated over Raney Nickel in water at 200°C, may be broken down into a mixture of oils (Boiling Point 95-250°C - 2mm), over Copper Chromite catalyst at 300°C and 350 atmospheres pressure of hydrogen. Yield 50% by weight in 12 hours.

Unfortunately the mixture of these oils decolourised bromine water, showing that although Copper Chromite has caused hydrogenolysis of the macro-molecule, it has still not been able to fully saturate the partly hydrogenated aromatic nuclei present. If on the other hand, full saturation did occur, then the double bonds must have been formed on distillation.

The process of obtaining the oils by hydrogenation of tannin over Raney Nickel followed by hydrogenolysis over Copper Chromite, was considered unnecessarily tedious and also wasteful in view of the first stage involved. Experiments were therefore planned in an attempt to obtain the oils direct from tannin itself, using Copper Chromite.

For this purpose it became necessary to find a solvent which would dissolve the tannin, the partly hydrogenated tannin and the oils from the cracking. Pure dry dioxan, although capable of dissolving the two latter, was unable to dissolve the tannin. After a number of experiments it was found that a solution containing 92% of dry dioxan and 8% of water, was the maximum strength in dioxan which would dissolve 20% of its weight of tannin, of partly hydrogenated tannin and of the oils.

Experiment VII was therefore conducted under the following conditions.

Experiment VII.

Substance.	40 gram of tannin,dried and freed of acetone.
Solvent.	200 ml of 92% Dioxan.
Pressure.	2300 lbs. per sq.in.,rising to 3100 lbs. per sq.in. and decreasing to 2400 lbs. per sq.in. in 3 hours, remaining constant at 2400 lbs. per sq.in. for 17 hours.

Catalyst. 15 gram Copper Chromite.

Temperature. $300^{\circ}C$.

Time. 20 hours continuous.

The solution after removal from the bomb was again light yellow, whereas it was black when introduced (see Experiment VI). The solvent was found, after removal of the catalyst and fractionation, to contain only water from hydrogenolysis and dioxan.

There was left after removal of the solvent, 40 gram of a brown viscous sludge which darkened to a black colour. On combustion:

.0661 gram gave .1492 gram CO_2 and .0384 gram H_2O, showing 61.6%C and 6.45%H.

On determination of the molecular weight by depression of freezing point in pure dioxan, as previously described,

a) .3151 gram gave a depression of .210°C (mean of .210, .210, .210 from graph).

Whence Molecular Weight = 270.

b) .4654 gram gave a depression of .301°C (mean of .301, .301, .301 from graph).

Whence Molecular Weight = 278.

On distillation of this substance under vacuum on a glycerol bath, some oils were liberated between 87-230°C (3 mm), leaving a black sludge which on further strong heating liberated more oils, and left a carbonised residue.

The result of this final hydrogenation is most encouraging since when consideration of its molecular weight is taken into account with the fact that some oils are present, as shown on distillation, it may be concluded either:-

1) That the tannin has largely been broken into elementary units (mean molecular weight 160), while some of the larger molecular units still remain (mean molecular weight 1800 (35)). Or

2) That the tannin has all been converted to units of molecular weight 274, which are easily split to a certain extent by vacuum distillation on a glycerol bath; the remainder of the molecular weight 274 units forming ethylenic links and condensing into a polymer which requires stronger heat for decomposition.

It may be noted that using a C_{15} basis as generally ascribed to tannin, a substance of empiric formula $C_{15}H_{19}O_6$ (molecular weight 295) would require 61.01%C and 6.485%H. Since the empiric formula generally used for tannin is $C_{15}H_{15}O_6$, the product obtained may have resulted from the reaction of each molecular unit with 4 atoms of hydrogen. This however is unlikely, even though Copper Chromite is not specific towards the saturation of aromatic rings. Consequently alternative 1 is to be preferred.

CHAPTER 15.

SUMMARY AND FURTHER MODES OF RESEARCH NECESSARY.

The preliminary section of this thesis will be found to include a dissertation on the chemistry of wattle tannin, followed by a summary of the general principles underlying the high pressure catalytic hydrogenation method. The results of the hydrogenation of lignin - a compound related to tannin in general properties - are presented, together with a discussion concerning the purification of the wattle tannin used as raw product.

The hydrogenation method has been applied to wattle tannin with the production of a black, amorphous, partly hydrogenated tannin, using Raney Nickel as catalyst. This has on destructive distillation yielded a mixture of high boiling point oils, the properties of which have been investigated after re-hydrogenation, by the usual techniques of organic chemistry. An examination of the results obtained has however indicated, that the use of water as a solvent for the reaction is unsuitable, and moreover that the process of destructive distillation employed has been too drastic, producing a number of unsaturated compounds.

The use of Copper Chromite as a catalyst for the hydrogenation of tannin in dioxan solution, has been shown to be more advantageous than the procedure just described, in that the oils have been obtained in certain proportion, by less drastic measures involving less chance of modification of the products.

Emphasis must be laid on the necessity of obtaining pure tannin as a starting product. Owing to the sensitive nature of the hydrogenation reaction, the presence of the slightest traces of impurities in the form of the non-tan constituents of the raw material, might so considerably modify the reaction products as to prevent any conclusions as to the nature of the tannin molecule being drawn from the results. Further research on the hydrogenation of tannin should therefore be accompanied by investigations directed towards the purification of the starting product, or at very least towards obtaining a substance of standard particle size.

Further effort should be directed towards increasing the yields of hydrogenation products, which have been found to be somewhat low. To this end,a continued study of the use of Copper Chromite, involving variations in the conditions of the reaction, would appear likely to prove profitable.

It is suggested that the problem might be approached from two angles.

1) Continued experimentation to obtain full yields of the elementary building units in the form of oils, direct from tannin using Copper Chromite in 92% dioxan or some suitable solvent. This to be followed by re-hydrogenation and identification of the products, after separation using more efficient fractionating columns. And

2) A mild hydrogenation to cause full saturation of the tannin molecule, preferably over Raney Nickel in a suitable solvent and under suitable conditions. This to be followed by further mild chemical degradations, designed to cause fragmentation with the production of compounds which might on analysis show the manner of bonding of the elementary units.

In each procedure, care must be taken that the process used should not be so drastic as to cause the formation of double bonds by disruption, and the consequent difficulty of separation of these partially saturated nuclei. The use of low pressure and low temperature hydrogenations over platinum or palladium, is suggested as likely to be helpful in this respect.

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