CXXXVI. THE DEGRADATION OF WOOD BY SIMULTANEOUS ACTION OF ETHYL ALCOHOL AND HYDROCHLORIC ACID.

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INTRODUCTION.

CONSIDERABLE interest attaches to the fact that by means of acid hydrolysis the carbohydrates of wood can be hydrolysed to sugars, some of which yield alcohol on fermentation. With a view to improving the yields of these fermentable sugars, numerous expedients have been applied, which for the most part have taken the form of variations in acid concentration, temperature, pressure, and duration of acid treatment, while at the same time attempts have been made to catalyse the hydrolysis. Detailed studies of the possible catalytic effect of a range of substances on the acid hydrolysis of wood have been made by Sherrard and Gauger [1923], but although positive effects were obtained in some instances, in no case were the yields of fermentable sugars increased by more than a small amount.

The nature of the results obtained by the above authors has stimulated interest in the effect on wood of other substances in the presence of acids. Of these ethyl alcohol has invited study, in view of its curious, and as yet unexplained, action on plant tissues in the presence of hydrochloric acid.

Mangin [1890], in his studies of the nature and composition of plant cell walls, used a solution of hydrochloric acid in ethyl alcohol as a macerating agent. He claimed that this solution was effective in dissolving the middle lamella of herbaceous plants, with the consequent separation of adjacent cells.

Holmberg and Runius [1925] have investigated the extract obtained from wood by acid-alcohol solutions, and claim that it contains lignin in solution. Moreover, as a result of their investigations, they advance the view that the lignin and cellulose in wood are chemically combined. Friedrich [1928] has also examined the acid-alcohol extract from wood with a view to finding the best conditions for obtaining the so-called soluble lignin. This author characterises the work of Holmberg and Runius [1925] as unconvincing, and produces evidence to show that chemical combination between the lignin and cellulose in wood has not been proved.

In the light of the above facts it has seemed desirable to investigate more closely the effect of acid-alcohol solutions on wood, for no satisfactory data are available with regard to the composition of the wood residue remaining after treatment, and its relationship to that of the original sound wood. Moreover, there would appear to be some reason for assuming that the term "soluble lignin" has been somewhat loosely applied to a precipitate obtained from the wood extract, whose relationship to the parent wood substance has not been fully established. In the present investigation an attempt has been made to deal with some aspects of the wood-acid-alcohol reaction which have been overlooked in previous work.

MATERIAL.

The material used was Sitka spruce heartwood sawdust of 60–80 mesh taken from the sample used in a previous investigation by Hawley and Campbell [1927], its composition (Table I) being determined by the analytical methods recommended by Schorger [1926, p. 505] and Hawley and Wise [1926]. The solubility in alcohol was determined by extracting a weighed sample for 6 hours at the boiling-point.

The results throughout are expressed as percentages by weight of the original oven-dry wood.

Table I. *Composition of original wood.*

Water-soluble	...	...	...	4.1
1 % alkali-soluble	...	...	...	12.0
Alcohol-soluble	...	...	...	2.9
Cellulose	...	...	...	62.5
Lignin	...	...	...	29.3
Total pentosans	...	...	...	9.9
Pentosans not in cellulose	...	...	...	6.2

EXPERIMENTAL.

Effect on air-dry wood of a solution consisting of one volume of concentrated aqueous hydrochloric acid and four volumes of 95 % ethyl alcohol.

In the first instance an acid-alcohol solution was prepared by mixing one volume of aqueous hydrochloric acid of Sp. Gr. 1.18 with four volumes of 95 % ethyl alcohol.

A series of six samples of the air-dry wood were thoroughly mixed with the reagent. One sample was maintained at room temperature for 24 hours and the remainder of the series were maintained at 100° over a time range of from $\frac{1}{2}$ to 6 hours. In each case a deep reddish brown extract was obtained, the colour becoming more intense as the treatment increased in severity. After filtering off the extract the residue was thoroughly washed with 95 % ethyl alcohol and then with water until free from acid. The material was then dried at 105° and analysed (Table II).

Table II. *Analysis of wood residue after treatment with acid-alcohol solution.*

Treating time and temperature	Loss due to treatment	Residue				Total pento- sans	Pentosans not in cellulose
		Alkali- soluble	Cellulose	Lignin	Methoxyl		
24 hours at 20°	6.8	11.2	61.2	25.5	4.7	7.6	4.4
$\frac{1}{2}$ hour at 100°	27.0	9.5	48.6	20.1	4.0	3.9	2.1
1 hour at 100°	32.7	8.8	44.5	18.3	3.8	3.0	1.6
$1\frac{1}{2}$ hours at 100°	33.7	7.14	46.2	17.8	3.42	2.7	0.3
3 hours at 100°	38.9	5.23	44.0	16.3	3.03	1.8	0.5
6 hours at 100°	43.6	5.8	37.6	14.9	2.7	1.3	0.4

Effect of ethyl chloride on oven-dry wood.

Since ethyl alcohol and hydrochloric acid react on heating to form ethyl chloride and water, the following experiments were carried out to determine firstly the effect of ethyl chloride on wood, and secondly the influence of water on the wood-acid-alcohol reaction.

40 cc. of pure ethyl chloride was prepared by the action of heat on ethyl alcohol and hydrogen chloride in the presence of zinc chloride, and 5 g. of the original wood, dried at 105°, was incorporated with this and maintained for 1 hour at 12.5°, the boiling-point of ethyl chloride. After removal of the ethyl chloride, washing with cold alcohol, and drying at 105° there was no loss in weight.

Effect of a weak acid-alcohol solution on oven-dry wood, in the absence of water.

An acid-alcohol solution was prepared by adding 23.9 cc. of hydrochloric acid of Sp. Gr. 1.18 to 1 litre of absolute ethyl alcohol. The acid concentration with respect to the alcohol was thus approximately 1 %. To this solution a large excess of fused zinc chloride was added. A 25 g. sample of the original wood, dried at 105°, was extracted with the solution in a Soxhlet apparatus for 3 hours, absence of water from the extraction thimble being secured by continuous contact of the boiling solution in the flask with zinc chloride. The extract had the characteristic red colour. The residue was washed with alcohol till free from acid, dried at 105°, and analysed (Table III). The loss in weight sustained by the sample during treatment was determined, first, directly, by comparing the dry weight of the residue with that of the original sample, then, by calculation, by comparing the data with those in Table I. The sum of the losses in cellulose, lignin and pentosans not in the cellulose gave the value for "calculated loss" recorded in Table III.

Table III. *Analysis of wood residue after extraction with 1 % acid-alcohol solution in absence of water.*

Loss due to treatment (determined)	...	3.8
Calculated loss	...	4.2
Cellulose	...	59.9
Lignin	...	29.0
Total pentosans	...	7.8
Pentosans not in cellulose	...	4.9

Effect of acid-alcohol solution on oven-dry wood in the presence of the water of reaction only.

An acid-alcohol solution was prepared by passing dry hydrogen chloride into cooled absolute alcohol. From this a solution of 8.36 % strength was prepared, and 25 g. of oven-dry wood were treated at 100°. The residue was washed as before, dried at 105°, and weighed; a loss of 51.5 % was sustained, and the lignin content had fallen to 12.6 % by weight of the original oven-dry wood.

A 29.5 % acid-alcohol solution was prepared by saturating absolute alcohol with dry hydrogen chloride at 15°. A 50 g. sample of the original wood, dried at 105°, was treated with 500 cc. of this solution for 1 week at 15°. A partial analysis of the residue is given in Table IV.

Table IV. *Analysis of wood residue after treatment with 29.5 % anhydrous acid-alcohol for 1 week at 15°.*

Loss due to treatment	...	...	58.9
1 % alkali-soluble	...	...	2.3
Cellulose	...	...	26.9
Lignin	...	...	12.1

Effect on wood of mild acid hydrolysis, followed by extraction with 95 % ethyl alcohol.

A sample of the original air-dry wood was hydrolysed for 6 hours with 1.5 % aqueous hydrochloric acid. The residue was washed with cold water till free from acid, and extracted with boiling 95 % alcohol for a further 6 hours. After washing, and drying at 105°, the loss in weight was determined, as well as the cellulose and lignin contents (Table V).

Table V. *Analysis of wood residue after hydrolysis with 1.5 % HCl followed by extraction with 95 % alcohol*

Loss due to treatment	...	...	20.9
Cellulose	...	...	49.7
Lignin	...	...	26.4

A hydrolysis similar to the above with 8 % acid followed by extraction with alcohol resulted in a total loss of 29.9 %, and the cellulose content of the residue was 45.7 % by weight of the original dry wood.

DISCUSSION.

In mild aqueous acid hydrolysis of wood there are three outstanding features. Carbohydrates are the most seriously attacked; lignin is affected only to a slight extent, and thirdly, as a direct result of hydrolysis, the residue becomes more soluble in alkali than the original wood. Comparison of Tables I and II shows that hydrolysis does not run true to type when ethyl alcohol is added to the hydrolysing medium. Carbohydrates are attacked as before, but at the same time lignin is largely removed, and the wood residue is less soluble

in alkali than the original wood. Clearly alcohol alone could not be responsible for the removal of so large a proportion of lignin, for according to Schorger [1926, p. 507] the alcohol extract of coniferous woods contains only tannins, linoxyn, highly oxidised resins, and substances related to lignin. In any case it has been shown above that after extraction with boiling alcohol for 6 hours the wood used in this investigation only lost 2.9 % of its oven-dry weight. There remains the possibility that lignin depletion may here be due to the action of ethyl chloride, but experimental evidence has been given to show that wood suffers no loss in weight when treated with this substance alone at atmospheric pressure. As ethyl chloride is volatile above 12.5° and is immiscible with water it can be concluded that it plays no part in the reaction.

Ethyl alcohol alone could not affect the carbohydrates of wood to any marked extent; dilute hydrochloric acid alone could not deplete lignin to the extent shown in Table II. Hence it follows that when wood is treated with an acid-alcohol solution at least two main reactions must take place simultaneously. First, there is hydrolysis of the carbohydrates influenced by the presence of alcohol, and secondly, there is action on lignin by alcohol, solution or combination, influenced by the presence of hydrogen chloride. Both reactions are influenced by the presence or absence of water.

Influence of alcohol on the acid hydrolysis of wood.

The results in Table II show that the hydrolysis has followed a different course from that followed in mild aqueous acid hydrolysis. Thus, on comparing the composition of the residue after treatment in this way for 6 hours at 100° with the composition of the residue from a sample of the same original wood which has been treated with 8 % aqueous hydrochloric acid for the same time at 100° [Hawley and Campbell, 1927], it is evident that the presence of alcohol in the hydrolysing medium has had the effect of increasing the percentage depletion of cellulose and pentosans, including the pentosans in the cellulose. The effect on the lignin of the wood will be discussed later. The most striking result of the addition of alcohol to the hydrolysing medium, however, is that the alkali-solubility of the residue decreases with increasing severity of treatment. It must therefore be concluded that the low alkali-solubility of the residue is partly due to the fact that the carbohydrate hydrolysis products have been removed with the acid-alcohol extract. It has been shown in previous work that after mild aqueous acid hydrolysis some of the products of hydrolysis are left in the residue. Evidence of this deviation from the normal course of acid hydrolysis caused by the addition of alcohol is supplied by the data in Tables I and II.

In Table I the sum of the main constituents, namely cellulose, lignin and pentosans not in cellulose, amounts to 98.0 % of the oven-dry weight of the original wood. In Table II the sum of the same constituents including the loss due to treatment amounts on the average to 97.86 % of the oven-dry weight of the original wood, the extreme variations in the series of six analyses being

96.5 % and 99.7 %. The close agreement of these totals proves conclusively that the residues contain nothing which cannot be estimated as cellulose, lignin or pentosans. Part of the decrease in the alkali-solubility of the residues is thus accounted for at once, while the removal of lignin from the wood accounts for still another portion. The question now arises as to whether the carbohydrate hydrolysis products of the action of acid-alcohol on wood are removed in the extract in a state of solution in, or combination with, alcohol.

If solution of the hydrolysis products alone takes place, then such solution should conceivably succeed hydrolysis, and be independent of acid. Experimental evidence, however, does not bear this out. Hawley and Campbell [1927] have shown that hydrolysis of the original wood with 1.5 % aqueous hydrochloric acid produces a loss of 17.6 % of its oven-dry weight. The results in Table V show that if the residue from a 1.5 % acid hydrolysis be extracted with alcohol for 6 hours the total loss due to the successive treatments amounts to 20.9 % of the oven-dry weight of the wood. Alcohol must therefore have removed 3.3 %, and thus the hydrolysis can only have increased the alcohol-solubility by 0.4 %. In the same way it can be shown that 8 % aqueous acid hydrolysis can only increase alcohol solubility by 2.1 % at the most. It thus becomes evident that during the acid-alcohol treatment of wood, the hydrolysis products must for the most part react with the alcohol in the presence of acid to form soluble compounds, which may possibly be of a glucosidic nature.

The action of alcohol on lignin in the presence of hydrochloric acid.

The comparatively slight effect of mild aqueous acid hydrolysis on the lignin of wood has been demonstrated in previous work. The results in Table II show that the addition of ethyl alcohol to the hydrolysing medium causes marked depletion of this constituent. In view of the fact that in wood analysis the lignin determination is always preceded by extraction of the samples with alcohol-benzene, it has not been shown previously whether the small lignin depletion noted after mild acid hydrolysis is due to solubility of lignin in alcohol as a result of hydrolysis. It has been shown above, however, that 1.5 % aqueous acid hydrolysis only increases alcohol solubility by 0.4 %, whereas comparison of Tables I and V shows that the extent of lignin depletion amounts to 2.9 % by weight of the oven-dry wood. In the same way it can be shown by reference to the data of Hawley and Campbell [1927] that after hydrolysis with 8 % hydrochloric acid the percentage of lignin depletion is in excess of the percentage increase in alcohol-solubility. It must therefore be concluded that the small lignin depletion determined after mild acid hydrolysis takes place during hydrolysis and not during the alcohol-benzene extraction which precedes the lignin determination in the analysis of the residue.

From the foregoing evidence it follows that, when wood is treated with acid and alcohol simultaneously, hydrolysis of the carbohydrates and of a portion of the lignin is independent of the action of alcohol in the presence of acid on the main body of the lignin. This contention is further strengthened

by the experimental data in Table II, which show that when wood is allowed to react with acid-alcohol solution at 20° for 24 hours the degree of carbohydrate hydrolysis is small in comparison with the extent of lignin depletion. It is therefore evident that in the presence of hydrochloric acid, alcohol reacts with a portion of the lignin in wood to form a soluble product, the rate of formation of which does not synchronise with the rate of hydrolysis of the carbohydrates. Holmberg and Runius [1925] have suggested that the formation of such a product is evidence of the presence of an acetal linkage between the lignin and cellulose in wood, and, further, that lignin is the carbonyl component of the acetal. In the wood-acid-alcohol reaction it is assumed that the ethyl group of the alcohol replaces cellulose in this acetal to give a soluble product. The results obtained in this investigation, however, are not consistent with such a suggestion. On the contrary, they rather favour the view of Friedrich [1928] that chemical combination between the lignin and cellulose in wood has not been proved.

The rôle of water in the wood-acid-alcohol reaction.

Holmberg and Runius [1925] have shown that when wood is treated with acid-alcohol containing water, the water has the effect of diminishing the rate of reaction. On the other hand, it has been shown above that the presence of some water is essential to the reaction, for the results in Table III show that, when precautions are taken to exclude water, attack on the wood is similar in effect to mild aqueous acid hydrolysis in that carbohydrates are depleted most and lignin is only affected to a slight extent. The close agreement in acid-alcoholic hydrolysis between the determined percentage loss and the calculated percentage loss is due, as shown above, to interaction between the carbohydrate hydrolysis products and alcohol.

It has also been shown above that the maximum effect of acid-alcohol on wood is secured when oven-dry wood is treated with a concentrated solution of dry hydrogen chloride in absolute alcohol. In this way the presence is obtained in the reaction mixture of the minimum amount of water. Friedrich [1928] has shown that the conditions most favourable to the attack on lignin are a long reaction time at a low temperature, coupled with a low water content of a concentrated acid-alcohol solution.

The acid-alcohol extract of wood.

The foregoing experimental evidence shows clearly that the extract obtained from wood by treatment with solutions of hydrochloric acid in ethyl alcohol under various conditions is in every case derived from portions of all the main constituents of wood substance. The results illustrate the fact that acid-alcohol cannot be regarded as a specific solvent for lignin. Holmberg and Runius [1925] claim that neutralisation of the extract with sodium hydroxide effects the precipitation of a substance to which they have applied the term "alcoholysis lignin," but in the light of the results of this investigation it

would appear that the term lignin cannot safely be applied to such a substance until its relationship to the parent wood substance has been fully established, in view of the possibility that it may reasonably be expected to contain material derived from wood constituents other than the lignin proper.

SUMMARY.

1. The simultaneous effect of ethyl alcohol and hydrochloric acid on the wood of Sitka spruce has been examined in detail.

2. Reasons are given for concluding that at least two main reactions are involved, namely, hydrolysis of carbohydrates, influenced by the presence of alcohol, and action of alcohol on lignin in the presence of hydrochloric acid.

3. Absence of water from the system favours depletion of carbohydrates, the maximum effect on the lignin in wood being secured by treating the oven-dry material with a concentrated solution of hydrogen chloride in absolute alcohol, the necessary water being formed by interaction of the acid and alcohol.

4. Experimental evidence is given which favours the view that the association of lignin and cellulose in wood is of a physical rather than a chemical nature.

5. It is shown that the extract obtained from wood after treatment with acid-alcohol solutions under various conditions is in each case derived from portions of all the main constituents, so that the precipitate obtained on neutralisation which has been termed "alcoholysis lignin" may reasonably be expected to contain material derived from wood constituents other than lignin.

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