LXIV. THE EFFECT OF PARTIAL DECAY ON THE ALKALI SOLUBILITY OF WOOD.

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Introduction.

It is generally accepted that at least two types of wood decay are caused by fungi, namely the "brown" and "white" rots. In the former type preferential attack is made on the carbohydrate components of wood substance, and lignin is in the main unaffected, the decayed residue being usually brown in colour. In the latter type lignin seems to be the main objective of the fungus, and in the decayed residue there remain patches or "pockets" of a white substance reputed to consist of pure cellulose. The type names are thus derived from the colour of the residues after attack.

In brown rots it has been shown by the work of Bray and Andrews [1924] that the causal fungi are consistent in their preferential attack on the carbohydrate components, but it cannot be said of the white rots that they are consistent in that lignin is always attacked in preference to carbohydrates. Only a few fungi of the white rot type have been studied in any detail, however, but Hawley and Wise [1926, 1] point out that while one of them, *Trametes pini*, may show a preference for lignin, another, *Polyporus hirsutus*, has a serious effect on the cellulose of the wood of white spruce. It is clear, therefore, that the terms "brown" and "white," as applied to different types of decay, can be accepted in an approximate sense only, since inconsistencies are encountered, in the case of the white rots at least, when the chemical effects on the host are taken into consideration.

A classification of decay types based on the chemical effects of the fungus on the host is suggested in the work of Falck and Haag [1927], Wehmer [1927], and Bavendamm [1927]. These authors favour the use of the terms "destruction" and "corrosion" respectively, the former type to include all forms of fungal decay in which carbohydrates are preferentially attacked, and the latter to include the forms in which lignin is preferentially attacked. According to Wehmer [1927], the "destruction" type is brought about by hydrolysis of carbohydrates, and in the "corrosion" type lignin is depleted by a process of oxidation. Hawley and Wise [1926, 2], however, are not disposed to consider decay purely as one chemical process, on the grounds that any decomposition of a nature so profound as the fungal decay of wood could not strictly be compared to a single type of chemical reaction.

In much of the work already done on the chemistry of decay, material has been examined in which decay has been allowed to proceed to a considerable extent, and there is little doubt that in its advanced stages fungal decay is a profound decomposition of a nature difficult of diagnosis by present methods of analysis. At the same time, however, there is evidence that decay takes place in stages [Hawley and Wise, 1926, 3], and the possibility must not be overlooked that, in the very early stages, reactions of a comparatively simple nature may be involved. Also, for all practical purposes the initial stages of decay are the most important, since it is against these that all preservative treatments must be applied. It is obvious, therefore, that a closer understanding of the mechanism of incipient decay should lead to better methods in wood preservation.

The one outstanding feature with regard to fungal decay in wood is that, as a direct result of infection, the residue is rendered more soluble in sodium hydroxide than the original sound wood. In fact Bray [1924] has pointed out that in the case of the brown rots, increase in alkali solubility serves as an index of the extent of cellulose depletion in any given sample of decayed wood. It has also to be noted that acid hydrolysis has the effect of increasing the alkali solubility of wood, and this fact has led Hawley and Campbell [1927] to conclude that there must exist a relationship between acid hydrolysis on the one hand and fungal decay on the other. That fungi are capable of producing acid in various media has been shown by Curtin [1927], and this further strengthens the contention of the above authors, since in the course of its action on wood the fungus may produce acid whereby hydrolysis is brought about. The present investigation has been undertaken in order to obtain a closer comparison between acid hydrolysis and decay than has hitherto been available.

Experimental.

The wood used was Sitka spruce heartwood sawdust of 60–80 mesh. The analytical methods were those recommended by Schorger [1926] and Hawley and Wise [1926, 4].

The general scheme employed was the same as that used by Hawley and Campbell [1927] in their study of acid hydrolysis. Analytical data were obtained for the main constituents of the original wood, and the effect of 1 % sodium hydroxide at 100° was determined on these as before. The results are given in Tables I and II.

Table I. *Analysis of original wood.*

Results on basis of weight of original dry wood.

Cold water-soluble	1·6 %
Hot water-soluble	3·6
1 % alkali-soluble	12·6
Cellulose	62·6
Lignin	26·2
Methoxyl	4·7
Total pentosans	8·4
Pentosans not in cellulose	5·1

Table II. *Analysis of residue after treatment with* 1 % *NaOH for* 1 *hour at* 100°.

Results expressed as percentages by weight of original dry wood.

Loss on alkali treatment	13·8
Cellulose	59·0
Lignin	24·3
Methoxyl	4·0
Total pentosans	6·8
Pentosans not in cellulose	3·9

In studying the effect of decay on alkali solubility, samples of decayed wood were analysed, treated with sodium hydroxide, and the residues analysed. The experiments were carried out in the following manner.

Three separate weighed samples of the 60–80 mesh material were placed in flasks, and moistened with water. The flasks were then plugged with cotton wool and sterilisation was effected by steaming for 30 minutes on each of three consecutive days. After inoculation with *Trametes serialis* Fr. one sample was left to decay for 3 months, and the other two for 4 months at 20°.

After decay each sample was collected on a linen filter and washed with cold water until free from acid. Drying was effected by suction as far as possible, and then, to arrest decay, the samples were further dried and sterilised by heating in weighing bottles at 105° for 16 hours. After cooling in desiccators the samples were weighed, and the loss in weight sustained by each was determined.

Each sample was now divided into two portions, one to be analysed without delay, and the second after treatment with 1 % sodium hydroxide for 1 hour at 100°. The analytical results are given in Tables III and IV.

Table III. *Analysis of residues after decay and washing with cold water.*

Results expressed as percentages by weight of original dry wood.

Duration of decay	Loss due to decay plus cold water washing	Hot water-soluble	Cellulose	Lignin	Methoxyl	Total pentosans	Pentosans not in cellulose
3 months	6·98	2·3	55·5	25·8	4·3	7·2	4·8
4 months (1)	8·0	2·9	53·6	25·9	4·2	6·9	4·7
4 months (2)	8·96	3·4	52·7	25·9	4·2	6·8	4·7

Table IV. *Analysis of residues after decay, washing with cold water, and subsequent treatment with* 1 % *NaOH for* 1 *hour at* 100°.

Results expressed as percentages by weight of original dry wood.

	Loss due to decay plus cold water washing	Loss on alkali treatment	Total loss	Cellulose	Lignin	Methoxyl	Total pentosans	Pentosans not in cellulose
(1)	6·98	23·1	30·08	44·7	22·6	3·6	4·6	2·6
(2)	8·0	22·4	30·3	42·9	23·0	3·5	4·4	2·4
(3)	8·96	24·9	33·86	40·0	22·5	3·5	4·1	2·4

Discussion.

As previously mentioned a steaming treatment was applied prior to inoculation of the wood with the fungus. That such a treatment has no detrimental effect on spruce wood has been shown by Hawley, Fleck and Richards [1928].

The results in Table III were obtained after the decayed residues had been washed with cold water and heated for 16 hours at 105°. These steps were considered necessary for the following reasons.

In the first place the decayed residues were found to be distinctly acid, hence it was imperative that all traces of acid should be removed prior to analysis. The loss due to decay and the cold water-soluble material was therefore determined as a whole. That some water-soluble material remained in the residues after the preliminary washing was proved by carrying out a hot water-soluble determination on each sample. Therefore, although the exact loss due to decay itself has not been determined, its effect on the wood can be visualised by a comparison of Tables I and III, for, even if all the water-soluble material had been left in the residues, it is certain to have been lost during subsequent analysis, and thus the analytical data would have been the same as those recorded.

As to the heat treatment applied after washing and prior to analysis, this was considered to be the only efficient means of arresting decay at the required time, and of getting the material into a convenient state for analysis. Peterson and Bray [1928] have pointed out that an oven-drying treatment has the effect of lowering cellulose yields, and of rendering the isolation of cellulose more difficult, but in this investigation no difficulties were experienced in isolating cellulose with a normal amount of chlorination after heating the residues for the time stated.

Fungal mycelium, if present in considerable amount in decayed residues, would tend to vitiate analytical results, but attempts to apply corrections for this source of error have proved unsatisfactory. In any case, where decay is only allowed to proceed for a short period, the actual amount of mycelium in the infected material could not be sufficient to detract from the purely comparative value of the analytical data. Care was taken thoroughly to mix the decayed material so that mycelial remains should be distributed as evenly as possible throughout the whole.

Comparison of Tables I and III shows that the fungus has behaved as a typical brown rot in the manner of its attack on wood. Cellulose and pentosans have been depleted, and lignin has been affected to a slight extent, the comparatively small loss in lignin being consistent with a corresponding fall in the methoxyl content. Moreover, it can be seen that the pentosan losses are chiefly due to depletion of the pentosans in the cellulose. That such behaviour is typical of brown rots has been amply demonstrated in previous work, but it was necessary to obtain these results for comparison with Table IV which

shows, firstly, the marked increase in alkali solubility due to decay, and secondly, the detailed effect of alkali treatment on decayed wood.

The increase in alkali solubility is largely accounted for by losses in cellulose and pentosans, the lignin in decayed wood being only slightly more soluble in alkali than the lignin in sound wood.

Whereas in Table I the sum of the four main constituents—namely water-soluble material, cellulose, lignin, and pentosans not in the cellulose—amounts to 99·1 % of the original wood, the sums of the main constituents in the samples of decayed wood, inclusive of the losses due to decay and water-soluble material, amount to 95·58, 95·1, and 95·66 % of the original wood respectively. These facts are in agreement with previous work in that they illustrate that there is in decayed wood a material which is insoluble in water, and is not determined as cellulose, lignin, or pentosans. That such material is probably a carbohydrate degradation product is illustrated by the fact that only the carbohydrates in the wood have been seriously affected by decay. Further, in Table IV, the sums of the main constituents, including the losses due to decay and alkali treatment, amount to 99·98, 98·7, and 98·76 % respectively of the original wood. The fact that these totals are approximately equal to the sum of the main constituents in the original wood indicates that, whatever the material undetermined in the decayed wood may be, it is largely soluble in 1 % sodium hydroxide.

Conclusions.

In comparing the foregoing experimental data with regard to decay and its effect on the alkali solubility of wood with those cited by Hawley and Campbell [1927] in their study of acid hydrolysis, a marked similarity in effect between the two processes is apparent.

The fact that both decayed and hydrolysed wood contain a material insoluble in water, but soluble in 1 % sodium hydroxide, which cannot be determined as cellulose, lignin, or pentosans, tends to strengthen the conviction that, in its early stages at least, fungal decay of the brown rot type is in effect an acid hydrolysis. The only possible objection to this conclusion is to be found in the apparently greater solubility of decayed wood in alkali. Hawley and Campbell [1927] emphasise that the alkali solubility of decayed wood is always greater than that of wood that has been hydrolysed to the same extent (as shown by equal loss in weight) but, all things considered, this is only to be expected. Whereas in the hydrolysis of wood with dilute acid all the water-soluble material is removed, wood that has been decayed still contains water-soluble material. Where the losses in weight are the same the alkali solubility of decayed wood will always be greater than that of hydrolysed wood in proportion to the amount of water-soluble material present in the former. If, in Table III, the percentage of hot water-soluble material be added to the loss sustained by decay plus cold water washing, and in Table IV deducted from the loss on alkali treatment, decay can be

strictly compared with hydrolysis. This can be illustrated by the following example.

In Table III the loss in weight sustained by one of the samples after 4 months' decay and cold water washing was 8·0 %. If the figure for the remaining water-soluble material be added to this a total of 10·9 % is obtained. This total is approximately equal to the loss obtained by Hawley and Campbell [1927] by hydrolysing Sitka spruce with 0·25 % hydrochloric acid. Furthermore, the losses due to decay, as expressed by a comparison of Tables I and III, agree very favourably with the losses involved in a hydrolysis with acid of the above concentration. Again, if in Table IV the amount of hot water-soluble material be subtracted from the loss due to alkali extraction, this latter is reduced from 22·4 to 19·5 % of the weight of the original wood. Hawley and Campbell [1927] have shown that Sitka spruce wood which has been hydrolysed with 0·25 % hydrochloric acid is soluble in 1 % sodium hydroxide to the extent of 18·2 %. Thus it can be seen that the agreement between the degree of alkali solubility of partially hydrolysed wood and that of partially decayed wood is in reality quite close, when the necessary allowance is made for the amount of water-soluble material in the latter.

With the advanced stages of decay this investigation is not strictly concerned, but it seems probable that the high degree of alkali solubility of the lignin in badly decayed wood is due, not so much to any direct effect of decay on the lignin complex, as to the large increase of surface area of the lignin caused by marked depletion of the carbohydrate components of the wood.

From the foregoing considerations the similarity of the effect on wood between acid hydrolysis on the one hand, and fungal decay of the brown rot type on the other, is so close as to warrant the conclusion that decay of the brown rot type should, in effect, be regarded as an acid hydrolysis.

Summary.

1. The effect of partial decay on the wood of Sitka spruce caused by *Trametes serialis* Fr. has been examined. This effect is typical of that produced on wood by fungi of the brown rot type.

2. The effect of partial decay on the alkali solubility of the wood of Sitka spruce has been examined, and reasons are given for concluding that, since this effect is of the same order as that produced in the same species of wood by acid hydrolysis, decay of the brown rot type should, in effect, be regarded as an acid hydrolysis.

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