CCXX. THE CHEMISTRY OF THE WHITE ROTS OF WOOD.

II. THE EFFECT ON WOOD SUBSTANCE OF *ARMILLARIA MELLEA* (VAHL.) FR., *POLYPORUS HISPIDUS* (BULL.) FR., AND *STEREUM HIRSUTUM* FR.

By WILLIAM GEORGE CAMPBELL.

From the Section of Chemistry, Forest Products Research Laboratory, Princes Risborough, Bucks.

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In a previous communication [Campbell, 1930] it has been pointed out that comparatively little experimental work has been done on the chemistry of the particular type of wood decay in which lignin is decomposed, and further, that it is unknown whether such decomposition is invariably accompanied by simultaneous decomposition of the wood carbohydrates. Analytical data were obtained, however, which showed clearly that in the decay of wood by *Polystictus versicolor* (Linn.) Fr. carbohydrates are depleted as well as lignin. Falck [1927] has concluded that in wood decayed by *Fomes annosus* cellulose is decomposed in the advanced stages. In the present investigation the study of the so-called white rots has been continued by examining the respective effects of *Armillaria mellea* (Vahl.) Fr. on beech wood, *Polyporus hispidus* (Bull.) Fr. on ash heartwood, and *Stereum hirsutum* Fr. on oak sapwood.

Experimental.

(1) The experimental procedure and analytical methods were the same as those employed in the previous work. Each sample of 60–80 mesh wood flour of known composition was first sterilised, then inoculated with the appropriate fungus and incubated at 20°. After decay had proceeded to the required stage, the wood residues were washed with cold water until free from acid, dried and sterilised at 105°. The comparative effects of 1 % sodium hydroxide on decayed and sound wood respectively were examined only in the case of beech wood. All analytical results are expressed as percentages by weight of the oven-dry original wood, except where it is stated otherwise.

(2) It was noted that oak sapwood decayed by *Stereum hirsutum* was much lighter in colour than the original sound wood, and furthermore, that in various localities the decayed residue was almost pure white in colour. As a rule these white patches were quite small, but in one culture flask there occurred an unusually large patch of white residue.

Table I. *The effect of 1 % NaOH on beech wood before and after decay by* Armillaria mellea.

	Original wood	Decayed wood	Original wood after alkali-extraction	Decayed wood after alkali-extraction
Duration of decay	—	16 months	—	—
Loss due to decay *plus* cold water washing	—	8·66	—	—
Cold water-soluble	0·64	0·17	—	—
Hot water-soluble	1·65	0·89	—	—
1 % NaOH-soluble	16·63	15·88	—	—
Cellulose	57·49	50·84	58·67	50·10
Lignin	23·79	24·00	19·79	18·42
Pentosans in cellulose	15·50	12·62	18·42	14·65
Pentosans not in cellulose	11·45	11·22	0·60	4·98
Methoxyl content	6·33	5·29	4·81	4·27

By carefully cutting the flask it was possible to remove the greater part of this white material. It was found to have retained the cellular structure of the original wood flour, and when dried to constant weight *in vacuo* over $CaCl_2$ and P_2O_5 it weighed 0·1668 g. After extraction with alcohol-benzene, a standard lignin determination was applied, using the appropriate volume of 72 % H_2SO_4. The lignin content of the sample was 0·0212 or 12·5 %. For

Table II. *Analysis of 60–80 mesh oak sapwood and ash heartwood before and after decay by* Stereum hirsutum *and* Polyporus hispidus *respectively.*

	S. hirsutum		*P. hispidus*	
	Original wood	Decayed wood	Original wood	Decayed wood
Duration of decay	—	13 months	—	12 months
Loss due to decay *plus* cold water washing	—	20·16	—	11·3
Cold water-soluble	2·97	1·40	1·38	0·90
Hot water-soluble	5·02	3·77	3·02	2·32
1 % NaOH-soluble	18·66	18·64	21·13	19·45
Cellulose	58·81	48·99	59·39	54·14
Lignin	21·51	15·66	20·30	17·30
Pentosans in cellulose	15·79	11·26	14·63	12·24
Pentosans not in cellulose	8·71	8·13	10·15	10·16
Methoxyl content	5·80	4·05	5·50	4·69

comparative purposes a lignin determination was applied to a small sample of decayed wood taken from the immediate vicinity of the white patch. 0·3408 g. of decayed wood contained 0·0698 g. or 20·48 % of lignin. While the white material was loosely packed together, the surrounding pale brown material was relatively compact, so that a complete separation was possible. During drying, the intensely white colour of the former was observed to change gradually to a pale brown of lighter tint than that of the latter.

Discussion of results.

It is generally accepted that *Polyporus hispidus* and *Stereum hirsutum* cause white rot in wood in the sense that the decayed wood assumes a lighter colour than the original sound wood, and that frequently the decayed material contains patches or pockets of a white material resembling cellulose in

appearance. This opinion has been confirmed in the experiments described above and definite white patches were observed in the case of the decay of oak sapwood by *Stereum hirsutum*. There appears to be some doubt, however, as to whether the decay of wood by *Armillaria mellea* can truly be described as a white rot. In this case the decayed wood was not markedly lighter in colour than the sound wood, despite the fact that Hubert [1924] has described the decay as a white rot. The data in Table I reveal however, that, at the stage of decomposition examined, *A. mellea* causes a type of decay whose chemical effect in wood has not hitherto been described in detail. It can be seen that after 16 months' decay the loss of 8·66 % of the oven-dry weight of the original wood is almost wholly accounted for by cellulose depletion. Of the pentosans, only those associated with the cellulose are attacked, and lignin appears to have been unaffected by the fungus. Thus far, the decay bears a close resemblance in effect to the several brown rots which have been described from time to time, but as brown rots in general have been shown to cause a marked increase in the alkali-solubility of the residual wood substance, the decay caused by *A. mellea* cannot be classified with them, for in this case no marked increase in alkali-solubility of the wood residue takes place. Undoubtedly had part of the water-soluble material not been removed from the decayed wood its alkali-solubility would have been greater than that recorded in Table I, but, at the same time, a tendency is here disclosed towards the reduction of the total alkali-solubility of the major constituents as decay proceeds. The same tendency has been observed in the white rot caused by *Polystictus versicolor* [Campbell, 1930] and the analytical data (Table I) reveal that its cause is to be sought in the marked reduction during decay in the alkali-solubility of the pentosans not in the cellulose. Thus even in the absence of analytical data to show whether lignin is in fact decomposed at a later stage, it is apparent that at the stage examined, decay by *A. mellea* possesses chemical characteristics of both brown and white rots, but that in view of the effect on the alkali-solubility of the decayed residue, it may, with reason, be described as a variety of white rot.

With regard to the respective effects on wood substance of *Stereum hirsutum* and *Polyporus hispidus*, it can be seen from the data in Table II that these are essentially the same, despite the fact that in the former case the loss in weight due to decay is approximately twice as great as in the latter. Lignin is decomposed, but in each case by far the greater proportion of the total loss in weight is accounted for by the depletion of the cellulose and its associated pentosans. The percentage amount of pentosans not in the cellulose remains practically constant throughout the decay, and the fall in the methoxyl content is much less than that of the lignin content. Finally, this type of decay does not cause a marked increase in the alkali-solubility of the principal components of wood substance, and it is probable that this fact can be ascribed to the same causes which are operative in the decay of wood by *Polystictus versicolor* and *Armillaria mellea*.

Consideration of the chemical composition of the patches of white material produced during the decay of oak sapwood by Stereum hirsutum.

It has long been considered by biologists that in certain white rots of wood, where patches or pockets of a white material are found to occur, the fungi concerned have a selective action on lignin, and that the white residue consists entirely of cellulose. This conclusion has been based primarily on the reaction of this material to the so-called cellulose stains, but, so far as is known, no purely chemical test has hitherto been applied to it. This has undoubtedly been due to the fact that the white patches in question are usually small, and that the isolation of samples sufficiently large for analysis has been a matter of difficulty. In the experiments recorded above, the samples were too small for more than one analytical determination in each case, but it was considered that lignin determinations would be comparatively easy to apply, and that, in spite of some degree of experimental error, they would provide a definite answer to the questions as to whether the white patch consisted entirely of cellulose, and whether the fungus had had a marked selective action on lignin.

In the first place, it is apparent that the white material still contains lignin, although its percentage amount cannot be directly compared with the lignin content of the original wood, since the loss in weight due to decay is not known. It may safely be deduced indirectly however that the portion of the original wood which gave rise to the white material must have lost considerably more than 20 % of its oven-dry weight before this residue attained a lignin content of 12·5 %, and, since the lignin content of the original wood (Table II) was 21·51 %, it is obvious that wood components other than lignin—and of these chiefly the cellulose—must have been decomposed. From the fact that the lignin content of the material immediately contiguous to the white patch is approximately the same as the actual lignin content of the decayed wood in Table II, it must be deduced that decay has not been confined to the material which ultimately became white.

Conclusions and summary.

From the above considerations it is to be concluded that the three examples of white rots examined have only one feature in common, and that this is shared by the white rot caused by *Polystictus versicolor*. In every case there is no marked increase in the total alkali-solubility of the major components of wood substance and in the case of *Polystictus versicolor* and *Armillaria mellea* this has been proved to be due to the fact that one component—namely the pentosans not in the cellulose—becomes less soluble in 1 % NaOH as decay proceeds. The white rots in question are thus sharply differentiated from the brown rots, for it has been found in some of the latter, that even in very advanced stages of decay the residual wood substance is much more soluble in alkali than the original sound wood. While it has been established

that the detailed chemical effect on wood substance of both *Polyporus hispidus* and *Stereum hirsutum* is essentially similar in all respects, this effect can in turn be differentiated from that of *Polystictus versicolor* when the manner in which pentosans are decomposed is considered. *Polystictus versicolor* attacks the pentosans not in the cellulose to a greater extent than the pentosans which are associated with the cellulose, whereas *Polyporus hispidus* and *Stereum hirsutum* attack the pentosans in the cellulose and have little or no effect on the pentosans not in the cellulose, at the stages of decay which were examined. In view of the effect on the alkali-solubility of wood substance of the decay caused by *Armillaria mellea*, and the fact that the decayed wood possesses to some extent the visual characteristics of a white rot, it must be concluded that in this type of rot a stage can exist in which lignin is apparently unaffected by the fungus.

In the case of the "pocket" rot caused by *Stereum hirsutum*, it is to be concluded that this fungus cannot be credited with a selective action on lignin. The white patches referred to above represent localities in a decaying mass in which decomposition has progressed to a greater extent than in the surrounding material. In these localities cellulose is decomposed as well as lignin, and even after the development of the white colour some lignin remains.

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