EFFECT OF DECAY ON THE CHEMICAL
COMPOSITION OF WOOD

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The comparative effects of decay on the chemical composition
of wood have been studied by analyzing several species of
wood before and after decay with both a white-rot and
brown-rot fungus. These analyses were confined
largely to the cellulose, with determinations
of pentosans in cellulose and of the
hydrolysis number of cellulose.

Previous chemical studies of wood decay have been
confined almost entirely to the effect of brown-rot fungi,[5]
all of which have shown a selective action on the Cross and
Bevan cellulose with little attack on the lignin. Part of
the cellulose is changed to some less stable intermediate

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[1] Received December 13, 1927.

[2] This article is respectfully dedicated by the authors to
L. M. Dennis. It will be reprinted in the Louis Munroe
Dennis Quarter Century Volume, to be published in 1928,
in commemoration of the completion by Professor Dennis
of twenty-five years of service as head of the Depart-
ment of Chemistry at Cornell University.

[3] Forest Products Laboratory.

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[5] A summary of the subject may be found in "The Chemistry of
Wood," by Hawley and Wise. The most important original
publications are Rose and Lisse, J. Ind. Eng. Chem., 9,
284 (1917); Mahood and Cable, Paper, 25, 1149 (1920);
Bray and Andrews, Ind. Eng. Chem., 16, 137 (1924); Smith,
Phytopathology, 14, 114 (1924).

product, and part is removed, probably as carbon dioxide and water. The pentosans also are attacked by the brown-rot type of decay, but previous analyses have not shown whether the pentosans in the cellulose or the pentosans not in cellulose are the more rapidly removed. Although the lignin is not much reduced in amount, yet it is modified, at least in its alkali solubility. The "lignin" referred to here is that isolated by the analytical method using 72 per cent sulfuric acid, which may not be the same as the lignin as it existed in the sample before isolation. The lignin in the original wood has probably been modified by decay to the extent of the partial removal of its methoxyl and acetyl groups.

Only one white-rot fungus, Trametes pini, has been included in published chemical studies of decayed wood, and even for this one not many analyses of the wood attacked are available. It is evident, however, that this fungus causes a different type of decay from that of the brown rots, since it has a preferential attack on the lignin and less effect on the cellulose.

(Note.--Since the above was written the recent work of Falck, Ber. deut. botan. Ges., 44, 652 (1927), and of Falck and Haag, Ber., 60, 225 (1927), has come to our attention. Falck had previously described two different types of decay, which he called "corrosion" and "destruction," but this is the first time he has given chemical analyses of the partly decayed mate-rial. Analyses of woods partly decayed by Fomes annosus and Merulius domesticus show that the former is like Trametes pini in its effect, while the latter is like the brown-rot fungi in making a preferential attack on the cellulose.

Falck endeavors to explain a fancied preference of the "corrosive" type of fungus--e.g., Fomes annosus--for heartwood and the "destructive" type-- e.g., Merulius domesticus--for sapwood by the greater prevalence of lignin in the heartwood and of cellu-lose in the sapwood. We doubt that there is any such preference; and even if there is, it cannot be so explained, since the assumed variations in lignin and cellulose do not exist.)

In order to obtain additional information on the comparative effects of decay on chemical composition, it was decided to analyze four species of wood before and after decay with one white-rot and with one brown-rot fungus, the analyses to be confined largely to the cellulose, with determinations of pentosans in cellulose, which had not been previously made, and of hydrolysis number of cellulose, for which a special method was developed.[6]

[6]Hawley and Fleck, Ind. Eng. Chem., 19, 850 (1927).

Many of the previous analyses of partly decayed wood have been made on samples in which the decay had been uncontrolled and the loss in weight due to decay was unknown. These conditions make it impossible to decide from the proportion of final constituents whether some one constituent, A, has remained intact or whether some other constituent, B, has been removed so much more rapidly than A that the constancy of A is only apparent. Attempts to overcome this difficulty have frequently been made by determining the specific gravity of the partly decayed samples and assuming that the loss in weight due to decay is exactly proportional to the loss in specific gravity; but this method of correcting the computations is not entirely satisfactory because of uncertainty as to the exact specific gravity of the original wood, and other unsound assumptions. It was not until the work of Bray and Andrews[5] that samples with known loss of weight due to decay were analyzed. Their method was followed in this work; weighed and analyzed samples of wood, after attack by pure cultures of known organisms, were weighed and analyzed again so that all determinations could be expressed as percentages of the weight of the original wood.

Selection of Materials

Polystictus hirsutus (Schräder) Fries was chosen as a representative fungus causing the so-called white rots, and Lenzites striata Swartz as one representing the brown-rot group. Both these fungi are common forms known to attack both hardwoods and softwoods.

The species of wood exposed to the action of these fungi were two softwoods, white spruce (Picea glauca (Moench) Voss) and southern cypress (Taxodium distichum (Linnaeus) Richard), and two hardwoods, red oak (Quercus borealis (Michaux)) and white oak (Quercus alba (Linnaeus)). The sapwood was used in each case because it is more susceptible to decay than the heartwood.

Preparation of Samples

Sawdust of the same grade was prepared from each species. Fifteen 3-gram samples of each kind of sawdust were placed in weighed flat-bottom extraction flasks of 100 cc. capacity. Enough distilled water was added in each flask to bring the moisture content of the sawdust up to

approximately 78 per cent by weight. The flasks were tightly plugged with cotton and sterilized at 100° C. for 30 minutes on three successive days. Some of the samples were then inoculated with small pieces of mycelium taken from cultures of Lenzites striata or Polystictus hirsutus that had been grown on a 2.5 per cent solution of Trommer's plain diastasic malt extract. Other samples were left uninoculated to serve as sterilization checks. Three similar sets, each set consisting of two samples of each species of wood inoculated with L. striata and two other samples of each species inoculated with P. hirsutus, were placed in a storage cabinet, where they remained for 2, 4, and 6 months, respectively, at room temperature.

When the sixteen 4-month samples were opened for examination it was found that in the majority of cases the moisture content had decreased so far that the action of the fungus was presumably inhibited. To prevent a further similar loss in the 6-month samples the following precautions were taken: The flasks were sterilized on the outside with a solution of mercuric chloride (1:1000) and were placed over water in sterile jars and opened; 5 cc. of sterile distilled water were then added to each sample, after which the jars were tightly capped with cotton to keep the contained air humid and thus prevent further excessive drying of the sawdust.

Analysis of Samples

In comparing the analyses of wood before and after decay, a question naturally arises as to the effect of the sterilization process, which is a part of the standard procedure for controlled decay. To obviate any uncertainty on this point, each species was analyzed for hot-water-soluble content, cellulose, and pentosans in cellulose, both before and after sterilization. The data in Table 1 show that the sterilization had very little effect on the composition of the wood. While there is a rather definite tendency toward higher hot-water solubility in the sterilized samples, the variations in the determinations of cellulose and of pentosans in cellulose are within the limits of experimental error. At any rate, the maximum possible change in all three constituents due to sterilization would be too small to affect the conclusions drawn from the analyses of the decayed samples.

At the time when the effects of sterilization were determined the method for the hydrolysis number determination had not been developed, and therefore no direct

determinations of the effect of sterilization on the hydrolysis number were possible. There are analyses in Table 4, however, which show that the maximum effect of the sterilization on the hydrolysis number is so slight as to be negligible. These are the two analyses of white oak and one of red oak infected with P. hirsutus, in which the maximum total effect of the decay plus the sterilization on the residue of stable cellulose (seventh column) has been to decrease it only 0.32 per cent.

Table 1.--Effect of sterilization on the constituents
of undecayed wood.

(All percentages are based on the dry (105° C.) weight
of the original wood.)

Material	Hot-water solubles	Cellulose	Pentosans in cellulose
	Per cent	Per cent	Per cent
White spruce:			
Original wood	3.73	55.43	4.36
Sterilized	4.71	55.87	4.43
White oak:			
Original wood	5.23	53.24	14.45
Sterilized	5.86	53.68	14.24
Red oak:			
Original wood	4.97	53.15	13.68
Sterilized	5.65	53.06	13.78

Before the determinations shown in Tables 1, 2, and 4 were made, the samples were extracted for 4 hours with a 1:2 alcohol-benzene mixture in order to remove any extractive material that might interfere with the cellulose determination. The cellulose was determined by the Cross and Bevan method as modified by Ritter,[7] and the pentosans in cellulose by the method used by Schorger.[8] Pentosan determinations

[7]Ind. Eng. Chem., 16, 947 (1924).
[8]Ibid., 9, 556 (1917).

(table 2) were made on the 2- and the 6-month samples, and both pentosan and hydrolysis number determinations on the 4-month samples (table 4).

Table 2.--Effect of decay on pentosans in cellulose.

(All percentages are based on the dry (105° C.) weight of the original wood.)

Duration of decay	Inoculum	Total loss in weight due to decay	Cellulose	Loss of cellulose due to decay	Pentosans in cellulose	Ratio pentosans to hexosans
Months		Per cent		Per cent		
			White spruce			
...	None	...	55.43	...	4.36	1:11.7
2	L.striata	15.5	35.98	19.45	1.26	1:27.5
4	L.striata	18.0	35.21	20.22	1.37	1:24.7
4	L.striata	20.2	32.38	23.05	1.28	1:24.3
6	L.striata	40.5	16.99	38.44	0.22	1:95.3
2	P.hirsutus	9.8	43.18	12.25	2.71	1:14.9
4	P.hirsutus	6.2	51.16	4.27	3.75	1:12.6
4	P.hirsutus	10.3	46.84	8.59	3.56	1:12.2
6	P.hirsutus	6.7	51.30	4.13	3.69	1:12.9
			Southern cypress			
...	None	...	52.65	...	5.05	1:9.4
2	L.striata	29.2	20.74	31.91	0.41	1:50
4	L.striata	39.1	12.04	40.61	...	...
4	L.striata	39.2	12.38	40.27	...	...
6	L.striata	56.9	1.78	50.87	0.00	1:00
2	P.hirsutus	1.6	49.26	3.39	4.32	1:10.4
4	P.hirsutus	0.7	50.70	1.95	4.81	1:9.5
4	P.hirsutus	0.8	50.42	2.23	4.21	1:10.9
6	P.hirsutus	2.3	50.41	2.24	4.87	1:9.35

(Continued)

Table 2. (Continued)

Dura-tion of decay	Inoculum	Total loss in weight due to decay	Cellu-lose	Loss of cellu-lose due to decay	Pento-sans in cellu-lose	Ratio pentosans to hexosans
Months		Per cent			Per cent	
			White oak			
...	None	...	53.24	...	14.45	1:2.7
2	L.striata	22.5	26.26	26.98	3.61	1:6.3
4	L.striata	20.0	28.84	24.40	3.90	1:6.4
4	L.striata	40.8	14.85	38.38	1.49	1:9.0
6	L.striata	64.8	2.11	51.13	0.00	1:00
2	P.hirsutus	1.7	51.88	1.36	13.60	1:2.8
4	P.hirsutus	1.9	52.29	0.95	12.90	1:3.3
4	P.hirsutus	2.3	52.76	0.48	12.28	1:3.1
6	P.hirsutus	3.8	51.77	1.47	12.40	1:3.2
			Red oak			
...	None	...	53.15	...	13.68	1:2.9
2	L.striata	17.5	33.96	19.19	5.40	1:5.3
4	L.striata	18.9	31.64	21.51	4.85	1:5.2
4	L.striata	25.0	26.32	24.83	4.53	1:5.5
6	L.striata	32.4	23.69	29.46	3.71	1:5.3
2	P.hirsutus	0.9	51.83	1.32	12.07	1:3.3
4	P.hirsutus	1.4	52.16	0.99	11.27	1:3.6
4	P.hirsutus	1.5	52.56	0.59	11.95	1:3.4
6	P.hirsutus	2.1	52.24	0.91	12.10	1:3.3

Discussion of Results

The loss of weight due to decay in a laboratory sample of wood cannot be taken as an exact measure of the usual effect of the fungus on that particular species of wood since it is difficult to control experiments in decay so as to get either reproducible results or those which might be found in practice. For instance, the attack of P. hirsutus on the sapwood of the oaks and cypress was very slight, and even on white spruce the maximum loss in weight due to this

decay was only 10.3 per cent, but such results do not necessarily mean that the sapwood of oak and cypress is commonly more resistant to the attacks of this fungus than is spruce sapwood, nor that P. hirsutus is commonly less destructive than L. striata. The amounts of decay indicated for these two fungi should be used only for correlation with the analytical data on changes in chemical composition of the woods.

In Table 2 are found the determinations of the cellulose and of the pentosans in cellulose, on both the original and the decayed wood. In every case but one the ratio of pentosans to hexosans is smaller in the partly decayed wood, indicating that the pentosans in cellulose are more rapidly attacked, in proportion to the amount present, than hexosans. The exception (southern cypress, 6 months L. striata) exhibits only a very small amount of decay, and because of the resulting minuteness of the quantities involved the assumption of only a slight error in the cellulose determination or a very slight error in the pentosan determination would fully explain this single deviation from the rule. In two cases, where nearly all of the cellulose had been removed, the residues contained no determinable amount of pentosans and in several cases at the other extreme, where only small amounts of cellulose had been removed, the pentosans formed a very large proportion of the cellulose destroyed. In fact, the analyses of two samples showed losses in the pentosans in cellulose greater than the losses in total cellulose; these discrepancies between the value of the part and the whole again[9] throw doubt on the reliability of our present analytical methods.

The general conclusions can safely be drawn from this investigation that the pentosans in cellulose are among the very first constituents of wood which are attacked by decay and that, in proportion to the amount present, they are more rapidly removed than the hexosans in the cellulose.

These conclusions are different from those reached by Rege,[10] who maintains that in straw and wood the pentosans not in cellulose are the very first constituents attacked by decay organisms, and that the pentosans in cellulose are highly resistant. He determined cellulose, however, only after an extraction for 20 minutes with hot 1 per cent sodium

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[9] Several examples of apparent unreliability of certain analytical methods for wood constituents are mentioned by Hawley and Campbell, Ind. Eng. Chem., 19, 742 (1927).

[10] Ann. Appl. Biol., 14, 1 (1927). This report also came to our attention after our experimental work was completed.

hydroxide solution. Although the recent work of Hawley and Campbell[11] shows that the actual results of this method of analysis probably differ only slightly from ours, it shows also that the nature of the disagreement in methods prevents strictly quantitative comparison of results. Dropping the question of such quantitative comparison, therefore, and looking more closely into his process of derivation, Rege's own figures, the present writers find, do not fully confirm his conclusions on the point in question. He reaches his conclusions about the high resistance to decay of the pentosans in cellulose by indirect methods, and does not offer actual comparisons of the amounts of the two kinds of pentosans removed by decay. Only five determinations of loss of the pentosans in cellulose are recorded in his paper, and these are tabulated by him merely for comparison with the corresponding loss of total cellulose. The materials and figures he reported for these determinations are shown in the first four columns of Table 3; the figures in the fifth column were calculated from the fourth column and from results recorded in Table 5 of Rege's original paper and are tabulated here for comparison. In only one case, a straw, is any considerably greater loss shown in Column 5 than in Column 4, and in two cases out of the five the loss of pentosans in cellulose is actually greater than that of pentosans not in cellulose; this difference in the case of wood, the material of most interest here, is by far the largest in the table. The figures in Columns 3 and 4 of this table do give indications contrary to the present writers' conclusions that the pentosans in cellulose are attacked more rapidly than the rest of the cellulose, but here again the differences are slight except in the first case, and the dissimilar analytical method used tends to make these pentosan figures lower than those of the writers.

The work of Smith,[5] on the other hand, tends toward direct confirmation of the writers' results, although on account of unlike analytical methods his results also are not strictly comparable; he found a greater percentage decrease in the pentosans in cellulose than in either pentosan-free cellulose or "hemicellulose pentosans."

Table 4 presents the hydrolysis number and the pentosan determinations on the 4-month samples. The decay was expected to affect first the readily hydrolyzable portions of the cellulose and to attack the more stable

[11]Ind. Eng. Chem., 19, 742 (1927).

Table 3.--Constituents removed by decay, expressed
in percentage of original values.

(Arranged from Rege's results)

Material	: Duration : of : decay	: Cellu-: : lose :	: Pentosans : in : cellulose	: Pentosans : not in : cellulose
	Days	P e r	c e n t	Per cent
Straw	8	21.3	9.0	21.3
Straw	12	45.0	40.0	43.4
Straw	40	75.6	73.0	81.6
Wood	60	63.2	52.4	39.0
Wood and straw	60	73.2	72.8	72.3

cellulose only after those portions had been largely removed.
Earlier indications to this effect[12] were not confirmed, how-
ever; the stable residue of unhydrolyzed cellulose was always
attacked by decay, even when the total loss of cellulose had
been very slight.

In three cases the hydrolysis number of the cellu-
lose was slightly increased by decay (showing preferential
attack on the stable cellulose), but in all other cases it
either remained the same, within the limit of error, or
actually decreased. Where the removal of cellulose by decay
amounted to more than 10 per cent, the pentosans in the un-
hydrolyzed residue were taken away more rapidly than the
hexosans (cf. columns 6 and 9 of Table 4); where the decay
was slight, however, an occasional apparent increase in
pentosans in the unhydrolyzed residue occurred but this was
almost within the limit of accuracy of the determination.

Although P. hirsutus is a typical white-rot fungus,
yet its method of attack apparently is not different from
that of the typical brown-rot fungus L. striata, at least
during the first stages of the decay. A loss in weight of
only 10.3 per cent is the greatest obtained by P. hirsutus
in this study, however, and a further attack, therefore,
might show different effects on the chemical composition of
the wood. Unfortunately, most of the chemical data on the

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[12]Rue, Miller, and Humphrey, Pulp Paper Mag. Can., 22, 93
(1924); Hawley and Wise, "The Chemistry of Wood," p.310.

Table 4.—Effect of decay on the hydrolysis number of cellulose.

(All percentages are based on the dry (105° C.) weight of the original wood.)

Inoculum	Total loss in weight due to decay	Cellu-lose	Loss of cellu-lose due to decay	Hydroly-sis No. of cellu-lose	Resi-due after hy-droly-sis	Loss in residue after hy-droly-sis	Pento-sans in cellu-lose	Pento-sans in residue after hydroly-sis
	Per cent	Per cent	Per cent		Per cent	Per cent	Per cent	Per cent
White spruce								
None	..:	55.43	..:	19.28	44.73	..:	4.36	1.29
P.hirsutus	6.2	51.16	4.27	19.90	40.98	3.75	3.75	1.50
P.hirsutus	10.3	46.84	8.59	21.29	36.87	7.86	3.56	1.38
L.striata	18.0	35.21	20.22	12.39	30.85	14.88	1.37	0.61
L.striata	20.2	32.38	23.05	11.51	28.57	16.16	1.28	0.55
Southern cypress								
None	..:	52.65	..:	16.41	44.00	..:	5.05	1.86
P.hirsutus	0.7	50.70	1.95	16.54	42.31	1.69	4.81	1.93
P.hirsutus	0.8	50.42	2.23	16.04	42.33	1.67	4.21	1.87
L.striata	39.1	12.04	40.61	18.14	9.86	34.14	a	0.00
L.striata	39.2	12.36	40.27	18.73	10.06	33.94	a	0.00

(Continued)

aNot determined.

Table 4. (Continued)

Inoculum	Total loss in weight due to decay	Cellulose	Loss of cellulose due to decay	Hydrolysis No. of cellulose	Residue after hydrolysis	Loss in residue after hydrolysis	Pentosans in cellulose	Pentosans in residue after hydrolysis
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
White oak								
None	..	53.24	..	25.85	39.48	..	14.45	2.94
P.hirsutus	2.3	52.76	0.48	25.52	39.30	0.18	12.28	3.03
P.hirsutus	1.9	52.29	0.95	25.10	39.16	0.32	12.90	3.24
L.striata	40.8	14.86	38.38	17.82	12.31	27.17	1.49	0.56
L.striata	20.0	28.84	24.40	19.49	23.22	16.26	3.90	0.96
Red oak								
None	..	53.15	..	26.40	39.13	..	13.62	2.79
P.hirsutus	1.5	52.56	0.59	26.16	38.81	0.32	11.95	2.71
P.hirsutus	1.4	52.16	0.99	26.34	38.42	0.71	11.27	2.72
L.striata	25.0	28.32	24.83	18.42	23.10	16.03	4.53	1.17
L.striata	18.9	31.64	21.51	18.27	25.86	13.27	4.85	0.83

effect of decay have been obtained on brown rots and as yet the data on white rots are insufficient for any generalizations.

Table 4 contains two sets of figures that should be discussed even though they do not deal with partly decayed wood, the figures in Columns 6 and 9 on the unhydrolyzed residue and the pentosans in the unhydrolyzed residue from uninfected wood. It is noticeable that the stable cellulose (cellulose not readily hydrolyzed) in the two softwoods is very nearly the same (about 44 per cent) and is much higher than in the two hardwoods (about 39 per cent); perhaps we have here another chemical distinction between hardwoods and softwoods. Further, the stable cellulose of the softwoods contains less pentosan than that of the hardwoods, although a greater proportion of the pentosans in cellulose remain unhydrolyzed in the softwoods (about one-third) than in the hardwoods (about one-fifth). The decision on the generality of these differences between softwoods and hardwoods, of course, requires first the determination of the pertinent factors on many more species.

Summary

1. In the decay of the sapwood of two hardwoods and two softwoods caused by one brown-rot and one white-rot fungus, the pentosans in cellulose were among the first constituents attacked and at all stages of decay they were removed more rapidly, in proportion to the amount present, than the hexosans in the cellulose.

2. Both the stable and the readily hydrolyzed portions of the cellulose were always attacked, but in most cases there was a preferential attack on the readily hydrolyzed portion.

3. Although the white-rot fungi are supposed to attack the lignin preferentially, Polystictus hirsutus, a white rot, during the first stages of decay is like the brown rots in its preferential attack on the cellulose. Further data on the effect of various white rots at different stages of decay are desirable.

4. The two softwoods had a larger amount of stable cellulose than the hardwoods, while the two hardwoods had more pentosans in this stable cellulose than did the softwoods.