Quantitative Changes in Structural Components of Conifer Woods During Decay by White- and Brown-Rot Fungi

T. K. Kirk and T. L. Highley

Plant Pathologists, Forest Products Laboratory, Forest Service, U.S. Department of Agriculture, Madison, Wisconsin 53705.

ABSTRACT

Quantitative changes in lignin, glucan, mannan, and xylan during decay of five conifer woods by three white-rot and three brown-rot fungi were determined. (Glucan, mannan, and xylan provided estimates of cellulose and the hemicelluloses galactoglucomannan and arabino-4-O-methylglucuronoxylan, respectively.) All the white-rot fungi removed all the major wood components progressively during decay; the brown-rot fungi removed the polysaccharides but not lignin. The white- and brown-rot fungi removed the mannan, and usually xylan, faster than glucan, but the difference was not as pronounced for the white-rot as for the brown-rot organisms. The brown-rot fungi all had similar effects on the chemical composition of all the woods. In the white-rot type of decay there was variation in the effects on the chemical composition; this appeared to depend more on the wood being decayed than the fungus involved.

Phytopathology 63:1338-1342

Additional key words: Polyporus versicolor, Ganoderma applanatum, Peniophora "G", Poria monticola, Lenzites trabea, Lentinus lepideus.

Very few studies have been made of the relative rates of removal of the structural components of wood (cellulose, hemicelluloses, and lignin) during decay by white-rot and brown-rot fungi (5). This is particularly true for conifer woods. To our knowledge, quantitative determinations of changes in the individual types of structural sugar polymers (glucan, mannan, and xylan) during the decay of conifer woods by either white-rot or brown-rot fungi have not been made. For hardwoods, such detailed analyses seem to have been done only by Cowling (3). The present study determined changes in the composition of representative conifer woods during decay by white- and brown-rot fungi commonly used in laboratory tests at the U.S. Forest Products Laboratory. The specific purposes of obtaining these

data were: (i) to provide information on the importance of hemicellulose decomposition during decay; (ii) to evaluate variation in the relative rates of removal of the major wood components, both among the different fungi with a given wood, and among different woods with a given fungus; and (iii) to better characterize the specific effects of our common wood-decay test organisms on the chemical composition of conifer woods.

MATERIALS AND METHODS.—*Wood samples and decay.*—Sapwood blocks 25.4 X 25.4 X 9.5 mm (1 X 1 X 3/8 inches), the small dimension with the grain, were cut from western hemlock [*Tsuga heterophylla* (Raf.) Sarg.], western white spruce [*Picea glauca* var. *albertiana* (S. Brown) Sarg.], Sitka spruce [*Picea sitchensis* (Bong.) Carr.], western white pine (*Pinus monticola* Dougl.) and southern pine (probably loblolly pine, *Pinus taeda* L.). These were decayed in soil block (1) or agar block (10) chambers for various periods of time to obtain samples of various extents of decay. Percentage weight loss, the measure of decay, was calculated from the weights of the decayed blocks after equilibration at 70% relative humidity and 27 C. The blocks decayed more slowly in the agar block chambers and most of the samples of small weight loss were from those chambers. Noninoculated blocks served as controls.

Blocks were decayed by three white-rot fungi, *Polyporus versicolor* (L. ex Fr.) (Madison 698), *Ganoderma applanatum* [Pers. ex Wallr. (Pat.)] (Madison 708), and *Peniophora* "G" (ME 461, not identified to species); and three brown-rot fungi, *Poria monticola* (Murr.) (Madison 698), *Lenzites trabea* (Pers. ex Fries) (Madison 617), and *Lentinus lepideus* (Fries) (Madison 534).

Analytical techniques.—Decayed and control blocks were ground to pass a 40-mesh screen and the wood meal dried in a vacuum oven at 45 C.

The wood meals were analyzed, without extraction, for sulfuric acid lignin, and for total reducing sugars in acid hydrolysates (determined colorimetrically as glucose) (9). Relative amounts of glucose, xylose, and mannose, and the total reducing sugars, as glucose, in acid hydrolysates were determined colorimetrically after paper chromatographic separation (9). From these values the glucan, xylan, mannan, and lignin and the losses of each during decay were calculated (12).

Acid hydrolysis of conifer woods yields 0.5-2% each of arabinose and galactose, which arise from the hemicelluloses (13). In the analysis used here, these two sugars are not separated from the main sugars (glucose, mannose, and xylose) and, therefore, contribute to the value obtained for total reducing sugars. On paper chromatograms, the galactose is not separated from the glucose, and the arabinose is not separated from the mannose. (To separate out these sugars requires an additional step and decreases the accuracy of the analyses of all the sugars) (9). Therefore, the presence of these two minor sugars leads to a slight overestimate of glucan and mannan and a slight underestimate of xylan. These errors, however, are considered to be insignificant in the present work.

Conifer wood is composed mainly of cellulose, a hemicellulose of the galactoglucomannan type (approximately 70% mannan), and lignin, plus a smaller percentage of a hemicellulose of the arabino-4-*O*-methylglucuronoxylan type (about 65% xylan) (13). Consequently, determination of glucan gave an estimate of cellulose (with a small error due to the glucose in glucomannan), mannan an estimate of the major hemicellulose, and xylan an estimate of the minor hemicellulose.

RESULTS.—Table 1 gives the composition of the sound woods. These woods contained from 27-32% lignin, 41-46% glucan (mostly cellulose), 15-17% mannan (in glucomannan), 4-7% xylan (in glucuronoxylan), and 6-10% "other" materials. The 6-10% of each sample labeled "other" materials includes extractives, acid-soluble lignin, acetyl, inorganic components, and uronic acid.

The percentage of this "other" material increased during decay by each fungus, up to 12-22% at the highest weight losses when expressed on the basis of the decayed sample. This increase is considered to reflect: (i) failure of the organisms to attack some of these materials (e.g., the inorganic components, certain extractives), and (ii) formation of additional materials (acid-soluble degraded lignin, fungus products) that did not analyze as one of the major wood components. These materials are not considered further in this report, since they do not affect our conclusions concerning the major structural components.

The analytical values for the decayed woods are summarized in Tables 2 and 3 as losses in lignin, glucan, mannan, and xylan, with results expressed as a percentage of the original amounts of each. In addition, data for the Sitka spruce decayed by *Polyporus versicolor* and *Poria monticola* are illustrated graphically in Figures 1 and 2.

Though lignin was removed progressively by all

TABLE 1. Analytical data for sound woods[a]

Wood species	lignin (%)	glucan (%)	mannan (%)	xylan (%)	other[b] (%)
Western hemlock	32.1	40.8	14.6	5.0	7.6
Southern pine	28.6	43.5	14.9	6.7	6.3
Western white pine	27.6	41.2	15.4	6.1	9.7
Sitka spruce	28.6	44.0	16.8	4.4	6.3
Engelmann spruce	27.0	45.9	15.0	5.9	6.2

[a] The analytical methods used here were developed to give accurate values with various wood samples (9). To estimate the precision of the methods, 12 replicate analyses were made over a period of time for a homogeneous sample of aspen wood, with statistical results as follows (data given in the following order: component analyzed, sample mean, sample standard deviation, 95% confidence interval for the true mean): glucan, 50.76, 0.31, 50.57 - 50.95; mannan, 2.36, 0.07, 2.31 - 2.41; xylan, 18.92, 0.33, 18.71 - 19.13; and lignin, 18.19, 0.32, 17.99 - 18.39.

[b] Includes extractives, acid-soluble lignin, acetyl, uronic acids, etc.

TABLE 2. Loss of major structural components[a] from conifer woods after various extents of decay by white-rot fungi

Wood, Fungus	In total weight (%)[b]	In lignin (%)[c]	In glucan (%)[c]	In mannan (%)[c]	In xylan (%)[c]
			Loss		
Western white pine, *Polyporus versicolor*	13	27	4	13	13
	22	33	17	22	21
	43	52	43	47	47
	61	62	65	68	67
	83	86	85	89	89
Western white pine, *Ganoderma applanatum*	16	26	12	16	19
	43	57	42	52	51
	52	68	49	63	64
Western white pine, *Peniophora* "G"	11	15	6	3	6
	30	34	29	39	41
	46	51	51	59	59
Sitka spruce, *Polyporus versicolor*	6	5	10	13	3
	21	20	27	29	27
	40	52	39	50	45
	61	65	65	72	66
Sitka spruce, *Ganoderma applanatum*	11	11	13	18	17
	35	48	33	47	44
	49	52	52	68	58
Southern pine, *Polyporus versicolor*	6	15	5	13	2
	21	19	24	28	33
	38	34	42	42	50
	61	62	65	68	63

[a] Expressed on the basis of the original amount of each component in the sound wood (Table 1).

[b] Decayed blocks were selected so that those combined for analysis were within a 3% weight loss interval.

[c] These data are based on a single determination of each component in each sample. The methods used have proven to give reproducible values (see footnote "a", Table 1).

the white-rot fungi, the rate of removal was not usually linear. The relative extents of removal of the lignin and other components also varied during the decay process; for example, at a 22% weight loss of western white pine inoculated with *P. versicolor*, 33% of the lignin and only 17-23% of the other components had been removed, whereas at a 55% weight loss all the components had been depleted to a comparable extent. There was also some variation in relative extents of removal of the wood components
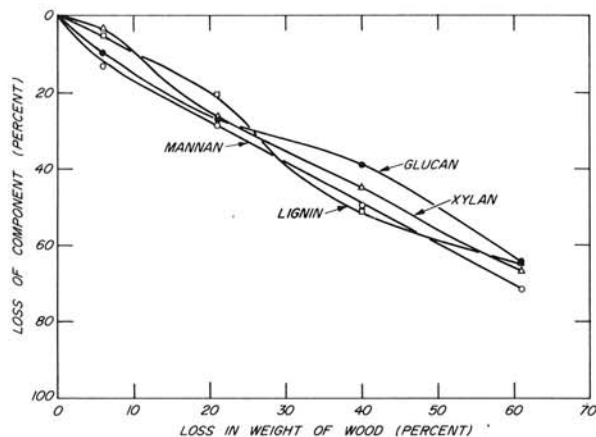

Fig. 1. Progressive loss of major structural components in the decay of Sitka spruce wood by *Polyporus versicolor*.
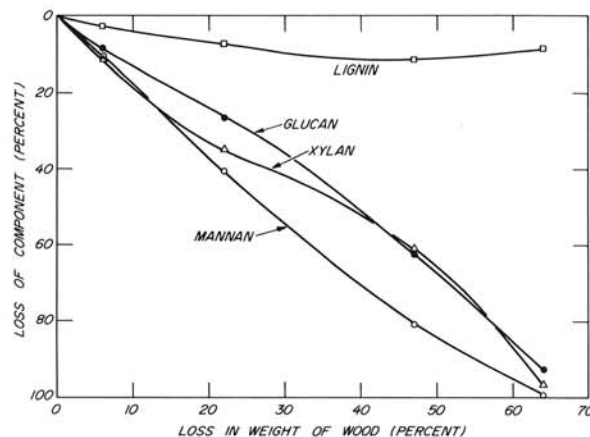

Fig. 2. Progressive loss of major structural components in the decay of Sitka spruce wood by *Poria monticola*.

TABLE 3. Loss of major structural components[a] from conifer woods after various extents of decay by brown-rot fungi

Wood, Fungus	Loss				
	In total weight (%)[b]	In lignin (%)[c]	In glucan (%)[c]	In mannan (%)[c]	In xylan (%)[c]
Western hemlock, *Poria monticola*	6	8	4	11	16
	26	4	26	38	39
	46	–2	79	88	75
Engelmann spruce, *Poria monticola*	12	6	13	26	22
	26	10	29	41	69
	49	–13	81	93	79
Sitka spruce, *Poria monticola*	6	3	9	11	11
	22	7	26	40	34
	47	12	62	81	62
	64	8	93	99	97
Sitka spruce, *Lenzites trabea*	10	9	12	14	18
	19	4	22	47	37
	43	11	55	80	65
Sitka spruce, *Lentinus lepideus*	6	3	12	6	19
	27	–4	37	68	49
	45	6	57	78	64
Southern pine, *Poria monticola*	9	–4	13	25	1
	24	2	29	58	26
	45	4	68	81	69

[a] Expressed on the basis of the original amount of each component in the sound wood (Table 1).

[b] Decayed blocks were selected so that those combined for analysis were within a 3% weight loss interval.

[c] These data are based on a single determination of each component in each sample. The methods used have proven to give reproducible values (see footnote "a", Table 1).

among different fungi on a given wood. For example, lignin was removed from white pine wood ahead of the other components by *Ganoderma applanatum*; whereas, with *Peniphora*, at weight losses above about 25%, the hemicellulose removal exceeded lignin removal (Table 2). The variation with a given fungus on different woods was somewhat more pronounced, and is well illustrated by comparing western white pine and Sitka spruce decayed by *P. versicolor* or these woods decayed by *Ganoderma applanatum* (Table 2). The lignin generally was removed by the white-rot fungi somewhat more preferentially than carbohydrates from the white pine, but not from southern pine or Sitka spruce (Table 2).

With the brown-rot fungi, the lignin was generally only slightly depleted but the values were irregular.

The lignin analysis is reproducible, but it is based simply on the acid-insolubles in the samples following acid hydrolysis. Although the analysis is as accurate as any other for sound conifer wood, it is clearly not definitive or absolute, and is particularly problematical for samples such as brown-rotted wood

(2), which contain modified lignin (4). Thus, the indicated decreases (and in some cases increases) in the lignin content of the brown-rotted samples, undoubtedly in part reflect idiosyncrasies of the analysis. White-rotted wood apparently contains only a small amount of degraded lignin (6), so the lignin analysis is more reliable.

The cellulose (glucan) was usually removed from the woods at a relatively constant, or slightly increasing, rate by both white- and brown-rot fungi. In the white rots, this rate was approximately the same as the loss in total weight; whereas, in the brown rots the loss of cellulose was always greater than the loss in total weight, which reflects the failure to deplete the lignin.

The rates of removal of the mannan and especially xylan were more variable than was the rate of removal of the glucan by white- and brown-rot fungi. In all of the woods, and with both white-rot and brown-rot fungi, the major hemicellulose (mannan) was removed faster than the cellulose (glucan) (Tables 2 and 3). This was much more pronounced with the brown rots.

Our results suggest a greater effect of the wood than of the decay fungus in determining the relative rates of removal of the major structural components by the white-rot fungi from the woods examined here. The similarities of the effects of different fungi on the same wood are illustrated by results with white pine and Sitka spruce. With white pine, the three fungi used were generally similar in their relative rates of removal of the mannan, glucan, and lignin—lignin and mannan being removed faster than the glucan during most of the decay. For Sitka spruce decayed with the two fungi used, the patterns of these rates of removal were very similar. With the same fungus on different woods, the effects were more variable. *P. versicolor* removed the major components at different relative rates from the three different woods, and the same was true of *G. applanatum* with Sitka spruce and white pine (Table 2).

The brown-rot fungi were similar with all the woods in the relative rates of removal of the glucan and mannan - mannan being removed faster in each case. The variation in xylan removal by the brown-rot fungi depended more on the wood than the fungus. Even so, with respect to the lignin, glucan, and mannan, neither the woods nor differences in fungi appeared to markedly influence the pattern of decay by the brown-rot type of organisms.

DISCUSSION.—The preferential depletion of mannan during brown rot, and to a lesser extent during white rot, has apparently not been noted previously. Seifert (11) analyzed cellulose, total pentosans (xylan, arabinan), and lignin in pine after various extents of decay by a brown-rot fungus, *Coniophora cerebella*. He did not assay for the major hemicellulose (glucomannan). In his study, the cellulose and pentosans were depleted approximately simultaneously, in a pattern similar to that with Sitka spruce and *Poria monticola* studied here. Kretsberg et al. (8) showed that the total pentosans are destroyed

faster than the cellulose, and the lignin more slowly than cellulose or pentosans, during the decay of spruce by the white-rot fungus *Trametes trogii* Berk. Again, however, the major hemicellulose was not analyzed. The pattern is similar to that in the 20-50% weight loss interval during decay of southern pine by *P. versicolor* in this study (Table 2).

In the brown-rot type of decay, the cellulose and possibly the hemicelluloses undergo an extensive depolymerization before much weight loss has occurred (3). Subsequent degradation and removal occurs progressively. Our results indicate that glucomannan is removed faster than cellulose from conifer woods and suggest that further degradation and removal of the depolymerized cellulose may depend on prior or concomitant removal of this major hemicellulose component. The same could be true for hardwoods. Cowling (3) found the mannan component to be preferentially removed from sweetgum by *Poria monticola*. However, in hardwoods (such as sweetgum) mannan is a minor component (13).

The white-rot type of decay differs biochemically from brown-rot. In the former, (i) no initial extensive depolymerization of the cellulose occurs (3), and (ii) the lignin is decomposed and removed. In other respects the two types are similar; i.e., the progressive removal of all the wood sugar polymers. The results here suggest that this similarity may go even further with conifer woods in that removal of glucomannan may precede removal of cellulose in both brown and white rots. However, analyses of additional wood/fungus combinations should be done before it can be established whether or not this is a valid generalization for white rots. It is clearly not as pronounced as with brown rots. In the white rot of hardwoods, neither the major hemicellulose, xylan, nor the mannan is consistently removed before the glucan (3, 7). Thus, it is possible that only in conifers is the major hemicellulose the most rapidly removed component.

Our results indicate that the selectivity of lignin removal by white-rot fungi depends strongly on the type of wood being decayed. Other recent studies also disclosed similar differences between birch and aspen wood and, more significantly, between hardwoods and conifer woods in this respect (7).

There was no clear relationship between relative rates of removal of the major components and the resistance of the woods to decay by the white- or the brown-rot fungi (the relative decay resistances are indicated by the average loss in weight after 12 weeks of decay by *Polyporus versicolor* and *Poria monticola*, Table 4).

CONCLUSIONS.—1) Three white-rot fungi removed all major wood components from conifer woods progressively during decay; three brown-rot fungi removed glucan, mannan, and xylan but not lignin.

2) The brown-rot fungi removed mannan and usually xylan faster than glucan from the five woods. The same was true for the white-rot fungi, but in these cases the difference was not as pronounced as with the brown-rot organisms.

3) The brown-rot fungi all had similar progressive effects on the chemical composition of all the woods. There was variation with the white-rot type of decay in the relative rates of removal of the major structural components—more so with a given fungus among different woods than with different organisms on the same wood.

LITERATURE CITED

1. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1963. Standard method for accelerated laboratory test of natural decay resistance of woods. ASTM D 2017, 1963 Book of ASTM Standards, Part 6:673-680.
2. COWLING, E. B. 1960. Methods for the chemical analyses of decayed wood. U.S. Dep. Agric., For. Serv., For. Prod. Lab. Rep. No. 2177, 23 p.
3. COWLING, E. B. 1961. Comparative biochemistry of the decay of sweetgum sapwood by white-rot and brown-rot fungi. U.S. Dep. Agric. Tech. Bull. 1258. 79 p.
4. KIRK, T. K. 1971. Effects of microorganisms on lignin. Annu. Rev. Phytopathol. 9:185-210.
5. KIRK, T. K. 1973. The chemistry and biochemistry of decay. p. 149-181. *In* D. Nicholas [ed.]. Wood deterioration and its prevention by preservative treatments. Syracuse University Press, Syracuse, N.Y.
6. KIRK, T. K., & K. LUNDQUIST. 1970. Comparison of sound and white-rotted sapwood of sweetgum with respect to properties of the lignin and composition of extractives. Sven. Papperstidn. 73:294-306.
7. KIRK, T. K., & W. E. MOORE. 1972. Removing lignin from wood with white-rot fungi and digestibility of resulting wood. Wood and Fiber 4:72-79.
8. KRETSBERG, Z. N., V. N. SERGEEVA, & Ya. K. GRABOVSKI. 1971. Investigation of wood destroyed by enzymes. IV. The effect of Trametes trogii on spruce wood. (In Russian). Khim. Drev. 7:115-118.
9. MOORE, W. E., & D. B. JOHNSON. 1967. Procedures for the chemical analysis of wood and wood products (as used at the U.S. Forest Prod. Lab.), USDA Forest Service, Madison, Wisc.
10. SCHEFFER, T., & C. G. DUNCAN. 1947. The decay resistance of certain Central American and Ecuadorian woods. Trop. Woods Yale Univ. Sch. For. 92:1-24.
11. SEIFERT, K. 1968. Zur Systematik der Holzfäulen, ihre Chemischen und Physikalischen Kennzeichen. Holz Roh-Werks. 26:208-215.
12. SPRINGER, E. L. 1966. Hydrolysis of aspenwood xylan with aqueous solutions of hydrochloric acid. Tappi 49:102-106.
13. TIMELL, T. 1967. Recent progress in the chemistry of wood hemicelluloses. Wood Sci. Technol. 1:45-70.

TABLE 4. Weight loss produced by *Poria monticola* and *Polyporus versicolor* in sapwood of conifers after 12 weeks in the soil-block test[a]

Wood species	Weight loss (%) caused by:	
	P. versicolor	*P. monticola*
Western hemlock	18 ± 4.0	55 ± 3.7
Sitka spruce	29 ± 8.4	65 ± 1.2
Southern pine	34 ± 9.1	51 ± 2.0
Western white spruce	35 ± 2.2	60 ± 2.5
Western white pine	50 ± 5.1	67 ± 1.5

[a] Average of six blocks with standard deviation.