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Characterization of acetylated wood decayed by brown-rot and white-rot fungi*

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Abstract The objective of this study was to characterize the decay of acetylated wood due to brown-rot and white-rot fungi by analysis of chemical composition, X-ray measurements, and ^{13}C-NMR spectroscopy. The decay by brown-rot fungus became inhibited at a weight percent gain (WPG) due to acetylation of more than 10%, and the mass loss (LOSS) due to decay became zero at a WPG of about 20%. The LOSS due to white-rot fungus decreased slowly with the increase in WPG, reaching zero at a WPG of about 12%. The losses of lignin by brown-rot decay increased initially with the decrease in LOSS owing to the progressing acetylation and then decreased at a LOSS of less than 60%. Polysaccharides were more easily decomposed than lignin during the decay of acetylated wood due to brown-rot fungus. The losses of both components due to white-rot decay decreased as the LOSS decreased with progressing acetylation. The white-rot fungus tended to preferentially decompose the lignin during the decay of acetylated wood. The brown-rot fungus decomposed the cellulose in the crystalline region to a large degree when the LOSS was more than 40%, whereas the white-rot fungus decomposed the crystalline region and the noncrystalline region in acetylated wood to the same degree. The brown-rot fungus preferentially decomposed unsubstituted xylose units in acetylated wood and partly decomposed the mono-substituted xylose units. It was suggested that the mono- and disubstituted cellulose were partly decomposed by brown-rot fungus.

Key words Acetylated wood · Brown-rot and white-rot decay · Chemical composition · Crystallinity · Acetyl distribution

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Introduction

Many studies have been carried out on chemical changes in wood caused during decay due to rotting fungi by means of chemical analysis[1–6] and solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy.[7–11] These studies have provided the following generally accepted information. Brown-rot fungus primarily decomposes carbohydrates in wood. The fungus removes the hemicelluloses more rapidly than cellulose during the early decay stages, and does not decompose preferentially the non-crystalline cellulose. The lignin is altered by demethoxylation during the decay. On the other hand, there are three types of white-rot fungus, which respectively act to (1) decompose all wood components essentially uniformly; (2) remove the lignin at a faster rate than the carbohydrates during early decay stages; and (3) remove initially the carbohydrates somewhat more rapidly than lignin. Amorphous carbohydrates are decomposed slightly faster than crystalline cellulose during the white-rot decay. The lignin is oxidized by white-rot fungus. Enoki et al.[4] showed that the brown-rot fungus *Tyromyces palustris*, which was also used in our study, decomposed the polysaccharides preferentially, whereas the white-rot fungus *Coriolus versicolor* decomposed the lignin somewhat preferentially.

Acetylation of wood has been studied by many researchers, and many results have been obtained on the reaction methods and the given properties, such as dimensional stability, durability, and resistance to termites.[12] It has been also shown in many studies that acetylated wood had biological resistance.[13,14] The changes in chemical composition in acetylated wood caused by decay have been little studied. The carbohydrate analysis of Peterson and Thomas[15] indicated that hemicellulose was more extensively decomposed than cellulose in acetylated wood decayed by brown-rot fungus, but this situation was reversed in the white-rotted acetylated wood.

In the present study we characterized the decayed acetylated wood by the analysis of chemical composition, X-ray measurements, and ^{13}C-NMR analysis.

Experimental

Acetylation of wood

Extractives-free makamba (*Betula maximowiczii* Regel) cross-section specimens [2 cm(R) × 2 cm(T) × 0.5 cm(L)] were acetylated with an acetic anhydride with or without a catalyst in liquid or vapor phase. In the case of the catalyst method, the specimens were first impregnated with a 4% aqueous solution of sodium acetate and then dried at 105°C. The dried specimens were reacted with liquid acetic anhydride for from 15 min to 6 hr at 110°C. For the noncatalyst method, the specimens were dried and then reacted with liquid or vapor acetic anhydride for from 10 min to 24 hr at 90°–120°C. After the end of reaction, all specimens were fully washed with water. The weight percent gain (WPG) due to acetylation ranged from 1.8% to 23.1%.

Decay test by brown-rot and white-rot fungi

The wood specimens were decayed by brown-rot fungus *Tyromyces palustris* (Berk. et Curt.) Murr. FFPRI 0507 and white-rot fungus *Coriolus versicolor* (L. ex. Fr.) Quel. FFPRI 1030 for 12 weeks at 26°C and 70% relative humidity (RH) according to JIS A 9201–1991. There were three specimens in the brown-rot decay test and 18 specimens in the white-rot test for each condition. The mass loss (LOSS) due to decay was measured after drying.

Determination of chemical composition

The decayed acetylated wood was milled to analyze its chemical composition. The lignin content of the samples was determined by preparing Klason lignin and acid-soluble lignin. The content of acid-soluble lignin was determined by the ultraviolet (UV) spectrometric analysis at 205 nm using an absorptivity of 113 l/gcm.

Relative neutral monosaccharide compositions in the decayed acetylated wood were analyzed in the hydrolysates in the Klason lignin preparation by ion-exchange chromatography using a TSK gel Sugar AXI column with 0.45 M borate buffer (pH 8.8) at a speed of 0.40 ml/min.

X-ray diffractometry

X-ray diffractograms of the decayed and nondecayed acetylated wood were obtained with 20 mm diameter disks prepared by compressing the milled samples under a vacuum. The X-ray diffractometer used was a JEOL JDX-8200. The equatorial diffraction pattern was measured over a range of $2\theta = 3°–40°$ at a rate of 0.02°/s using Ni-filtered Cu-Kα radiation generated at 50 kV and 120 mA. The slit widths used were 1-1-0.4-0.5°. The crystallinity index (CrI) was estimated by measuring the areas of the crystalline and noncrystalline regions in the X-ray diffractograms according to Jayme and Knolle's method.[16,17]

^{13}C-NMR analysis

The changes of acetyl distribution in the wood due to decay were examined by ^{13}C-NMR spectroscopy. The milled samples were dissolved in a mixture (1:4) of *N*-methylmorpholine *N*-oxide monohydrate (MMNO) and dimethyl-d_6 surfoxide (DMSO-d_6) after light delignification in the same way as described in a previous paper.[18] The ^{13}C-NMR spectra were recorded on a JEOL JNM-GSX400 spectrometer operating at 100.4 MHz in a proton noise-decoupled mode. The spectra were obtained at 80°C using a 5-mm tube. The measurement conditions were the same as reported previously.[18]

Results and discussion

Mass losses of acetylated wood due to decay

The relation between the LOSS and the WPG is shown in Fig. 1. With the decay by the brown-rot fungus, the LOSS of nonacetylated wood was 72.8%. The LOSS was large at a WPG of less than 10% but quickly decreased thereafter, reaching zero at a WPG of about 20%. This indicates that the decay by brown-rot fungus was inhibited at a WPG of more than 10%. The decay power of white-rot fungus was lower than that of brown-rot fungus because the LOSS of the nonacetylated wood was just 23.0%. The LOSS decreased slowly as the WPG increased, reaching zero at a WPG of about 12%.

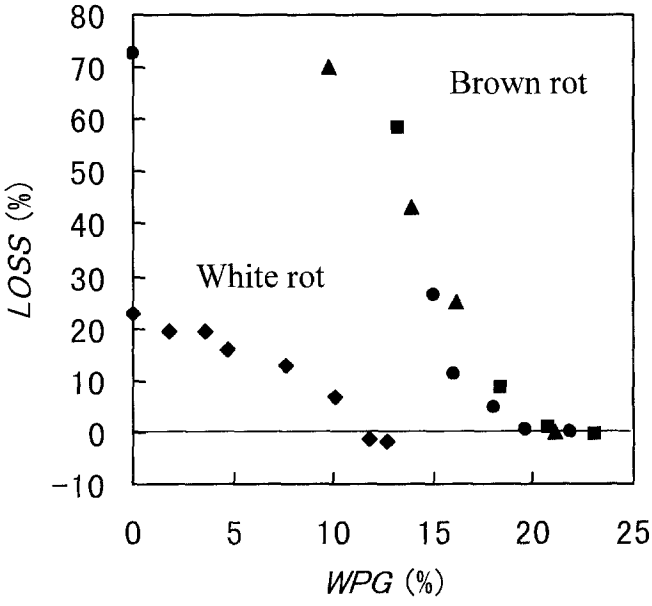

Fig. 1. Relation between mass loss (*LOSS*) due to decay and weight percent gain (*WPG*) due to acetylation in the decay test of acetylated wood. *Circles*, acetylated with catalyst; *triangles* and *rhombi*, without catalyst in liquid phase, *squares*, without catalyst in vapor phase

Changes of chemical composition due to decay

The content of various types of lignin measured for the decayed acetylated wood is shown in Table 1 together with the LOSS. The contents of Klason, acid-soluble, and total lignin were 21.4%, 3.0%, and 24.4% in the nondecayed nonacetylated control, respectively. In the brown-rotted nonacetylated wood (LOSS 72.8%), the lignin contents were 69.8%, 5.3%, and 75.0%, respectively, being considerably higher than that in the nondecayed control. This suggests that the polysaccharides were highly decomposed during the process of decay. The lignin content in the decayed acetylated wood decreased with increasing WPG.

In the white-rotted nonacetylated wood (LOSS 23.0%), the lignin contents were 19.8%, 3.2%, and 23.1%, respectively, being slightly lower than that in the control. There was little change in the lignin content of the decayed acetylated wood with an increase in WPG.

The lignin content mentioned above refers to the quantity of lignin based on the weight of decayed wood. Therefore, to obtain the lignin content in the decayed wood based on the weight before decay, the mass losses due to decay have to be taken into account. Moreover, because the acetyl groups were probably removed by the sulfuric acid used during the preparation of Klason lignin, the weight gains due to acetylation must also be counted. The corrected content of lignin can be calculated by multiplying the measured content by (1 − LOSS/100) and (1 + WPG/100), assuming that the WPGs of wood specimens do not change during the decay.

$$\text{Corrected content} = \text{measured content} \times (1 - \text{LOSS}/100) \times (1 + \text{WPG}/100) \quad (1)$$

The corrected lignin content in the decayed acetylated wood is shown versus the LOSS in Fig. 2. The corrected contents of Klason, acid-soluble, and total lignin were 19.0%, 1.4%, and 20.4%, respectively, in the brown-rotted nonacetylated wood (LOSS 72.8%). These values were lower than those in the nondecayed control (21.4%, 3.0%, and 24.4%, respectively). In the decayed acetylated wood, the corrected content of Klason lignin initially dropped with the decrease in LOSS resulting from the increase in WPG but then increased as the LOSS fell below 58.2% (WPG 13.3%). The corrected content of acid-soluble lignin increased evenly as the LOSS decreased. As a result, the corrected content of total lignin had the same tendency of change as the Klason lignin. When LOSS was more than 25.3% (corresponding to a WPG of less than 16.2%), the corrected content of total lignin in the decayed acetylated wood was lower than that in decayed nonacetylated wood (LOSS 72.8%). This indicates that more lignin was decomposed over this range of LOSS. We reported in a previous paper[18] that the acetyl substitution in hydroxyl groups of xylan and cellulose in the amorphous region occurred at a WPG of 5.7% during the acetylation of wood. Therefore, the reason for the lower lignin content may be that the brown-rot fungus needed to decompose more lignin to survive because of the rising difficulty of degrading acetylated polysaccharides. For a LOSS of less than 8.8% (WPG more than 18.4%), the corrected content of lignin in the decayed acetylated wood was higher than that in decayed nonacetylated wood (LOSS 72.8%). This indicates that the lignin decomposition became difficult because of the progressing acetylation of lignin.[19]

With the white-rot decay, the corrected contents of Klason, acid-soluble, and total lignin in the decayed nonacetylated wood (LOSS 23.0%) was 15.3%, 2.5%, and 17.8%, respectively. The corrected content increased evenly with the reduction in LOSS caused by the increase in WPG, unlike the brown-rot decay. This indicates that the decomposition of lignin by white-rot fungus became difficult with the increase in WPG.

Table 1. Lignin content in decayed acetylated wood

WPG (%)	LOSS (%)	Klason lignin (%)	Acid-soluble lignin (%)	Total lignin (%)
Brown rot				
0	72.8	69.8	5.3	75.0
9.7	70.0	52.6	6.2	58.8
13.3	58.2	32.6	4.9	37.6
13.9	43.1	25.0	4.4	29.4
16.2	25.3	19.4	4.0	23.3
18.4	8.8	17.3	3.6	20.9
21.0	−0.1	16.5	3.5	20.0
–	–	21.4	3.0	24.4
White rot				
0	23.0	19.8	3.2	23.1
1.8	19.3	20.9	2.9	23.8
3.6	19.3	19.9	3.0	22.9
4.7	15.8	20.3	3.0	23.3
7.6	12.9	20.4	3.3	23.7
10.1	7.0	19.9	3.2	23.1
11.8	−1.5	18.8	3.1	21.9
12.7	−1.6	17.8	3.3	21.0

WPG, weight percent gain; LOSS, mass loss

The polysaccharide content was also corrected in the same manner as the lignin content estimated by Eq. (1). The ratios of the corrected contents of glucose and xylose in the decayed acetylated wood to those in the nondecayed control are shown versus the LOSS in Fig. 3. The ratios of glucose and xylose in the brown-rotted nonacetylated wood (LOSS 72.8%) were 0.05 and 0.08, respectively. This indicates that most polysaccharides in the wood were decomposed by the brown-rot fungus. The ratios in the decayed acetylated wood increased with a decrease in LOSS caused by the rising WPG. This indicates that the decomposition of polysaccharides by brown-rot fungus became difficult with the increase in WPG.

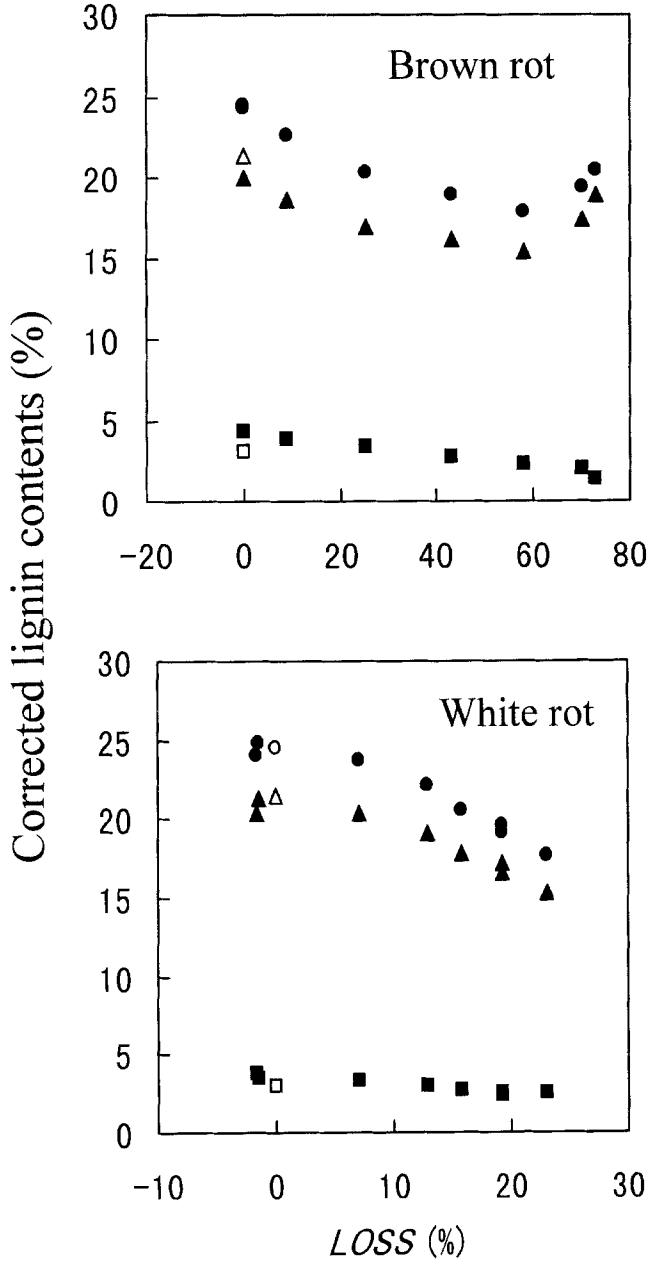

Fig. 2. Relation between corrected lignin content and mass loss of decayed acetylated wood. *Triangles*, Klason lignin; *squares*, acid-soluble lignin; *circles*, total lignin; *unshaded symbols*, nonacetylated and nondecayed control

The ratios of the corrected content of glucose and xylose in the white-rotted nonacetylated wood (LOSS 23.0%) were 0.81 and 0.75, respectively. The decrease in LOSS due to rising WPG increased these ratios, but there was no consistent tendency in the difference between them.

Relation between the losses of each chemical composition and the LOSS

The losses of lignin and polysaccharides due to decay were calculated from the differences between their respective corrected content in the nondecayed control and the decayed acetylated wood. These losses are shown versus LOSS in Fig. 4. With the brown- rotting, the loss of lignin in the decayed nonacetylated wood (LOSS 72.8%) was 16.4%.

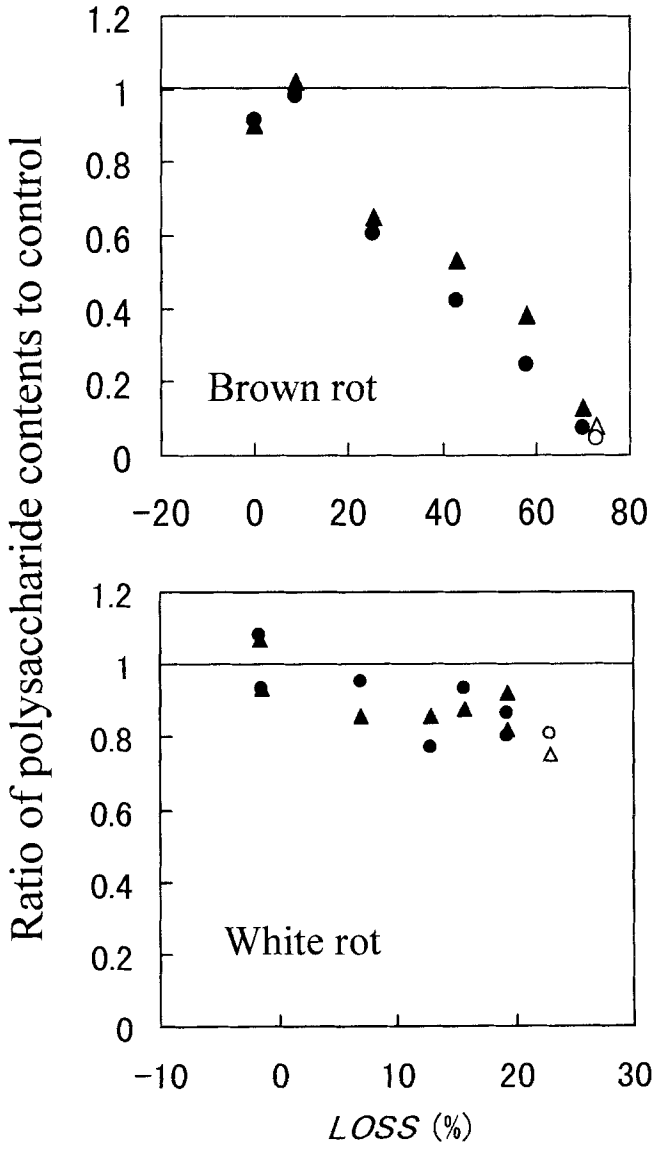

Fig. 3. Relation between the ratio of corrected polysaccharide content to control and the mass loss of decayed acetylated wood. *Circles*, glucose; *triangles*, xylose; *unshaded symbols*, decayed nonacetylated wood

The loss of lignin increased first with decreasing LOSS in the decayed acetylated wood and then decreased when LOSS fell below 58.2%. The reason for the increase in losses was mentioned earlier. The loss of lignin was smaller than the LOSS, defined as the loss of whole wood, when LOSS was more than 25.3%. This indicates that the decomposition of lignin by brown-rot fungus was difficult. The loss of polysaccharides in the decayed nonacetylated wood was 91.9% but decreased with the dropping LOSS in the decayed acetylated wood. The loss of polysaccharides was larger than the LOSS over a whole range of LOSS. This indicates that the brown-rot fungus decomposed the polysaccharides easily. From these results, it is concluded that brown-rot fungus preferentially decomposed the polysaccharides in acetylated wood similarly to that in nonacetylated wood.

With the white-rot decay, the losses of lignin and polysaccharides were 27.4% and 17.5%, respectively, in the decayed nonacetylated wood (LOSS 23.0%). This indicates that the white-rot fungus decomposed fewer polysaccharides than did the brown-rot fungus. Both losses decreased as the LOSS decreased in the decayed acetylated wood. The loss of lignin was more than that of polysaccharides above a LOSS of 15.8%. This indicates that the white-rot fungus decomposed lignin somewhat preferentially during the decay of acetylated wood and nonacetylated wood.

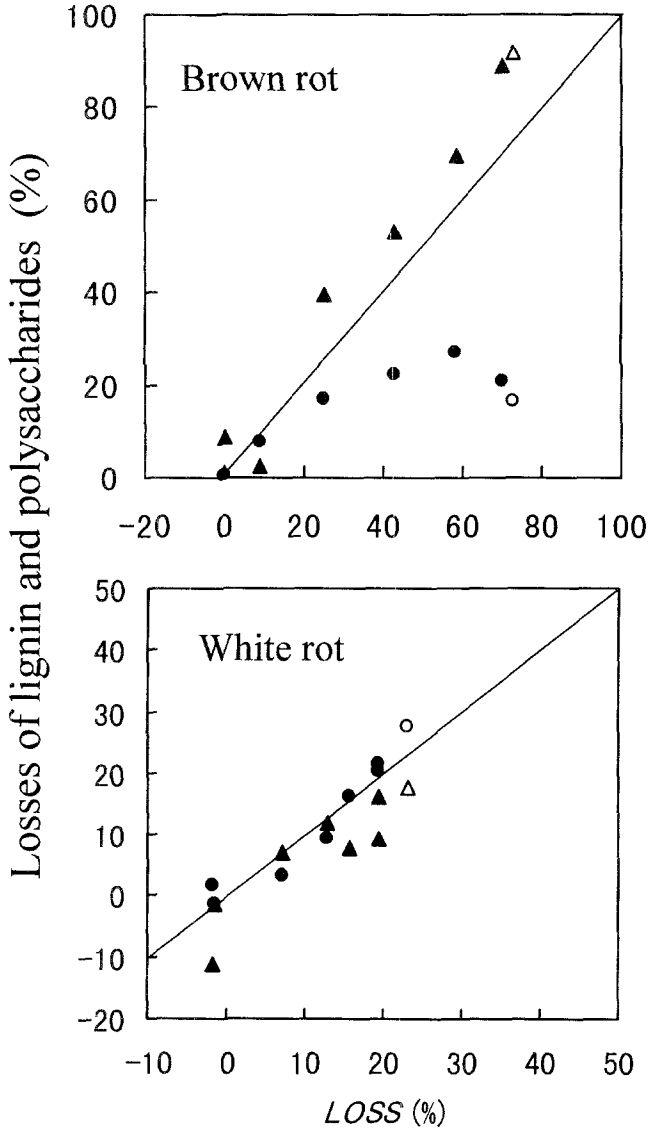

Fig. 4. Relation between the losses of lignin and polysaccharides and the mass loss of decayed acetylated wood. *Circles*, lignin; *triangles*, polysaccharides; *unshaded symbols*, decayed nonacetylated wood

X-ray diffraction curves of decayed acetylated wood

The X-ray diffraction curves of the nondecayed and brown-rotted acetylated wood are shown in Fig. 5. In the nondecayed acetylated wood, the height of peaks of the ($1\bar{1}0$), (110), and (200) diffraction planes (2θ = 14.7°, 16.5°, and 22.7°, respectively) decreased with increasing WPG. These small changes in the diffraction pattern may have been caused by acetylation of the noncrystalline components in the wood.[20] In the decayed acetylated wood, the pattern changed dramatically from that of the nondecayed one at a LOSS of more than 58.2%, whereas there was a little difference between the diffraction pattern before and after decay at a LOSS of less than 43.1%.

The crystallinity indices (CrI) were estimated from the diffraction curves. The ratios of CrI in the decayed wood to the nondecayed wood are plotted against the LOSS in Fig. 6. The ratio was 0.63 in the brown-rotted nonacetylated wood (LOSS 72.8%), increasing with the decrease in LOSS when the LOSS was more than 40% in the decayed acetylated wood. This indicates that the brown-rot fungus de-

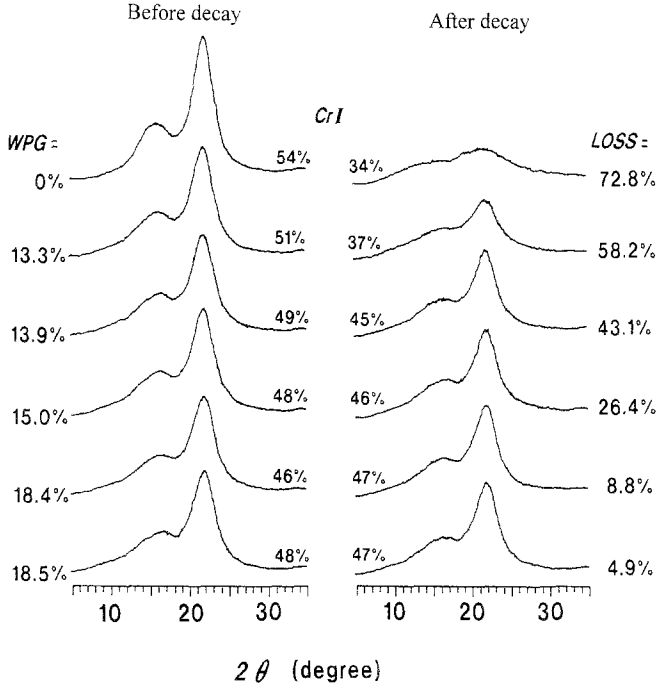

Fig. 5. X-ray diffraction curves of the acetylated wood before and after decay by brown-rot fungus. *CrI*, crystallinity index

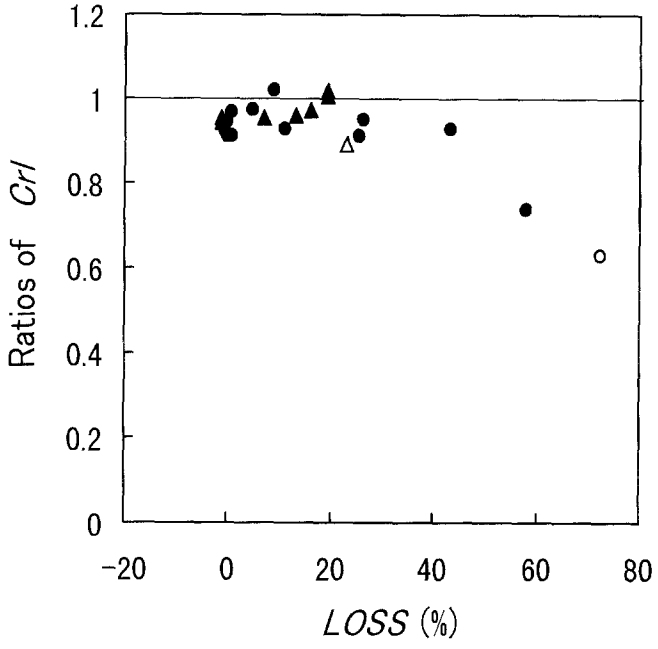

Fig. 6. Relation between the ratios of crystallinity index and the mass loss of decayed acetylated wood. *Circles*, brown rot; *triangles*, white rot; *unshaded symbols*, decayed nonacetylated wood

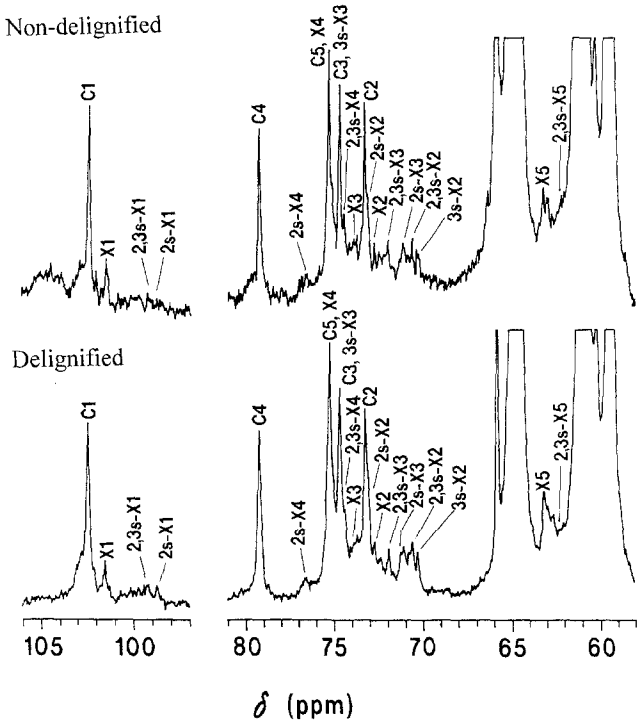

Fig. 7. ^{13}C-NMR spectra in the ring carbon region of acetylated wood (WPG 13.3%) decayed by brown-rot fungus (LOSS 58.2%) before and after delignification in MMNO/DMSO-d_6. *C*, cellulose; *X*, xylose; *s*, substituted. *Numbers* indicate carbon positions

composed the cellulose in the crystalline region in large degrees above this LOSS. With white-rot decay, the ratio of decayed nonacetylated wood (LOSS 23.0%) was 0.89, indicating that the fungus somewhat decomposed the cellulose in the crystalline region. The ratio of white-rotted acetylated wood was approximately 1 over the range of tested LOSS. This suggests that the white-rot fungus decomposed the crystalline region and the noncrystalline region in acetylated wood to the same degree.

^{13}C-NMR spectra of decayed acetylated wood

The acetylated wood largely decayed by brown-rot fungus (LOSS of more than 43.1%) could be dissolved in a mixture of MMNO/DMSO-d_6 without delignification. This may be because of the alteration or decomposition of the lignin and cellulose in the crystalline region by the fungus. The ^{13}C-NMR spectrum in the ring carbon region of polysaccharides of the nondelignified decayed wood (WPG 13.3%, LOSS 58.2%) is shown together with the spectrum of the delignified wood in Fig. 7. The assignment and the chemical shift of the signals were shown in detail in a previous paper.[18] There was no difference between the two spectra except that the spectrum without delignification had more noise, which indicates that the delignification caused no change in the acetyl distribution of the decayed acetylated wood, such as the removal and migration of acetyl groups.

The ^{13}C-NMR spectra in the ring carbon region of the acetylated wood (WPG 16.2%) before and after decay by brown-rot fungus (LOSS 25.3%) are shown in Fig. 8. In the postdecay spectrum, the intensity of unsubstituted signals of xylan (X1, X2, X3) became lower than that of the mono-

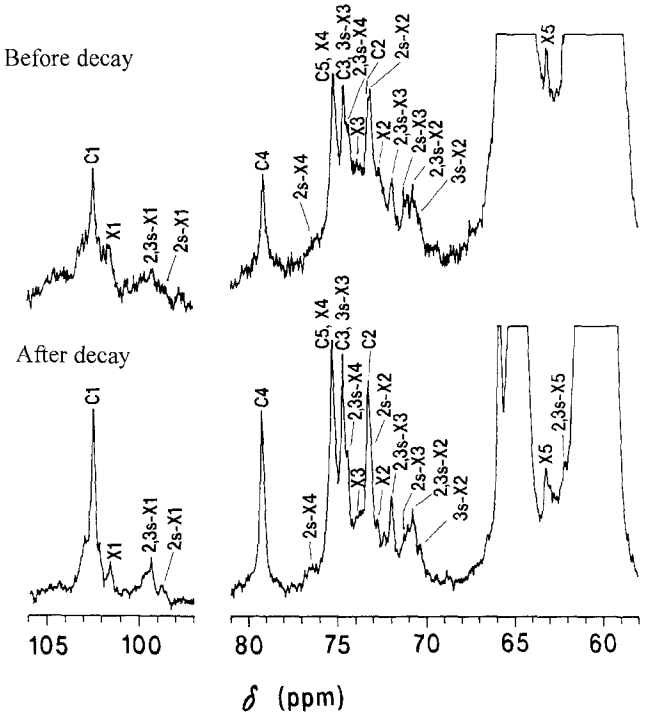

Fig. 8. ^{13}C-NMR spectra in the ring carbon region of acetylated wood (WPG 16.2%) before and after decay by brown-rot fungus (LOSS 25.3%). Abbreviations are the same as in Fig. 7

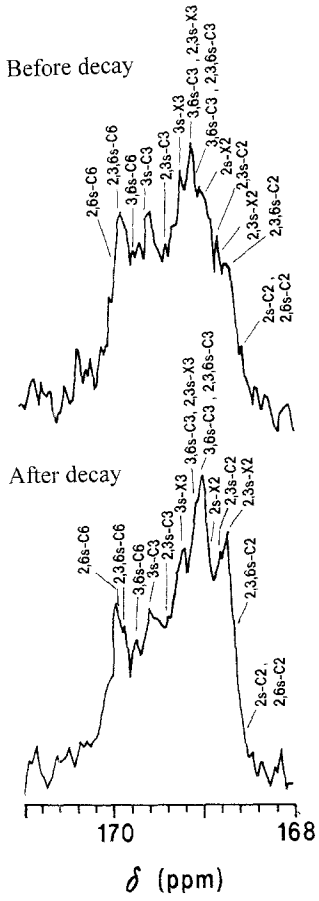

Fig. 9. ^{13}C-NMR spectra in the acetyl carbonyl carbon region of acetylated wood (WPG 16.2%) before and after decay by brown-rot fungus (LOSS 25.3%). Abbreviations are the same as in Fig. 7

and disubstituted signals (having the abbreviation "s", such as 2s-X1, 2,3s-X1, and so on), compared with those before decay. This indicates that the unsubstituted xylose units in acetylated wood were preferentially decomposed by the brown-rot fungus. Furthermore, the intensity of monosubstituted signals (2s-X1, 3s-X2, 2s-X3) became relatively small in comparison with the disubstituted signals (2,3s-X1, 2,3s-X2, 2,3s-X3) after decay, suggesting that the brown-rot fungus was able to decompose the monosubstituted xylose units to the some degree. On the other hand, substituted signals of cellulose were not observed in these spectra. However, this does not necessarily mean that the acetyl substitution of cellulose did not occur, because some substituted signals might have overlapped or been hidden by other signals owing to their small intensities.

The ^{13}C-NMR spectra in the acetyl carbonyl carbon region of the polysaccharides of acetylated wood (WPG 16.2%) before and after decay by brown-rot fungus (LOSS 25.3%) are shown in Fig. 9. The shapes of the two spectra were different. The intensity of the signals existing between 169.2 and 169.8 ppm in the spectra after decay was slightly less than before decay. The signals in this range were assigned to mono-substitution (3s-C3) and disubstitution (3,6s-C6 and 2,3s-C3) of cellulose.[18] This suggests that the mono- and disubstitutions of cellulose in the acetylated wood were partly decomposed by brown-rot fungus.

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