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Author(s)	TAKAHASHI, Munezoh; NISHIMOTO, Koichi
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Studies on the Mechanism of Wood Decay (2)^{***}

Changes in Infrared Spectra of BUNA and SUGI Wood
as Decay Proceeds*

Munezoh TAKAHASHI** and Koichi NISHIMOTO**

高橋旨象**・西本孝一**：木材の腐朽機構に関する研究（第2報）***
腐朽にともなうブナおよびスギ材の赤外スペクトルの変化*

Introduction

Infrared spectroscopy is one of the effective methods for structural analysis of polymers. It has been widely used to elucidate many of the properties of macromolecules¹⁾. Nowadays, it is not difficult to collect many literature data on the infrared spectra of cellulose and lignin, important natural high polymers and main wood constituents. The application of infrared spectral method, however, to the study of wood itself has not been so many, and especially of the wood components degraded enzymatically by wood-destroying fungi, has been scarce^{2) 3)}.

The authors, in the course of investigations on the mechanism of wood decay, reported in previous paper⁴⁾ on the changes in strengths of wood as decay proceeds, and assumed that the observed different courses of reduction in strengths would be correlated to the differences of degradation of wood constituents according to the three types of wood decay, namely brown-, white-, and soft-rots.

In this paper, in purpose to clarify the differences in mode of degradation in some details, the changes in infrared spectra of wood were recorded as decay proceeds. As described above, however, the application of infrared spectroscopy to the study of wood itself is in the early stage, and the assignment of absorption bands in wood is not yet established invariably at present. For this reason, the observed changes in infrared spectra in this experiment were not always connected to the changes in molecular structure of wood constituents.

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** Division of Wood Biology (木材生物部門)

*** Among three reports, titled "Studies on the Mechanism of Wood Decay (1), (2) and (3)", presented at the 16th and 17th Meeting of the above society, the first and the second were put together into the previous paper, and the third into the present paper.

Experimental

Compulsory decay of wood

Wood blocks were cut from sapwoods of BUNA (*Fagus crenata* BLUME) and SUGI (*Cryptomeria japonica* D. DON), and exposed to decay by three species of wood-rotting fungi, namely *Corirolellus palustris* MURR. (Government Forest Experiment Station of Japan No. 0507), *Coriolus versicolor* (FR.) QUEL (the same No. 1030), and *Chaetomium globosum* KUNZE (the same No. 8059). These fungi are brown-, white- and soft-rot fungi respectively.

The sizes of wood blocks were $1.5(T) \times 1.5(R) \times 3.0(L)$ (cm) and $1.5(T) \times 3.0(R) \times 1.5(L)$ (cm). The former size of block shall be called as block A and the latter as block B hereafter.

For the incubating vessels, glass bottles, 9 cm in diameter and 16 cm in height, were used. These bottles, containing 350 g of quartz sand and 120 ml of the nutrient solution⁴⁾, were screwed up by metal caps and then autoclaved.

Small pieces of mycelium of the test fungi from ten days cultures on agar plates were inoculated in the bottles for cultivating.

After recording of the dry weights and sterilizing in vapor of propylene oxide, wood blocks were soaked into sterilized water and placed on the surface of mycelium fully developing in the bottles. The temperature in incubating room had been maintained at $28 \pm 3^\circ\text{C}$ during each 10, 25, 45, 70 and 100 day decay test.

Preparation of the samples

The decayed wood blocks, after measurements of their weights and compressive strengths after every prescribed period, were cut off by small hand-saw at the distances of 2, 6 and 10 mm in block A, and 2 and 6 mm in block B, from a cross sectional end of blocks.

The sawdust was collected and ground in a mortar. Samples for infrared spectroscopy were prepared from the ground meal passed through a 300 mesh sieve.

Spectroscopic measurement

Measurement of infrared spectra was carried out according to the KBr-disk method⁵⁾. The procedure was as follows:

Coarse KBr powder was ground in an agate mortar to pass through a 200 mesh sieve and dried for 48 hours at 130°C . Each sample of the ground wood meal was dried separately *in vacuo* for 8–10 hours at 65°C . 3 mg of the dried samples was then well mixed with 600 mg of the dried and cooled KBr powder in an agate mortar. The mixture was then pressed in a disk-press at 190 kg/cm^2 for 5 minutes under vacuum conditions produced by a normal backing pump. The resulting disk was submitted to spectroscopic measurement through the $1800\text{--}650 \text{ cm}^{-1}$ region under operation of infrared spectrophotometer, Japan Spectroscopic **DS-402G**.

Results

Infrared spectra of the wood samples are recorded separately in Figs. 1-10. In each figure, *A* shows the spectra of wood decayed by *C. palustris*, and *B* by *C. versicolor*. The used samples were prepared from the sawdust collected by cutting off at the distance of 6 mm from cross sectional ends of block A and B, as described in the experimental section. The spectra of BUNA wood decayed by *C. globosum* showed little change despite of considerable weight loss in blocks (Fig. 11), which was attributed to the surface action of this fungus reported previously⁴⁾. Thus, newly prepared samples from the wood meal collected by surface shaving were used in the spectroscopic measurement. The spectra of these samples are recorded in *C* in Figs. 1, 3, 5, 7 and 9.

C. globosum did not cause the appreciable weight loss in SUGI wood. Consequently, significant changes were not observed in the spectra of the samples (Fig. 12). Thus, in SUGI, the comparison of the spectral change among the three types of decay was not possible.

Changes in spectra observed in this experiment were described as follows :

1. In the 1800-1500 cm^{-1} region (Figs. 1, 2 and 12).
 - a) The absorption at 1730 cm^{-1} in BUNA decreased markedly during the degradation by *C. globosum*, whereas only slightly by *C. palustris* and *C. versicolor*.
 - b) On the other hand, the same absorption in SUGI was reduced constantly due to the brown- and white-rots. The progress of the reduction in the white-rotted wood was always ahead of the brown-rotted one. The reduction was also observed in the wood scarcely decayed by the soft-rot fungus. The occurrence of absorptions at about

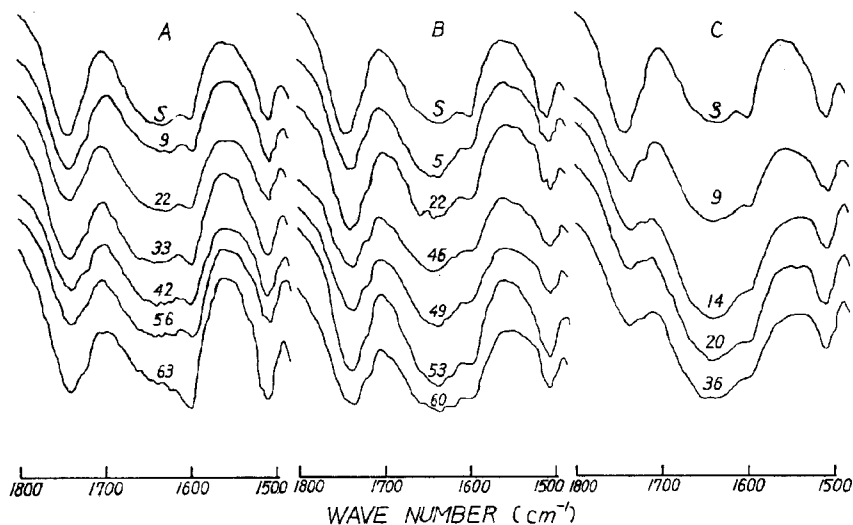


Fig. 1. Infrared spectra of BUNA wood decayed by *C. palustris* (A), *C. versicolor* (B) and *C. globosum* (C) in the 1800-1500 cm^{-1} region. S: sound, figures on spectra: percents weight loss of decay wood blocks.

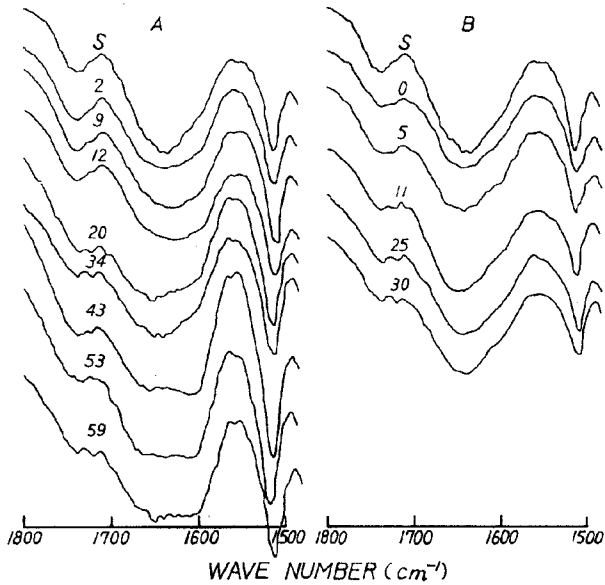


Fig. 2. Infrared spectra of SUGI wood decayed by *C. palustris* (A) and *C. versicolor* (B) in the 1800-1500 cm^{-1} region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

2. In the 1500-1300 cm^{-1} region (Figs. 3 and 4).

a) The absorption at 1460 cm^{-1} increased with the progress of decay in both woods

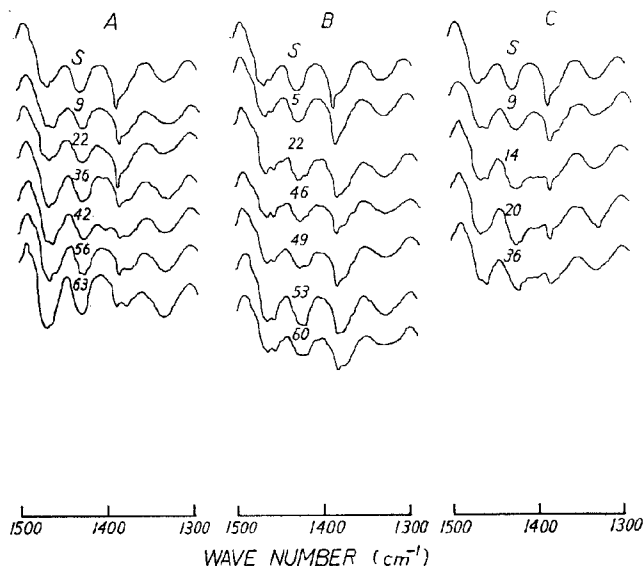


Fig. 3. Infrared spectra of BUNA wood decayed by *C. palustris* (A), *C. versicolor* (B) and *C. globosum* (C) in the 1500-1300 cm^{-1} region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

- 1715 cm^{-1} was realized in both decayed woods, especially in SUGI, with the decrease in 1730 cm^{-1} .
- c) The absorption band centered at 1640 cm^{-1} was broadened in SUGI exposed to *C. palustris*.
- d) The absorptions at 1595 and 1510 cm^{-1} were sharpened in BUNA decayed by *C. palustris*, and the latter absorption in SUGI decayed by the same fungus was also increased severely. These two absorptions were conversely decreased in BUNA decayed by *C. versicolor* and *C. globosum*, and the absorption at 1510 cm^{-1} in SUGI decayed by the former weakened, too.

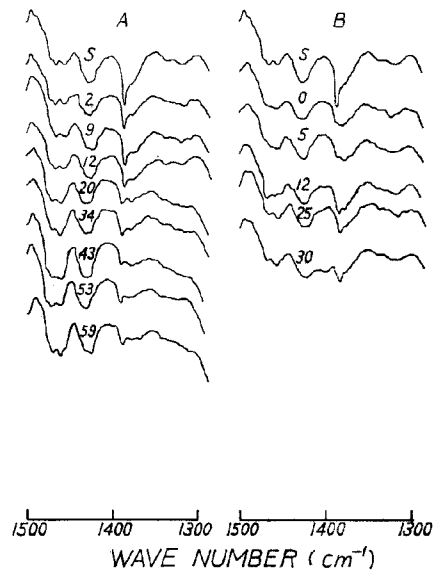


Fig. 4. Infrared spectra of SUGI wood decayed by *C. palustris* (A) and *C. versicolor* (B) in the 1500-1300 cm^{-1} region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

exposed to *C. palustris*. Especially in BUNA, it was more remarkable. Thus, the situation in the intensity of absorptions 1460 and at 1420 cm^{-1} reversed itself as decay proceeds.

- b) The absorption at about 1405 cm^{-1} , not present in original sound wood, was visualized after decay, especially in the soft-rotted BUNA and white-rotted SUGI.
- c) The absorption at 1380 cm^{-1} decreased to some degree during the degradation, which was common to all samples tested.
- d) The absorption at $1330\text{--}1310\text{ cm}^{-1}$ seemed to increase slightly in BUNA exposed to *C. palustris*, while it decreased in SUGI decayed by the same fungus.

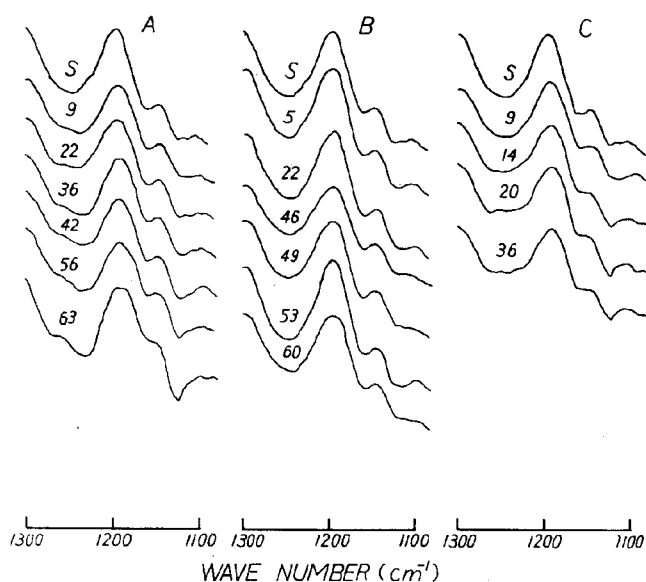


Fig. 5. Infrared spectra of BUNA wood decayed by *C. palustris* (A), *C. versicolor* (B) and *C. globosum* (C) in the $1300\text{--}1100\text{ cm}^{-1}$ region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

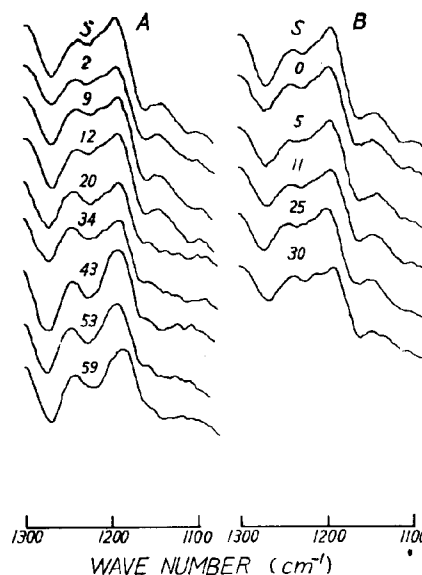


Fig. 6. Infrared spectra of SUGI wood decayed by *C. palustris* (A) and *C. versicolor* (B) in the $1300\text{--}1100\text{ cm}^{-1}$ region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

3. In the $1300\text{--}1100\text{ cm}^{-1}$ region (Figs. 5 and 6).

- a) The broad absorption band at $1300\text{--}1200\text{ cm}^{-1}$ in BUNA took the different shape with the progress of decay by *C. palustris*, followed by the occurrence of two distinct absorptions which were present originally in SUGI. One was at 1270 cm^{-1} and another was at 1230 cm^{-1} . These absorptions increased similarly in SUGI with increase of degree of decay by the same fungus.
- b) The broader band at $1200\text{--}1000\text{ cm}^{-1}$ was weakened, as a whole, progressively due to decay as recorded in Figs. 7 and 8. Details in the change, however, were differently specific to the species of wood or fungus. The absorption at 1160 cm^{-1} decreased in BUNA exposed to *C. palustris* and *C. globosum*, and in SUGI decayed by the former. The absorption at 1120 cm^{-1} was sharpened in BUNA degraded by

C. palustris and *C. globosum*, but not in SUGI decayed by *C. palustris* and *C. versicolor*.

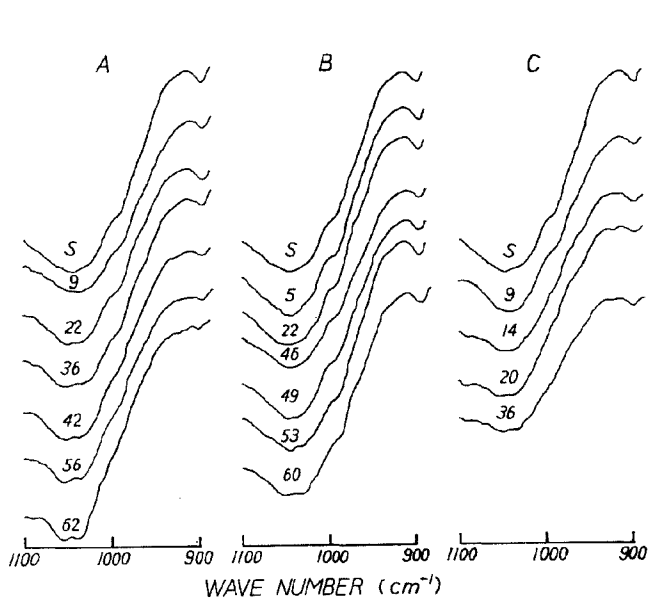


Fig. 7. Infrared spectra of BUNA wood decayed by *C. palustris* (A), *C. versicolor* (B) and *C. globosum* (C) in the 1100-900 cm^{-1} region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

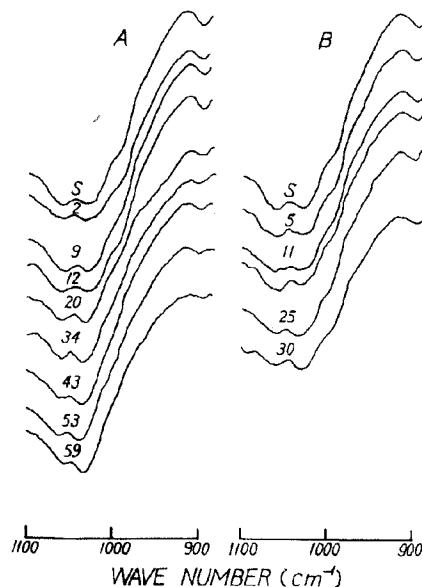


Fig. 8. Infrared spectra of SUGI wood decayed by *C. palustris* (A) and *C. versicolor* (B) in the 1100-900 cm^{-1} region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

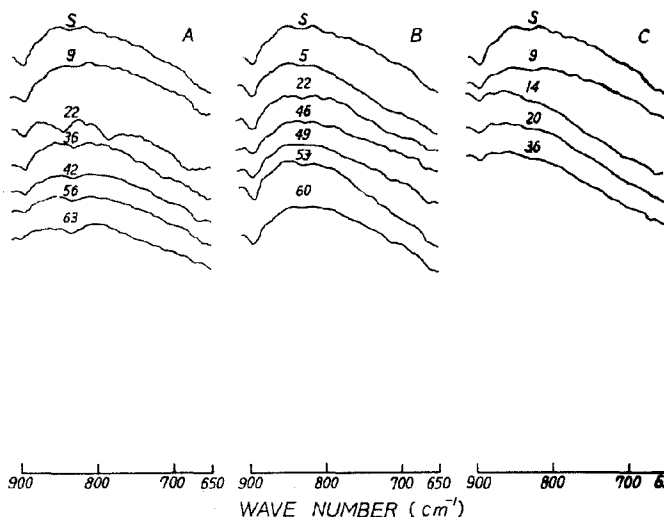


Fig. 9. Infrared spectra of BUNA wood decayed by *C. palustris* (A), *C. versicolor* (B) and *C. globosum* (C) in the 900-650 cm^{-1} region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

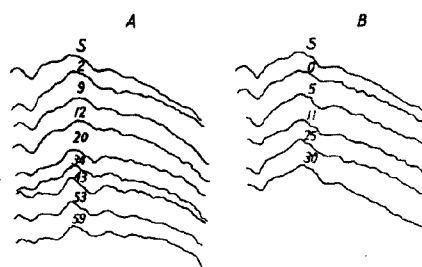


Fig. 10. Infrared spectra of SUGI wood decayed by *C. palustris* (A) and *C. versicolor* (B) in the 900-650 cm^{-1} region. S: sound, figures on spectra: percent weight loss of decayed wood blocks.

4. In the $1100\text{--}900\text{ cm}^{-1}$ region (Figs. 7 and 8).

- a) The absorption band at $1050\text{--}1030\text{ cm}^{-1}$ in BUNA were divided into two weak bands after decay by *C. palustris*.
- b) Meanwhile, in SUGI, these two bands were noticeable before decay at 1050 and 1030 cm^{-1} respectively. The situation of the absorption intensity reversed itself gradually due to decay by *C. palustris* and *C. versicolor*.

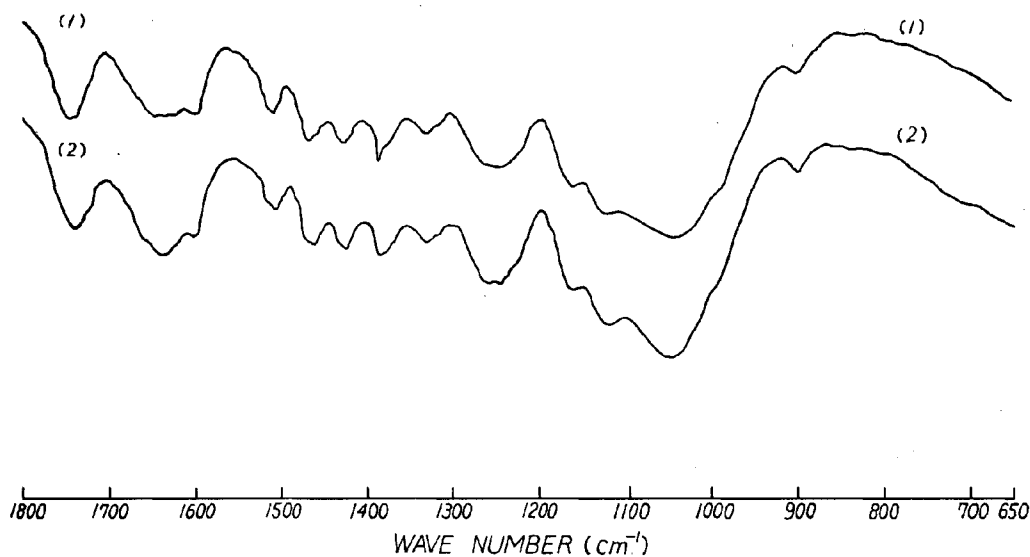


Fig. 11. Infrared spectra of BUNA wood. (1): sound; (2): exposed to *C. globosum* to the extent of 19% of weight loss. Each sample was prepared from the sawdust.

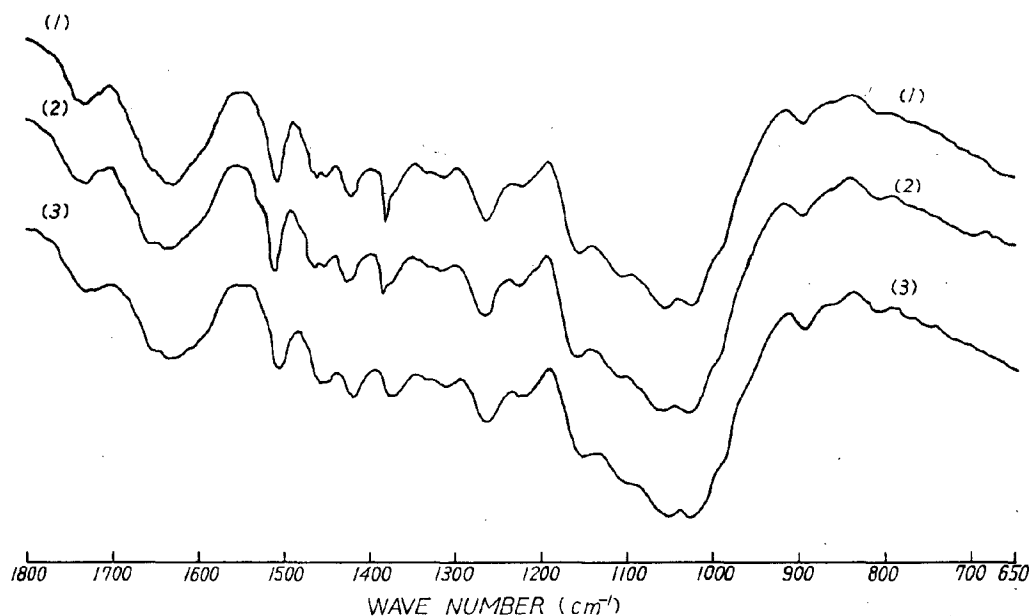


Fig. 12. Infrared spectra of SUGI wood. (1): sound; (2) and (3): exposed to *C. globosum* to the extent of 1 and 3% of weight loss, respectively. Each sample was prepared from the sawdust.

5. In the 900–650 cm^{-1} region (Figs. 9 and 10).
- a) The absorption at 895 cm^{-1} decreased progressively in BUNA decayed by *C. palustris* and *C. globosum*. Such decrease was also observed in SUGI decayed by the former.
 - b) The decrease of same absorption due to decay by *C. versicolor* was not noticeable in BUNA, but slight in SUGI.

Discussion

The purpose of this study is clarifying some differences in mode of degradation of wood constituents among the three types of decay. Thus, changes in the infrared spectra of wood samples due to decay were recorded. And, as the sub-purpose, possibility of the application of infrared spectral method to the measurement of degree of decay was examined. Complying with these purposes, sample wood meal was collected from the three locations depending on the distance from a cross sectional end of each decayed block, and its infrared spectrum was recorded separately. It was due to a following reason: wood meal prepared collectively from a whole block tends to contain much non-decayed portion so that if it is supposed that decay commence from a surface of wood, particularly from a cross sectional one, progressively into an inner part, the effect of decay on the infrared spectrum should be hidden especially in the early stage of decay. On the other hand, the comparison of infrared spectrum of each sample different from the location decided by the distance from a cross sectional end of block, was expected to answer the question whether such a process in the development of decay would be present or not.

As the results, the difference of infrared spectral changes due to the location of sample meal collection were scarcely observed, and followed by the suggestion that decay does not invariably proceeds from a cross sectional end in such a experimental compulsory decay of wood block.

Changes in infrared spectra have been recorded with the comparison to the increase of weight loss from the original wood blocks. Duration as well as weight loss is the well used index in study concerning to wood decay. As discussed previously⁴⁾, however, the situation between percent weight loss and duration of decay has been variable depending on the combination of fungi and wood used in the experiment.

Changes in infrared spectra were followed almost conclusively by the percent weight loss as shown in figures. The weight loss in wood, however, indicates the degree of removal of wood substance in the form of water and carbon dioxide due to the enzymatic degradation and metabolism by fungi, but never shows the degree of degradation of residual wood constituents. Such a degree will be noticeable even in the very early stage of decay in which a little weight loss will not yet be found. Consequently, it had been expected from this study that some changes in molecular structures of wood compo-

nents would appear even at the initial stage of decay. As the results, however, nearly all absorptions did not change in such a stage with few exceptions, namely at 1730, 1380 and 1050 cm^{-1} . Thus, infrared spectral method with KBr-disk preparation must be much useful on the general qualitative examination of wood decay, but less effective on the structural analysis of wood constituents at the very early stage of decay.

The maximum values and the intervals of percent weight loss were not similar in each combination of fungus and wood tested. For this reason, it has been hard to say that the comparison between spectral changes on the mode of degradation was carried out satisfactorily in all cases. In addition to it, the sample meal of BUNA decayed by *C. globosum* was collected from the surface of block. Considering the surface action of the fungus, the ratio of the degree of degradation in residual substances to that of weight loss in the soft-rotted wood block must be larger than that in brown- or white-rotted one. Thus, keeping these in view and setting the soft-rot fungus to the center, following discussion has been brought up on the degradation characteristics.

The absorption at 1730 cm^{-1} in BUNA decreased rapidly due to decay by *C. globosum* (Fig. 1-C). The decrease was not noticeable in SUGI slightly decayed by this fungus as well as in BUNA by *C. palustris* and *C. versicolor* (Figs. 12 and 1). The absorption is assigned to the C=O stretching vibration of carboxyl and acetyl groups in xylan, precisely the *O*-acetyl (4-*O*-methylglucurono)xylan in hardwoods, and the arabino-(4-*O*-methylglucurono)xylan in softwoods⁶⁾. The absorptions at 1460 and 1230 cm^{-1} are due to the CH_2 deformation vibration in lignin and xylan+benzene ring vibration in lignin, and the acetyl and carboxyl vibration in xylan+C=O stretching vibration in lignin, respectively⁷⁾. These absorptions did not change in BUNA decayed by *C. globosum* and *C. versicolor* but increased in the same wood decayed by *C. palustris*. Considering these and other spectral changes associated to lignin discussed later, the above two absorptions will be more strongly related to lignin than to xylan.

Among several absorptions referred to cellulose and hemicellulose, the absorptions at 1380, 1160 and 895 cm^{-1} decreased not only due to decay by *C. globosum* but also *C. palustris*. It is possible as to these results to suggest that *C. globosum* as well as *C. palustris* attacks cellulose and hemicellulose in the course of decay of hardwoods and that the soft-rot type of degradation of hemicellulose, mainly consisted of xylan, is characterized by the specific action on carboxyl and acetyl groups in it.

The absorptions at 1595 and 1510 cm^{-1} are due to the well known stretching vibrations of the benzene ring in lignin. These absorptions increased due to decay by the brown-rot fungus, *C. palustris*, and conversely decreased by the white-rot, *C. versicolor*, which is surely anticipated by the general view that the former can not metabolize lignin in wood but the latter can do it.

The five absorptions at 1460, 1420, 1270, 1230 and 1030 cm^{-1} are also referred to

lignin. Among them, 1460 cm^{-1} is assigned to the CH_2 deformation + benzene ring vibration and 1420 cm^{-1} is to the CH_3 bending vibration⁷⁾. The other absorptions are due to the $\text{C}=\text{O}$ stretching vibrations, but they are also associated with cellulose or hemicellulose⁷⁾. The above five absorptions increased or not during the decay by *C. palustris*, but never increased by *C. versicolor*. These changes, however, were not remarkable, which is supposedly due to their references to cellulose and hemicellulose.

Meanwhile, the changes in some absorptions relating lignin in the case of soft-rot were quite different from that of the brown-rot, while followed by the similarity to the white-rot contrary to expectations. LEVI and PRESTON⁸⁾ as a result of their chemical investigation drew the following conclusions about the relation among brown- white- and soft-rot fungi: there are similarities between brown-rots and soft-rot, *Chaetomium*, e. g. the effect on lignin, and between white-rots and soft-rot, e. g. the effect on the alkali-soluble fraction. Furthermore, all types of wood destroying fungi remove methoxyl from lignin and, in the cases of brown- and soft-rot fungi, this appears to be the main effect on lignin. According to their conclusions, soft-rot fungi can not metabolize lignin but can only modify it. SAVORY and PINION⁹⁾, on the contrary, concluded, as a result of their investigation, that lignin in the secondary wall of hardwood was completely metabolized.

As a result of this study, it is possible to conclude about the action of soft-rot fungus, *C. globosum*, upon lignin that this fungus causes the important changes in the chemical structure of lignin, which are quite different to the case of brown-rot fungus, *C. palustris*, even if they are only modification.

The ability of soft-rot fungi to degrade hardwoods to a greater extent, and more rapidly, than they can degrade softwoods has been generally attributable to the differences in lignin content in the secondary walls of the both types of wood^{8) 10)}. This difference in such a ability, however, would seem to be also concerned with differences in the chemical structure of lignin, considering the strong action of *C. globosum* on lignin in hardwoods, BUNA.

COWLING¹¹⁾ has been reviewed the properties of white-rot fungi and concluded that all wood components are attacked at rates dependent on their concentration, which is followed by some characteristics of the white-rot, such as the slow lowering of the degree of polymerization and the gradual decrease of the alkali soluble content.

Changes in infrared spectra of wood decayed by *C. versicolor* were merely apparent at a few absorptions, namely at 1595 , 1510 and 1380 cm^{-1} , although the weight loss in original wood blocks were not small. Based on such a spectral change and the COWLING's view described above, it has been suggested that chemical structures of the residual components are not much altered in the case of the white-rot.

The broad absorption band in the region of 1640 cm^{-1} is undoubtedly due to the major contribution to the H-O-H deformation of adsorbed water^{7) 12)}. SUMIYA and his

co-workers³⁾ reported that this band was more broadened progressively in BUNA exposed to *C. palustris*. In this study, however, such a change was less noticeable.

The absorptions at 870 and 800 cm^{-1} , specific to the softwood, SUGI, assigned to mannan mainly composed of glucomannan¹²⁾, are originally very weak at the measurement by the KBr-disk method and then changes in these spectra were hardly observed.

The absorptions at about 1715 and 1405 cm^{-1} which were visible after decay and shown in Figs. 1-4, were not discussed in this study, since their assignment has not been known at present.

Finally, it must be in mind that effective investigation on mechanism of wood decay requires some physical, chemical and biological examination to be carried out comprehensively with a single piece of wood. Consequently, the use of thin wood section should be recommended for the coming study, despite of some technical difficulty associated with it.

Summary

Infrared spectra of BUNA and SUGI wood decayed by *Corirolellus palustris*, *Coriolus versicolor* and *Chaetomium globosum* were recorded and compared with each other. The decreases of the absorption at 1380 cm^{-1} in both woods decayed by the three fungi were apparent in the early stage of decay. Among several absorptions referred to lignin in wood, the 1595 and 1510 cm^{-1} absorptions increased in the case of brown-rot, while decreased in the white- and soft-rot. Other absorptions referred to lignin at 1460, 1420, 1270, 1230 and 1030 cm^{-1} , sharing the contributions with other fractions, were also inclined to increase in the brown-rot. But they showed little change in the white- and soft-rot. The absorption at 1730 cm^{-1} weakened rapidly in SUGI exposed to the three fungi. Such a fact was remarkable in BUNA decayed by the soft-rot fungus.

Based on the results described, the characteristics of brown-, white- and soft-rot fungi on their modes of degradation of wood substances have been discussed briefly. And the possibility of application of infrared spectroscopy with KBr-disk procedure to the measurement of degree of decay was examined.

摘 要

ブナおよびスギ辺材の腐朽にともなう赤外スペクトルの変化を KBr 法により測定し、褐色腐朽菌 *Corirolellus palustris*, 白色腐朽菌 *Coriolus versicolor* ならびに軟腐朽菌 *Chaetomium globosum* の木材成分分解様式について考察し、同時に赤外分光法の木材の腐朽度判定に対する適用の可否を検討した。

(1) セルロースならびにヘミセルロースの CH 変角振動に由来する 1380 cm^{-1} の吸収は、いずれの腐朽材においても腐朽にともなうすみやかに減少した。

(2) リグニンのベンゼン環伸縮振動にもとづく 1595 ならびに 1510 cm^{-1} の吸収は、褐色腐朽材では増加し、白色腐朽材では減少した (Fig. 1, 2)。

(3) $1460, 1420, 1270, 1230, 1030\text{ cm}^{-1}$ の吸収は、リグニンにも関係するといわれ、褐色腐朽材では増加の傾向にあるが、白色腐朽材ではほとんど変化がみとめられず顕著な対照を示さなかつた。

(4) 白色腐朽材ではこれらの吸収を含めて全般にスペクトルの変化は著しくなく、残存成分の構造はリグニンを除いてあまり変化を受けていないと推察された。

(5) キシランのカルボキシル基ならびにアセチル基の $\text{C}=\text{O}$ 伸縮振動を示す 1730 cm^{-1} の吸収は、すぎにおいては腐朽によつてすみやかに減少した (Fig. 2)。軟腐朽菌に侵されたブナにおいてはこの減少はとくに著しく、同菌によるブナ材中のキシランの分解は、とくにこの $\text{C}=\text{O}$ 部分に集中するものと考えられた。

(6) 軟腐朽菌のブナ材中のリグニンに対する作用は、Fig. 1 に示したように白色腐朽菌同様ベンゼン環におよんでおり、褐色腐朽菌と同じくリグニンの単なる modification にとどまるという従来の見解にはあらためて検討が必要である。

(7) 軟腐朽菌は針葉樹材よりも広葉樹材を強く侵害するといわれ、本研究においても同様の結果を得た。しかし、上記の結果から、その理由としてあげられている両者間のリグニン含量の差ならびに細胞膜中の分布状態および化学的性質の相違に対しては、腐朽菌による酵素作用の立場からも新たな検討を要する。

(8) KBr 法による腐朽材の赤外スペクトル測定は、重量減少率測定と同様に腐朽度判定手段に対する適用が可能である。しかし、重量減少のみとめられないような腐朽のごく初期における材成分の構造変化を記録しうる程鋭敏ではなかつた。

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