CHEMICAL COMPONENTS OF WOOD DECAYED UNDER NATURAL CONDITION AND THEIR PROPERTIES

By

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I. Introduction and Historical Review of the Chemical Literature on Decayed Wood

HARTIG[47] (1878) indicated that a certain type of wood decay must have been always caused by the same species of fungus on the same species of wood. The characteristic changes in wood caused by the action of the enzymes from wood-destroying fungi are noticeable not only in physical appearance but also in the type and properties of the chemical components.

There is much scientific literature concerning chemical studies on decayed wood or dealing with such subjects collectively.[10,11,37,41,45,50,52,132,141,142] The early studies on decayed wood were begun with an ultimate analysis. BULLER[141] (1905) found that the wood decayed by *Polyporus aquamosus* had a little higher carbon content and lower nitrogen content than that of the sound wood. And WEHMER[136] (1915), FALCK and HAAG[28] (1927), CAMPBELL[20] (1941) and FUKUYAMA, HANZAWA and KAWASE[37] (1953) also made ultimate analyses and indicated similarly that the carbon content of decayed wood increased in the case of brown rot and decreased or hardly changed in the case of white rot.

The study of decayed wood involving the determination of the composition by the method for wood analysis was first carried out by KATAYAMA[67] (1914), who indicated that the cellulose, pentosan and water soluble matter as well as the ash in decayed wood were decreased by decay while the rest of the components (mainly lignin) were increased, and also found in the alcohol extract of decayed wood the presence of soluble lignin by a color reaction with aniline

acetate and phloroglucinol. The subsequent work on the chemical composition of decayed wood has been done by the use of various sorts of fungi and wood species as follows. WEHMER[135] (1914) compared decayed spruce wood with sound wood as to its solubility in water, alkaline solution, ether and ethanol. ROSE and LISSE[114] (1917) divided Douglas-fir decayed wood into three stages and analyzed it for its chemical components (except lignin). MAHOOD and CABLE[89] (1920) observed the change of chemical composition of wood by means of a mixed culture of fungi on wood, and BRAY and ANDREWS[13] (1924) investigated the relation between the weight of wood lost by decay and the chemical composition of the wood decayed by means of a pure culture of a fugus. Before this, BRAY and STAIDL[12] (1922) analyzed decayed wood and prepared sulfite and ground wood pulp from it. According to the tests for the properties of the pulp, decayed wood pulp was inferior to sound wood pulp. FALCK[27] (1926) studied the types of rot of wood and divided them into two groups according to their color and chemical properties: "Korrosionsfäule" and "Destruktionsfäule". In the former, the decomposition of both carbohydrates and lignin takes place (white rot). In the latter, on the other hand, only carbohydrates are decomposed, leaving the lignin very little affected, and the wood becomes dark brown (brown rot).

It was reported SCHWALBE and EKENSTAM[124] (1927) that the lignin (Pilzlignin) in brown rotted wood (Pilzholz) was more soluble in alkaline solution and had less methoxyl groups than those of sound wood. Thus it became evident that every component of wood was more or less decomposed during decay by fungi. In addition to these, much work was carried out by FALCK and his co-workers[28~32] (1927~1930), in which they investigated not only the chemical composition but also many phases of the subject such as estimating the loss of components by the weight present in a unit volume of the wood and decomposition of cellulose by means of copper number or that of lignin by methoxyl group content.

BARTON-WRIGHT and BOSWELL[5] (1929) analyzed spruce wood decayed by *Merulius lacrymans* and found that cellulose, galactan and mannan were consumed. CAMPBELL[14] (1929) reported that the process of the fungal decay was regarded as acid hydrolysis.

A systematic examination of the white rot of wood was reported by CAMPBELL[15~17] (1930~1932) and types of white rot were classified into the following three groups:

Group I

White rots in which lignin and pentosan are attacked in the early stages and in which the incidence of the attack on the cellulose proper is delayed.

Group II

White rots in which cellulose and its associated pentosans are attacked in the early stages and in which the incidence of the attack on lignin and pentosans not associated with cellulose is delayed.

Group III

White rots in the early stages of which both lignin and cellulose are attacked but in varying proportions.

So far as white rots are concerned, it was reported by NARAYANAMURUTI and VERMA[103] (1953) that the ratio of cellulose to lignin in decayed wood increased in proportion to the period of decay. There are also similar reports dealing with classification of decayed wood according to its chemical composition.

Especially, FUKUYAMA, HANZAWA and KAWASE[37] (1953) studied the chemical composition of the wood decayed under natural condition and reported that decayed wood could be divided into three types as follows; (a) white rot—attacks lignin in preference to cellulose, (b) brown rot—attacks cellulose more rapidly than lignin, and (c) intermediate rot—attacks both lignin and cellulose to an equal extent.

Lately, fifty-eight kinds of decayed wood were analyzed by KAWASE[75] (1958) and classified numerically into three groups according to the ratio of holocellulose to lignin as follows:

1. Brown rot type
   The decayed wood in which the ratio of holocellulose to lignin is below 1.
2. White rot type
   The decayed wood in which the ratio of holocellulose to lignin is very high.
3. Intermediate type
   The decayed wood in which the ratio of holocellulose to lignin is not far from that of sound wood.

Another group, HARAGUCHI and YAMAGUCHI[46] (1958) studied the classification of wood-destroying fungi by the index number of the wood-decomposing type and reported that the classification depended upon the chemical composition of the decayed wood. Thus they suggested index numbers of wood-decomposing types (I. D.), the values of which were between zero and ten. I. D.=(Lignin decomposed/Cellulose decomp.+Lignin decomp.)×10. I. D. seemed to vary depending on the species of wood meal used as a culture medium and the period of decay, but these value might be useful in the practical classification of wood-destroying fungi.

On the other hand, BAVENDAMM[6] (1928) recognized that the white rot fungi produced a wide darkened zone around the mycelial mat by cultivating some of fungi in an agar medium containing either tannic or gallic acid.

The most extensive examination of wood-destroying fungi with respect to their reaction on gallic or tannic acid media was performed by DAVIDSON, CAMPBELL and BLAISDELL[24] (1938). The result of the observation employing BAVENDAMM's technique showed that this method was, for the most part, correct and useful when applied to fungi.

There are many other substantial reports dealing with the chemical nature of decayed wood. In addition to the reports above-mentioned, many studies were carried out by FALCK[32] (1930), HAWLEY, WIERTELAK and RICHARDS[49] (1930), BARTON-WRIGHT and BOSWELL[6] (1931), MIURA[94] (1931), NISHIDA and NAKA[104] (1931), YAMANO[143] (1931), KAWAMURA, TANIGUCHI and SHÔJINO[68] (1932), WIERTELAK and DOMINIK[140] (1936), KOMAROV and FILIMONOVA[85] (1937), SCHEFFER[120] (1937), STORCH[131] (1937), SCHULZE, THEDEN and VANPEL[123] (1938) and BOSWELL[8] (1938).

In the 1940's owing to World War II, only a few studies were reported by CAMPBELL and BRYANT[19] (1940), HILBORN and STEINMETZ[57] (1943), MIURA and MIGITA[96,97] (1943), MIZUMOTO[98,99] (1944, 1948) and HEUSER and co-workers[51] (1949).

Recently, the reports dealing with chemical composition of decayed wood were those by APENITIS, ERDTMAN and LEOPOLD[2] (1952), ASANO and FUJII[4] (1953), FUKUYAMA, HANZAWA and KAWASE[37] (1953), HIGUCHI, KAWAMURA and KAWAMURA[53] (1955), KAYAMA[79] (1955), NAKAMURA[102] (1955), KAWASE[71] (1956), KAWASE and IKEDA[72] (1956), KAWASE and MIYAKE[74] (1957), HARAGUCHI and YAMAGUCHI[46] (1958), KAWASE[75] (1958), KAWASE and MIYAKE[76] (1958), KAWASE[77] (1959), KAWASE[78] (1959), MORIMOTO[101] (1960), and REIS and LIBBY[112] (1960).

In many reports dealing with fungal degradation of wood components, degradation of lignin was often discussed. Reviews on this subject that have appeared recently are those by GOTTLIEB and PELCZAR[41] (1951), BRAUNS[10] (1952), HIGUCHI[42] (1954), COOKE[22] (1957), and by BRAUNS and BRAUNS[11] (1960).

Recent studies on degradation of lignin specifically are those by SCHUBERT and NORD[121] (1950) who found that the lignin in wood decayed by *Lentinus lepideus* had a lower content of carbon and methoxyl group; HIGUCHI, KAWAMURA and KAWAMURA[53] (1955), and by GROH[42] (1960) who analyzed spruce wood after various periods of decay for methoxyl group in Klason lignin and for methoxyl group in alcoholextracted wood and found that the methoxyl group in either case decreased almost linearlly with the degree of decay, and the slopes of the curves obtained were reproducible. It was also found that

the alteration of lignin, as expressed by this decrease in the content of methoxyl group, was due mainly to enzymatic activity. The native character of the lignin liberated by enzymes according to NORD and SCHUBERT (1947) was contradicted.

On the other hand, according to the systematic studies by NORD and co-workers[105,106,121,122,125] (1950～1961), it was suggested that the route by which the wood-destroying fungus *Lentinus lepideus* synthesized methyl p-methoxycinnamate from simple organic compounds, such as glucose, xylose or ethanol, might be similar to the route by which lignin was synthesized in the growing plant.

From the point of utilization of the decayed wood, there are many interesting reports, in one of which KÜRSCHNER[86] (1927) described the presence of vanillin and vanillic acid in the hot water extract from the wood decayed by *Merulius lacrymans*; in another NORDENSKJOLD[107] (1953) found that when vanillin was prepared by oxidation with nitrobenzene from decayed wood, the yield was higher than that from sound wood, while the consumption of nitrobenzene was less. HIGUCHI et al[53,54] (1955) prepared aldehydes by a similar oxidation process with nitrobenzene from decayed beechwood and found that the yield from white-rotted wood was extremely low and even from brown-rotted wood was a little less than that from sound wood.

As to the constructive utilization of decayed wood, HUBER[58] (1944) used it for a polishing agent and KAWASE[69,70,75] (1950～1958) prepared the active carbon from various kinds of decayed wood, some of which gave high adsorptive ability especially in the purification of penicillin. From a conservative point of view, there are many reports dealing with the estimated value of decayed wood for pulp wood, and such reports were published in a single volume by the Technical Association of the Pulp and Paper Industry[132] (1955).

On the strength of decayed wood, there are studies by COLLEY[21] (1921), LIESE and STAMER[88] (1934), TRENDELENBURG[133] (1940), YAZAWA[145] (1943) and by PECHMAN and SCHAILE[110] (1950) who examined in detail the chemical and physical properties of decayed wood.

For the measurement of the degree of decay, SOSHIRODA[128] (1952) studied the method by strength, while SOSHIRODA[129] (1952) and FUKUYAMA and KAWASE[39] (1954) used its nail-holding power, while RUE, MILLER and HUMPHERY[115] (1924), MORGAN[100] (1931) and MARTYNOV[132] (1940) used solubility in one per cent sodium hydroxide. FUKUYAMA and KAWASE[38] (1954) found a simpler method for determining the degree of wood decay with dilute alkaline solution and KAWASE[75] (1958) applied this method to various kinds of decayed wood. PEARL[109] (1953) presented a method for the estimation of the amount and type of decay in Douglass-fir wood chips from the color of ethanol, hot water or caustic

solution extract of the chips.

As mentioned above, chemical studies on decayed wood have been successively carried out. But there are some other problems about chemical properties of decayed wood which can not be solved by the usual methods of wood analysis. The comparatively simple and recently improved method for preparing holocellulose and the quantitative or qualitative analysis by chromatographic method is most helpful for the investigation of carbohydrates in decayed wood.

By the method used for the analysis of ordinary wood the author analyzed various kinds of wood decayed by fifty-one species of wood-destroying fungi under natural conditions. He also examined the separate monosaccharides from holocellulose of the decayed wood after hydrolysis. Using the ratio of holocellulose to lignin, decayed woods were divided into three types by the author as follows:

1. Lignin-rich decayed wood—the decayed wood in which the ratio is below one (0.18～0.99, it means that lignin content is higher than holocellulose content).
2. Cellulose-rich decayed wood—the decayed wood in which the ratio is very high (16.92～∞).
3. "Normal-like" decayed wood—the decayed wood in which the ratio is similar to that of sound wood (1.83～5.07, those of sound wood ranged from 1.46 to 4.40).

According to this classification, typical samples were selected from each group of decayed wood and tested for their holocellulose by their resistance to alkali, calorific value and monosaccharides and for their lignin by their resistance to alkali and methoxyl group and carbon content.

With reference to determining the degree of wood decay, it was found that the more wood was decayed, the more alkali was consumed during the treatment with hot dilute alkaline solution. The consumption means the dis appearance of alkali by neutralization, adsorption and other factors. This property of decayed wood was applicable for determining the degree of wood decay. The degree of decay can be determined by this simple treatment within a short time.

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II. Samples

Samples for this study were prepared from various woods decayed under natural conditions in the forest and the species of each fungus was identified by the specialist at the Department of Forest Pathology of Agricultural College, Hokkaido University.

Each sample was divided into four decay stages such as sound (0), discolored (1), more rotted (2) and most rotted (3) by its appearance to the naked eye. For instance, in the case of softwood, fir wood decayed by *Fomitopsis annosa* was shown as 1_0, 1_1, 1_2 and 1_3, while in hardwood, oak wood decayed by *Fomitopsis castanea* was shown as I_0, I_1, I_2 and I_3 according to the stage. From each stage, some typical parts were picked out and measured for density. Every sample was sawed by a special small power-driven disc saw to produce saw dust: if the sample was fragile enough, it was crushed with a Wiley mill and then sieved. A sample which passed a 40-mesh sieve and was retained on a 60-mesh sieve was used for the analysis of holocellulose and that which passed a 60-mesh sieve and was retained on a 100-mesh sieve was usually used for the analysis of the other components.

The samples of the various species of decayed wood were collected at the places listed in Table 1, and those places are located widely in Hokkaido Island as shown roughly in Fig. 1.

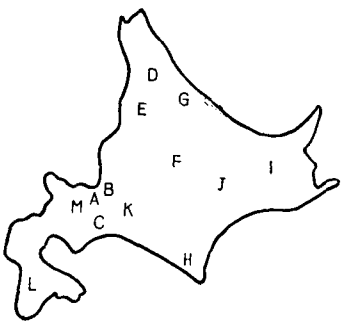

Fig. 1. The distribution of the localities where the samples were taken.

A: Sapporo
B: Nopporo
C: Tomakomai
D: Kamiotoineppu
E: Kitamoshiri
F: Sōunkyo
G: Ōmu
H: Samani
I: Teshikaga
J: Ashoro
K: Ōyubari
L: Katsuraoka
M: Jōzankei

TABLE 1. Samples

Wood species	Fungus species	Locality
Larix Kaempferi	*Sparassis crispa*	Sapporo
Larix Kaempferi	*Phaeolus schweinitzii*	
Larix Kaempferi	*Phaeolus schweinitzii*	
Picea jezoensis	*Gyrophana lacrymans*	
Picea jezoensis	*Stereum fasciatum*	Tomakomai
Picea jezoensis	*Lentinus Kauffmanii*	
Picea jezoensis	*Fomitopsis pinicola*	
Quercus crispula	*Fomitopsis castanea*	
Acer palmatum var. *Matsumurae*	*Phellinus igniarius*	
Ulmus Davidiana var. *japonica*	*Rigidoporus ulmarius*	
Sorbus alnifolia	*Coriolus hirsutus*	
Prunus Maximowiczii	*Coriolus hirsutus*	
Tilia japonica	*Elfvingia applanata*	
Acer palmatum var. *Matsumurae*	*Fomes fomentarius*	
Acer mono var. *glabrum*	*Irpex lacteus*	
Alnus hirsuta	*Inonotus cuticularis*	
Acer palmatum var. *Matsumurae*	*Oxyporus populinus*	
Prnus Sargentii	*Phellinus pomaceus*	
Betula Maximowicziana	*Daedaleopsis confragosa*	
Quercus crispula	*Trametes dickinsii*	
Tilia japonica	*Trametes gibbosa*	
Acer mono var. *glabrum*	*Daedaleopsis tricolor*	
Quercus crispula	*Laetiporus sulphureus*	
Populus Maximowiczii	*Ischnoderma resinosum*	
Syringa reticulata	*Phellinus baumii*	
Fraxinus mandshurica var. *japonica*	*Stereum* sp.	
Cercidiphyllum japonicum	*Coriolus versicolor*	
Phellodendron amurense	*Bjerkandera fumosa*	
Alnus hirsuta	*Hymenochaete intricata*	
Taxus cuspidata var. *latifolia*	*Coniophora* sp.	Nopporo
Fraxinus mandshurica var. *japonica*	*Tyromyces* sp.	
Betula Maximowicziana	*Fuscoporia obliqua*	
Picea jezoensis	*Cryptoderma yamanoi*	Kamiotoineppu

Wood species	Fungus species	Locality
Abies sachalinensis	*Phellinus hartigii*	Kitamoshiri
Abies sachalinensis	*Stereum sanguinolentum*	
Abies sachalinensis	*Sparassis crispa*	
Picea Glehnii	*Tyromyces borealis*	
Picea Glehnii	*Phaeolus schweinitzii*	
Picea Glehnii	*Tyromyces balsameus*	
Abies sachalinensis	*Favolus alveolarius*	
Abies sachalinensis	*Cryptoporus volvatus*	
Betula platyphylla	*Phellinus igniarius*	
Quercus crispula	*Laetiporus sulphureus*	
Acer mono var. *glabrum*	*Poria* sp.	
Quercus crispula	*Stereum frustulosum*	
Ulmus Davidiana var. *japonica*	*Coriolus consors*	
Picea jezoensis	*Fuscoporia weirii*	Sōunkyo
Picea jezoensis	*Fomitopsis reseozonata*	
Picea jezoensis	*Ischnoderma resinosum*	
Abies sachalinensis	*Hirschioporus fusco-violaceus*	Ōmu
Quercus crispula	*Tyromyces* sp.	
Abies sachalinensis	*Fomitopsis insularis*	Samani
Quercus crispula	*Lentinus edodes*	
Prunus Ssiori	*Fomitopsis pinicola*	
Quercus crispula	*Grifola* sp.	
Abies sachalinensis	*Laetiporus sulphureus* var. *miniatus*	Teshikaga
Abies sachalinensis	*Poria subacida*	
Abies sachalinensis	*Fomitopsis annosa*	Ashoro
Fagus crenata	*Coriolus hirsutus*	Katsuraoka
Abies Mayriana	*Phaeolus schweinitzii*	Jōzankei

III. Methods of Investigation

A. Analysis of Wood

The properties of decayed wood are usually different from those of sound wood, for this reason suitable methods of analysis should be applied, but in this study the following usual methods which are convenient for comparison of decayed and sound woods were used.

a. Density

Two or three of typical specimens from each stage of wood decay were picked out and the volume of each specimen determined by measuring of length, width and height with calipers after squaring it off, or by xylometer. After drying for about 2 days at 105°C, the specimen was weighed after cooling in a desiccator. Density value was calculated as follows:

$$\text{Density} = \frac{\text{Moisture-free weight (g)}}{\text{Green volume (ml)}}$$

b. Ash

About 1 gram of an ovendry sample was accurately weighed into a crucible and incinerated carefully in an electric furnace or on a triangle until carbonaceous materials were eliminated, and the crucible was then removed to a desiccator, cooled and weighed. The ash was calculated to percentage of the ovendry sample.

c. Carbon and Hydrogen

Two or three miligrams of an ovendry sample were used for the analysis of carbon and hydrogen by PREGL's micro methods.

d. Solubility in Cold Water

About 1 gram of an accurately weighed ovendry sample was placed in an ERLENMEYER flask. 200 ml of cold water were added to the flask and allowed to stand with occasional shaking at room temperature for 48 hours. Then, the sample was filtered off in a tared fritted-glass crucible, washed with cold water, dried overnight at 105°C, cooled in a desiccator and weighed.

e. Solubility in Hot Water

About 1 gram of accurately weighed an ovendry sample was placed in an ERLENMEYER flask. 100 ml of water were added to the flask and the flask was placed in a boiling water bath with occasional shaking for 3 hours. Then, the wood was transferred to a tared fritted-glass crucible and washed with hot water. It was also dried and weighed.

f. Solubility in Alcohol-Benzene

Two tared fritted-glass crucibles (1 G 2), containing accurately weighed 1 or 2 grams of an ovendry sample were placed in a SOXHLET's extractor and treated with the mixture of the equal volume of 95 per cent alcohol and benzene until the solvent in the siphon became completely colorless (within about 20 hours). The solvent was removed from the crucible by suction and the crucible and the contents were treated for 4 hours at 105°C, cooled in a desiccator and weighed. From the difference in weight, solubility in alcohol-benzene was calculated.

g. Solubility in 1 Per Cent Sodium Hydroxide

About 1 gram of accurately weighed sample was placed in an ERLENMEYER flask and 100 ml of 1 per cent sodium hydroxide solution were added. The flask was placed in a boiling water bath with occasional shaking for 1 hour. Then, the sample was filtered by suction on a tared fritted-glass crucible, washed thoroughly with hot water and the crucible and contents were dried at 105°C, cooled and weighed.

h. Total Pentosan

About 1 gram of accurately weighed ovendry sample was placed in a distilling flask, together with 100 ml of 12 per cent hydrochloric acid. Distillation was carried out so as to distill 30 ml in 10 minutes and continued until the distillate amounted to 360 ml. To the distillate 40 ml of phloroglucinol solution were added. After allowing this to stand for 16 hours, the precipitate was collected on a tared fritted-glass crucible and washed with 150 ml of water, dried for 4 hours at 105°C, cooled and weighed with the crucible in a stoppered weighing bottle. The precipitate was dissolved in hot 95 per cent ethanol and the residue was weighed also. Pentosan was calculated from the weight of the residue according to KRÖBER's table. And methyl-pentosan was calculated from the weight of soluble phloroglucide. The sum of these amounts was expressed as total pentosan.

i. Cross and Bevan Cellulose

About 1 gram of accurately weighed extractive-free sample in a tared fritted-glass crucible (1 G 2) was moistened with cold water, and excess water was removed by suction. The sample with the crucible was transferred to a chlorinating apparatus and treated with a given amount of chlorine for 15 minutes. After that, the sample was treated with 2 per cent sulfurous acid and washed with water. The crucible with contents was placed in a 50-ml beaker, in which 3 per cent sodium sulfite was added and the beaker was then placed in a boiling water bath to digest for 1 hour. After this treatment the sodium

sulfite solution was removed by suction and the sample was washed with hot water followed by cold water and excess water was removed. The chlorination, washing cycle (the time of the second and the third chlorination was 10 minutes and following chlorination was reduced to 5 minutes) was repeated until chlorinated sample showed white or sometimes only a faint pink color on addition of the sodium sulfite solution. Finally, the cellulose was washed thoroughly with hot water, 50 per cent ethanol, and ether, successively, dried at 105°C, cooled and weighed in a stoppered weighing bottle.

In case of the some brown rotted woods, one or two chlorinations made the sample unfilterable. Therefore, the sample which was once or twice treated by the treating cycles was weighed and analyzed for lignin by usual analytical method. From the difference of these two values the cellulose content was calculated. The Cross and Bevan cellulose content was presented as percentage of the ovendry unextracted sample.

j. Holocellulose

According to the procedure of WISE,[141] about 5 grams of 40 to 60 mesh accurately weighed sample were extracted for 6 hours with 95 per cent ethanol and 2 hours with ether. The extractive-free sample was treated in a 200-ml ERLENMEYER flask with 160 ml of water containing 1.5 grams of sodium chlorite and 0.5 ml of glacial acetic acid, and heated under hood for 1 hour at 70 to 80°C. The flask was covered by a watch-glass, and shaked gently at intervals during the reaction. After 1 hour, 0.5 ml of acetic acid and 1.5 grams of sodium chlorite were added without cooling the mixture, and heating continued for an additional hour. Four such treatments were used for coniferous woods, whereas three treatments for hardwood. After the chloriting was completed, the suspension was cooled and filtered through a coarse fritted-glass crucible (1 G 2). The residue was washed with water followed by acetone, dried at 105°C, cooled and weighed. The residue was transferred to a beaker and treated with 72 per cent sulfuric acid for 1 hour at 30°C. The mixture was diluted with water to a 3 per cent acid concentration and heated in an autoclave for 4 hours at 115°C. The residue was filtered on a fritted-glass crucible, dried at 105°C, cooled and weighed as lignin. True holocellulose content was corrected by subtracting the value for lignin from the value for crude holocellulose. The holocellulose content is given as percentage of the ovendry unextracted sample.

k. Lignin

About 1 gram of the accurately weighed extractive-free sample was placed in a beaker and treated with 20 ml of 72 per cent sulfuric acid for 4 hours at

room temperature. The mixture was diluted with water to a 3 per cent acid concentration and boiled for 2 hours. After all the carbohydrates were completely hydrolyzed the mixture was cooled and the residue was filtered on a tared fritted-glass crucible (1 G 3), washed with water, dried and weighed. The lignin obtained was presented as percentage of the ovendry unextracted sample.

1. Hydrogen-Ion Concentration

A cold-water extract of the sample was used for the measurement of pH value of the sample wood. The hydrogen-ion concentration was measured roughly with pH test paper made by The Toyo Filter Paper Co. Ltd..

B. Alkali Consumption

One tenth gram of ovendry sample was transferred to a glass-stoppered 100-ml ERLENMEYER flask, and 15 ml of 0.1 *N* sodium hydroxide solution were added. The flask was heated on a boiling water bath for 2 hours. After cooling, the mixture was filtered and an aliquot of the filtrate was titrated with 0.1 *N* hydrochloric acid using fluoresceinnatrium (few drops of 0.1 per cent aqueous solution) as indicator. The value in ml of 0.1 *N* sodium hydroxide consumed was calculated from the difference between the amounts of added and remaining alkali.

The fluorescent indicator was effective for the purpose of finding the end point of titration even in a dark brownish-red colored solution of brown rotted woods.

C. Calorimetry

An accurate measurement of calorific value was made with Berthelot-Mahler bomb calorimeter. As a rule, samples that passed the 100-mesh sieve were used. About 1 gram of the sample was wrapped in a piece of paper, the calorific value of which was already known and moistend in a bottle for several days at a high humidity. The wrapped sample was fixed in a stainless-steel crucible. After the nickel wire was coiled in a small spiral at the middle part of it, it was connected between the terminals passing through a small hole in the paper. The crucible was put in place in the stainless-steel bomb and oxygen was then admitted slowly from the supply tank until the pressure reached 20 to 25 atmospheres. The burning was done by the usual method. The measured value was corrected by the Pfaundler's formula for the radiation of heat and also corrected for the calorific value of the paper.

Wood samples should be burned after moistening and under rather low

pressure such as 20 atmospheres; if not, combustion does not proceed smoothly and a carbonized sample may sometimes be found inside the bomb.

D. Properties of Holocellulose

In order to investigate the sugar constituents of decayed wood, holocellulose prepared from the wood by the method of WISE[141], was hydrolyzed by the procedure of SAEMAN et al.[117], and the sugars were separated chromatographically from the hydrolyzate.

The experimental details were as follows : 0.3 gram of holocellulose together with 3 ml of 72 per cent sulfuric acid was placed in a small ERLENMEYER flask in a water bath held at 30°C for 1 hour. The contents of the flask were then transferred to a 250-ml beaker with distilled water to make the solution of a 3 per cent acid concentration, and digested for 1 hour in an autoclave at a steam pressure of 15 p.s.i..

After cooling, the hydrolyzate was filtered, the filtrate was neutralyzed to pH 6 with 1 *N* sodium hydroxide. The aliquot of the hydrolyzate was used for the determination of reducing sugar as glucose by means of BERTRAND's method. The rest of the hydrolyzate was concentrated and a large amount of ethanol was added. The alcoholic solution of the sugar was filtered and the residue was washed with ethanol repeatedly. After the solution was evaporated on a water bath, the resultant sugar condensate was dissolved again in small quantities of distilled water.

To separate and identify the sugar constituents in the purified solution, paper chromatography was carried out with the multiple ascending method on the Toyo filter paper No. 50, using a solvent mixture of n-butanol, acetic acid and water (4 : 1 : 5). The sugar spots were made visible by spraying with aniline hydrogen phthalate, and identified by the comparison with known sugar spotted simultaneously on the paper.

The determination of the degree of polymerization of holocellulose was made by viscosity measurement in cuprammonium hydroxide solution. Calculation was made by STAUDINGER's formula.

E. Properties of Lignin

Lignin for this investigation was prepared by the method mentioned above for the determination of lignin. Using a part of the lignin sample, the contents of carbon and hydrogen were determined by the above-mentioned analytical method, and with the other part the content of methoxyl group was determined by the following method.

In a small cup made from tin-foil, 20 to 30 milligrams of lignin were

weighed, wrapped up and placed in the reaction flask with 5 ml of hydriodic acid (d=1.70) and a small amount of phenol and acetic anhydride. The reaction flask was then boiled constantly by passing a slow, uniform stream of carbon dioxide through it, then methyl iodide in the stream was led into pyridine in a reaction tube through the mixture of equal volumes of 5 per cent cadmium sulfate and 5 per cent sodium thiosulfate in the scrubber. The reason for using pyridine is that the lignin prepared by above-mentioned method contained sulfur. The pyridine solution was transferred quantitatively to a evaporating dish with small amount of water and evaporated thoroughly on a water bath. The residue in the dish was dissolved in a small amount of water and titrated with 0.1 *N* silver nitrate using 0.5 per cent eosin solution as indicator and the methoxyl group content was calculated from following equation:

$$1 \text{ ml } N/10 \text{ } AgNO_3 = 0.0031 \text{ g } CH_3O$$

F. Properties of Alkali Soluble Matter

One gram each of wood samples from one kind of sound and from two kinds of decayed oak wood (*Quercus crispula*) were treated with 100 ml of 1 per cent sodium hydroxide for 1 hour in a boiling water bath. After cooling, the solution of alkali soluble matter was obtained by filteration, sulfuric acid was then added to the filtrate to give an acid concentration of 3 per cent and the mixture was boiled for 2 hours to hydrolyze the carbohydrates in it. The hydrolyzate was filtered, the filtrate was neutralyzed with barium carbonate and filtered. After concentration, a large amount of ethanol was added to the filtrate and the alcoholic solution of sugars was filtered. The solution was evaporated and the condensate was dissolved in small quantities of water. Paper chromatography was carried out using a solvent mixture of n-butanol, benzene, pyridine and water (10 : 2 : 5 : 5).

According to the hot alkaline solution treatment, clear spots of sugars could not be found, so a cold alkaline solution treatment was carried out as follows; 1 gram each of one sound and three kinds of decayed oak wood (*Q. crispula*) was extracted with 5 per cent sodium hydroxide for 2 hours at room temperature. Hydrolysis with sulfuric acid (3 per cent) for 2 hours, neutralization with sodium hydroxide to pH 6, and purification with ethanol and the paper chromatography using a solvent mixture of n-butanol, benzene, pyridine and water (10 : 2 : 5 : 5) were carried out successively. The total reducing sugar of the hydrolyzate was determined as glucose by means of BERTRAND's method.

In addition, the precipitate produced by hydrolysis of the solution with sulfuric acid was filtered on a fritted-glass crucible, and the content of carbon, hydrogen and methoxyl group was determined.

IV. Results of Experiment

The author has used the following terms for types of decay brown rot (b. r.), white rot (w. r.) and intermediate rot (i. r.) in the previous reports[37,75] and also uses them for the explanation of the results in this paper but from the results of this analytical work it seems better based on the chemical constitution of various decayed woods to suggest a new classification which is discussed later.

The results of this work are as follows.

A. Chemical Composition of Decayed Wood

Chemical composition of the decayed softwood is presented in Table 2 and that of hardwood is in Table 3.

B. Alkali Consumption

Results of the measurements which are given in Table 4 to Table 9 show that the more the decay of wood is advanced the more alkali is consumed by wood with a few exception.

C. Calorific Value

Calorific value of the decayed wood is given in Table 10.

D. Properties of Holocellulose

Raw holocellulose prepared from brown-rotted wood was generally higher in lignin content and dark color than that from sound wood. With regard to the yield of the reducing sugars obtained from holocellulose by hydrolysis, that from decayed wood is usually lower than that from sound wood except in *Picea jezoensis* decayed by *Cryptoderma yamanoi*, *Ulmus Davidiana* var. *japonica* by *Rigidoporus ulmarius* and *Coriolus consors*, *Fraxinus mandshurica* var. *japonica* by *Stereum* sp. and *Quercus crispula* by *Lentinus edodes* and *Grifola* sp..

Paper chromatogram of the sugar was observed by the naked eye qualitatively without quantitative examination. According to the comparison of the spots of glucose, xylose and mannose from decayed wood in size and depth of color with those of the sugars from sound wood, decayed softwoods could be divided into four groups and decayed hardwood into three groups as follows:

Softwood:

1. Decayed wood, the chromatogram of which is like that of sound wood. The woods of *Abies sachalinensis* decayed by *Fomitopsis annosa*, *Phellinus*

hartigii, *Stereum sanguinolentum*, *Favolus alveolarius* and *Cryptoporus volvatus*, *Picea Glehnii* by *Tyromyces borealis* and *Picea jezoensis* by *Fuscoporia weirii* and *Cryptoderma yamanoi*.

2. Decayed wood in which the spot of mannose on the chromatogram is smaller than that of sound wood. The woods of *Abies sachalinensis* decayed by *Sparasis crispa* (4_4), *Larix Kaempferi* by *S. crispa* ($4'_3$), *Larix Kaempferi* by *Phaeolus schweinitzii* ($7a_4$, $7b_3$) and *Picea Glhenii* by *Tyromyces balsameus*.

3. Decayed wood in which the spots of mannose and xylose on the chromatogram are smaller than those of sound wood. The woods of *Abies Mayriana* decayed by *Phaeolus schweinitzii* ($7'_3$), *Abies sahalinensis* by *Laetiporus roseozonata* and *Ischnoderma resinosum* and *Abies sachalinensis* by *Poria subacida*.

4. Decayed wood in which the spots of glucose and mannose are smaller than those of sound wood. The wood of *Taxus cuspidata* var. *latifolia* decayed by *Coniophora* sp. According to the results of chromatographic examination in decayed softwood, many of the intermediate rotted woods have sound-like chromatograms while the spot of mannose in the brown rotted wood is generally small.

Hardwood:

1. Decayed wood in which the chromatogram is like that of sound wood. The woods of *Acer palmatum* var. *Matsumurae* decayed by *Phellinus igniarius* (II_3), *Betula platyphylla* by *Phellinus igniarius*, *Acer palmatum* var. *Matsumurae* by *Coriolus hirsutus*, *Fomes fomentarius* and *Oxyporus populinus*, *Tilia japonica* by *Elfvingia applanata* and *Trametes gibbosa*, *Acer mono* var. *glabrum* by *Irpex lacteus*, *Daedaleopsis tricolor* and *Poria* sp., *Alnus hirsuta* by *Inonotus cuticularis*, *Prunus Sargentii* by *Phellinus pomaceus*, *Betula Maximowicziana* by *Daedaleopsis confragosa* and *Fuscoporia obliqua*, *Populus Maximowiczii* by *Ischnoderma resinosum*, *Syringa reticulata* by *Phellinus baumii*, *Fraxinus mandshurica* var. *japonica* by *Stereum* sp. and *Tyromyces* sp., *Quercus crispula* by *Stereum frustulosum*, *Coriolus consors*, *Inonotus hispidus*, *Inonotus dryadeus*, *Fomitopsis castanea*, *Lentinus edodes* and *Grifola* sp., *Cercidiphyllum japonicum* by *Coriolus versicolor* and *Phellodendron amurense* by *Bjerkandera fumosa*.

2. Decayed wood in which the spot of glucose is small. The wood of *Acer palmatum* var. *Matsumurae* decayed by *Coriolus hirsutus*.

3. Decayed wood in which the spot of xylose is small. The woods of

TABLE 2-a. The composition of decayed softwood (%)

Fungus species	*Fomitopsis annosa*	*Phellinus hartigii*	*Stereum sanguinolentum*
Wood species	*Abies sachalinensis*	*Abies sachalinensis*	*Abies sachalinensis*
Sample number	1_3	2_3	3_3
Density	0.17	0.20	0.32
Ash	1.0	1.4	1.5
Carbon	49.4	50.0	49.3
Hydrogen	6.5	6.4	6.2
Solubility in:			
Alcohol-benzene	2.2	3.2	3.0
Cold water	6.8	5.9	5.5
Hot water	10.5	11.5	10.1
1% NaOH	27.0	25.7	24.4
Cross and Bevan cellulose	51.7	49.7	53.0
Total pentosan	10.5	12.9	13.7
Holocellulose	64.6	65.1	65.3
Lignin	28.1	27.8	23.6

TABLE 2-b. The composition of decayed softwood (%)

Fungus species	*Sparassis crispa*	*Sparassis crispa*	*Cryptoderma yamanoi*	*Tyromyces borealis*
Wood species	*Abies sachalinensis*	*Larix Kaempferi*	*Picea jezoensis*	*Picea Glehnii*
Sample number	4_3	$4'_3$	5_3	6_3
Density	0.22	0.25	—	0.34
Ash	0.7	0.4	0.1	1.4
Carbon	58.0	54.8	43.9	49.2
Hydrogen	6.4	5.9	6.3	5.9
Solubility in:				
Alcohol-benzene	18.0	9.8	0	0.9
Cold water	44.2	6.8	—	3.9
Hot water	11.6	17.6	—	8.6
1% NaOH	70.6	65.6	60.4	21.8
Cross and Bevan cellulose	19.7	33.0	84.8	54.7
Total pentosan	13.6	12.6	5.7	9.6
Holocellulose	16.3	26.0	86.3	69.8
Lignin	52.4	45.3	0	27.4

TABLE 2-c. The composition of decayed softwood (%)

Fungus species	*Phaeolus schweinitzii*	*Phaeolus schweinitzii*	*Phaeolus schweinitzii*
Wood species	*Abies Mayriana*	*Abies Mayriana*	*Picea Glehnii*
Sample number	7_3	$7'_3$	$7d_3$
Density	0.29	0.33	0.34
Ash	0.7	0.6	0.6
Carbon	52.0	53.9	54.6
Hydrogen	6.3	6.4	5.8
Solubility in :			
Alcohol-benzene	3.7	5.1	9.8
Cold water	—	—	5.4
Hot water	7.3	7.4	11.9
1% NaOH	40.5	44.8	48.5
Cross and Bevan cellulose	32.4	19.0	14.1
Total pentosan	10.5	11.4	17.7
Holocellulose	—	39.5	—
Lignin	45.6	56.8	45.2

TABLE 2-d. The composition of decayed softwood (%)

Fungus species	*Phaeolus schweinitzii*	*Phaeolus schweinitzii*	*Phaeolus schweinitzii*	*Phaeolus schweinitzii*
Wood species	*Larix Kaempferi*	*Larix Kaempferi*	*Larix Kaempferi*	*Larix Kaempferi*
Sample number	$7a_3$	$7b_3$	$7b'_3$	$7c_3$
Density	0.23	0.26	0.27	0.30
Ash	0.5	0.2	0.2	1.0
Carbon	56.8	58.8	—	—
Hydrogen	6.0	6.3	—	—
Solubility in :				
Alcohol-benzene	9.5	20.3	18.7	7.6
Cold water	4.1	6.7	4.2	4.8
Hot water	14.0	16.4	11.4	21.6
1% NaOH	69.0	72.4	76.7	66.3
Cross and Bevan cellulose	23.3	16.8	9.8	2.2
Total pentosan	12.1	4.4	2.9	13.6
Holocellulose	16.1	22.1	21.5	—
Lignin	54.1	56.5	65.0	63.0

TABLE 2-e. The composition of decayed softwood (%)

Fungus species	*Stereum fasciatum*	*Lentinus Kaufmanii*	*Fomitopsis pinicola*	*Coniophora* sp.
Wood species	*Picea jezoensis*	*Picea jezoensis*	*Picea jezoensis*	*Taxus cuspidata* var. *latifolia*
Sample number	8_2	9_3	10_3	11_3
Density	0.33	—	0.24	0.28
Ash	0.5	0.4	0.6	0.6
Carbon	49.4	61.5	54.2	59.5
Hydrogen	6.7	5.9	6.3	5.8
Solubility in :				
Alcohol-benzene	3.0	8.6	10.4	7.6
Cold water	3.0	—	6.6	1.9
Hot water	7.3	—	12.3	8.8
1% NaOH	20.0	63.7	58.0	57.7
Cross and Bevan cellulose	54.6	15.9	37.0	9.7
Total pentosan	13.5	9.7	12.4	10.4
Holocellulose	68.5	12.4	40.8	16.9
Lignin	31.5	69.1	41.3	71.5

TABLE 2-f. The composition of decayed softwood (%)

Fungus species	*Tyromyces balsameus*	*Fuscoporia weirii*	*Fomitopsis roseozonata*	*Favolus alveolarius*
Wood species	*Picea Glehnii*	*Picea jezoensis*	*Picea jezoensis*	*Abies sachalinensis*
Sample number	12_3	13_3	14_3	15_2
Density	0.31	0.13	0.27	—
Ash	1.3	0.4	0.5	0.4
Carbon	52.9	50.1	55.0	48.7
Hydrogen	5.7	6.4	6.0	6.1
Solubility in :				
Alcohol-benzene	3.1	7.1	13.0	3.4
Cold water	3.5	8.3	5.2	4.8
Hot water	9.3	15.9	14.7	9.7
1% NaOH	50.6	35.5	59.2	27.3
Cross and Bevan cellulose	24.4	46.8	28.8	42.7
Total pentosan	10.2	10.0	11.0	16.8
Holocellulose	41.7	62.3	28.8	60.8
Lignin	48.3	28.4	42.6	30.5

TABLE 2-g. The composition of decayed softwood (%)

Fungus species	*Cryptoporus volvatus*	*Hirschioporus fuscoviolaceus*	*Fomitopsis insularis*
Wood species	*Abies sachalinensis*	*Abies sachalinensis*	*Abies sachalinensis*
Sample number	16_2	17_3	18_3
Density	0.33	0.14	0.16
Ash	0.4	0.8	1.3
Carbon	49.4	48.8	49.5
Hydrogen	6.4	6.4	7.0
Solubility in:			
Alcohol-benzene	2.0	2.8	4.5
Cold water	4.3	6.6	10.0
Hot water	9.2	11.2	16.3
1% NaOH	22.8	26.7	33.2
Cross and Bevan cellulose	57.0	55.4	49.5
Total pentosan	11.8	10.5	11.6
Holocellulose	72.7	69.0	62.4
Lignin	22.5	26.3	27.1

TABLE 2-h. The composition of decayed softwood (%)

Fungus species	*Ischnoderma resinosum*	*Laetiporus sulphureus* var. *miniatus*	*Poria subacida*
Wood species	*Picea jezoensis*	*Abies sachalinensis*	*Abies sachalinensis*
Sample number	19_3	20_3	21_3
Density	—	0.13	0.09
Ash	—	0.6	1.7
Carbon	43.4	58.8	48.3
Hydrogen	6.5	7.0	6.0
Solubility in:			
Alcohol-benzene	1.4	15.0	6.3
Cold water	—	5.5	11.4
Hot water	—	13.9	22.0
1% NaOH	57.0	57.0	45.2
Cross and Bevan cellulose	88.1	17.3	43.4
Total pentosan	7.1	11.4	10.2
Holocellulose	85.7	14.7	57.6
Lignin	0	57.9	29.6

TABLE 3-a. The composition of decayed hardwood (%)

Fungus species	*Fomitopsis castanea*	*Phellinus igniarius*	*Phellinus igniarius*	*Rigidoporus ulmarius*
Wood species	*Quercus crispula*	*Acer palmatum* var. *Matsumurae*	*Betula platyphylla*	*Ulmus Davidiana* var. *japonica*
Sample number	I_3	II_3	II'_3	III_3
Density	0.23	0.21	0.22	—
Ash	3.3	2.6	0.5	4.3
Carbon	53.6	49.4	50.3	42.9
Hydrogen	6.0	6.4	6.0	6.2
Solubility in:				
Alcohol-benzene	1.0	1.3	3.5	2.7
Cold water	2.8	2.9	2.3	11.7
Hot water	26.6	5.6	5.7	16.9
1% NaOH	79.8	28.1	29.6	50.5
Cross and Bevan cellulose	27.6	50.0	51.8	75.0
Total pentosan	11.7	23.8	28.0	7.4
Holocellulose	28.2	67.7	70.8	75.7
Lignin	60.0	28.1	24.3	4.5

TABLE 3-b. The composition of decayed hardwood (%)

Fungus species	*Coriolus hirsutus*	*Coriolus hirsutus*	*Coriolus hirsutus*	*Coriolus hirsutus*
Wood species	*Acer palmatum* var. *Matsumurae*	*Fagus crenata*	*Sorbus alnifolia*	*Prunus Maximowiczii*
Sample number	IV_3	IV'_3	IV''_3	IV'''_3
Density	—	0.25	0.18	—
Ash	2.9	0.7	0.3	3.5
Carbon	46.7	48.7	48.6	48.0
Hydrogen	6.0	6.2	6.6	6.3
Solubility in:				
Alcohol-benzene	1.2	1.0	1.0	1.4
Cold water	10.6	3.7	2.0	3.0
Hot water	20.3	6.1	4.1	6.3
1% NaOH	44.7	27.2	23.3	36.1
Cross and Bevan Cellulose	47.8	54.2	56.4	47.7
Total pentosan	23.8	26.2	25.1	27.0
Holocellulose	60.8	78.3	76 3	72.2
Lignin	30.3	21.5	20.7	26.5

TABLE 3-c. The composition of decayed hardwood (%)

Fungus species	*Elfvingia applanata*	*Fomes fomentarius*	*Irpex lacteus*
Wood species	*Tilia japonica*	*Acer palmatum* var. *Matsumurae*	*Acer mono* var. *glabrum*
Sample number	V_3	VI_3	VII_3
Density	0.24	0.30	0.16
Ash	0.5	1.7	1.7
Carbon	48.5	49.3	48.5
Hydrogen	6.2	6.4	6.4
Solubility in :			
Alcohol-benzene	3.8	1.1	2.2
Cold water	3.9	2.7	7.3
Hot water	7.4	13.0	13.5
1% NaOH	29.1	23.1	37.5
Cross and Bevan cellulose	60.6	55.5	51.7
Total pentosan	23.8	25.7	23.4
Holocellulose	79.1	72.5	70.6
Lignin	15.6	25.1	23.7

TABLE 3-d. The composition of decayed hardwood (%)

Fungus species	*Inonotus cuticularis*	*Oxyporus populinus*	*Phellinus pomaceus*	*Daedaleopsis confragosa*
Wood species	*Alnus hirsuta*	*Acer palmatum* var. *Matsumurae*	*Prunus Sargentii*	*Betula Maximowicziana*
Sample number	$VIII_3$	IX_3	X_3	XI_3
Density	0.22	—	0.23	0.27
Ash	0.9	1.5	1.4	1.7
Carbon	48.9	47.7	48.8	47.1
Hydrogen	6.7	6.1	6.3	6.2
Solubility in :				
Alcohol-benzene	2.1	0.8	1.1	1.8
Cold water	3.2	—	2.9	8.1
Hot water	7.3	—	4.8	11.2
1% NaOH	27.8	34.8	26.7	32.4
Cross and Bevan cellulose	56.9	43.2	53.2	52.1
Total pentosan	22.7	23.8	27.5	28.4
Holocellulose	75.4	—	77.7	73.4
Lignin	22.3	27.4	22.6	20.8

TABLE 3-e. The composition of decayed hardwood (%)

Fungus species	*Trametes dickinsii*	*Trametes gibbosa*	*Daedaleopsis tricolor*
Wood species	*Quercus crispula*	*Tilia japonica*	*Acer mono* var. *glabrum*
Sample number	XII_3	$XIII_3$	XVI_3
Density	0.32	0.07	0.23
Ash	1.2	1.9	1.2
Carbon	52.7	48.7	48.7
Hydrogen	5.6	6.2	6.2
Solubility in:			
Alcohol-benzene	18.4	4.6	1.4
Cold water	6.2	10.1	4.4
Hot water	23.7	15.6	6.7
1% NaOH	73.8	47.7	26.7
Cross and Bevan cellulose	28.5	46.1	52.4
Total pentosan	11.9	20.0	24.1
Holocellulose	32.2	63.8	73.4
Lignin	37.1	20.8	25.7

TABLE 3-f. The composition of decayed hardwood (%)

Fungus species	*Laetiporus sulphureus*	*Ischnoderma resinosum*	*Phellinus baumii*	*Stereum* sp.
Wood species	*Quercus crispula*	*Populus Maximowiczii*	*Syringa reticulata*	*Fraxinus mandshurica* var. *japonica*
Sample number	XV_3	XVI_3	$XVII_3$	$XVIII_3$
Density	0.21	0.12	0.21	0.31
Ash	1.0	2.8	0.3	0.5
Carbon	54.1	48.1	50.2	47.7
Hydrogen	6.1	6.4	6.0	6.1
Solubility in:				
Alcohol-benzene	12.5	7.3	4.4	3.0
Cold water	3.6	15.4	2.5	4.1
Hot water	15.7	23.2	7.0	6.8
1% NaOH	80.4	59.2	34.3	27.0
Cross and Bevan cellulose	22.1	49.8	47.9	55.7
Total pentosan	8.7	15.0	23.4	21.7
Holocellulose	14.3	62.1	64.2	76.9
Lignin	44.4	14.5	27.7	20.8

TABLE 3-g. The composition of decayed hardwood (%)

Fungus species	*Coriolus versicolor*	*Lentinus edodes*	*Bjerkandera fumosa*
Wood species	*Cercidiphyllum japonicum*	*Quercus crispula*	*Phellodendron amurense*
Sample number	XIX_3	XX_3	XXI_3
Density	0.12	0.29	0.21
Ash	0.4	1.6	1.1
Carbon	47.5	46.4	48.4
Hydrogen	6.7	6.5	6.3
Solubility in:			
Alcohol-benzene	0.8	4.8	4.1
Cold water	2.4	9.1	6.3
Hot water	4.7	11.8	9.1
1% NaOH	29.9	36.1	34.2
Cross and Bevan cellulose	54.8	59.7	52.4
Total pentosan	23.3	20.8	26.5
Holocellulose	70.4	76.4	74.2
Lignin	23.8	18.8	19.9

TABLE 3-h. The composition of decayed hardwood (%)

Fungus species	*Hymenochaete intricata*	*Tyromyces* sp.	*Fomitopsis pinicola*	*Poria* sp.
Wood species	*Alnus hirsuta*	*Quercus crispula*	*Prunus Ssiori*	*Acer mono* var. *glabrum*
Sample number	$XXII_3$	$XXIII_3$	$XXIV_3$	XXV_3
Density	0.18	—	0.26	—
Ash	1.0	2.7	0.6	4.4
Carbon	49.0	47.7	54.1	45.2
Hydrogen	6.7	6.3	5.9	6.2
Solubility in:				
Alcohol-benzene	3.9	3.3	16.8	0
Cold water	5.8	12.4	4.2	7.5
Hot water	10.3	15.5	16.8	10.5
1% NaOH	31.3	35.0	89.4	29.1
Cross and Bevan cellulose	48.0	41.7	18.9	60.0
Total pentosan	26.0	27.7	11.0	19.1
Holocellulose	73.1	—	21.8	73.5
Lignin	26.0	26.1	51.1	20.6

TABLE 3-i. The composition of decayed hardwood (%)

Fungus species	*Tyromyces* sp.	*Fuscoporia obliqua*	*Stereum frustulosum*
Wood species	*Fraxinus mandshurica* var. *japonica*	*Betula Maximowicziana*	*Quercus crispula*
Sample number	$XXVI_3$	$XXVII_3$	$XXVIII_3$
Density	0.15	0.21	0.29
Ash	2.7	3.4	1.5
Carbon	48.9	49.6	49.9
Hydrogen	6.3	6.0	6.0
Solubility in:			
Alcohol-benzene	1.4	4.6	5.9
Cold water	3.0	5.6	5.1
Hot water	5.6	14.5	14.3
1% NaOH	29.3	46.4	36.3
Cross and Bevan cellulose	44.8	40.0	43.7
Total pentosan	24.4	22.8	25.9
Holocellulose	72.8	58.3	64.3
Lignin	32.9	31.8	29.5

TABLE 3-j. The composition of decayed hardwood (%)

Fungus species	*Coriolus consors*	*Grifola* sp.	*Inonotus hispidus*	*Inonotus dryadeus*
Wood species	*Ulmus Davidiana* var. *japonica*	*Quercus crispula*	*Quercus crispula*	*Quercus crispula*
Sample number	$XXIX_3$	XXX_3	$XXXI_3$	$XXXII_3$
Density	0.26	—	0.22	0.28
Ash	0.8	—	3.7	0.8
Carbon	49.5	44.1	—	—
Hydrogen	6.1	6.7	—	—
Solubility in:				
Alcohol-benzene	2.1	0	0.7	1.3
Cold water	3.1	3.5	5.3	4.5
Hot water	5.2	5.1	8.3	6.4
1% NaOH	24.6	51.7	31.0	24.7
Cross and Bevan cellulose	53.8	91.2	50.5	53.9
Total pentosan	23.3	12.4	27.1	27.4
Holocellulose	74.7	91.7	66.4	73.8
Lignin	23.7	3.1	26.7	23.8

TABLE 4. Amount of alkali consumed by 0.1 g of brown rotted softwood in ml of 0.1 *N* sodium hydroxide

Sample number	Wood species	Fungus species	Decay stage			
			0	1	2	3
4	*Abies sachalinensis*	*Sparasis crispa*	1.00	1.23	3.76	3.83
4′	*Larix Kaempferi*	*Sparasis crispa*	1.77	2.53	4.06	4.68
7	*Abies Mayriana*	*Phaeolus schweinitzii*	1.23	1.45	4.17	4.22
7′	*Abies Mayriana*	*Phaeolus schweinitzii*	0.65	0.62	3.93	4.27
7a	*Larix Kaempferi*	*Phaeolus schweinitzii*	—	2.23	4.22	4.60
7b	*Larix Kaempferi*	*Phaeolus schweinitzii*	1.84	—	—	4.52
7d	*Picea Glehnii*	*Phaeolus schweinitzii*	—	—	—	4.34
9	*Picea jezoensis*	*Lentinus Kaufmanii*	—	1.39	—	3.83
10	*Picea jezoensis*	*Fomitopsis pinicola*	1.08	1.39	3.76	4.22
11	*Taxus cuspidata* var. *latifolia*	*Coniophora* sp.	2.00	1.77	—	3.68
12	*Picea Glehnii*	*Tyromyces balsameus*	1.26	1.14	3.45	4.01
14	*Picea jezoensis*	*Fomitopsis roseozonata*	—	2.53	—	4.52
20	*Abies sachalinensis*	*Laetiporus sulphureus* var. *miniatus*	—	—	—	3.47
	Average		1.35	1.63	3.91	4.17

TABLE 5. Amount of alkali consumed by 0.1 g of white rotted softwood in ml of 0.1 *N* sodium hydroxide

Sample number	Wood species	Fungus species	Decay stage			
			0	1	2	3
5	*Picea jezoensis*	*Cryptoderma yamanoi*	1.22	1.55	2.22	6.85
19	*Picea jezoensis*	*Ischnoderma resinosum*	—	—	—	5.07
	Average		1.22	1.55	2.22	5.96

TABLE 6. Amount of alkali consumed by 0.1 g of intermediate rotted softwood in ml of 0.1 *N* sodium hydroxide

Sample number	Wood species	Fungus species	Decay stage			
			0	1	2	3
1	*Abies sachalinensis*	*Fomitopsis annosa*	1.31	1.23	1.46	2.00
2	*Abies sachalinensis*	*Phellinus hartigii*	1.39	1.31	—	1.77
3	*Abies sachalinensis*	*Stereum sanguinolentum*	1.00	1.39	—	1.92
6	*Picea Glehnii*	*Tyromyces borealis*	1.48	1.26	—	1.89
8	*Picea jezoensis*	*Stereum fasciatum*	—	—	1.62	—
13	*Picea jezoensis*	*Fuscoporia weirii*	—	—	—	2.69
15	*Abies sachalinensis*	*Favolus albeorarius*	—	—	2.38	—
16	*Abies sachalinensis*	*Cryptoporus volvatus*	1.08	—	1.84	—
17	*Abies sachalinensis*	*Hirschioporus fuscoviolaceus*	—	1.23	—	2.38
18	*Abies sachalinensis*	*Fomitopsis insularis*	—	1.46	—	2.99
21	*Abies sachalinensis*	*Poria subacida*	—	—	—	3.32
	Average		1.25	1.31	1.83	2.37

TABLE 7. Amount of alkali consumed by 0.1 g of brown rotted hardwood in ml of 0.1 *N* sodium hydroxide

Sample number	Wood species	Fungus species	Decay stage			
			0	1	2	3
I	*Quercus crispula*	*Fomitopsis castanea*	2.61	2.46	4.14	3.76
XII	*Quercus crispula*	*Trametes dickinsii*	—	2.76	—	4.75
XV	*Quercus crispula*	*Laetiporus sulphureus*	—	1.33	—	3.77
XXIV	*Prunus Ssiori*	*Fomitopsis pinicola*	2.38	—	—	4.52
	Average		2.50	2.18	4.14	4.20

TABLE 8. Amount of alkali consumed by 0.1 g of white rotted hardwood in ml of 0.1 *N* sodium hydroxide

Sample number	Wood species	Fungus species	Decay stage			
			0	1	2	3
III	*Ulmus Davidiana* var. *japonica*	*Rigidoporus ulmarius*	1.92	—	—	3.76
XXX	*Quercus crispula*	*Grifola* sp.	—	2.84	—	4.45
	Average		1.92	2.84	—	4.11

TABLE 9. Amount of alkali consumed by 0.1 g of intermediate rotted hardwood in ml of 0.1 *N* sodium hydroxide

Sample number	Wood species	Fungus species	Decay stage			
			0	1	2	3
II	*Acer palmatum* var. *Matsumurae*	*Phellinus igniarius*	1.62	1.39	2.00	2.38
II′	*Betula platyphylla*	*Phellinus igniarius*	—	—	—	2.15
IV	*Acer palmatum* var. *Matsumurae*	*Coriolus hirsutus*	—	2.15	2.46	2.92
IV′	*Fagus crenata*	*Coriolus hirsutus*	—	1.48	—	2.32
IV″	*Sorbus alnifolia*	*Coriolus hirsutus*	—	—	—	2.53
IV‴	*Prunus Maximowiczii*	*Coriolus hirsutus*	—	—	—	2.61
V	*Tilia japonica*	*Elfvingia applanata*	2.53	2.00	2.30	2.84
VI	*Acer palmatum* var. *Matsumurae*	*Fomes fomentarius*	—	—	2.54	2.30
VII	*Acer mono* var. *glabrum*	*Irpex lacteus*	—	—	—	2.84
VIII	*Alnus hirsuta*	*Inonotus cuticularis*	—	—	2.38	2.53
IX	*Acer palmatum* var. *Matsumurae*	*Oxyporus populinus*	1.49	—	1.77	2.30
X	*Prunus Sargentii*	*Phellinus pomaceus*	—	2.38	2.53	2.61
XI	*Betula Maximowicziana*	*Daedaleopsis confragosa*	—	2.07	2.46	2.92
XIII	*Tilia japonica*	*Trametes gibbosa*	—	—	—	4.16
XIV	*Acer mono* var. *glabrum*	*Daedaleopsis tricolor*	1.84	—	2.23	2.38
XVI	*Populus Maximowiczii*	*Ischnoderma resinosum*	—	—	—	3.99
XVII	*Syringa reticulata*	*Phellinus baumii*	—	—	2.30	2.46
XVIII	*Fraxinus mandshurica* var. *japonica*	*Stereum* sp.	1.84	—	2.23	—
XIX	*Cercidiphyllum japonicum*	*Coriolus versicolor*	2.99	—	—	2.84

TABLE 9. (continued)

Sample number	Wood species	Fungus species	Decay stage 0	1	2	3
XX	*Quercus crispula*	*Lentinus edodes*	—	2.46	—	3.45
XXI	*Phellodendron amurense*	*Bjerkandera fumosa*	—	—	—	2.69
XXII	*Alnus hirsuta*	*Hymenochaete intricata*	—	2.00	—	2.84
XXIII	*Quercus crispula*	*Tyromyces* sp.	—	—	—	2.53
XXV	*Acer mono*	*Poria* sp.	2.07	—	—	1.62
XXVI	*Fraxinus mandshurica* var. *japonica*	*Tyromyces* sp.	1.69	—	2.53	2.53
XXVII	*Betula Maximowicziana*	*Fuscoporia obliqua*	2.00	1.54	—	2.69
XXVIII	*Quercus crispula*	*Stereum frustulosum*	—	2.69	—	2.61
XXIX	*Ulmus Davidiana* var. *japonica*	*Coriolus consors*	—	2.07	—	2.61
XXXI	*Quercus crispula*	*Inonotus hispidus*	1.84	—	—	1.71
XXXII	*Quercus crispula*	*Inonotus dryadeus*	1.82	—	—	1.91
	Average		1.97	2.02	2.31	2.63

TABLE 10. Relation between the calorific value and the main components in the decayed wood

Sample number	Decay type	Calorific value cal	Component Carbon %	Lignin %	Holocellulose %
$5_{2.5}$	w. r.	4,640	48.6	22.6	75.4
7_3	b. r.	5,650	58.8	56.5	22.1
10_3	b. r.	5,280	54.2	41.3	40.8
6_3	i. r.	4,760	49.2	27.4	69.8
17_3	i. r.	4,620	48.8	26.3	69.0
III_0	sound	4,810	50.1	29.9	71.0
III_3	w. r.	3,880	42.9	4.5	75.7
XXX_3	w. r.	4,170	44.1	3.1	91.7
I_3	b. r.	5,080	53.6	60.0	28.2
II_3	i. r.	4,680	49.4	28.1	67.7
V_3	i. r.	4,630	48.5	15.6	79.1
XI_3	i. r.	4,550	47.1	20.8	73.4

Ulmus Davidiana var. *japonica* decayed by *Rigidoporus ulmarius*, *Quercus crispula* by *Trametes dickinsii* and *Laetiporus sulphureus* and *Prunus Ssiori* by *Fomitopsis pinicola*.

According to the results of the chromatographic tests on hardwood, almost all of intermediate rotted woods show sound-like chromatograms like those shown in softwood, and many of the brown rotted woods have small spots of xylose.

Table 11 shows the result of measuring the calorific value and degree of polymerization of the holocellulose isolated from wood. Nearly every holocellulose has about 4,200 calories and no difference can be found between the holocellulose of soft- and hardwood, and of decayed and sound woods, except that *Ulmus Davidiana* var. *japonica* decayed by *Rigidoporus ulmarius* which is considered natural holocellulose in itself isolated by the fungus shows lower value. The degree of polymerization of the holocellulose of decayed wood is lower than that of sound-wood holocellulose.

TABLE 11. Calorific value and degree of polymerization of various holocelluloses

Original wood		Holocellulose			
Sample number	Decay type	Yield %	Lignin content %	Calorific value cal	Degree of Polymerization
10_0	sound	75.1	2.8	4,260	—
$5_{2.5}$	w. r.	79.7	5.4	4,170	1,840
10_3	b. r.	40.8	2.3	4,140	—
17_3	i. r.	75.1	8.2	4,280	—
III_0	sound	79.1	10.2	4,270	1,570
III_3	w. r.	78.0	3.0	4,210	570
II_3	i. r.	72.5	6.6	4,200	920
V_3	i. r.	83.2	5.0	4,210	—
5_3	w. r.	100 (wood itself)	0	—	180
III_3	w. r.	100 (wood itself)	4.5	3,880	240

E. Properties of Lignin

Sulfuric acid lignins from both decayed and sound woods were investigated as to the contents of carbon, hydrogen and methoxyl group and the results are given in Table 12.

Table 12 shows that carbon and methoxyl group content of the lignin from brown rotted wood is a little lower than that in the lignin from sound

TABLE 12. Carbon, hydrogen and methoxyl contents in lignin from decayed and sound woods (%)

Wood species	*Quercus crispula*		*Quercus crispula*		*Fagus crenata*	
Fungus species	*Fomitopsis castanea*		*Inonotus dryadeus*		*Coriolus versicolor*	
Decay type	b. r.		i. r.		i. r.	
Sound or decayed	Sound	Decayed	Sound	Decayed	Sound	Decayed
Sample number	I_0	I_3	$XXXII_0$	$XXXII_3$	—	—
Yield of lignin	26.1	60.0	27.2	23.8	17.5	23.9
Carbon	61.7	60.2	61.3	62.1	62.6	62.3
Hydrogen	5.2	5.0	5.2	5.4	5.5	5.6
Methoxyl	18.2	14.6	19.0	20.1	20.5	20.3

wood, but on the whole there seem almost no differences between decayed and sound wood lignins. Hydrogen content is almost the same in each lignin.

F. Properties of Alkali Soluble Matter

Properties of the matter precipitated from the extractives of decayed wood with 1 per cent sodium hydroxide solution by acidifying with sulfuric acid are given in Table 13. According to the data, the amount of the precipitate is relatively small about 3 per cent in sound wood and 6 per cent in intermediate

TABLE 13. Properties of 1% NaOH-extractive in decayed oak wood

Fungus species	—	*Inonotus hispidus*	*Fomitopsis castanea*
Decay type	Sound	i. r.	b. r.
Sample number	$XXXI_0$	$XXXI_3$	I_3
Yield of extract, %[a]	22	33	78
Yield of precipitate, %[a]	3	6	39
Precipitate Carbon content, %	61.6	61.6	61.5
Hydrogen content, %	5.1	5.7	5.6
Methoxyl content, %	16.7	17.5	16.8
Methoxyl content of lignin in the residue, %	20.2	19.3	—[b]

a) On the basis of ovendry wood.

b) After extraction, the residue became such a hard cake that isolation of lignin was impossible. The methoxyl group content of the residue was 8.8 per cent.

rotted wood, it is however as large as 39 per cent in brown rotted wood on the basis of ovendry wood. The above figures correspond to 14, 18 and 50 per cent of total extract, respectively. There is no difference in carbon, hydrogen and methoxyl contents among the three precipitates and these precipitates may be considered as soluble lignin from the analytical results. According to the results above mentioned, the main part of alkali soluble matter must be lignin in brown rotted wood. The amount of methoxyl group in the precipitate is equivalent to 75 per cent of that in sulfuric acid lignin, while the amount remaining in the residue is equivalent to only 23 per cent in the case of the brown rotted wood. Thus, the main part of lignin became soluble in alkali. But alkali soluble lignin has a lower methoxyl group content than insoluble lignin remaining in the residue in both sound and intermediate rotted wood. This is almost the same property shown in the case of brown rotted softwood. On the other hand, after the hydrolysate of the extractives was filtered and concentrated the sugar constituents were tested by paper chromatography, but clear spots could not be obtained, except a dim spot of xylose because of the degradation of the sugars with hot alkaline solution. For this reason, decayed wood was extracted with cold 5 per cent sodium hydroxide and the extractives were treated as mentioned before. The result of the test of extracted sugars and precipitates is given in Table 14.

TABLE 14. Reducing matter and precipitate separated from cold 5% NaOH-extractive after acid hydrolysis (%)

Sample number	Decay type	Yield of extract	Reducing matter (as glucose)		Precipitate		
			Total extract basis	Original wood basis	Total extract basis	Original wood basis	Color
$XXXI_0$	sound	17.5	59.6	10.4	9.5	1.7	greyish brown
$XXXI_3$	i. r.	26.5	55.5	14.7	13.5	3.6	bright greyish brown
I_3	b. r.	53.3	19.7	10.5	49.9	26.6	greyish brown
XXX_3	w. r.	38.8	59.9	23.2	27.9	10.8	black

In the chromatogram of the hydrolysate obtained from 5 per cent sodium hydroxide extractive of white rotted wood, two clear spots of xylose and glucose were observed of the same size, and between these spots one faint spot which seemed to correspond to mannose was also observed. While in the case of sound, brown rotted and intermediate rotted woods, only a spot of xylose could

be observed distinctly. By acid hydrolysis of the extractive from brown rotted wood with 5 per cent sodium hydroxide, much precipitate was observed as well as in the case of the extractive with 1 per cent sodium hydroxide. The color of the precipitates from sound and brown rotted woods was greyish brown, while that of the precipitate from intermediate rotted wood was bright greyish brown. A large quantity of black precipitate from white rotted wood amounting to 10.8 per cent on the basis of the original wood contained 1.2 per cent of methoxyl group.

V. Discussion

In the chemical analysis of decayed wood it is sometimes difficult to apply the usual analytical methods used with common sound wood. If it is possible to make use of the usual method for the analysis of decayed wood, the chemical components analyzed sometimes differ greatly from that of sound wood. Before discussing the properties of the components of decayed wood, the analytical results by the usual methods must be discussed.

When the chemical composition of decayed wood is discussed, it is convenient to classify the type of decay into several groups as has already been done by some workers.[7,17,27,46,103] As a standard for the classification of decay types certain principal components of wood which can be easily analyzed should be selected. Cross and Bevan cellulose has been considered as one of the favourable components for the classification, but it is not so easy to analyze. On the contrary, lignin is another important principal component connected with the properties of decayed wood, and moreover relatively easy to analyze. The author has tried to classify the decayed woods on the basis of the content of lignin and holocellulose. Methods of isolation have been so improved recently that the procedure is easy and holocellulose as well as lignin also one of the most important principal components, has a great influence upon the properties of decayed wood.

Table 15 and Table 16 show that there are differences among sixty-four kinds of decayed wood analyzed by the author in the ratio of holocellulose to lignin, by which the decayed woods can be classified into three groups as follows:

1. Lignin-rich decayed wood—the decayed wood in which the ratio is below 1.0 or the lignin content is higher than the holocellulose content.
   (a) Softwood decayed by *Lentinus Kaufmanii*, *Coniophora* sp., *Laetiporus sulphureus* var. *miniatus*, *Phaeolus schweinitzii*, *Sparassis crispa*, *Fomitopsis roseozonata*, *Tyromyces balsameus* and *Fomitopsis pinicola* (Their ratios range from 0.18 to 0.99 in Table 15-a).

TABLE 15-a. The ratio of holocellulose to lignin in decayed softwood

Sample number	Wood species	Fungus species	Ratio
9_3	*Picea jezoensis*	*Lentinus Kaufmanii*	0.18
11_3	*Taxus cuspidata* var. *latifolia*	*Coniophora* sp.	0.24
20_3	*Abies sachalinensis*	*Laetiporus sulphureus* var. *miniatus*	0.25
$7a_3$	*Larix Kaempferi*	*Phaeolus schweinitzii*	0.30
4_3	*Abies sachalinensis*	*Sparassis crispa*	0.31
$7b'_3$	*Larix Kaempferi*	*Phaeolus schweinitzii*	0.33
$7b_3$	*Larix Kaempferi*	*Phaeolus schweinitzii*	0.39
$4'_3$	*Larix Kaempferi*	*Sparassis crispa*	0.57
14_3	*Picea jezoensis*	*Fomitopsis roseozonata*	0.68
$7'_3$	*Abies Mayriana*	*Phaeolus schweinitzii*	0.70
12_3	*Picea Glehnii*	*Tyromyces balsameus*	0.86
10_3	*Picea jezoensis*	*Fomitopsis pinicola*	0.99

TABLE 15-b. The ratio of holocellulose to lignin in decayed softwood

Sample number	Wood species	Fungus species	Ratio
21_3	*Abies sachalinensis*	*Poria subacida*	1.95
15_2	*Abies sachalinensis*	*Favolus alveolarius*	2.00
8_2	*Picea jezoensis*	*Stereum fasciatum*	2.17
13_3	*Picea jezoensis*	*Fuscoporia weirii*	2.19
1_3	*Abies sachalinensis*	*Fomes annosa*	2.30
18_3	*Abies sachalinensis*	*Fomitopsis insularis*	2.31
2_3	*Abies sachalinensis*	*Phellinus hartigii*	2.34
6_3	*Picea Glehnii*	*Tyromyces borealis*	2.55
17_3	*Abies sachalinensis*	*Hirschioporus fusco-violaceus*	2.62
3_3	*Abies sachalinensis*	*Stereum sanguinolentum*	2.77
16_3	*Abies sachalinensis*	*Cryptoporus volvatus*	3.23

(b) Hardwood decayed by *Laetiporus sulphureus*, *Fomitopsis pinicola*, *Fomitopsis castanea* and *Trametes dickinsii* (Their ratios range from 0.32 to 0.87 in Table 16-a).

2. Cellulose-rich decayed wood—the decayed wood in which the ratio is very high, or that sometimes contains only holocellulose without lignin.

TABLE 15-c. The ratio of holocellulose to lignin in decayed softwood

Sample number	Wood species	Fungus species	Ratio
5_3	*Picea jezoensis*	*Cryptoderma yamanoi*	∞
19_3	*Picea jezoensis*	*Ischnoderma resinosum*	∞

(a) Softwood decayed by *Cryptoderma yamanoi* and *Ischnoderma resinosum* (Their ratios are in Table 15-c).

(b) Hardwood decayed by *Rigidoporus ulmarius* and *Grifola* sp. (Their ratio are 16.93 and 29.76 respectively in Table 16-c).

3. "Normal-like" decayed wood—the decayed wood in which the ratio is similar to that of sound wood.

(a) Softwood decayed by *Poria subacida*, *Favolus alveolarius*, *Stereum fasciatum*, *Fuscoporia weirii*, *Fomitopsis annosa*, *Fomitopsis insularis*, *Phellinus hartigii*, *Tyromyces borealis*, *Hirschioporus fusco-violaceus*, *Stereum sanguinolentum* and *Cryptoporus volvatus* (Their ratios range from 1.95 to 3.23 in Table 15-b).

(b) Hardwood decayed by *Fuscoporia obliqua*, *Coriolus hirsutus*, *Stereum frustulosum*, *Tyromyces* sp., *Phellinus baumii*, *Phellinus igniarius*, *Inonotus hispidus*, *Fomes fomentarius*, *Coriolus versicolor*, *Irpex lacteus*, *Trametes gibbosa*, *Inonotus dryadeus*, *Coriolus consors*, *Inonotus cuticularis*, *Phellinus pomaceus*, *Daedaleopsis confragosa*, *Poria* sp., *Stereum* sp., *Bjerkandera fumosa*, *Lentinus edodes*, *Ischnoderma resinosum* and *Elfvingia applanata* (Their ratios range from 1.83 to 5.07 in Table 16-b).

If the composition of decayed wood differs from that of sound wood, it is evident that decomposition of wood has started, but even when there is no

TABLE 16-a. The ratio of holocellulose to lignin in decayed hardwood

Sample number	Wood species	Fungus species	Ratio
XV_3	*Quercus crispula*	*Laetiporus sulphureus*	0.32
$XXIV_3$	*Prunus Ssiorii*	*Fomitopsis pinicola*	0.43
I_3	*Quercus crispula*	*Fomitopsis castanea*	0.47
XII_3	*Quercus crispula*	*Trametes dickinsii*	0.87

TABLE 16-b. The ratio of holocellulose to lignin in decayed hardwood

Sample number	Wood species	Fungus species	Ratio
$XXVII_3$	*Betula Maximowicziana*	*Fuscoporia obliqua*	1.83
IV_3	*Acer palmatum* var. *Matsumurae*	*Coriolus hirsutus*	2.00
$XXVIII_3$	*Quercus crispula*	*Stereum frustulosum*	2.18
$XXVI_3$	*Fraxinus mandshurica* var. *japonica*	*Tyromyces* sp.	2.21
$XVII_3$	*Syringa reticulata*	*Phellinus baumii*	2.32
II_3	*Acer palmatum* var. *Matsumurae*	*Phellinus igniarius*	2.41
$XXXI_3$	*Quercus crispula*	*Inonotus hispidus*	2.48
IV_3'''	*Prunus Maximowiczii*	*Coriolus hirsutus*	2.73
$XXII_3$	*Alnus hirsuta*	*Hymenochaete intricata*	2.81
XIV_3	*Acer mono* var. *glabrum*	*Daedaleopsis tricolor*	2.85
VI_3	*Acer palmatum* var. *Matsumurae*	*Fomes fomentarius*	2.89
II_3'	*Betula platyphylla*	*Phellinus igniarius*	2.92
XIX_3	*Cercidiphyllum japonicum*	*Coriolus versicolor*	2.96
VII_3	*Acer mono* var. *glabrum*	*Irpex lacteus*	2.99
$XIII_3$	*Tilia japonica*	*Trametes gibbosa*	3.07
$XXXII_3$	*Quercus crispula*	*Inonotus dryadeus*	3.10
$XXIX_3$	*Ulmus Davidiana* var. *japonica*	*Coriolus consors*	3.16
$VIII_3$	*Alnus hirsuta*	*Inonotus cuticularis*	3.38
X_3	*Prunus Sargentii*	*Phellinus pomaceus*	3.43
XI_3	*Betula Maximowicziana*	*Daedaleopsis confragosa*	3.53
XXV_3	*Acer mono* var. *glabrum*	*Poria* sp.	3.57
IV_3'	*Fagus crenata*	*Coriolus hirsutus*	3.64
IV_3''	*Sorbus alnifolia*	*Coriolus hirsutus*	3.69
$XVIII_2$	*Fraxinus mandshurica* var. *japonica*	*Stereum* sp.	3.69
XXI_3	*Phellodendron amurense*	*Bjerkandera fumosa*	3.72
XX_3	*Quercus crispula*	*Lentinus edodes*	4.06
XVI_3	*Populus Maximowiczii*	*Ischnoderma resinosum*	4.29
V_3	*Tilia japonica*	*Elfvingia applanata*	5.07

apparent difference between the analytical results on sound wood and on "normal-like" decayed wood, it does not always mean that decay has not progressed. For example, if the density of decayed wood is compared with that of sound wood coexisting in the same trunk attacked by wood-destroying fungus, the average value for the density in lignin-rich decayed softwood is

TABLE 16-c. The ratio of holocellulose to lignin in decayed hardwood

Sample number	Wood species	Fungus species	Ratio
III_3	*Ulmus Davidiana* var. *japonica*	*Rigidoporus ulmarius*	16.93
XXX_3	*Quercus crispula*	*Grifola* sp.	29.76

64 per cent (range 85–48 per cent) on the basis of sound wood, in "normal-like" decayed softwood 58 per cent (range 97–37 per cent), in lignin-rich decayed hardwood 42 per cent (range 50–35 per cent), and in "normal-like" decayed hardwood 43 per cent (range 65–26 per cent). If the shrinkage of wood by decay is not taken into account; about 40 per cent of wood in weight on the basis of sound wood is decreased in softwood and 60 per cent in hardwood. Though the author has studied only a few samples, completely decayed woods of the cellulose-rich decayed wood, cannot retain their original structure, thus the tendency can not be defined. In *Picea jezoensis* decayed by *Cryptoderma yamanoi*, about 50 per cent of wood is consumed from 5_0 (sound wood) to $5_{2.5}$ (most rotted wood as far as it can keep its structure). According to the loss in weight, therefore, the decayed woods used in this work are all considered to be in an advanced stage of decay. Accordingly, it means that in lignin-rich decayed wood the principal components, especially lignin decomposed by fungus remains in the wood, while in "normal-like" decayed wood every component has been used up and only slightly changed part of original components remains in the wood.

A. Chemical Composition of Decayed Wood

a. Ash Content

The ash content of decayed wood is higher than that of sound wood except that of cellulose-rich decayed softwood. Ash presents some problems not only in determining its content but also in its properties, which must be further investigated.

b. Carbon Content

If wood is sound, the carbon content is about 50 per cent in both soft- and hardwood, but it varies with changes in its chemical composition by decay and becomes higher in lignin-rich decayed wood, lower in cellulose-rich decayed wood and is about the same in "normal-like" decayed wood. Table 17 in which the average values for carbon content in each type of decay are presented,

TABLE 17. Average value of carbon content in each decayed wood type

Decay type	Wood kind	Carbon content in:	
		Sound wood	Decayed wood
Lignin-rich	Softwood	50.0	55.7
	Hardwood	49.6	53.6
Cellulose-rich	Softwood	48.5	43.7
	Hardwood	50.1	43.5
"Normal-like"	Softwood	50.4	49.3
	Hardwood	48.7	48.5

shows clearly the tendency as above described. Conversely, from the carbon content of decayed wood, the type of decay becomes evident. Since about 6 per cent of hydrogen is present in all kinds of wood and all types of decay, this shows that the hydrogen content is not effected by decay.

c. Solubility in Alcohol-Benzene, Cold Water and Hot Water

The solubility in alcohol-benzene mixture is very high for lignin-rich decayed wood, but for "normal-like" decayed wood it does not differ from that of sound wood. The solubility in cold water is generallally not different from that of sound wood, while the solubility of most of decayed woods in hot water is higher than that of sound wood. But it was sometimes found that some lignin-rich decayed woods were not so hydrophylic that the extraction with cold water was considered to be unsatisfactory. From the results of the analyses of some

TABLE 18. Chemical composition of lignin-rich decayed wood by Dore's method of wood analysis (%)

Wood species	*Larix Kaempferi*	*Abies sachalinensis*	*Quercus crispula*	*Quercus crispula*
Fungus species	*Phaeolus schweinitzii*	*Laetiporus sulphureus* var. *miniatus*	*Fomitopsis castanea*	*Laetiporus sulphureus*
Sample number	$7b_3$	20_3	I_3	XV_3
Moisture	26.2	18.3	6.6	23.2
Solubility in:				
Benzene	3.1	1.4	0.6	0.8
Alcohol	15.9	12.0	4.9	12.1
Hot water	3.9	6.5	17.2	10.0
1% NaOH	40.0	23.7	50.5	44.8

lignin-rich decayed woods by the Dore's method[25] of wood analysis as shown in Table 18, it can be known that the content of resins, essential oils, oils, fats and waxes are low. Accordingly, alkali soluble matter in lignin-rich decayed wood must be the degraded products from the principal components such as lignin, cellulose and pentosan. Alkali soluble matter in decayed wood will be discussed fully in the next section.

d. Solubility in 1 Per Cent Sodium Hydroxide

Nearly everyone who has investigated the chemical composition of decayed wood recognizes without exception that the more wood is decayed, the more soluble it becomes in alkaline solution and some[100,115,132] of the reseach workers have tried practically to use the solubility in 1 per cent sodium hydroxide as a measure of the degree of wood decay. Also in the author's research, the solubility in 1 per cent sodium hydroxide of almost every decayed wood is higher than that of sound wood except *Tilia japonica* decayed by *Elfvingia applanata*. The average values for the solubility in 1 per cent sodium hydroxide for each type of decay are listed in Table 19. From the table, it will be noted that each type of decay of hardwood may be inferred from the solubility, while in softwood lignin-and cellulose-rich decayed woods have almost the same solubility but differ from "normal-like" one in the solubility.

TABLE 19. Average value of solubility in 1% NaOH (%)

Decay type	Wood kind	Content	
		Sound	Most rotted
Lignin-rich	Softwood	16.3	59.1
	Hardwood	27.8	80.9
Cellulose-rich	Softwood	13.7	60.2
	Hardwood	22.6	51.1
"Normal-like"	Softwood	13.2	29.9
	Hardwood	22.5	33.3

Moreover, from the ratio of solubility in 1 per cent sodium hydroxide of decayed wood of each type to that of sound wood (sound wood=100) listed in Table 20, the tendency above described is more clearly shown.

It is necessary to know which component among the principal components become soluble in alkaline solution during decay. First of all, pentosan can not be considered as a main part of the increment of alkali soluble matter in decayed wood because it is already soluble in alkaline solution even in the sound state.

TABLE 20. Ratio of solubility of decayed wood in 1% NaOH to that of sound wood (sound wood=100)

Decay type	Ratio		
	Maximum	Minimum	Average
Softwood			
Lignin-rich	754 ~	186	401
Cellulose-rich	440		440
"Normal-like"	219 ~	135	189
Hardwood			
Lignin-rich	308 ~	301	305
Cellulose-rich	223		223
"Normal-like"	234 ~	99	148

Concerning the cellulose, for example, *Picea jezoensis* decayed by *Cryptoderma yamanoi* (5_3), that is, white fibrous material containing mainly degraded cellulose with 5.7 per cent pentosan, is a carbohydrate according to elementary analysis, and 60.4 per cent of this carbohydrate substance is soluble in 1 per cent sodium hydroxide. In *Ulmus Davidiana* var. *japonica* decayed by *Rigidoporus ulmarius* (III_3) containing mainly cellulose with 4.5 per cent lignin and 7.4 per cent pentosan, 50.5 per cent of this wood is soluble in 1 per cent sodium hydroxide. In *Picea jezoensis* decayed by *Ischnoderma resinosum* (19_3) containing mainly cellulose with 7.1 per cent pentosan, 57.0 per cent of this wood is soluble in 1 per cent sodium hydroxide. According to these data listed above, a great deal of degraded cellulose in each cellulose-rich decayed wood is dissolved in 1 per cent sodium hydroxide.

On the other hand, lignin is also changed to become soluble in alkaline solution during decay. For example, in *Larix Kaempferi* decayed by *Phaeolus schweinitzii* ($7b_3'$) containing 65.0 per cent lignin, 76.7 per cent of it is soluble in 1 per cent sodium hydroxide, accordingly, even if the residue after sodium hydroxide extraction is all lignin, alkali soluble lignin is equivalent to 41.7 per cent of the original decayed wood and is 64.1 per cent of the total lignin. In the other lignin-rich decayed woods the same tendency is observed. For this reason, it can be understood that the increments of alkali soluble matter in decayed wood consist mainly of degraded cellulose and lignin. This tendency is in accord with the fact that 1 per cent sodium hydroxide-solubility is very high both in cellulose- and lignin-rich decayed woods. Alkali solubility in "normal-like" decayed wood is not so high, because the wood does not contain so much decomposed material as do the lignin- and cellulose-rich decayed woods.

e. Cross and Bevan Cellulose Content

It is already known that cellulose is decomposed by wood-destroying fungi and is changed into alkali soluble matter, but it is also important to know how it is decomposed and how much of it remains in the wood. As cellulose is the main reason for its utilization in the pulp and wood hydrolysis industries, the decomposition of cellulose needs to be fully investigated. The average values of Cross and Bevan cellulose content in the woods listed in Table 21 show

TABLE 21. Average value of Cross and Bevan cellulose content (%)

Decay type	Wood kind	Content	
		Sound	Most rotted
Lignin-rich	Softwood	54.7	21.0
	Hardwood	50.1	24.3
Cellulose-rich	Softwood	51.2	86.4
	Hardwood	53.3	83.1
"Norma-like"	Softwood	57.3	50.5
	Hardwood	57.7	51.0

distinguishing characteristics in types of decay. This value is low in lignin-rich decayed wood, high in cellulose-rich decayed wood and does not differ from that of sound wood in "normal-like" decayed wood. From this fact it seems that if the content of Cross and Bevan cellulose of decayed wood is determined, the type of decay can be judged. And according to the ratio of Cross and Bevan cellulose content in decayed wood to the content in sound wood (sound wood=100) listed in Table 22, the tendency for variation in decay described above is more clearly known. The data in Table 22 show the characteristic value for each decay type. In comparison with Cross and Bevan cellulose content of sound wood, that of some decayed woods is rather high in the case of softwood decayed by *Cryptoderma yamanoi* and hardwoods by *Rigidoporus ulmarius*, *Elfvingia applanata*, *Coriolus versicolor*, *Lentinus edodes*, *Poria* sp., *Stereum frustulosum* and *Grifora* sp., while that of wood decayed by the all other organisms is lower. From the survival ratio $\left(\frac{\text{g in 100 ml of decayed wood}}{\text{g in 100 ml of sound wood}} \times 100\right)$, it is found that many of lignin-rich decayed woods are rather low in cellulose and in all softwoods it ranges from 10 to 93 per cent, average 43 per cent, while in hardwood from 14 to 67 per cent, average 37 per cent. Accordingly, it appears that one half to two

TABLE 22. Ratio of Cross and Bevan cellulose content in decayed wood to that in sound wood (sound wood=100)

Decay type	Ratio		
	Maximum	Minimum	Average
Softwood			
Lignin-rich	67	21	43
Cellulose-rich	165		165
"Normal-like"	102	8	93
Hardwood			
Lignin-rich	55	38	47
Cellulose-rich	141		141
"Normal-like"	108	63	88

thirds of Cross and Bevan cellulose in sound wood is consumed by fungus. From these results, it is understood that Crooss and Bevan cellulose is decomposed and consumed by every fungus irrespective of the type of decay. And further the author should like to add that in lignin-rich decayed wood, Cross and Bevan cellulose can not often be isolated so that the content of holocellulose and pentosan is suitable as a basis for calculation of cellulose.

f. Total Pentosan Content

As already reported,[12,13,28,104,114,124] some of wood-destroying fungi consume pentosan readily, and the author's analytical result shows the same tendency. According to the average value in each type of decay listed in Table 23, the

TABLE 23. Average value of total pentosan content (%)

Decay type	Wood kind	Content	
		Sound	Most rotted
Lignin-rich	Softwood	12.1	11.5
	Hardwood	23.7	10.8
Cellulose-rich	Softwood	12.8	5.7
	Hardwood	24.0	9.9
"Normal-like"	Softwood	13.8	11.1
	Hardwood	22.9	24.1

total pentosan content is lower than that of sound wood in every type of decayed wood except "normal-like" decayed hardwood. From the ratio of total pentosan content of decayed woods to that of sound wood (sound wood=100) listed in Table 24, it is obvious that the pentosan content is reduced by decay to the

greatest extent in cellulose-rich decayed hardwood and in the other decayed woods to a lesser extent while in "normal-like" decayed hardwood there is no loss in pentosan.

Concerning the survival ratio of total pentosan, it ranges from 29 to 87 per cent, average 56 per cent in softwood while in hardwood it ranges from 12 to 65 per cent, average 38 per cent, accordingly, one half to two thirds of the total pentosan is consumed by fungus as well as in the case of Cross and Bevan cellulose. The survival ratio is low in the "normal-like" decayed softwoods by *Fomitopsis insularis*, *Hirschioporus fusco-violaceus*, *Fomitopsis annosa*, *Cryptoderma Yamanoi* and so on, but on the contrary, the woods decayed by *Cryptoporus volvatus* and *Stereum sanguinolentum*, which have high survival ratio, also belong to the "normal-like" decayed wood, and between the two groups there are most of the lignin-rich decayed softwoods which have a survival ratio of over 50 per cent. In hardwood, on the other hand, the ratio of all lignin-rich woods decayed by *Laetiporus sulphureus*, *Fomitopsis castanea* and *Trametes dickinsii* is very low, ranging from 12 to 14 per cent. The relationship of total pentosan content to type of decay is rather more irregular than in the case of Cross and Bevan cellulose, but in the total pentosan content some regular tendencies are still noticed.

TABLE 24. Ratio of total pentosan content in decayed wood to that in sound wood (sound wood=100)

Decay type	Ratio		
	Maximum	Minimum	Average
Softwood			
Lignin-rich	121	~ 50	88
Cellulose-rich		45	45
"Normal-like"	94	~ 78	84
Hardwood			
Lignin-rich	48	~ 47	48
Cellulose-rich		31	31
"Normal-like"	116	~ 85	107

g. Holocellulose Content

A considerable part of holocellulose in decayed wood is lost when it is isolated from the wood by the usual analytical method with sodium chlorite. For example, cellulose-rich decayed wood (5_3) free from lignin as shown by color reaction is obviously considered to be a carbohydrate from the result of carbon

and hydrogen analyses, but about 15 per cent of this almost pure naturally-formed holocellulose is lost by the usual treatment of holocellulose with sodium chlorite. In the analysis of Cross and Bevan cellulose in some lignin-rich decayed woods, the repetition of delignifying treatment is so difficult that after only one treatment the content of the Cross and Bevan cellulose is calculated as the difference between the amount of the residue and that of the lignin in the residue, therefore, the content of Cross and Bevan cellulose is sometimes higher than that of holocellulose. This fact means that in holocellulose analysis a part of the degraded holocellulose is lost by several delignifying treatments. For this reason, it would be desirable to use a more suitable analytical method or close observation of the decayed wood. As the proper analyticl methods for decayed wood have not yet been established, analyses have been done by the usual methods of wood analysis in this study. The classification of types of decay is made on the basis of holocellulose and lignin content, therefore, it is natural that the characteristics of each type of decay are observed on the basis of holocellulose content. The average value of holocellulose content and the ratio of the content in decayed wood to that in sound wood are listed respectively in Table 25 and Table 26. In "normal-like" decayed woods, only

TABLE 25. Average value of holocellulose content (%)

Decay type	Wood kind	Content	
		Sound	Most rotted
Lignin-rich	Softwood	69.9	25.0
	Hardwood	75.5	24.1
Cellulose-rich	Softwood	76.5*	86.0
	Hardwood	71.0	83.7
"Normal-like"	Softwood	73.5	64.5
	Hardwood	78.5	70.7

* Discolored wood.

two kinds of wood, a softwood decayed by *Cryptoporus volvatus* and a hardwood decayed by *Phellinus pomaceus*, have higher holocellulose contents than those of sound wood. The survival ratio of holocellulose ranges from 11 to 92 per cent, average 42 per cent in softwood, and in hardwood from 6 to 65 per cent, average 36 per cent.

Accordingly, severe degradation and consumption of holocellulose are observed in all types of decayed woods.

TABLE 26. Ratio of holocellulose content in decayed wood to that in sound wood (sound wood=100)

Decay type	Ratio		
	Maximum	Minimum	Average
Softwood			
Lignin-rich	56	22	38
Cellulose-rich	113*		113
"Normal-like"	92	85	88
Hardwood			
Lignin-rich	38	29	33
Cellulose-rich	132*	107	119
"Normal-like"	100	69	88

* Discolored wood basis.

h. Lignin Content

Some research workers[27,67] have long had an interest in the lignin content as well as cellulose content, as one of indicators showing the characteristics of decayed wood. Lignin is decomposed by every wood-destroying fungus as is cellulose. The average value for the lignin content and ratio in decayed wood to that in sound wood are listed respectively in Table 27 and Table 28. According to the tables, both the average value for lignin content and the ratio of lignin content distinguish clearly each type of decayed wood. The survival ratio of lignin ranges from 35 to 173 per cent, average 100 per cent, in softwood and from 27 to 94 per cent, average 54 per cent in hardwood. Among these values, the survival ratio in lignin-rich decayed softwood ranges from 98 to 173 per cent, average 125 per cent, and means that lignin increases during decay. Such phenomenon was observed by the other research workers[104] but this

TABLE 27. Average value of lignin content (%)

Decay type	Wood kind	Content	
		Sound	Most rotted
Lignin-rich	Softwood	27.7	53.5
	Hardwood	24.9	48.2
Cellulose-rich	Softwood	27.7	0
	Hardwood	30.3	3.8
"Normal-like"	Softwood	28.1	27.3
	Hardwood	22.1	24.2

TABLE 28. Ratio of lignin content in decayed wood to that in sound wood (sound wood = 100)

Decay type	Ratio		
	Maximum	Minimum	Average
Softwood			
Lignin-rich	297 ~	150	190
Cellulose-rich	0 ~	0	0
"Normal-like"	100 ~	77	93
Hardwood			
Lignin-rich	230 ~	216	223
Cellulose-rich	31* ~	30	30
"Normal-like"	175 ~	90	117

* Discolored wood basis.

increment was only an apparent one due to the shrinkage of wood as already pointed out by the authors.[37] Abundant cracks in lignin-rich decayed wood show that extreme shrinkage is caused in wood during decay.

According to the comparison of the chemical composition of decayed wood with that of sound wood, the tendency does not always coincide completely

TABLE 30. Contents of components in decayed wood in comparison with that in sound wood

Decay type	Lignin-rich		Cellulose-rich		"Normal-like"	
Wood kind	Soft.	Hard.	Soft.	Hard.	Soft.	Hard.
Carbon	+	+	−	−	±	±
Hydrogen	±	±	±	±	±	±
Solubility in:						
Alcohol-benzene	+	+			±	±
Hot water	+	+			+	+
1% NaOH	+	+	+	+	+	+
Cross and Bevan cellulose	−	−	+	+	−	−
Total pentosan	±	−	−	−	±	±
Holocellulose	−	−	+	+	−	−
Lignin	+	+	−	−	±	±

\+ Higher than sound wood.
− Lower than sound wood.
± Hardly different from sound wood.

for each wood with the same type of decay. But from an outline of the tendencies one is able to distinguish from the results of analysis the various type of decayed woods. A summary of all the components in decayed wood is given in Table 30 using the following marks to show higher (+), lower (−) or hardly different (㊣) in comparison with sound wood. From this table the characteristics of decay type can be judged.

B. Hydrogen-Ion Concentration

Hydrogen-ion concentrations of the cold water extractives of decayed woods listed in Table 29 are a little lower than those of sound wood, but the difference is very small. And also there is almost no difference between the hydrogen-ion concentration value of decayed woods and the average value of 5.4 (ranged 5.0 to 5.6) of sound woods taken from completely sound trees.

TABLE 29. Average value of hydrogen-ion concentration in decayed wood

Decay type	Wood kind	pH	
		Sound	Most rotted
Lignin-rich	Softwood	5.2	4.9
	Hardwood	5.6	5.4
Cellulose-rich	Softwood	—	5.5
	Hardwood	5.9	5.6
"Normal-like"	Softwood	5.3	5.0
	Hardwood	5.5	5.4

C. Amount of Alkali Consumed by Wood

The amount of 0.1 normal sodium hydroxide solution consumed by 0.1 gram of ovendry decayed wood is different for each type of decay. The average value for lignin-rich decayed woods is 4.17 ml for softwood and 4.20 ml for hardwood, that of cellulose-rich decayed wood is 5.96 ml and 4.11 ml, and that of "normal-like" decayed wood is 2.37 ml and 2.63 ml respectively. In the case of sound wood the amount in hardwood is more than that in softwood, and the difference between decayed and sound woods is larger in softwood than in hardwood. Consumption of alkaline solution is approximately in proportion to solubility in 1 per cent sodium hydroxide of decayed wood as known in Figure 2 and Figure 3. Because of the high content of alkali soluble matter such as pentosan consuming much alkali in hardwood, the consumption of alkali by sound hardwood is more than that by sound softwood.

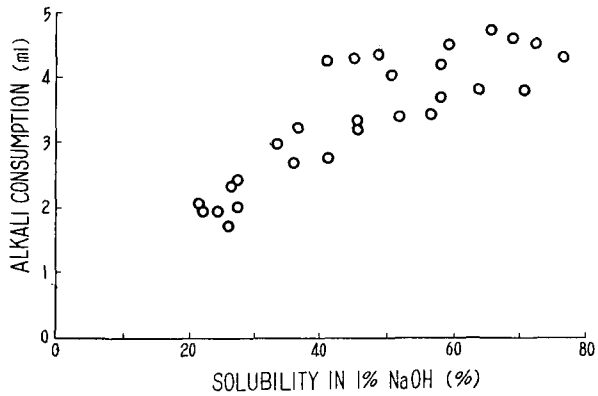

Fig. 2. Relation between consumption of alkaline solution and solubility in 1% NaOH of decayed softwood.

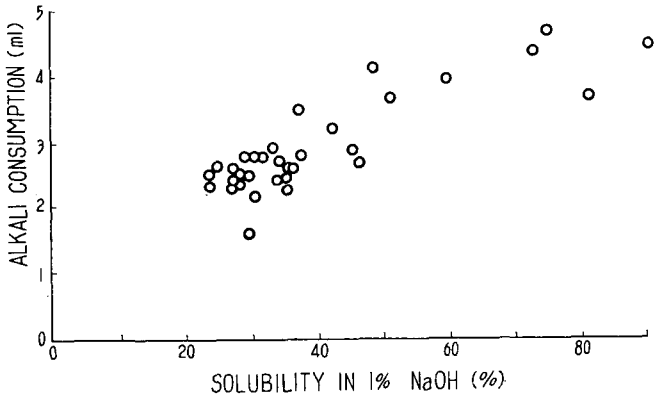

Fig. 3. Relation between consumption of alkaline solution and solubility in 1% NaOH of decayed hardwood.

TABLE 31. Effect of extracting treatment on consumption of alkali

Sample number	Amount of alkaline solution consumed by the residue after extraction (ml)			
	7_0	7_3	5_3	*Picea jezoensis* by *Gyrophana lacrymans*
Non-treated	0.83	3.14	4.27	3.55
Alcohol-benzene	0.75	2.86	—	—
Hot water	0.68	2.79	—	—
0.1 *N* NaOH	0.22	1.88	1.17	—
1% NaOH	0.07	0.86	0.72	1.28

The effect of the soluble component which has a relation to the consumption of alkali in decayed wood was tested and the result is given in Table 31. According to the results, the consumption is most affected by 1 per cent sodium hydroxide-soluble matter; 0.1 normal sodium hydroxide comes second; next in order are the factors soluble in hot water and alcohol-benzene mixture, but these factors have almost no effect on the consumption of alkali.

From the findings that the longer the heating time, the more alkali is consumed by wood as shown in Figure 4, that the hydrogen-ion concentration of the cold water extractives of decayed wood is only a little lower than that of sound wood, and that only a little alkali is consumed by treating wood with cold alkaline solution, it can not be considered that the increment of alkali consumption is due to free organic acid in decayed wood. Accordingly, it is concluded that alkaline solution reacts gradually on the main wood components such as holocellulose and lignin and is consumed by them.

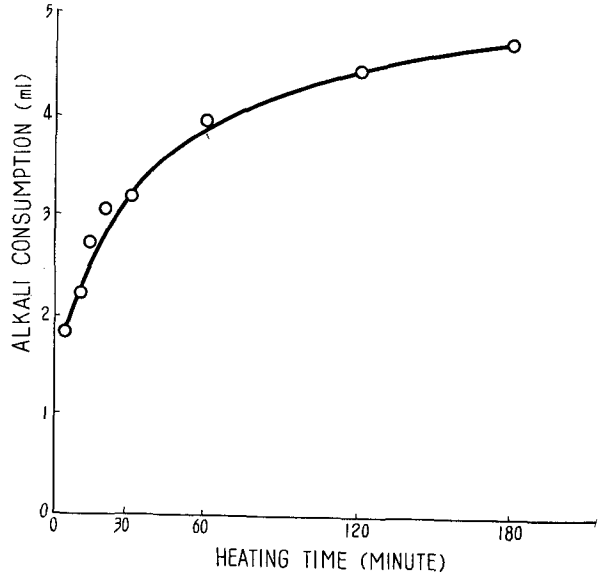

Fig. 4. Relation between alkali consumption and heating time.

On the study of the controversial subject of alkali consumption by holocellulose and lignin, holocellulose isolated from fir wood (7_3) decayed by *Phaeolus schweinitzii* consumed 2.03 ml of 0.1 normal sodium hydroxide which is more than 1.36 ml consumed by that from sound wood (7_0), and on the other hand, lignin isolated from fir decayed wood (7_3) consumed 2.29 ml of the alkaline solution which is more than 1.65 ml consumed by that from sound wood (7_0).

It is not always recognized that those isolated components consume the same amount of alkali as they do in the original wood, but it can be assumed that those components in decayed wood consume much more alkali than those in sound wood. Moreover, cellulose-rich decayed spruce wood (5_5) by *Cryptoderma yamanoi*, which is almost pure holocellulose isolated naturally by fungus, consumed 4.27 ml of the alkaline solution which is more than three times the 1.36 ml consumed by sound wood (7_0) holocellulose and 0.11 ml of a commercial rayon pulp. Accordingly, holocellulose in decayed wood is in the degraded state as above described.

D. Properties of Holocellulose

The yields of reducing materials, calculated as glucose, prepared from the holocellulose isolated from decayed woods are listed in Table 32. The yield from cellulose-rich decayed wood is the highest and that from "normal-like" decayed wood is second, followed by that from lignin-rich decayed wood in accordance with their own properties. It must be noticed that the isolation of holocellulose from decayed wood is done with considerable loss of holocellulose in spite of the application of today's most suitable method using sodium chlorite. In cellulose-rich decayed woods which show no color reaction of lignin, the yield of holocellulose by the usual analytical method is 85.7 per cent in 19_3, 78.0 per cent in III_3 and 91.7 per cent in XXX_3, which means that 8.3 to 22.0 per cent of loss resulted from the treatment. Even from perfectly lignin-free decayed wood (III_3), 3.0 per cent of a lignin like substance appears as a residue after hydrolysis. The author examined thoroughly the properties of the residue as well as the alkali soluble matter, as described later.

TABLE 32. Yield of reducing materials calculated as glucose on hydrolysis of holocellulose (%)

Decay type	Yield (original wood basis)		
	Maximum	Minimum	Average
Softwood			
Lignin-rich	38.0	9.3	20.9
Cellulose-rich	76.5	70.2	73.3
"Normal-like"	62.4	46.7	56.3
Hardwood			
Lignin-rich	26.2	11.3	18.3
Cellulose-rich	69.0	68.0	68.5
"Normal-like"	70.6	44.1	57.9

Calorific value of decayed wood holocellulose which approximates the values of 4,260 to 4,270 calories for sound wood holocellulose irrespective of the kinds of decayed wood, shows that calorific properties of holocellulose isolated from various kinds do not differ from each other.

The degree of polymerization of the holocellulose of decayed hardwood is lower than that of sound wood holocellulose, and among the values of decayed wood holocellulose, the degree of polymerization of non-treated III_3 which is considered as a natural holocellulose, is as low as 240, while that of holocellulose from III_3 is 570. This means that when holocellulose is isolated from decayed wood, holocellulose which has a low degree of polymerization is removed. And the fact that the degree of polymerization of natural holocellulose (5_3) is as low as 180, while that of holocellulose from one of most rotted wood ($5_{2,5}$) is as high as 1,840, shows that not only holocellulose in lignin-containing decayed wood such as $5_{2,5}$ has still a rather high degree of polymerization but also that a part of the holocellulose which has low degree of polymerization is removed by treatment. That is also evidenced by the fact that yield and strength of kraft pulp from some of the decayed woods were by no means inferior to those of pulp from sound wood according to the author's observation.[75]

E. Carbon, Hydrogen and Methoxyl Group Contents in Lignin

The fact that lignin is degraded by fungi has been observed by many research workers.[2,16,42,116,124] Though the ability of fungus to degrade lignin is low for some fungi which produce lignin-rich decayed wood while rather high for other fungi, the high content of degraded lignin in decayed wood does not mean necessarily the high ability of the fungus to degrade lignin. That is, as above described, the lignin in lignin-rich decayed wood is more degraded than that in "normal-like" decayed wood. It means that the fungus which produces lignin-rich decayed wood has such a low ability to degrade lignin that it can not digest lignin completely and thus leave the lignin degraded in the wood, while the fungus which produces "normal-like" decayed wood digests a part of the lignin thoroughly and does not leave it in a degraded state in the wood. It can be observed from the result of wood analysis that lignin in lignin-rich decayed wood is soluble in alkaline solution, and lignin is also soluble in very dilute hot alkaline solution such as 0.5 to 0.05 per cent of sodium hydroxide. The lower the concentration of alkali, the less methoxyl group the soluble lignin contains, and methoxyl group content in soluble lignin is lower than that in the insoluble form. Methoxyl group content in the lignin isolated from lignin-rich decayed wood such as softwood decayed by *Phaeolus sehweinitzii* or *Tyromyces balsameus* is lower than that in lignin isolated from sound wood,

and this tendency is also observed from the value of the lignin content calculated from methoxyl group and lignin content determined directly in original decayed and sound woods. On the other hand, methoxyl group content in lignin calculated from that in the original wood such as "normal-like" or cellulose-rich type wood decayed by *Tyromyces borealis* or *Cryptoderma yamanoi* shows almost no difference but is a little lower than that in sound wood.

F. Properties of Alkali Soluble Matter

Alkali soluble matter in wood, as shown in Table 14, is mainly hemicellulose in sound wood, and in cellulose-rich and "normal-like" decayed woods, but in lignin-rich decayed wood the matter is mainly degraded lignin. This phenomenon can also be satisfactorily explained by the fact that the saccharification rate of holocellulose isolated from "normal-like" decayed wood is 58 per cent while that for cold 5 per cent sodium hydroxide soluble matter is 60 per cent in both sound wood and cellulose-rich decayed wood, 56 per cent for "normal-like" decayed wood and 20 per cent for lignin-rich decayed wood. The results of examination by paper chromatography of the hydrolysate after hydrolysis of hemicellulose extracted with alkaline solution show that the hemicellulose consists mainly of xylan in sound wood, lignin-rich and "normal-like" decayed woods, and in cellulose-rich decayed wood it consists mainly of xylan and glucan. The hemicellulose from cellulose-rich decayed wood is changed to humin-like substance by treatment with acid and is sometimes determined as lignin. Assuming that the saccharification rate of hemicellulose (alkali soluble carbohydrate) in lignin-rich decayed wood is 60 per cent as well as in cellulose-rich decayed wood, the hemicellulose is equivalent to 33 per cent of total soluble matter, and the precipitate is equivalent to 50 per cent of total soluble matter, then the rest of the 17 per cent should be considered as a soluble and non-precipitated lignin.

According to the results above described, not only the chemical composition of one decayed wood is different from another type but also properties of components are considerably different in each type of decayed wood. The characteristics in each type of decayed wood, are distinctive; lignin-rich decayed wood contains highly degraded lignin and cellulose-rich decayed wood contains much degraded holocellulose, while "normal-like" decayed wood does not contain such degraded components as lignin or holocellulose and differs slightly from sound wood.

VI. Summary

The chemical composition and properties of fifty-eight kinds of wood decayed under natural conditions in the forest of Hokkaido by the action of each one kind of several wood-destroying fungi were investigated. These decayed woods were observed to be degraded considerablly according to losses ranging from 40 to 60 per cent in weight on the basis of original sound wood calculated from the density of sound and decayed woods. Furthermore, alkali consumption of wood was measured in order to determine the degree of wood decay. Important results are summarized as follows:

1. Decayed wood can be divided into three groups by the ratio of holocellulose content to lignin content as follows:
   a. Lignin-rich decayed wood.
   b. Cellulose-rich decayed wood.
   c. "Normal-like" decayed wood.

Decayed woods which belong to lignin-rich group have a brown color, are called brown rotted wood, while those which belong to cellulose-rich or "normal-like" decayed wood and have usually bright color, are called white rotted wood mainly from the dendropathologic standpoint. However, from the chemical stand point on the basis of chemical composition of decayed wood, the method of classification and the name of groups suggested by the author seem to be more suitable.

2. A decayed wood which belongs to one of these three groups has its own characteristics not only in chemical composition but also in properties of each component. For example, lignin in lignin-rich decayed wood is more soluble than that in others and has a lower methoxyl-group content, while that in "normal-like" decayed wood is slightly different from that in sound wood but has almost the same properties as those in cellulose-rich decayed wood. Holocelluloses in lignin-rich decayed wood and in cellulose-rich type both have high alkali solubility, but the former has low mannan content while the latter has low xylan content. Holocellulose in "normal-like" decayed wood is not so different from that in sound wood. And degree of polymerization of holocellulose is low in lignin- and cellulose-rich decayed woods and rather higher in "normal-like" decayed woods. Moreover, the calorific value is high in lignin-rich decayed wood, low in the cellulose-rich type and lies between the two in "normal-like" type which is only slightly different from that of sound wood.

3. When decayed wood is treated with hot dilute alkaline solution, considering the chemical composition and properties of components, it is obvious that the more the wood is decayed, the more alkali is consumed by the decayed

wood. The same phenomenon is also observed in lignin and holocellulose isolated from wood, and high consumption value indicates progressive degradation of the components. Using this method, the amount of alkali consumption is large in lignin- and cellulose-rich decayed woods but relatively small in "normal-like" decayed wood. Using a little sample and simple treatment, the degree of wood decay can be determined quickly with considerable accuracy by this alkali consumption method, so this method is applicable to determining the degree of wood decay.

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