J Wood Sci (2002) 48:245–249

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Physical and chemical characteristics of the blackened portion of Japanese persimmon (*Diospyros kaki*)

Received: March 29, 2001 / Accepted: August 10, 2001

Abstract The heartwood of the Japanese persimmon tree (*Diospyros kaki*) becomes black on rare occasions and has been highly esteemed as a substitute for ebony. We attempted to clarify how the physical, mechanical, chemical, and biodegradation properties differ between sapwood and blackened heartwood. The specific gravity, equilibrium moisture content, modulus of rupture, and modulus of elasticity in the blackened heartwood were higher, and the loss tangent was lower, than those in sapwood. Furthermore, the blackened portion was more resistant to fungal and termite attacks. A section of heartwood was dark-brown, and the specific gravity and mechanical properties of this portion were slightly lower than those in sapwood. The dark-brown portion was speculated to be a sign or interrupted state of fungal attack. The blackening substance was bound tightly to cell wall components and could not be extracted with any of the organic solvents used. The findings of trace element analysis using inductively coupled plasma-mass spectrometry showed that the boron content was markedly high in the blackened portion. The findings obtained here suggest a role of boron in the antifungal properties and the blackening phenomenon of Japanese persimmon.

Key words Japanese persimmon · Mechanical property · Decay resistance · Trace element · Boron

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Part of this work was presented at the 50th Annual Meeting of the Japan Wood Research Society, Kyoto, April 2000

Introduction

About 500 species of *Diospyros* grow in the tropical to temperate regions. Among them are many species of which the heartwood is black to dark-brown, black-spotted, or black-striped.[1] In particular, some *Diospyros* species in India, Southeast Asia, and tropical Africa usually have black heartwood. The heartwood of these species is called ebony; it is highly valued, and is used for furniture, carvings, musical instruments, etc. because of its high density, hardness, excellent durability, and ornamental value.[2]

The heartwood of Japanese persimmon (*Diospyros kaki*) does not usually blacken, although it can on rare occasions. The blackened portion of Japanese persimmon has been called "kurogaki"; it is also highly prized and is used for purposes similar to those of ebony. Neither the actual properties of kurogaki nor the mechanism of the blackening phenomenon has been fully clarified. Only the chemical structures of some extracts are known.[3] In this study, we examined the physical, mechanical, and chemical characteristics of kurogaki and its resistance to biological attacks.

Materials and methods

Sample

The sample of kurogaki, which was grown in the garden of a private home in Hiyoshi-cho, Kyoto Prefecture, was cut on February 1999. The height and diameter at breast height (DBH) were about 13 m and 60 cm, respectively; the age of the tree could not be confirmed because of the indistinctness of the annual rings. A disk was obtained from the upper part of the DBH and was cut into 2 mm (T) × 12 mm (R) × 150 mm (L) specimens for physical and mechanical property tests. Each specimen was numbered, from sapwood to pith; samples 1–12 were sapwood, and samples 13+ were blackened parts, among which 15–19 were not completely black but were dark-brown. Another series of 20 mm (T) × 20 mm (R) × 10 mm (L) test pieces were prepared for termite and decay tests, but here the completely black and dark-brown portions were not distinguished. For convenience, we refer to the white portion as sapwood and the black or dark-brown portion as heartwood, although they may not be purely sapwood or heartwood in the strictest sense.

Bending tests

After measuring the specific gravity and equilibrium moisture content at 20°C and 65% relative humidity (RH), the oven-dried specimens were subjected to a free-free flexural vibration test[4] at 20°C and 65% RH. They were then used for a static bending test. The test was conducted at 20°C and 65% RH using an instrument with a constant cross-head speed (50 mm/min), with loading at the center while being supported at two points 100 mm apart. The rather high cross-head speed was chosen to facilitate comparisons between parts. The vibrating and loading directions were in the tangential direction.

Biodegradation tests

The resistance to termites (*Coptotermes formosanus* Shiraki) was tested using a force-feeding method in an acrylic vessel. Three wood block samples of sapwood and heartwood were subjected to the test. Mortalities among 150 worker termites and 15 solider termites were counted over 3 weeks at 26° ± 2°C while maintaining the humidity with a moist cotton mat. The specimen weight loss was determined from the difference in oven-dried weights before and after testing.

The decay tests were carried out for 2 months at 26° ± 2°C and higher than 70% RH using brown rot fungus [*Fomitopsis palustris* (Berk. et. Curt.) Murr.] and white rot fungus [*Coriolus versicolor* (L. ex. Fr.) Quel.]. Nine specimens were used for each test. The specimen weight loss was calculated on the basis of the difference in oven-dried weights before and after testing.

Determination of the amount of extracts

Wood meals were prepared from sapwood and blackened heartwood and used to determine the amount of the extracts. Extractions were successively carried out with *n*-hexane, ethyl acetate, methanol, and water using a Soxhlet extractor for about 10 h for each. The extracts were weighed after condensation and drying.

Quantitative analysis of trace elements

In addition to the 24 specimens from the mechanical strength tests, three more oddly shaped pieces were broken into splinters, reduced to ashes at 420°C for 4 h in an electric furnace, and then dissolved in concentrated nitric acid. After filtration through a membrane filter and dilution with ultrapure water to a specified concentration, the solutions were subjected to trace element analysis. The analysis was carried out by inductively coupled plasma-mass spectrometry (ICP-MS) (HP4500; Yokogawa Analytical Systems). ^{115}In was used as an internal standard, and 16 elements (B, Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Pb, U) were analyzed quantitatively. The vanadium used for standardization was the reagent for atomic absorption spectrometry (Wako Pure Chemical Industries), and the other elements were multielement mixed solutions (XSTC469; SPEX CertiPrep). These elements were appropriately diluted with 0.1 N nitric acid.

Results and discussion

Physical and mechanical properties

Figure 1 shows the oven-dried specific gravity, equilibrium moisture content, and volumetric swelling for 24 specimens prepared from sapwood to heartwood. The specific gravity was higher in heartwood than in sapwood except for the

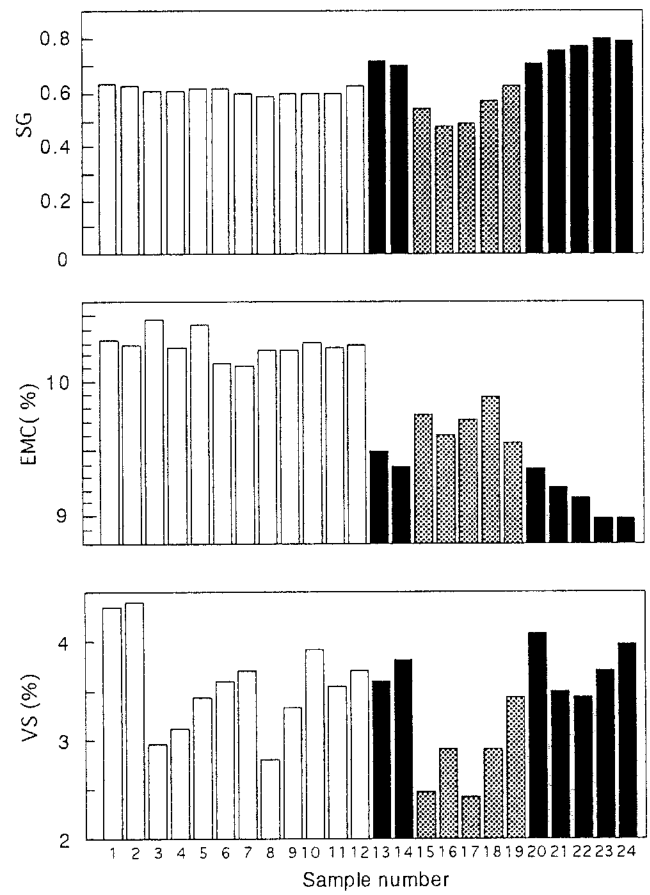

Fig. 1. Changes in specific gravity (*SG*), equilibrium moisture content (*EMC*), and volumetric swelling (*VS*) of Japanese persimmon specimens along with annual rings. *Open bars*, sapwood; *shaded bars*, dark-brown portion; *filled bars*, blackened portion

dark-brown portion (nos. 15–19). It is plausible that the dark-brown portion was a sign of or interrupted state of fungal attack, although no distinct decay could be observed. Signs of slight decay were also observed in the mechanical properties, as described below. The equilibrium moisture content was higher in sapwood than in heartwood. Substances related to blackening would be hydrophobic and apparently lower the moisture content. The volumetric swelling varied widely and did not show any correlation with equilibrium moisture content.

Figure 2 shows the loss tangent ($\tan\delta$) and specific dynamic Young's modulus (E/γ) of a series of specimens prepared along with annual rings. The loss tangent was highest in sapwood, intermediate in the dark-brown portion, and lowest in completely blackened heartwood. For some wood species, it is known that low loss tangent values are attributable to their extracts.[5,6] This may also be applicable to persimmon in that the substances related to blackening lower the loss tangent. The dynamic Young's modulus obtained from resonance frequency tended to increase from sapwood to heartwood.

The modulus of rupture (MOR) and modulus of elasticity (MOE) are shown in Fig. 3. The MOE and MOR of the blackened portion in heartwood was higher than those of sapwood, but they were lower in the dark-brown portion in heartwood than in sapwood. These findings also suggest that the dark-brown portion is a sign of fungal attack, but that the progress of decay was interrupted due to the formation of some protective substance. When the protective substance is stored in the sound portion of heartwood, it may bind tightly to cell wall components to give strong mechanical properties and a black color.

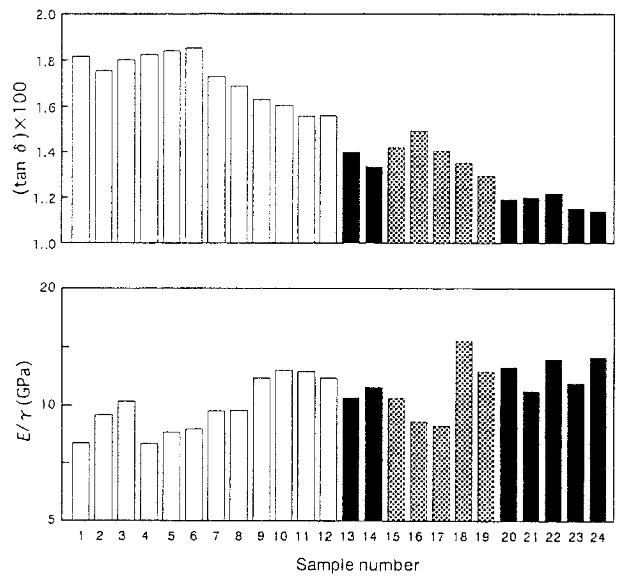

Fig. 2. Changes in loss tangent ($\tan\delta$) and specific dynamic Young's modulus (E/γ) of Japanese persimmon specimens along with annual rings. *Bars*, same as in Fig. 1

Resistance to biodegradation

Tables 1 and 2 are the mortality of *Coptotermes formosanus* during 3 weeks of a forced-feeding test and specimen weight loss after testing, respectively. The mortality of worker termites was similar in sapwood and heartwood, suggesting

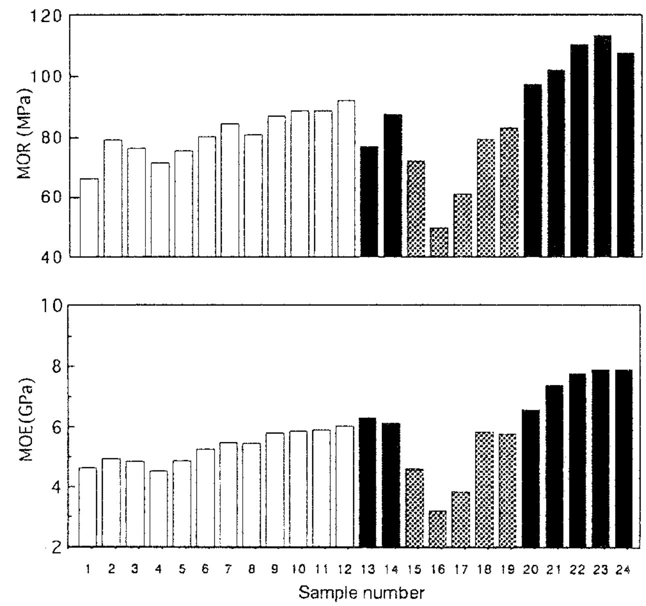

Fig. 3. Changes in moduli of rupture (*MOR*) and elasticity (*MOE*) of Japanese persimmon specimens along with annual rings. *Bars*, same as in Fig. 1

Table 1. Mortality of worker termites (*Coptotermes formosanus*)

Test period (week)	Mortality (%)	
	Sapwood	Heartwood
1	8.2	7.1
2	13.6	15.3
3	19.8	20.7

The heartwood contained both black and dark-brown portions

Table 2. Weight loss after 3 weeks of termite testing and 2 months of decay testing

Sample	Termite test with *Coptotermes formosanus*	Decay test	
		Fomitopsis palustris	*Coriolus versicolor*
Sapwood	20.6 ± 12.1	52.8 ± 3.1	44.2 ± 7.6
Heartwood[a]	9.7 ± 7.3	9.6 ± 10.7	17.2 ± 10.7

Results are given as the percent weight loss and its 95% confidence limits
[a] The heartwood contained both black and dark-brown portions

Table 3. Weight yields from oven-dried wood meal after successive extractions with organic solvents and hot water

Sample	*n*-Hexane	Ethyl acetate	Methanol	Hot water	Total
Sapwood	0.23	0.70	3.33	2.62	6.89
Heartwood[a]	0.20	0.30	0.86	2.45	3.82

Results are percents
[a]The dark-brown portion in heartwood was excluded

that the substances contained in the blackened portion are not toxic to termites. Nevertheless, the weight loss differed significantly between sapwood and heartwood; moreover, it was observed macroscopically that the termites attacked the blackened portion less. Therefore, the blackening substances appear to retard termite attacks.

The specimen weight loss was significantly less in heartwood than in sapwood for both brown and white rot fungi (Table 2). Although the blackening in Japanese persimmon may be related to some protective function against decay, this was not an unexpected finding as higher decay resistance in heartwood is also seen in other wood species.

Chemical components

Extracts

The yields after successive extractions with organic solvents are summarized in Table 3. The total yield was higher in sapwood; in particular, the greatest amount was extracted with polar solvents. The blackening substance barely colored any extract.

It has been reported that 4,5-dihydroxy-8-methoxy-2-naphthaldehyde and related substances are precursors for the blackening process. Those substances localize mostly in heartwood and immediately form quinones by the actions of phenol oxidase, peroxidase, and the sap of persimmon; they then further polymerize to an insoluble black substance.[3] Therefore, it is reasonable that the blackening substance could not be extracted.

Trace elements

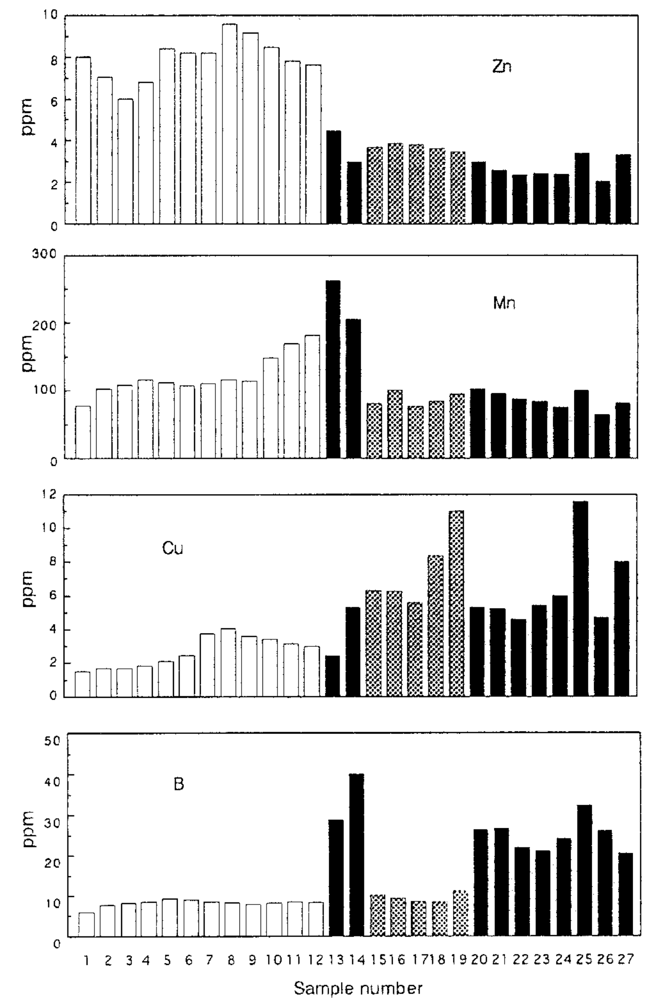

Fig. 4. Concentration changes of trace elements in Japanese persimmon specimens along with annual rings. *Bars*, same as in Fig. 1

Figure 4 shows the concentration changes of trace elements along with annual rings. Characteristic patterns were found for B, Mn, Cu, and Zn. Among them, the concentrations of Mn, Cu, and Zn changed notably in the vicinity of the sapwood–heartwood border. These changes appear to be related to heartwood formation, and similar tendencies have been reported in sugi (*C. japonica*)[7,8] and mizunara (*Quercus mongolica*).[9]

Boron was distributed densely in the black portion. It is known that boron is an essential element for higher plants and that its lack causes decreased peroxidase activity. Furthermore, it forms a complex and participates in the formation of cell wall components and physiological functions.[10,11] The boron contents in sugi (*C. japonica*) and sakura (*Prunus* spp.) are reported to be constant (2–5 ppm) throughout the wood stem (T. Aoki, unpublished data). The boron content of Japanese persimmon in sapwood (5–10 ppm) did not differ much from that of sugi and sakura, whereas that in the black portion was markedly higher (20–40 ppm).

Recently, much attention has been paid to the protective function of boron compounds against fungal attack.[12] As stated above, the black portion of Japanese persimmon was highly resistant to fungi, suggesting that the accumulation of boron in Japanese persimmon is related to the protection against fungal attack. Moreover, the substances related to blackening, which probably coexist with boron, could not be extracted with any solvent tested. The leaching of boron from wood impregnated with boron compounds is an important unsolved problem. Therefore, clarifying the mechanism of boron fixation in the black portion of Japanese persimmon may suggest ways to prevent the leaching of boron compounds from wood.

Conclusions

The characteristics of the blackened portion of Japanese persimmon (*D. kaki*) were examined for physical, mechanical, biodegradation, and chemical properties. Blackened heartwood showed a higher specific gravity, equilibrium moisture content, MOR, and MOE and a lower loss tangent than sapwood. Furthermore, this portion was more resistant to fungal and termite attacks. These properties may be the reason kurogaki is so highly esteemed. Because the blackening substance was insoluble in various organic solvents, it was thought that the substance bound tightly to cell wall components and formed a polymer.

Among the many trace elements, the boron content was especially high in the black portion, which suggests some relation of boron with the blackening phenomenon in Japanese persimmon. Because the blackening was associated with antifungal properties, the findings obtained here are interesting from the viewpoint of the antifungal effects of boron compounds and their fixation in wood substances.

Acknowledgments The authors thank Dr. K. Nishimura, University Forests, Kyoto University, for supplying the invaluable sample of Japanese persimmon. The authors also thank Professor Y. Imamura, Wood Research Institute, Kyoto University, for conducting biodegradation tests.

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