PREVENTION OF SUGI (*CRYPTOMERIA JAPONICA* D. DON) FROM TURNING BLACK BY SMOKE HEATING

Futoshi Ishiguri and *Saori Maruyama*
Graduate Students
Faculty of Agriculture, Utsunomiya University
Utsunomiya 321-8505, Japan

Koetsu Takahashi
Associate Professor
Faculty of Agriculture, Yamagata University
Tsuruoka 997-8555, Japan

Minoru Andoh
Lecturer

Shinso Yokota
Associate Professor

and

Zensaku Abe and *Nobuo Yoshizawa*
Professors
Faculty of Agriculture, Utsunomiya University
Utsunomiya 321-8505, Japan

(Received November 2000)

ABSTRACT

Green sugi logs (tree A, normal heartwood color; tree B, heartwood color gradually turned to black after harvesting) were smoke-heated for 5, 10, 20, and 40 h to investigate the influence of smoke heating on the color change of heartwood. After the treatment, changes in color, pH, and content of norlignan were examined. The heartwood was also saturated with $KHCO_3$ in order to examine the relationship between pH and changes in heartwood color. The results revealed that smoke heating the logs for at least 5 h prevented the heartwood from turning black; instead, the treated heartwoods turned yellowish-white. The pH value of the tree B decreased significantly from 7.4 to 6.5 after a 5-h smoke heating; from then on, the pH remained nearly constant with additional exposure. When smoke-heated, tree A- and tree B-heartwood specimens were saturated with a $KHCO_3$ solution (pH 8.6), the brightness decreased, and the color turned black, suggesting that the blackening substances did not deteriorate when exposed to smoke heating. In the tree A heartwood, on the other hand, the contents of sequirin-C and agatharesinol barely changed before and after smoke heating. In the tree B heartwood, however, the amounts of agatharesinol and sequirin-C decreased significantly compared with those in the fresh heartwood before it turned black, whereas a large amount of norlignans, in particular, sequirin-C, was found in the smoke-heated heartwood. The results obtained in the present study suggest that the chemical changes of norlignans accompanied with pH changes are closely involved in color changes in the sugi heartwood.

Keywords: *Cryptomeria japonica* D. Don, blackening heartwood, smoke heating, pH, norlignans.

Wood and Fiber Science, 35(2), 2003, pp. 209–216

INTRODUCTION

Although sugi (Japanese cedar, *Cryptomeria japonica* D. Don) usually shows a reddish-brown to rose-pink heartwood, known as ''red heartwood,'' it sometimes shows a black-brown or black heartwood that is known as ''black heartwood.'' In black sugi heartwood, the wood turns from red to black within a few hours of felling. Many studies have focused on the blackening phenomenon in sugi heartwood (Kitamura 1962; Abe and Oda 1994; Abe et al. 1994; Oda et al. 1994; Takahashi 1996a, 1998; Kubo and Ataka 1998). Studies have shown that oxidative conditions under weak alkalinity (pH 8.4–8.6) cause the blackening. In addition, Abe and Oda (1994) and Takahashi (1996a) found that potassium hydrogencarbonate ($KHCO_3$) is a causative compound increasing the pH value in black sugi heartwood.

In general, the color of wood is related to the kinds and amounts of wood extractives. In the heartwood of sugi, the involvement of norlignans in wood color has been reported (Kai et al. 1972; Takahashi 1981). In particular, sequirin-C and agatharesinol, which are the primary norlignans in sugi heartwood, seem to be involved in the blackening process. In addition, under weak alkaline conditions, these compounds change chemically to cause a rapid change to black (Takahashi 1996a, 1998).

On the other hand, black sugi heartwood has been reported to fade when green logs are exposed to smoke heating (Okuyama et al. 1990; Ishiguri et al. 2000; Maruyama et al. 2001). Our report (Ishiguri et al. 2000) has shown that pH changes from weak alkalinity to weak acidity were related to color changes in the black heartwood, and that the amounts of potassium in the black heartwood did not differ greatly whether the wood was treated or not. Okuyama et al. (1990) reported that the amounts of hemicellulose in sugi sapwood decrease rapidly when they are smoke-heated for more than 40 h above 80°C, suggesting that the decrease in pH may occur as a result of thermal degradation of hemicellulose by smoke heating.

In the present study, the influence of the exposure time to smoke heating was investigated with a focus on the changes in the heartwood color and pH. In addition, the color change in heartwood by saturation with $KHCO_3$ was evaluated to clarify the relationship between pH and heartwood color. Furthermore, the amounts of norlignans were determined along with their involvement in color changes.

EXPERIMENTAL

Materials

Two green sugi logs (Japanese cedar, *Cryptomeria japonica* D. Don) trees were used in this experiment. The 3-m logs were harvested in the Kanuma district of the Tochigi Prefecture, Japan, two weeks before the experiments (May 9, 2000). Tree A was a 34-year-old tree with rose-pink heartwood (ca. 200 mm in diameter). Tree B was a 39-year-old tree with black heartwood (200 mm in diameter); neither heartwood had changed its original color before the experiments began. The heartwood sample of tree B was reddish-brown immediately after being harvested, but it changed color gradually, turning finally brownish-black.

Smoke heating of logs

Five 500-mm log sections with intact bark were cut from the long logs. They were then treated by smoke heating with a modified food smoker (Shinsei Sangyo, FS-50N) according to the method of Ishiguri et al. (2000, 2003). The log sections were smoke-heated at 100–120°C in a chamber. The temperature inside the log sections was measured at the center of each log section by thermocouples inserted in depth 100 mm from the log surface, and was maintained at 80°C for 5, 10, 20, and 40 h during the treatment. The untreated log sections were used as the control for the tree A and B heartwoods. After each treatment, wood specimens and wood meal (42–80 mesh) were prepared from the heartwood of each log section and used in the experiment.

Color measurement

Wood specimens of 30 (L) × 30 (T) × 10 (R)-mm were taken from the heartwood of the control and treated log sections. The color of the air-dried wood specimens was measured with a CIE L*a*b* system, described in Tappi testing method, using a colorimeter (Minolta, CF-200). L*a*b* system gives the brightness (L*), redness (a*), and yellowness (b*). The resulting total color difference (ΔE*ab) was evaluated using the following equation: $\Delta E^*ab = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$.

pH measurement

For measurement of pH, wood blocks of heartwood were taken at the center of log sections of both the control and treated wood and then crushed by using Willy type meal. One gram of wood meal (42–80 mesh) was suspended in 20 ml of distilled water overnight. The wood meal was removed from the suspension by passing through filter paper (Advantec, No. 1); then pH of the filtrates was measured with a pH meter (TOA Electronics, Ltd., HM-20E).

Color changes in heartwood by $KHCO_3$ treatment

Five heartwood specimens (30 (L) × 30 (T) × 10 (R)-mm) from the control and smoke-heated (40 h) woods were saturated with an aqueous solution of $KHCO_3$ (2 g/400 ml, pH 8.6) for 10 days at 25°C. After air-drying, the specimens' color was measured as described above.

Norlignan content in heartwood

For norlignan analysis, non-color-changes fresh samples of small wood chips (3–5 mm) were prepared from the heartwood immediately after cutting before they turned black. The chips were immediately extracted with several solvents, as described later. Samples from heartwood that had turned black (control) and from the heartwood smoke-heated for 5 and 40 h were also prepared. Each sample (1 g) was extracted for 9 h with 120 ml of methanol, acid methanol (0.1% acetic acid in methanol), and reductive methanol (0.1% ascorbic acid in methanol), respectively. After that, 1 ml of each extract solution was transferred into a micro test tube, and 10 μl of veratrum acid was added to the solution as an internal standard. After the solvent evaporated, the extracts were trimethylsilylated with the mixture of chlorotrimethylsilane and *N,O*-bis (trimethylsilyl) acetamide and analyzed by gas chromatography. The analytical conditions were as follows: instrument, Hitachi G-3000 Gas chromatograph; column, OV-1 bonded capillary column (25 m); column temperature, 150–280°C (5°C/min); carrier gas, He. Norlignans were quantified by comparing the peak areas of gas chromatograms with those from the internal standard.

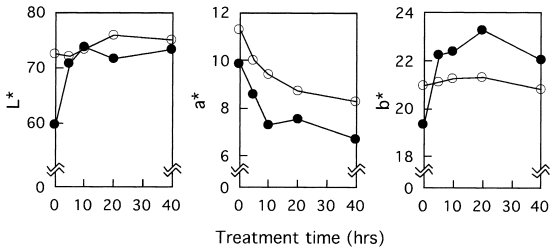

FIG. 1. Changes in heartwood color caused by different durations of smoke heating. Symbols: Open circles, red heartwood; filled circles, black heartwood.

RESULTS AND DISCUSSION

Observation of heartwood color with the naked eye

The color of the heartwood obtained from the green logs immediately after being harvested was rose-pink to reddish-brown. Tree B had characteristically blackening heartwood that gradually, after being felled, changed color and finally turned brownish-black. After the green logs were smoke-heated for 5, 10, 20, and 40 h, the color changes in the heartwood were observed (Fig. 1). There were no obvious differences in color that could be perceived with the naked eye from the control and smoke-heated heartwood in tree A. In the tree

B heartwood, on the other hand, the heartwood was light brown to yellowish-white after smoke heating. In either case, ΔE*ab had greater values (Fig. 1). Smoke heating for at least 5 h helped to prevent the heartwood from turning black.

Influence on heartwood color change from exposure time to smoke heating

In previous papers, thermal treatment was found to help in preventing sugi heartwood from turning black (Ishiguri et al. 2000; Maruyama et al. 2001). In the present study, therefore, influence on the heartwood color change from exposure time to smoke heating was investigated (Fig. 1). The L* value increased slightly as a result of smoke heating in tree A heartwood, the b* value had almost no changes, and the a* value decreased significantly, especially within 10 h of smoke heating. As a result, the tree A (normal) heartwood that was smoke-heated for 5, 10, 20, and 40 h produced total color differences (ΔE*ab) of 1.4, 2.0, 4.1, and 3.9, respectively (Fig. 1). These results indicate that color changes in the normal heartwood as a result of smoke heating increase with exposure time.

On the other hand, the a* value decreased significantly as a result of smoke heating in tree B heartwood, whereas the L* and b* values significantly increased. Although the control wood showed an L* value of 59.7, all of the smoke-heated heartwood had L* values greater than 70. This fact indicates that the blackening heartwood became lighter after exposure to smoke heating (Fig. 1). ΔE*ab of heartwood exposed to smoke heating for 5, 10, 20, and 40 h were 11.6, 14.6, 12.7, and 14.1, respectively, indicating that the colors of all the wood exposed to smoke heating differed significantly from those of the control. Previous studies have also shown similar effect on L* and b* of blackening heartwood after smoke heating (Okuyama et al. 1990; Ishiguri et al. 2000; Maruyama et al. 2001). The values of L* and a* of normal sugi heartwood have been reported so far to be higher than 65 and 10, respectively, and the value of b* hs been reported to be about 20 (Kitamura 1987; Abe 1995). Although the value of a* decreased in the smoke-heated blackening heartwood in the present study, the L* and b* values increased more than 70 and 20, respectively, indicating that blackening was prevented by smoke heating. In addition, the rapid change in heartwood color occurred within the first 10 h of smoke heating (Fig. 1).

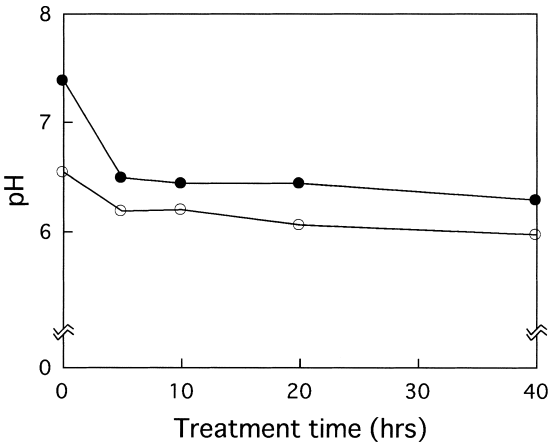

FIG. 2. Changes in pH values caused by smoke heating. Symbols: Open circles, red heartwood; filled circles, black heartwood.

pH change

Figure 2 shows the change in the pH value of sugi heartwood exposed to smoke heating. The pH was 6.5 for the tree A heartwood and 7.4 for the tree B heartwood before smoke heating. In general, the pH of normal red heartwood in sugi is weakly acid, whereas that of black heartwood is weakly alkaline (Abe et al. 1994; Takahashi 1996a; Takenami 1964). This was also true according to the results obtained here. The pH decreased to 6.2 in tree A heartwood after smoke heating for 5 h. It then decreased slightly with time of exposure to smoke heating until it reached 6.0 after 40 h. Similarly, pH decreased from 7.4 to 6.5 in tree B heartwood after a 5 h of smoke heating, then became stable. The pH changes nearly corresponded to the changes in the color of

the heartwood that were caused by smoke heating (Fig. 1). Previous studies have shown that pH of the blackening heartwood decreased with thermal treatment and became weakly acidic (Ishiguri et al. 2000; Maruyama et al. 2001). The present study also revealed that changes in both pH value and heartwood color occurred within 10 h of exposure to smoke heating, suggesting that pH changes from weak alkaline to weak acidic in blackening heartwood are involved in the color change in the heartwood.

Abe and Oda (1994) found that potassium hydrogencarbonate, which is present in considerable amounts in blackening heartwood, is one of the substances that causes the blackening of sugi heartwood. According to Takahashi (1996a), a large amount of K^+ increases the pH value of sugi heartwood, and norlignans, extractives of the heartwood, are chemically changed under a condition of weak alkalinity, resulting in the blackening of the heartwood. We found that the pH of black heartwood decreased when exposed to smoke heating and that the amount of potassium in the black heartwood differed little in the control and thermal-treated woods (Ishiguri et al. 2000). This fact suggests that the amount of K^+ is not related to the pH change.

Okuyama et al. (1990) reported that the amounts of holocellulose in sugi sapwood decreased rapidly when the wood was heated for more than 40 h above 80°C. They concluded that this was caused by the thermal degradation of hemicellulose, leading to the darkening of the wood. They also noted that the pH decreased noticeably, irrespective of exposure to smoke heating for fewer than 40 h. A slight thermal degradation of hemicellulose as a result of exposure to smoke heating might have caused the pH value to decrease, but the cause of pH changes that occur as a result of exposure to smoke heating should be investigated more thoroughly.

Color changes in heartwood as a result of $KHCO_3$ treatment

Abe and Oda (1994) found that the color of normal heartwood changed from reddish-brown to black when the wood was saturated with an aqueous solution of $KHCO_3$ (pH 8.4–8.6). In the present study, the control and smoke-heated woods obtained from the tree A and tree B heartwood were saturated with an aqueous solution of $KHCO_3$ (pH 8.6) to confirm the change in color with the use of the alkaline solution (Table 1). The L* values of the specimen used were apparently characteristic of black heartwood (Abe 1995).

The color change from rose-pink to black in tree A heartwood could be seen clearly with the naked eye after a $KHCO_3$ treatment. The ΔE^*ab values was 24.1 for the control and 26.3 for the smoke-heated wood after $KHCO_3$ saturation. The L* values of the control and smoke-heated woods were 69.2 and 67.8, respectively, before the treatment. Both values decreased after the treatment to 46.5 and 42.8, respectively. Although the b* values of the control and smoke-heated woods also decreased after the treatment, the a* values did not show a significant decrease. Our results agree with those of Abe and Oda (1994). We assume that the substances that cause the color to change to black under weakly alkaline conditions are present in normal heartwood.

The L* value of smoke-heated heartwood in tree B heartwood also showed a noticeable decrease from 65.8 to 49.6 after the treatment and the ΔE^*ab value of 17.3. The color of the smoke-heated black heartwood changed from yellowish-white to black, just as the red heartwood changed to black, and the color changes could be seen with the naked eye. These findings indicate that the substances that cause the wood to turn black under weak alkaline conditions are also present in smoke-heated blackening heartwood. These results suggest that the pH change from weakly alkaline to weakly acidic resulting from smoke heating prevented heartwood blackening.

Content of norlignans in heartwood

Sequirin-C and agatharesinol are the primary norlignans in sugi wood, and these substances have been identified as the primary

substances responsible for heartwood blackening (Takahashi 1996a, 1998). The norlignan content was determined in the heartwoods that were non-treated or smoke-heated for 5 and 40 h. In addition, quantitative analysis was also done with fresh samples of heartwood collected immediately after the trees were felled (in the case of the blackening heartwood, the samples were collected before they blackened) because the amounts of sequirin-C and agatharesinol in the black part of sugi heartwood decrease remarkably within one day of cutting (Takahashi 1996a) (Table 2).

Levels of agatharesinol and sequirin-C in the fresh sample in the tree A heartwood were about 4 mg/g and 7 mg/g, respectively. These levels decreased in the air-dried (control) and smoke-heated heartwoods more than in the fresh sample. On the other hand, notable results were obtained in the tree B heartwood. In the fresh sample, methanol extracts contained only 3 mg/g agatharesinol and sequirin-C, whereas large amounts of sequirin-C were observed in the acid-methanol and reductive-methanol extracts. These results suggest that sequirin-C tends to undergo certain chemical changes when it is extracted with methanol alone; in contrast, sequirin-C, when extracted with acid methanol or reductive methanol, does not deteriorate as much because acid methanol is effective for keeping pH acidic and reductive methanol prevents the norlignans from oxidizing. These findings suggest that norlignans were present in relatively large amounts in the fresh sample of tree B heartwood. After the control wood turned black, however, the amounts of both agatharesinol and sequirin-C decreased markedly in all extracts. Sequirin-C, in particular, could not even be detected. The results suggest that the blackening occurred through the chemical changes of agatharesinol and sequirin-C. On the other had, it is noteworthy that, when compared to the control, relatively large amounts of both agatharesinol and sequirin-C were present in the heartwood exposed to smoke heating, which prevented blackening.

Balogh and Anderson (1965) isolated the

TABLE 1. *Color changes in heatwood caused by saturation with an aqueous solution of $KHCO_3$.*

Material	Treatment	L*			a*			b*			ΔE*ab
		Before	After	Dif. (%)	Before	After	Dif. (%)	Before	After	Dif. (%)	
Tree A (normal HW)	Control	69.2	46.5	−32.8	10.2	8.0	−21.6	22.9	15.1	−34.1	24.1
	Smoke-heated	67.8	42.8	−36.9	9.5	8.8	−7.4	22.4	14.5	−35.3	26.3
Tree B (blackening HW)	Control	57.9	51.1	−11.7	10.4	7.8	−25.0	20.0	14.1	−29.5	9.3
	Smoke-heated	65.8	49.6	−24.6	8.9	8.4	−5.6	23.2	17.0	−26.7	17.3

Note: HW, heartwood; Dif. (%), percentage difference between before and after.

TABLE 2. *Norlignan contents in sugi heartwood.*

Material	Treatment	Solvent	Norlignans (mg/g)	
			Agatharesinol	Sequirin-C
Tree A (normal heartwood)	Fresh sample	M	4.09	7.21
	Control	M	2.16	3.62
	Smoke heating (5 h)	M	3.65	6.16
	Smoke heating (40 h)	M	2.78	4.11
Tree B (blackening heartwood)	Fresh sample	M	3.22	2.88
		A	4.08	20.34
		R	2.99	14.14
	Control	M	0.79	—
		A	0.54	—
		R	0.39	—
	Smoke heating (5 h)	M	2.25	10.50
	Smoke heating (40 h)	M	1.80	8.37

Note: Fresh sample, samples obtained from the wood immediately after cutting (blackening heartwood, before discoloration); Control, air-dried samples (blackening heartwood, after discoloration); M, extracts with MeOH; A, extracts with acid MeOH (0.1% acetic acid in MeOH); R, extracts with reductive MeOH (0.1% ascorbic acid in MeOH);—, not detected.
Values were calculated in milligrams per gram of the dried sample.

colorless sequirin-C from red wood (*Sequoia sempervirens*), and found that the compound underwent rapid oxidation in an alkaline solution, resulting in a violet color solution. Takahashi (1996b) also reported that the sequirin-C isolated from sugi heartwood changed to dark purple compounds as a result of a treatment with a weak alkaline solution (1% $KHCO_3$). These findings reveal that sequirin-C can undergo chemical changes under weak alkalinity in non-thermal-treated heartwood, producing a darkened heartwood. We suspect that sequirin-C remained largely unchanged chemically in the smoke-heated blackening heartwood because of the decrease in pH as a result of thermal treatment, that also limits the color change to black. It is of interest to note that the pH rapidly decreased during smoke heating for the first 5 h, which resulted in preventing the heartwood from blackening under weak acidity. Further research should be undertaken to better understand the role of norlignans in color changes and pH decreases.

CONCLUSIONS

(1) The color of tree B (blackening) heartwood exposed to smoke heating for at least 5 h did not turn black, and that of the thermal-treated heartwood was yellowish-white.
(2) The pH value of tree B heartwood decreased from 7.4 to 6.5 after a 5-h smoke heating, at which time it became quite stable. The change corresponded to the color change in the heartwood, which occurred as a result of smoke heating.
(3) When a heartwood specimen was saturated with an aqueous solution of $KHCO_3$, the color of the smoke-heated heartwood changed from yellowish-white to black.
(4) In tree A (normal) heartwood, the contents of sequirin-C and agatharesinol did not change significantly before or after exposure to smoke heating. In the tree B heartwood, however, the amounts of both agatharesinol and sequirin-C decreased significantly when compared with the fresh heartwood before blackening, whereas a large amount of norlignans, in particular sequirin-C, was found to be present in the heartwood exposed to smoke heating.

These results reveal that, in the blackening heartwood, the norlignans underwent almost no change from the chemical point of view under an acidic condition as a result of the decrease in pH caused by smoke heating, thus preventing the blackening of the wood.

ACKNOWLEDGMENTS

This research was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science.

REFERENCES

ABE, Z. 1995. Discoloration of sugi heartwood; a review of the mechanisms. Wood Industry 50:2–6.

———, AND K. ODA. 1994. The color change of sugi (*Cryptomeria japonica*) heartwood from reddish brown to black. II. Identification of potassium hydrogencarbonate as one of the causative materials. Mokuzai Gakkaishi 40:1126–1130.

———, ———, AND J. MATSUMURA. 1994. The color change of sugi (*Cryptomeria japonica*) heartwood from reddish brown to black. I. The color changes and its causes. Mokuzai Gakkaishi 40:1119–1125.

BALOGH, B., AND A. B. ANDERSON. 1965. Chemistry of the genus *Sequoia*—II. Isolation of sequirins, new phenolic compounds from the coast red wood (*Sequoia sempervirens*). Phytochemistry 4:569–575.

ISHIGURI, F., K. SAITOH, M. ANDOH, Z. ABE, S. YOKOTA, AND N. YOSHIZAWA. 2000. Improvement of heartwood color of black-colored (*Cryptomeria japonica* D. Don) by UV irradiation after smoke heating. Holzforschung 54:294–300.

———, M. MASTUI, M. ANDOH, S. YOKOTA, AND N. YOSHIZAWA. 2003. Time-course changes of chemical and physical properties in sugi (*Cryptomeria japonica* D. Don) logs during smoke heating. Wood Fiber Sci. (in press).

KAI, Y., H. KURODA, AND F. TERATANI. 1972. On the phenolic constituent from *Cryptomeria japonica* D. Don. VI. Hydroxysugiresinol and coloration of heartwood. Mokuzai Gakkaishi 18:315–321.

KITAMURA, Y. 1962. On the black-stained heartwood of *Cryptomeria japonica* D. Don. Bull. Gov. For Exp. Sta. 146:133–142.

———. 1987. Measured colour values of important domestic and imported wood (Research note). Bull. For. and For. Prod. Res. Inst. 347:203–239.

KUBO, T., AND S. ATAKA. 1998. Blackening of sugi (*Cryptomeria japonica* D. Don) heartwood in relation to metal content and moisture content. J. Wood Sci. 44:137–141.

MARUYAMA, S., F. ISHIGURI, M. ANDOH, Z. ABE, S. YOKOTA, K. TAKAHASHI, AND N. YOSHIZAWA. 2001. Reddening by UV irradiation after smoke-heating in sugi (*Cryptomeria japonica* D. Don) black heartwood. Holzforschung 55:347–354.

ODA, K., J. MATSUMURA, J. TSUTSUMI, AND Z. ABE. 1994. Black-heartwood formation and ash contents in the stem of sugi (*Cryptomeria japonica* D. Don). Sci. Bull. Fac. Agr. Kyushu Univ. 48(3–4):171–176.

OKUYAMA, T., H. YAMAMOTO, AND I. KOBAYASHI. 1990. Quality improvement in small log of sugi by direct heating method (2). Wood Industry 45:63–67.

TAKAHASHI, K. 1981. Heartwood phenols and their significance to color in *Cryptomeria japonica* D. Don. Mokuzai Gakkaishi 27:654–657.

———. 1996a. Relationships between the blacking phenomenon and norlignans of sugi (*Cryptomeria japonica* D. Don) heartwood. I. A case of partially black heartwood. Mokuzai Gakkaishi 42:998–1005.

———. 1996b. The relationships between the structural difference of norlignans and coloration. Transactions of the Materials Research Society of Japan 20:159–162.

———. 1998. Relationships between the blacking phenomenon and norlignans of sugi (*Cryptomeria japonica* D. Don) heartwood. II. On blacking heartwood containing two main norlignans, sugiresinol and hydroxysugiresinol. Mokuzai Gakkaishi 44:125–133.

TAKENAMI, K. 1964. Studies on the discoloration of wood. I. Sensitivities of various wood species for the dyeing effect with ion. Mokuzai Gakkaishi 10:22–29.