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Extractives relating to heartwood color changes in sugi (*Cryptomeria japonica*) by a combination of smoke-heating and UV radiation exposure

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Abstract Sugi green logs with red or black heartwood were smoke-heated, and the changes in the color of the heartwood after ultraviolet (UV) (λ = 365 nm) radiation exposure were then observed. After UV radiation exposure, the redness and yellowness increased in both the red and black heartwoods, whereas the brightness decreased. In the black heartwood, the resulting color turned from yellowish white to reddish brown. Reddening in black heartwood after exposure to a combination of smoke heating and UV radiation is thought to be due to a decrease in brightness and an increase in both redness and yellowness. However, the degree of change in heartwood color by UV radiation exposure was not greatly affected by smoke-heating treatments of various lengths. When methanol extracts were fractionated and exposed to UV radiation, the yellowness increased in the *n*-hexane-soluble portion and the redness increased in the acetone-soluble fractions from the *n*-hexane-insoluble portion. These results suggest that the *n*-hexane-soluble fraction contains the substances that allow heartwood color to change to yellow after UV radiation exposure, and the acetone-soluble-fraction from the *n*-hexane-insoluble portion contains the substances that allow it to change to red.

Key words Sugi black heartwood · Smoke heating · UV radiation exposure · Photodiscoloration · Norlignans

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Introduction

During the utilization of wood the surface view of the wood, which includes qualities such as color, grain, and gloss, is an important factor, particularly when wood is used as an interior material for houses or for the manufacture of furniture; the mechanical properties are important as well. In general, the tree forms heartwood as an interior xylem core as the tree ages. The heartwood usually shows a deeper color than the sapwood, the specific tone of which varies among wood species. Heartwood with a rare and peculiar color has a value all its own, and such heartwood is favored for use as interior materials. On the other hand, dirty-colored heartwood has a displeasing appearance, and its price is therefore lower. Thus, wood color is an important factor when establishing the price of wood.

Sugi (Japanese cedar, *Cryptomeria japonica* D. Don) is a softwood species with beautifully colored heartwood in Japan. Sugi wood has been utilized widely in various sectors of the wood industry, and its value is frequently influenced by the heartwood color. The heartwood of this species is usually reddish brown to rose pink, also known as red heartwood, but it sometimes has a blackish brown or black color.[1–3] Unfortunately, sugi wood with black heartwood has been traded at a lower price than the usual red heartwood because of its “dirty” appearance.

Photodiscoloration is one of the major causes of the change in wood color, and many researchers have investigated this phenomenon. It is well known that wood color is changed by light exposure. Exposure to light mainly causes the wood to darken and in rare cases to fade.[4] It has been determined that photodiscoloration takes place in the phenolic constituents of wood extracts.[5]

In sugi wood, the redness of normal red heartwood can be enhanced by exposure to light at wavelengths longer than 600 nm.[6] We also reported that, in sugi heartwood, the redness and yellowness of not only red heartwood but also smoke-heated black heartwood increased after ultraviolet (UV) radiation exposure.[7] Recently, we found that the coloring substances relating to the reddening as a result of thermal treatment and UV radiation exposure in sugi heartwood could be extracted with organic solvents, particularly methanol.[8]

In the present study, we investigated the effects of the length of smoke-heating treatment on the photo-induced color change of sugi black heartwood. Furthermore, involvement of the extracts causing color changes under UV radiation exposure is discussed based on the results obtained.

Materials and methods

Materials

Two green logs (20 cm in diameter) from sugi (*Cryptomeria japonica* D. Don) trees were used in this experiment. One of them, a 39-year-old tree, had black heartwood. The other, a 24-year-old tree, had reddish brown heartwood.

Smoke heating of logs

Green logs were smoke-heated using a modified food smoker (Shinsei Sangyo, FS-50N) according to a method reported elsewhere.[7] To investigate the effect of the duration of the smoke-heating treatment on heartwood color change by UV radiation exposure, the logs were smoke-heated at 100°–120°C in a chamber. The temperature inside the logs was kept at 80°C for 5, 10, 20, and 40 h during treatment.

Soluble and insoluble fractions with *n*-hexane

Air-dried wood meal was prepared from black heartwood smoke-heated for 5 h. It was then extracted with methanol at 60°C for 9 h. After evaporating methanol with a rotary evaporator, the methanol extracts were further extracted with *n*-hexane at 60°C. After collecting the *n*-hexane-soluble fraction, the insoluble residue was extracted with acetone at 60°C. Each fractionated solution was absorbed on filter papers (Advantec, No. 1) and used for color measurement after removing the solvents.

UV radiation exposure

Ultraviolet radiation was applied to the wood specimens [3 (L) × 3 (T) × 1 (R) cm], wood meal, and extracts with a handheld UV lamp (Spectronics, model ENF-280C/J). The exposure conditions were as follows: distance from the light source 25 cm; wavelength λ 365 nm, which had the effect of significantly changing the color[7,8]; exposure time 12 h. The color of the samples was measured by a colorimeter (Minolta, CR-200) at 1-h intervals during UV radiation exposure and evaluated with an $L^*a^*b^*$ color system. Color index values indicating the brightness (L^*), redness (a^*), and yellowness (b^*) were obtained from the $L^*a^*b^*$ system based on Japanese Industrial Standard (JIS) Z8729. The resulting total color difference (ΔE^*ab), based on JIS Z8730, was calculated using the following equation.

$$\Delta E^*ab = \left(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}\right)^{1/2}$$

Results and discussion

Effects of duration of smoke-heating on color change after UV radiation exposure

As shown in Fig. 1, in red heartwood both a^* and b^* values increased with the increase of UV radiation exposure time in the control and all of the smoke-heated heartwoods, whereas L^* decreased. The rapid increase of the a^* and b^* values occurred within the first 8 h of UV radiation exposure; then both values became almost constant. There were no obvious differences in the increased ratio of redness (Δa^*) among smoke-heating treatments of different lengths (Table 1), although the a^* value decreased when the treatment time was longer.

On the other hand, in black heartwood the color change of the control wood was small (ΔE^*ab = 3.2); that is, not all

Table 1. Color changes of heartwood after UV radiation exposure

Smoke heating (h)	Before UV radiation exposure			After UV (λ = 365 nm) radiation exposure			
	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*ab
Red heartwood							
0 (control)	72.6	11.3	21.0	−5.2	2.9	4.5	7.4
5	72.0	10.0	21.1	−5.6	3.4	5.4	8.5
10	73.3	9.4	21.3	−5.2	3.0	5.2	7.9
20	75.8	8.7	21.3	−6.3	3.8	5.3	9.0
40	75.0	8.3	20.8	−5.6	2.9	4.2	7.5
Black heartwood							
0 (control)	59.7	9.8	19.3	−3.2	0.3	0.3	3.2
5	70.9	8.6	22.3	−8.1	6.1	5.6	11.6
10	73.8	7.3	22.4	−8.7	7.5	7.2	13.6
20	71.6	7.5	23.3	−8.0	7.5	7.4	13.3
40	73.3	6.7	22.0	−8.9	7.6	6.1	13.0

UV, ultraviolet; L^*, brightness; a^*, redness; b^*, yellowness

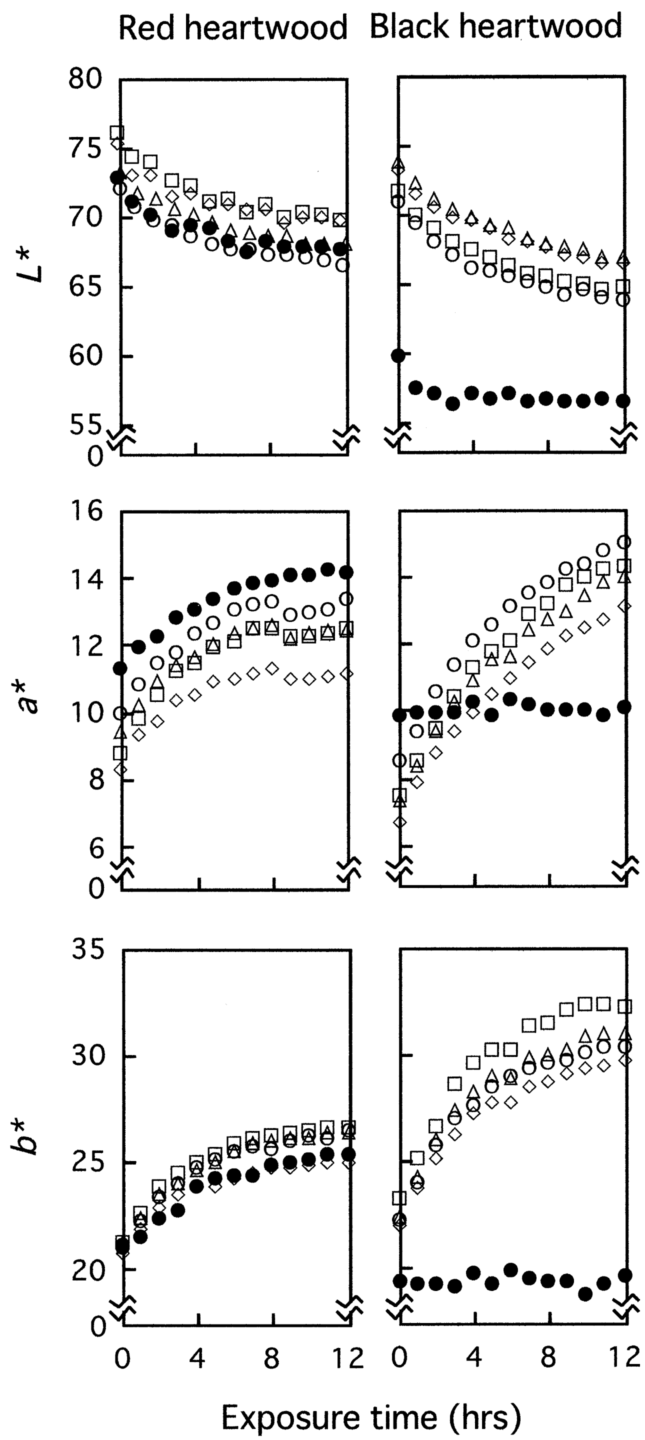

Fig. 1. Color changes in smoke-heated heartwood after ultraviolet (UV) radiation exposure. *Filled circles*, control; *open circles*, smoke-heated for 5h; *open triangles*, smoke-heated for 10h; *open squares*, smoke-heated for 20h; *open diamonds*, smoke-heated for 40h

of the L^*, a^*, and b^* values showed great variation, irrespective of the increase in UV radiation exposure time (Fig. 1). On the contrary, the values of a^* and b^* increased noticeably in all the smoke-heated heartwoods with increased UV radiation exposure time. As a result, the ΔE^*ab achieved values above 11.0 after exposure to UV radiation in all of the smoke-heated heartwoods (Table 1), although there were almost no large differences in the total color change among smoke-heating times.

These results indicate that significant reddening of black heartwood by UV radiation exposure can be obtained by means of smoke-heating for at least 5h. We found that pH changes from the weakly alkaline to the weakly acidic conditions as a result of smoke-heating for 5h could prevent the blackening of heartwood.[9] It is thought that UV radiation exposure, in conjunction with the pH change, caused the reddening of smoke-heated black heartwood.

Table 2. Color changes of the extracts from smoke-heated black heartwood by UV radiation exposure

Solvent	Before UV radiation exposure			After UV (λ = 365nm) radiation exposure for 12h			
	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*ab
Acetone[a]	63.6	15.7	23.7	−9.9	6.7	−3.6	12.5
n-Hexane	82.9	1.3	16.5	−0.9	−0.8	5.9	6.0

[a] Acetone-soluble fraction in the *n*-hexane-insoluble portion

n-Hexane-soluble and *n*-hexane-insoluble fractions

In our study on sugi heartwood, the extracts, especially methanol extracts, were responsible for the color after UV radiation exposure.[8] In fact, when wood meal extracted with methanol was exposed to UV radiation, the redness did not increase. Among the many extractives from sugi heartwood, norlignans have been isolated and identified as phenol constituents that are responsible for heartwood color.[10,11] It has been reported that ferruginol, one of the terpenoids, and agatharesinol and sequirin-C, two norlignans, exist abundantly in the heartwood and are the main contributors to sugi heartwood color.[12] The former is *n*-hexane-soluble, and the latter are acetone-soluble. In the present study, therefore, to investigate the substances that bring about heartwood color change by UV radiation exposure methanol extracts from sugi heartwood were fractionated into *n*-hexane-soluble and acetone-soluble fractions, and the color changes of the extracts in these fractions caused by UV radiation exposure were examined. The results are shown in Table 2.

In acetone extracts the a^* value increased significantly in smoke-heated black heartwood, whereas the L^* and b^* values decreased. On the other hand, in the *n*-hexane extracts almost no changes were found in the a^* value, whereas the b^* value increased. These results suggest that the *n*-hexane-soluble fraction contains the substances that turn the color to yellow after UV exposure and that the acetone-soluble fraction from the *n*-hexane-insoluble fraction contains the substances that allow the color to turn to red. As shown in Fig. 2, it was clear that in the acetone extracts only the Δa^* value increased with the increased UV radiation exposure time, whereas in the *n*-hexane extracts only the Δb^* value increased.

It has been reported that sequirin-C, abundantly present also in redwood (*Sequoia sempervirens*), is responsible for

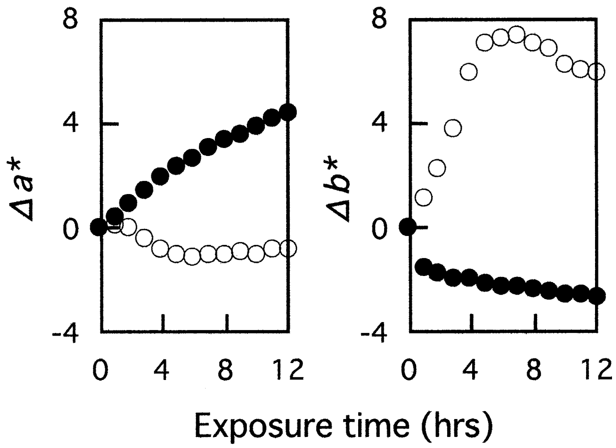

Fig. 2. Color changes of the extracts from black heartwood smoke-heated for 5 h and then subjected to UV radiation exposure. *Open circles*, *n*-hexane extracts; *filled circles*, acetone extracts

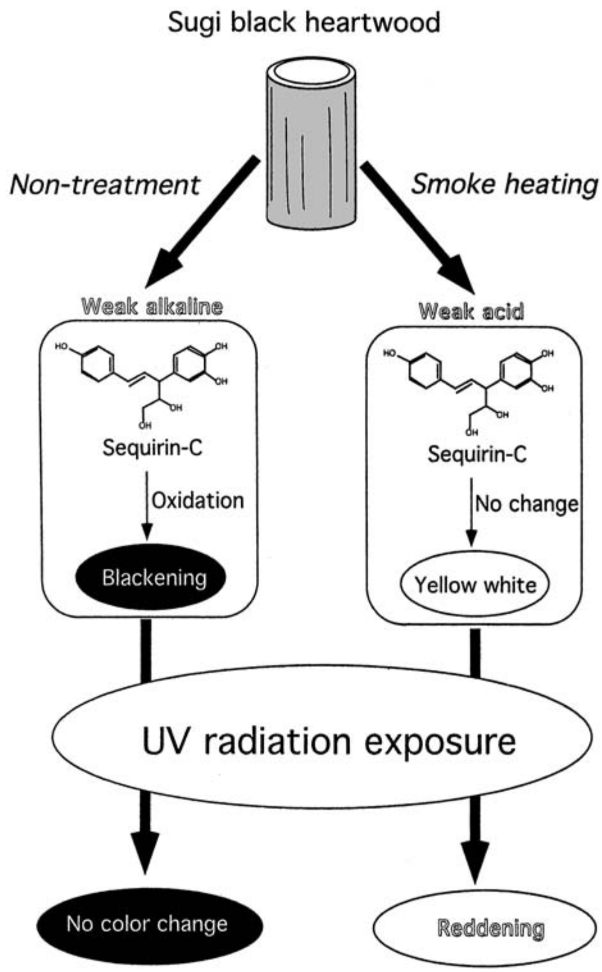

Fig. 3. Proposed mechanism of color change in sugi black heartwood subjected to UV exposure after smoke-heating

reddening during light exposure.[13] This supports the fact that sequirin-C, which is one of the main norlignans in sugi wood according to Takahashi,[14] might have brought about the color change to red after UV radiation exposure. Sequirin-C is thought to cause black coloration of heartwood under a weakly alkaline condition.[14] In black heartwood, it is also thought that the oxidation of certain substances (e.g., sequirin-C) was prevented by a pH decrease due to thermal treatment,[9] which allowed the substances to turn reddish brown after UV radiation exposure. Furthermore, it has been reported that ferruginol is involved in the color change to light yellow and that other diterpenes also participate in the color change to yellow.[12] These findings indicate that norlignans might be related to the reddening, and diterpenes might be responsible for the yellowing. However, Kawamura et al.[15] concluded that in western hemlock photodiscoloration depends on the coexistence of many biosynthetic intermediates of lignans. Therefore, it is thought that the mechanism of photodiscoloration in sugi heartwood is complicated. It is necessary to identify the compounds that cause the color change of sugi heartwood after UV radiation exposure.

Heartwood color change after UV radiation exposure

The present study revealed that UV radiation exposure apparently increased the *a** and *b** values of heartwood in both nonthermally treated and thermally treated woods of normal red heartwood (Table 1). We reported similar results in the red heartwood.[7] Interestingly, however, this finding differs from the results with the black heartwood obtained in the present study, which showed a color change accompanied by an increase in redness only in the thermally treated wood.

Figure 3 proposes a mechanism of color change in black heartwood. It is thought that thermal treatment of green logs before air exposure, which causes the heartwood color to fade to yellowish white, first changes the pH to a weakly acidic condition, resulting in the prevention of heartwood blackening. Thereafter, the heartwood color changes from yellowish white to reddish brown when the heartwood, which had retained a yellowish white color even after exposure to air, is exposed to UV radiation. The results obtained here suggest that wood extractives contributing to the heartwood's black coloring remained chemically unmodified by smoke-heating. After smoke-heating, these extractives might have changed chemically after UV radiation exposure under weakly acidic conditions.

Balogh and Anderson[13] reported that sequirin-C isolated from redwood underwent rapid oxidation in an alkaline solution, resulting in the appearance of a violet color. Takahashi[14] found that the contents of sequirin-C and agatharesinol decreased during the process of blackening, where the pH value was higher than that of the normal red portion. Takahashi[16] also reported that sequirin-C isolated from sugi heartwood changed its color to dark purple when it was treated with a weakly alkaline solution (1% $KHCO_3$). It is thought that a weakly alkaline pH in the heartwood, which causes blackening within a few hours by air oxidation, changed to a weakly acidic pH after thermal treatment of the logs. As a result, the coloring compounds contributing to the reddening (e.g., norlignans such as sequirin-C) seem to undergo photodiscoloration by UV radiation exposure, changing the color to reddish brown instead of causing blackening. A full understanding of black heartwood color change by heating and subsequent UV radiation exposure has not yet been achieved. An investigation to clarify the color changes in heartwood by a combination of smoke-heating and UV radiation exposure, in addition to pH changes, is needed.

Conclusions

In the present study changes in sugi heartwood color caused by a combination of smoke-heating and UV radiation exposure were observed. The effects of the duration of the smoke-heating treatment on the color change followed by UV radiation exposure were investigated. The involvement of extractives in color changes was also discussed.

1. Sugi heartwood turned yellowish white when it was smoke-heated (before turning black) to prevent blackening.
2. Ultraviolet radiation exposure after smoke heating changed the heartwood color from yellowish white to reddish brown.
3. Different durations of smoke-heating treatment did not result in any significant differences in the total color change by the UV radiation exposure.
4. When fractionated methanol extracts were exposed to UV radiation, the yellowness increased in the *n*-hexane soluble fractions, and the redness increased in the acetone-soluble fractions from the *n*-hexane-insoluble portion.

These results indicate that the coloring substances relating to the reddening of heartwood by UV radiation exposure were contained in the methanol extracts, especially in the acetone-soluble fraction from the *n*-hexane-insoluble portion.

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