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ORIGINAL ARTICLE

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Chemical changes in terpenes of sugi (*Cryptomeria japonica*) wood during steam drying in kiln at high temperature

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Abstract Sawdusts of sugi (*Cryptomeria japonica*) wood prepared before and after steam drying at 120°C in a kiln were extracted with *n*-hexane and ethyl acetate to give *n*-hexane extracts and ethyl acetate extracts. From gas chromatography-mass spectrometry analysis of the ethyl acetate extracts from woods before and after steam drying, the components of 4-*epi*-cubebol, cubebol, and 2,7(14),10-bisabolatrien-1-ol-4-one, which existed in the raw sugi wood, were proved to disappear in the steam-dried wood. These components were also absent in the ethyl acetate extract of the steam-condensed solution of waste steam from the kiln outlet. When these three components were treated with 0.2% (v/v) acetic acid solution at 120°C, δ-cadinene was produced as a major product from both 4-*epi*-cubebol and cubebol by dehydration and cleavage of the cyclopropane ring, and cryptomerone from 2,7(14),10-bisabolatrien-1-ol-4-one by hydration. The chemical changes of the three components presumably occur during steam drying of the sugi wood.

Key words Steam drying of sugi (*Cryptomeria japonica*) wood · Chemical changes · 4-*epi*-Cubebol · Cubebol · 2,7(14),10-Bisabolatrien-1-ol-4-one

Introduction

The high-temperature and low-humidity drying of sugi (*Cryptomeria japonica*) boxed timber using steam has been widely adopted. Influences of drying conditions on physical properties of sugi timber, such as moisture content, impact bending, and shear stress and on colorization, have been investigated.[1–7] For high-temperature-dried sugi wood, decreases in durability[8] and termite resistance[9] were also reported. However, few studies on chemical changes of components in sugi wood during steam drying have been conducted. Kano et al.[9] recently reported that the termite resistance decreased due to the loss of antitermite norlignans such as sequirin C and agatharesinol during steam drying. Further investigation of chemical changes of sugi wood components during steam drying is important to elucidate the cause of decreased durability and termite resistance of sugi steam-dried timber. We report herein a study on chemical changes of resin components in sugi wood after steam drying at high temperature.

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Materials and methods

Materials and instruments

Boxed-heart square timbers of sugi wood (130 × 130 × 3000 mm) produced in Miyazaki Prefecture were used and about 1000-mm-long specimens were made from the timber. One of the specimens was left undried and the others were dried using a steam-drying kiln MHB-5MR (Kyushu Olympia, Japan) under the following schedule: initial step at 90°C [dry-bulb temperature (DBT)] for 7 h and then at 85°C (DBT) for 17 h; second step at 120°C (DBT) and 95°C [wet-bulb temperature (WBT)] for 27 h; third step at 110°C (DBT) and 90°C (WBT) for 49 h; fourth step at 100°C (DBT) and 80°C (WBT) for 49 h. The waste steam from the kiln outlet was cooled with a water condenser during the second and third steps to give the steam-condensed solution. The pH of the steam-condensed solution was obtained by measurement with a pH meter D-50 (Horiba, Japan). The specimens before and after drying were cut into small pieces and crushed into the respective sawdusts. The sawdust of the raw wood was dried at room temperature for 1 week.

The water content of the sawdust of the raw wood was 10.7% (w/w) and that of the steam-dried wood was 10.8% (w/w) determined by a Kett moisture meter F-1 (Kett, Japan). A filter paper No. 2 (Advantec Toyo, Japan) was used for filtration. All purchased solvents were of high purity and were redistilled before use. Silica gel BW-300 and activated alumina (45 μm) for column chromatography were purchased, respectively, from Fuji Silysia (Japan) and Wako (Japan). Silica gel 60 F254 plates for thin-layer chromatography (TLC) and preparative thin-layer chromatography (PLC) were purchased from Merck (Germany). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on an AC-250P (Bruker, USA) or JNM AL-300 (JEOL, Japan) spectrometer in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were measured in $CHCl_3$ solution on a IR 270-30 spectrometer (Hitachi, Japan). Gas chromatography (GC) was performed on a GC-14B (Shimadzu, Japan) with a flame ionization detector (FID) and a C-R4A data processor (Shimadzu, Japan) under the following conditions: sample solution, 1 μl; split ratio, 1/30; column, DB-WAX (0.25 mm I.D. × 25 m, J&W Scientific, USA); carrier gas, He (1.0 ml/min); injector temperature, 300°C; detector temperature, 300°C; column temperature, 40°C (1 min), from 40°C to 245°C (10°C/min), 245°C (28.5 min). Gas chromatography-mass spectrometry (GC-MS) was performed on a GC 6890 (Agilent, USA) with a JMS-AMSUM (JEOL, Japan) or a GCMS-QP2010 (Shimadzu, Japan) under the following conditions: sample solution, 1 μl; split ratio, 1/20; column, DB-WAX (0.25 mm I.D. × 25 m); carrier gas, He; injector temperature, 250°C; interface temperature, 250°C; ion source temperature, 200°C; column temperature, 40°C (1 min), from 40°C to 245°C (10°C/min), 245°C (28.5 min). Acetic acid content in the steam-condensed solution was determined by single-ion-mode GC-MS.

Extraction of sawdusts of raw or steam-dried woods with *n*-hexane or ethyl acetate

The sawdusts of the raw and steam-dried woods were extracted with *n*-hexane or ethyl acetate as follows. The sawdust (100.0 g) was extracted with *n*-hexane (1.0 l) at room temperature for 48 h, and the solution was filtered to remove the sawdust. The *n*-hexane extraction was repeated three times. The *n*-hexane solution was evaporated to give *n*-hexane extract. Sawdust (100 g) was also extracted with ethyl acetate (1.0 l) by the method described above to give the ethyl acetate extract. The *n*-hexane and ethyl acetate extracts from the raw and steam-dried woods were dissolved in ethyl acetate, respectively, and the solutions were analyzed by GC-MS.

Extraction of steam-condensed solution of waste steam from the kiln outlet with ethyl acetate

The steam-condensed solution (2000 ml) was extracted by magnetic stirring at 500 rpm with ethyl acetate (3 × 400 ml). The ethyl acetate layer was dried over anhydrous sodium sulfate, filtered, and evaporated to give 1.078 g of ethyl acetate extract as brown oil.

Chromatographic separation of components **A**, **B**, and **C** from the *n*-hexane extract of raw wood

The *n*-hexane extract (10.20 g) of raw wood was separated into 51 fractions by silica gel column chromatography with *n*-hexane (500 ml), *n*-hexane–diethyl ether [20:1 (320 ml), 15:1 (320 ml), 8:1 (360 ml), 4:1 (850 ml)], and ethyl acetate (500 ml) as shown in Fig. 1. Components **A**, **B**, and **C** were

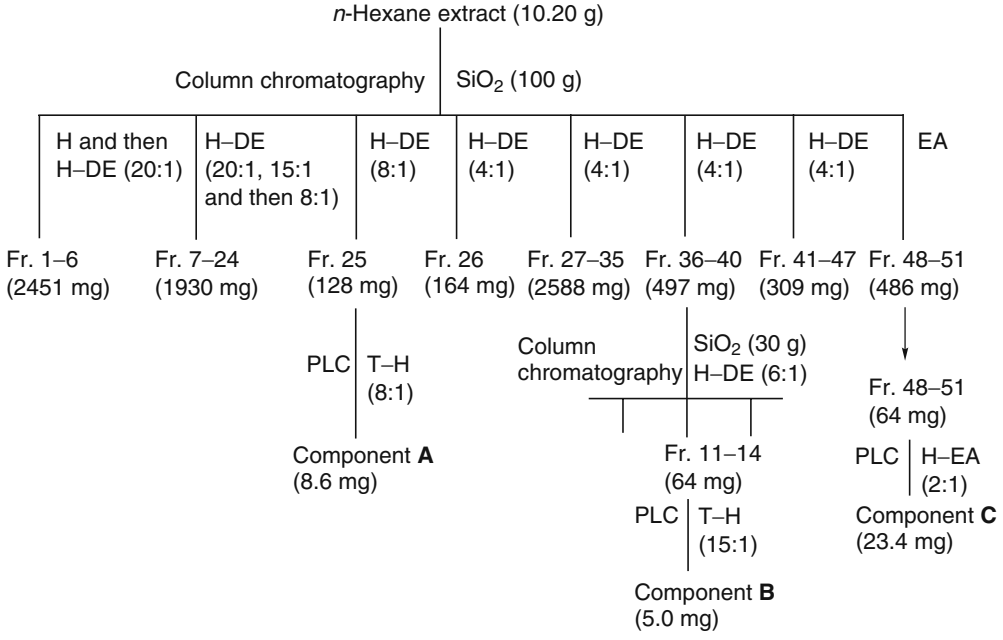

Fig. 1. Isolation of components **A**, **B**, and **C** from the *n*-hexane extract of raw sugi wood. *H*, *n*-hexane; *DE*, diethyl ether; *EA*, ethyl acetate; *T*, toluene

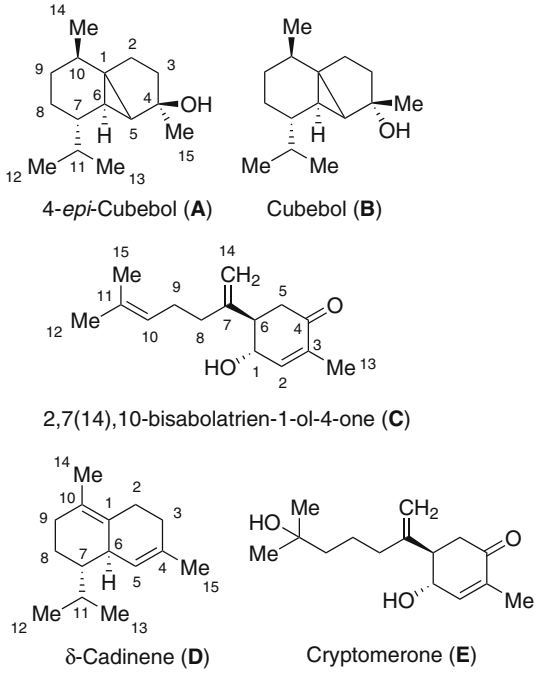

Fig. 2. Isolated components **A**–**E**

isolated from the corresponding fractions and identified as shown in Fig. 2 from IR and NMR spectral data.

Component ***A***. Colorless oil; GC retention time (t_R) = 16.12 min; IR ($CHCl_3$): ν 3650 (O-H), 3050, 2950, 2900 (C-H), 1480, 1475 (C-H), and 1100 cm^{-1} (C-O); ^1H NMR (400 MHz, $CDCl_3$) δ 0.41 (1H, dd, J = 3.2, 3.2 Hz, H-6), 0.51 (1H, dddd, J = 12.4, 12.4, 11.1, 1.9 Hz, H-9b), 0.75–0.88 (3H, m, H-5, H-7, H-8b), 0.90 and 0.93 (each 3H, d, J = 6.8 Hz, H-12, H-13), 1.00 (3H, d, J = 6.0 Hz, H-14), 1.20–1.68 (6H, m, H-2b, H-3a, H-3b, H-8a, H-9a, H-10), 1.33 (3H, s, H-15), 1.77 (1H, sept, J = 6.0 Hz, H-11), 2.06 ppm (1H, ddd, J = 12.0, 12.0, 8.7 Hz, H-2a); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.2 (C-12), 19.8 (C-13), 20.0 (C-14), 25.0 (C-6), 25.3 (C-8), 27.1 (C-15), 29.7 (C-2), 30.2 (C-10), 31.8 (C-9), 33.7 (C-11), 34.9 (C-1), 36.6 (C-3), 39.9 (C-5), 44.6 (C-7), 81.0 ppm (C-4).

Component ***B.*** Colorless oil; t_R = 16.70 min; IR ($CHCl_3$): ν 3650 (O-H), 3050, 2950, 2900 (C-H), 1480 (C-H), and 1100 cm^{-1} (C-O); ^1H NMR (400 MHz, $CDCl_3$) δ 0.51 (1H, dddd, J = 12.4, 12.4, 11.2, 2.0 Hz, H-9b), 0.74–1.00 (4H, m, H-5, H-6, H-7, H-8b), 0.92 and 0.93 (each 3H, d, J = 6.8 Hz, H-12, H-13), 0.97 (3H, d, J = 7.2 Hz, H-14), 1.20–1.40 (2H, m, H-3b, H-9a), 1.28 (3H, s, H-15), 1.45–1.72 (5H, m, H-2b, H-3a, H-8a, H-10, H-11), 1.84 (1H, ddd, J = 12.0, 12.0, 8.7 Hz, H-2a) ppm; ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.8 (C-12), 19.7 (C-13), 20.1 (C-14), 22.6 (C-6), 26.5 (C-8), 28.0 (C-15), 29.6 (C-2), 30.9 (C-10), 31.7 (C-9), 33.5 (C-1), 33.7 (C-11), 36.4 (C-3), 39.1 (C-5), 44.2 (C-7), 80.3 ppm (C-4).

Component ***C***. Colorless oil; t_R = 26.08 min; IR ($CHCl_3$): ν 3600, 3500 (O-H), 3040, 2970, 2950, 2880 (C-H), 1680 (C=O), and 1220 cm^{-1} (C-O); ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (3H, s, H-13), 1.69 (3H, s, H-12), 1.80 (3H, s, H-15), 2.08 (2H, m, H-8), 2.16 (2H, m, H-9), 2.33 (1H, dd, J = 16.6, 13.8 Hz, H-5a), 2.52 (1H, dd, J = 16.6, 3.8 Hz, H-5b), 2.66 (1H, ddd, J = 13.8, 9.8, 3.8 Hz, H-6), 4.47 (1H, dt, J = 9.8, 2.0 Hz, H-1), 5.00 (2H, s, H-14), 5.07 (1H, tt, J = 6.7, 1.4 Hz, H-10), 6.72 ppm (1H, t, J = 1.4 Hz, H-2); ^{13}C NMR (63 MHz, $CDCl_3$) δ 15.2 (C-15), 17.7 (C-13), 25.6 (C-12), 26.2 (C-9), 33.3 (C-8), 41.5 (C-5), 51.8 (C-6), 69.2 (C-1), 112.7 (C-14), 123.4 (C-10), 132.5 (C-11), 135.1 (C-3), 147.3 (C-2), 147.4 (C-7), 198.4 ppm (C-4).

Chromatographic separation of component **D** from the *n*-hexane extract of steam-dried wood

The *n*-hexane extract (2.00 g) was separated on silica gel (50 g) with *n*-hexane (400 ml) into 15 fractions. The content of compound **D** (t_R = 14.58 min) in each fraction was estimated from the area ratio of peak **D** and total peaks on the GC chromatogram: fraction 2 (480 mg; content 21.8%), fraction 3 (536 mg; 52.6%), fraction 4 (195 mg; 48.1%), and fraction 5 (16 mg; 11.5%). Component **D** (35 mg) was isolated from 83 mg of fraction 3 by column chromatography on alumina (5.0 g) with *n*-hexane: ^1H NMR (240 MHz, $CDCl_3$) δ 0.79, 0.96 (each 3H, d, J = 7.0 Hz, H-12, H-13), 0.8–2.1 (9H, m, methylene and methine protons), 1.65 (3H, brs, H-15), 1.67 (3H, brs, H-14), 2.48 (1H, brd, H-6), 2.71 (ddd, 1H, J = 12.6, 3.2, 3.2 Hz, H-9a), 5.45 ppm (1H, brs, H-5); ^{13}C NMR (63 MHz, $CDCl_3$) δ 15.7 (C-13), 18.5 (C-12), 21.2 (C-14), 21.8 (C-8), 23.6 (C-15), 26.7 (C-11), 26.8 (C-2), 32.0 (C-9 or C-3), 32.3 (C-3 or C-9), 39.5 (C-7), 45.4 (C-6), 124.5 (C-1), 124.7 (C-5), 129.9 (C-10), 134.2 ppm (C-4).

Treatment of components **A** and **B** with water or 0.2% acetic acid at 120°C

Component **A** (ca. 1.0 mg) was treated with 1 ml of water (pH 6.0) or 0.2% (v/v) acetic acid (pH 3.1) in a sealed tube at 120°C for 4 h. The reaction mixture was cooled at room temperature, and extracted with diethyl ether (3 × 5 ml). The ethereal solution was dried over anhydrous sodium sulfate, filtered, and evaporated to afford oily product. Reaction of component **B** (ca. 0.6 mg) in the same manner as described above gave oily product. Dichloromethane solution of each product was analyzed by GC-MS.

Treatment of component **C** with water or 0.2% acetic acid at 120°C

Component **C** (ca. 15 mg) was treated with 10 ml of water for 4, 8, and 24 h at 120°C in a manner similar to that described above. The reaction of **C** with 0.2% (v/v) acetic acid instead of water was carried out under the same conditions. After the post-treatment described above, the product obtained from each reaction was dissolved in dichlorometh-

Table 1. Amounts of *n*-hexane and ethyl acetate extracts of sawdust (100 g) of raw or steam-dried sugi wood

Solvent	Sugi wood[a]	Amount of extract (g)			
		First extraction	Second extraction	Third extraction	Total
n-Hexane	Raw	2.324	0.524	0.184	3.032
	Steam-dried	1.876	0.399	0.160	2.435
Ethyl acetate	Raw	4.224	0.745	0.170	5.139
	Steam-dried	2.699	0.742	0.165	3.606

[a]Water content of the sawdust: raw wood, 10.7% (w/w); steam-dried wood, 10.8% (w/w)

ane and analyzed by GC and GC-MS. The crude product (15.1 mg) obtained from the reaction of **C** (15.5 mg) with 0.2% (v/v) acetic acid for 8 h was purified by PLC with *n*-hexane–ethyl acetate (1:4) to give component **E** (7.3 mg) as colorless oil from the band of Rf, 0.18–0.26. IR ($CHCl_3$): ν 3620 (O-H), 3030, 2950, 2870 (C-H), 1690 (C=O), and 1100 cm^{-1} (C-O); ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H × 2, s, H-12, H-13), 1.80 (3H, dd, J = 1.8, 1.8 Hz, H-15), 2.36 (1H, dd, J = 16.4, 13.8 Hz, H-5a), 2.56 (1H, dd, J = 16.4, 3.7 Hz, H-5b), 2.69 (1H, ddd, J = 13.8, 10.0, 3.7 Hz), 4.52 (1H, dd, J = 2.0, 1.0 Hz, H-1), 5.04 (2H, s, H-14), 6.72 ppm (1H, dq, J = 1.8, 1.8 Hz, H-2); ^{13}C NMR (63 MHz, $CDCl_3$) δ 15.3 (C-13), 22.3 (C-9), 29.3 (C-12 or C-15), 29.5 (C-15 or C-12), 34.0 (C-8), 41.8 (C-5), 43.1 (C-10), 51.7 (C-6), 69.4 (C-1), 70.9 (C-11), 112.5 (C-14), 135.2 (C-3), 147.4 (C-2), 147.7 (C-7), 198.3 ppm (C-4).

Results and discussion

The sugi wood sawdusts obtained before and after steam drying at 120°C were extracted with *n*-hexane and ethyl acetate, respectively. Table 1 summarizes the results of the solvent extraction. The amounts of both the *n*-hexane and ethyl acetate extracts of the stream-dried wood were lower than those of the raw wood. This suggests that volatile components were removed from the sugi wood during steam drying in the kiln.

The GC chromatograms of the ethyl acetate extracts obtained from the raw and steam-dried woods are shown in Fig. 3. Nineteen components were observed as major peaks on the GC chromatogram of the extract of the raw wood. Three components **A**, **B**, and **C** (peak numbers 8, 9, and 15) were found to disappear in the extract of the wood after steam drying. Except for the peaks of components **A**, **B**, and **C**, the GC-MS chromatogram of the steam-dried wood extract resembled that of the raw wood extract. Kano et al.[9] reported that ferruginol and two norlignans (sequirin C and agatharesinol) were included in the *n*-hexane extract and the methanol extract of sugi heartwood as major antitermite components. The norlignans decreased during steam drying but ferruginol did not. Although ferruginol (peak 19) likewise remained unchanged in the ethyl acetate extract of steam-dried wood, the loss of the other components **A**, **B**, and **C** was newly observed.

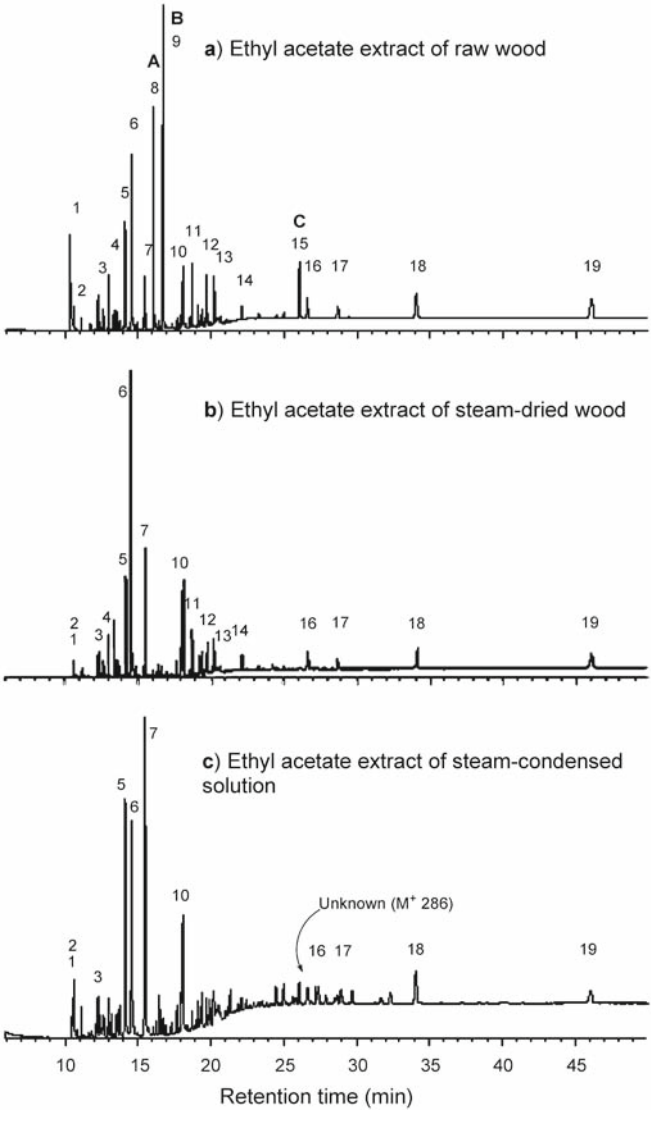

Fig. 3a–c. Gas chromatography-mass spectrometry (GC-MS) chromatograms of the ethyl acetate extracts of sawdusts of **a** the raw wood and **b** the steam-dried wood, and **c** the ethyl acetate extract of the steam-condensed solution of waste steam from the kiln outlet. GC-MS was performed on a Shimadzu GCMS-QP2010 under the conditions described in the experimental section: peak *1*, acetic acid; *2*, α-cubebene; *3*, cedrene; *4*, thujopsene; *5*, α-muurolene; *6*, δ-cadinene; *7*, calamenene; *8*, 4-*epi*-cubebol (**A**); *9*, cubebol (**B**); *10*, 1-*epi*-cubenol; *11*, cubenol; *12*, eudesmol; *13*, cryptomerione; *14*, abietadiene; *15*, 2,7(14),10-bisabolatrien-1-ol-4-one (**C**); *16*, sandaracopimarinal; *17*, phyllocladanol; *18*, sandaracopimarinol; *19*, ferruginol

We next investigated the components of the condensed solution of waste steam in order to ascertain whether the components **A**, **B**, and **C** were distilled away during steam drying of the sugi wood. The steam-condensed solution was extracted with ethyl acetate to give ethyl acetate extract. The components **A**, **B**, and **C** were also found to be absent in the extract by GC-MS (Fig. 3c). From these results, the disappearance of components **A**, **B**, and **C** from sugi wood presumably occurs during steam drying under high-temperature conditions.

In order to determine the structures of these components, the *n*-hexane extract of the raw wood was chromatographed on a silica gel column. The fractions including the components **A**, **B**, and **C** were purified by PLC. Components **A** and **B** proved to be 4-*epi*-cubebol and cubebol, respectively, on the basis of their GC-MS, IR, ^{1}H NMR, and ^{13}C NMR spectral data compared with those reported previously (Fig. 2).[10–12] Component **C** was identified as 2,7(14),10-bisabolatrien-1-ol-4-one in agreement with published data.[12,13]

4-*epi*-Cubebol (**A**) and cubebol (**B**) have been found commonly in the wood oils from various varieties of sugi.[12–22] 2,7(14),10-Bisabolatrien-1-ol-4-one (**C**) was first isolated from sugi wood[13] and its absolute configuration was determined by Kim et al.[23] It was also reported to be included in the wood oils from different varieties of sugi.[12,13,15,17–22] Cubebol and 2,7(14),10-bisabolatrien-1-ol-4-one were reported as strong antifeedants against a snail species *Acusta despesta*, which is a pest of vegetables and crops.[12] Morisawa et al.[24] also reported that a mixture of sandaracopimarinol and 2,7(14),10-bisabolatrien-1-ol-4-one acted as a repellent against the pill-bug *Armadillidium vulgare*, which is an unpleasant pest in the house and a vegetable pest, although each compound alone showed no activity. The steam drying of sugi wood at high temperature may change these biological activities of sugi wood oil because of the disappearance of components **A**, **B**, and **C**.

Components **A**, **B**, and **C** were considered to disappear from sugi wood by chemical change under slightly acidic conditions during steam drying. In practice, the steam-condensed solution showed a pH of 3.3 and was found to contain 0.18% of acetic acid by GC-MS. Therefore, the isolated components were reacted in water or 0.2% acetic acid (pH 3.1) at 120°C.

Figure 4 shows GC chromatograms before and after the treatment of components **A** and **B** with water or 0.2% acetic acid at 120°C for 4 h. 4-*epi*-Cubebol (**A**) and cubebol (**B**) easily changed under these conditions and production of new compounds was observed. Major product **D** was considered to be δ-cadinene from GC-MS data. Compound **D** was isolated from the *n*-hexane extract of the steam-dried wood by column chromatography on silica gel and on alumina and proved to be δ-cadinene by comparison of its ^{1}H and ^{13}C NMR spectra with those reported previously.[25,26]

On the other hand, component **C** scarcely reacted with distilled water at 120°C for 4 h, and a considerable remained after reaction with 0.2% (v/v) acetic acid at 120°C for 4 h. Therefore, the reaction period was extended up to 8 h and

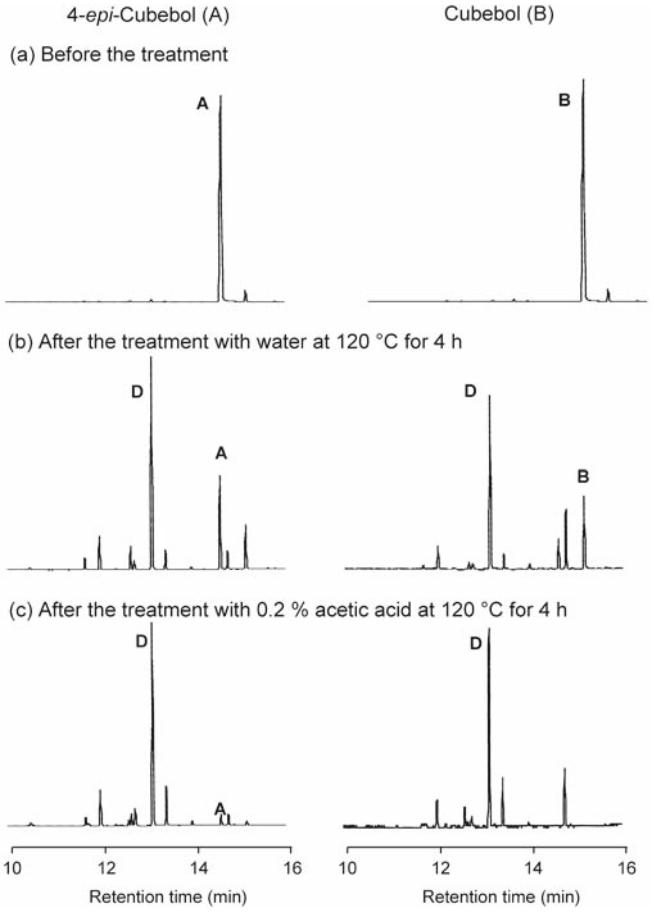

Fig. 4a–c. GC-MS chromatograms of **a** 4-*epi*-cubebol (**A**) and cubebol (**B**), and the products obtained by the treatment of 4-*epi*-cubebol (**A**) and cubebol (**B**) with **b** water at 120°C for 4 h and **c** 0.2% acetic acid aqueous solution at 120°C for 4 h

24 h. Figure 5 shows GC-MS chromatograms of the products after treatment with 0.2% acetic acid for 8 h (Fig. 5b) and 24 h (Fig. 5c). A new product **E** (t_R = 36.7 min) appeared as a major peak after 8 h (together with unchanged **C**), and was isolated by PLC and identified as cryptomerone by comparison of its ^{1}H and ^{13}C NMR spectra with those reported previously.[16,27] However, both component **C** and product **E** disappeared after 24 h, and the resulting mixture was complicated and inseparable.

Morita et al.[16] proposed a mechanism for aging production of cubenols and calamenene from 4-*epi*-cubebol (**A**) and cubebol (**B**) in the trunk of yakusugi. A mechanism of production of **D** from **A** and **B** is likely to be analogous to their mechanism via dehydration along with cleavage of the cyclopropane ring (Fig. 6). On the other hand, it would seem that **E** is initially produced from **C** by hydration of the olefin moiety and secondarily transformed into complicated products.

Thus, the three components of 4-*epi*-cubebol (**A**), cubebol (**B**), and 2,7(14),10-bisabolatrien-1-ol-4-one (**C**) were found to change during steam drying of sugi wood and to disappear in both the steam-dried wood and the steam-condensed solution from the waste steam.

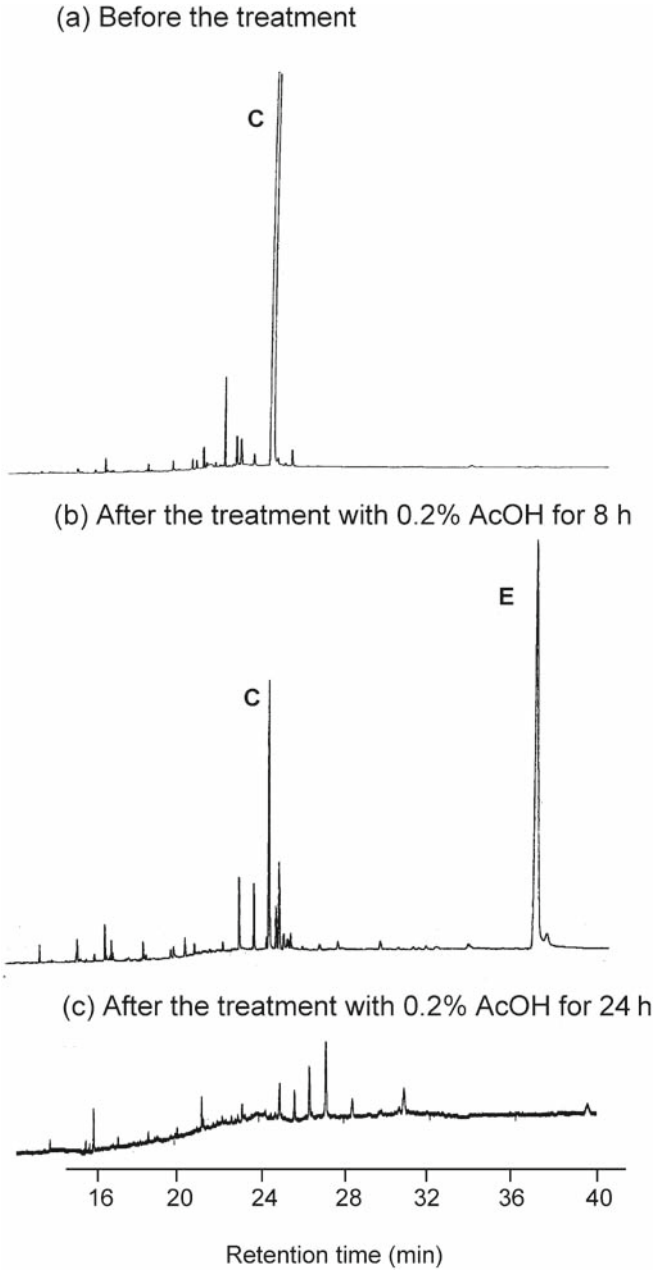

Fig. 5. **a** GC chromatogram of 2,7(14),10-bisabolatrien-1-ol-4-one (**C**). GC chromatograms of the product obtained by treatment of **C** with 0.2% acetic acid at 120°C for **b** 8 h and **c** 24 h

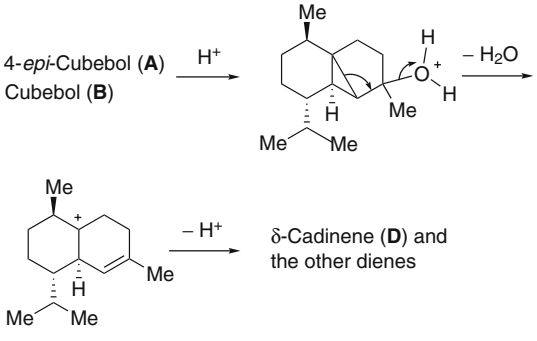

Fig. 6. Proposed mechanism of production of **D** from **A** and **B**

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