

## NOTE

Shizuo Nagahama · Tomoaki Sanetika · Masato Tazaki

**Absolute configuration of new bisaboranoids from Yaku-sugi (*Cryptomeria japonica*) wood**

Received: August 9, 1999 / Accepted: January 26, 2000

**Abstract** The absolute configuration of bisabolanoids isolated from Yaku-sugi wood were compared with those of dihydrocarvone and dihydrocarveol isomers based on their  $^{13}\text{C}$  nuclear magnetic resonance data and optical rotations.

**Key words** *Cryptomeria japonica* · Bisabolanoids ·  $^{13}\text{C}$  NMR of dihydrocarveols

**Introduction**

During the course of examining sugi (*Cryptomeria japonica* D. Don) wood constituents we found eight new bisabolanoids, a group of monocyclic sesquiterpenoids with a cyclohexane ring, in a tree grown in Yakushima, Kagoshima, Japan.<sup>1</sup> The configurations of the 7-methyls (carbon numbering coincides with that of *p*-menthane and not bisabolane, a 15-methyl described in a previous paper<sup>1</sup>) of these bisabolanoids were undecided. Among them, compound **28** (numbers are the same as those designated in the previous paper<sup>1</sup> as a matter of convenience) was a sesquiterpene related to monoterpene dihydrocarvone or isodihydrocarvone; and **32c**, **43b**, **47b**, and **48c** were related to dihydrocarveol derivatives. Thus (+)dihydrocarvone (**1**), (+)isodihydrocarvone (**2**), (–)dihydrocarveol (**3**), (+)neodihydrocarveol (**4**), (+)neoisodihydrocarveol (**5**), and (+)isodihydrocarveol (**6**) were prepared from (–)carvone or (+)limonene oxide by known methods, and their  $^{13}\text{C}$  nuclear magnetic resonance (NMR) was measured and compared with that of the bisaboranoids. The optical rotations of these compounds were measured, and their stereochemistry is discussed.

**Experimental**

The  $^{13}\text{C}$  NMR spectra were measured by JEOL JNM-EX270 FT-NMR in  $\text{CDCl}_3$  at 67.8 MHz. Optical rotations were measured by JASCO DIP-1000 Digital Polarimeter in  $\text{CHCl}_3$  solution. (+)Dihydrocarvone (**1**)  $[\alpha]_{\text{D}}^{18.9} + 14.1^\circ$  ( $c = 1.18$ ) and (+)isodihydrocarvone (**2**)  $[\alpha]_{\text{D}}^{21.6} + 2.0^\circ$  ( $c = 0.11$ ) were obtained from (–)carvone (Wako Chemicals  $[\alpha]_{\text{D}} - 56^\circ$ ) by reduction with zinc and alkali.<sup>2</sup>

(–)Dihydrocarveol (**3**)  $[\alpha]_{\text{D}}^{22.6} - 22.2^\circ$  ( $c = 0.67$ ), lit.  $-34.1^\circ$  was obtained from (–)carvone by reduction with Na in ammonia.<sup>3</sup> (+)Neodihydrocarveol (**4**)  $[\alpha]_{\text{D}}^{22.5} + 30.5^\circ$  ( $c = 1.64$ ) lit.  $+ 35.16^\circ$  and (+)neoisodihydrocarveol (**5**)  $[\alpha]_{\text{D}}^{22.7} + 28.6^\circ$  ( $c = 1.44$ ) were obtained from the reduction of (+)limonene oxide (Aldrich, 99% ee) by cyanoborohydride-borontrifluoride etherate  $\text{NaBH}_3\text{CN}\cdot\text{BF}_3\text{OEt}_2$ <sup>4</sup> or  $\text{LiAlH}_4$ .<sup>5</sup> (+)Isodihydrocarveol (**6**)  $[\alpha]_{\text{D}}^{21.8} + 4.4^\circ$  was obtained from **2** by the Meerwein-Ponndorf reduction.<sup>2</sup>

Specific rotation: **28**  $[\alpha]_{\text{D}}^{17} + 4.2^\circ$  ( $c = 0.32$ ); **32c**  $+ 1.4^\circ$  ( $c = 0.76$ ); **43b**  $+ 36^\circ$  ( $c = 0.21$ ); **45**  $+ 27^\circ$  ( $c = 0.17$ ); **47b**  $+ 15.1^\circ$  ( $c = 1.41$ ); **47c**  $+ 1.5^\circ$  ( $c = 0.27$ ); **48b**  $+ 14.5^\circ$  ( $c = 0.14$ ); **48c**  $+ 3.5^\circ$  ( $c = 0.23$ ).

Acetylation of **47b**: A 50-mg aliquot of **47b** was treated with 0.5 ml of acetic anhydride and 1 drop of pyridine for 2 days. It afforded 41 mg of **43b**,  $[\alpha]_{\text{D}}^{25.7} + 36^\circ$  ( $c = 0.32$ ).

**Results and discussion**

The  $^{13}\text{C}$  NMR data for dihydrocarvone and dihydrocarveol isomers (Fig. 1) are shown in Table 1. Their assignments had been made through two-dimensional NMR as  $^1\text{H}$ - $^{13}\text{C}$  correlated spectroscopy (COSY) and long range COSY, homonuclear decoupling (HOM), and nuclear Overhauser effect (NOE) difference techniques for each isomer. We then compared our results with those of Bradesi et al.,<sup>6</sup> but their work had been done on mixtures of isomers by computer-aided analysis, and the assignment of carbons 5

S. Nagahama (✉) · T. Sanetika · M. Tazaki  
Kumamoto Institute of Technology, 4-22-1 Ikeda, Kumamoto 860-0082, Japan  
Tel. +81-96-326-3111; Fax +81-96-326-3000  
e-mail: nagahama@chem.kumamoto-it.ac.jp

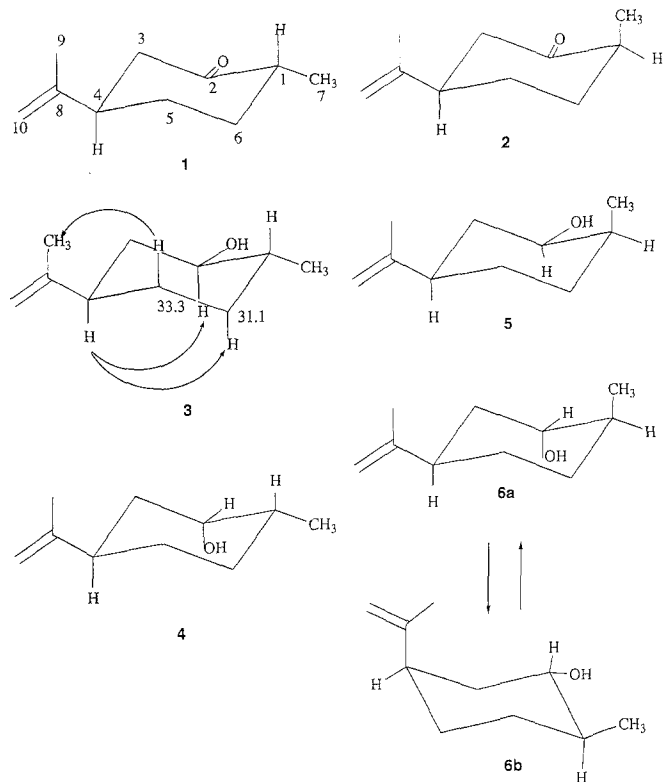


Fig. 1. Diastereomers of dihydrocarvone and dihydrocarveol

Table 1.  $^{13}\text{C}$  NMR data for dihydrocarvone and dihydrocarveol diastereomers ( $\text{CDCl}_3$ , TMS)

Carbon	1	2	3	4	5	6
1	44.7	43.9	40.0	36.2	33.7	36.5
2	212.5	214.0	76.3	70.8	72.6	72.1
3	47.0	44.6	40.6	38.7	33.9	34.5
4	46.9	44.2	44.2	37.8	44.1	38.9
5	34.9	30.6	33.3 <sup>a</sup>	31.5	24.6	26.1
6	30.8	26.4	31.1 <sup>a</sup>	28.2	30.7	27.2
7	14.4	15.6	18.4	18.4	10.8	17.3
8	147.6	146.9	149.4	150.3	149.5	149.1
9	20.5	21.6	20.9	21.0	20.9	21.6
10	109.6	111.6	108.6	108.4	108.6	109.2

NMR, nuclear magnetic resonance; TMS, tetramethylsilane

<sup>a</sup>Interchanged at the assignment by Bradesi et al.<sup>6</sup>

and 6 for **3** were interchanged. Dihydrocarveol (**3**) showed two methylene carbons at  $\delta$  31.1 and 33.3. On NOE difference spectroscopy, irradiation of axial H on the carbon at  $\delta$  33.3 enhanced the methyl proton on the double bond plus two equatorial protons (on C5 and C6). On the other hand, irradiation of the methine proton on C4 (axial) enhanced the axial protons on carbon  $\delta$  31.1 and C2. Thus  $\delta$  33.3 carbon is C5 and  $\delta$  31.1 is C6. On  $^{13}\text{C}$  NMR, **3** and **4**, which have equatorial methyl, show a signal at  $\delta$  18.4; and **5**, with an axial methyl, shows a signal at  $\delta$  10.8. However, isodihydrocarveol (**6**), having conformers **6a** and **6b**, shows a signal at  $\delta$  17.3. The  $^1\text{H}$  NMR patterns of these samples were identical with that reported by Decouzon et al.<sup>7</sup>

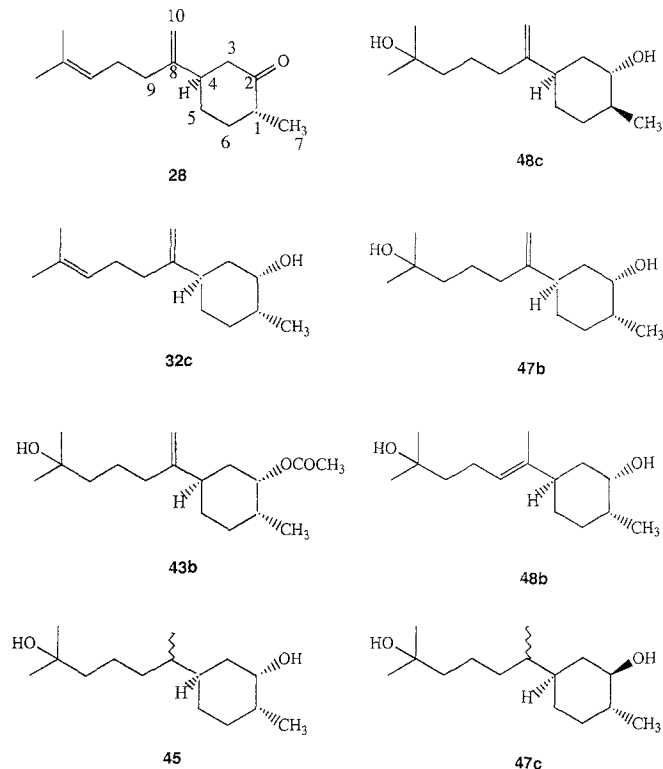


Fig. 2. Bisabolane derivatives from Yaku-sugi wood

Compound **28** (Fig. 2) shows that  $\delta$  14.4 of C7 on  $^{13}\text{C}$  NMR corresponds to **1** and exhibits dextrorotation. Thus its absolute configuration is 1R,4R. The formula for **28**, shown in a previous paper,<sup>1</sup> must be levorotatory despite an uncertain methyl configuration, as it corresponds to (-)dihydrocarvone or (-)isodihydrocarvone. Compound **48c**, the only one that shows a signal of C7 at  $\delta$  17.3, must correspond to **6**. Because it shows the same order of dextrorotation as (+)**6**, it is reasonable to propose the same absolute configuration as for (+)**6**, namely, 1S,2S,4R. Compounds **32c** and **47b** (the previous value<sup>1</sup> for  $\delta$  17.3 was erroneous) show a signal of C7 at  $\delta$  18.3 and the methyls must be equatorial. Because the OH bond was axial<sup>1</sup> they relate to **4**. They also show dextrorotation, so the configurations are considered to be 1R,2S,4R. Because acetylation of **47b** gave (+)**43b**, their absolute configuration must be same. Compound **48b** also shows a signal of C7 at  $\delta$  18.4, indicating the presence of equatorial methyl. Thus it also corresponds to **4**. As it is dextrorotatory, the configuration is 1R,2S,4R.

The remaining compounds, **45** and **47c**, have an additional chiral center at C8, the configuration of which remains obscure. However, they show signals of C7 at  $\delta$  18.3–18.4, respectively, indicating the presence of equatorial methyl. Thus **47c** corresponds to **3**, and **45** corresponds to **4**. Among the diastereomers dihydrocarveol (**3**) is the only member with levorotation, and the weak dextrorotation of **47c** may be attributed to the new chiral center at C8, rather than an enantiomeric configuration of ring substituents.

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