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HYDROPEROXYLATED GUAIANE-TYPE SESQUITERPENES FROM *VIBURNUM AWABUKI*

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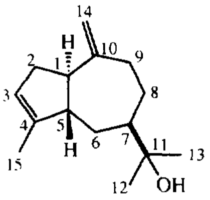
Key Word Index—*Viburnum awabuki*; Caprifoliaceae; wood; awabukinol; 4-hydroperoxyawabukinol; 3-hydroperoxyawabukinol; guaiane sesquiterpene; hydroperoxylated sesquiterpene.

Abstract—Three new guaiane-type sesquiterpenes named awabukinol, 4-hydroperoxyawabukinol and 3-hydroperoxyawabukinol, which are characterized by the presence of a hydroperoxy function, have been isolated from the wood of *Viburnum awabuki*. Their structures have been elucidated as (1α,5β,7β)-3,10(14)-guaiadien-11-ol, (1α,5β,7β)-4β-hydroperoxy-2,10(14)-guaiadien-11-ol and (1α,7β)-3β-hydroperoxy-4,10(14)-guaiadien-11-ol, respectively, by extensive analysis of spectroscopic data and some chemical transformations. The absolute configuration of awabukinol has been assigned as (1*R*), (5*S*) and (7*R*) on the basis of the CD octant rule applied to its 10-oxo-derivative.

INTRODUCTION

Viburnum awabuki has been often cultivated as a hedge and a windbreak in the south part of Japan, because it is an evergreen and also strongly resistant against air pollution and fire [1]. Its leaves are known to have been used as fish poison for the purpose of catching fish in Okinawa islands [2]. Kawazu [3, 4] reported that a pisicidal principle of *V. awabuki* was vibsanine A with a novel skeleton consisting of an 11-membered diterpene, along with inactive vibsanines B, C, D, E and F. However, chemical constituents of the wood of *V. awabuki* have not been studied. In the course of our search for antioxidant natural products in subtropical and tropical plants [4], the methanol extract of the wood of *V. awabuki* has been found to inhibit lipid peroxidation. This prompted us to investigate the chemical constituents of *V. awabuki*. As a result, we have isolated three new guaiane-type sesquiterpenes **1**, **2**, and **3**, named awabukinol, 3-hydroperoxyawabukinol and 4-hydroperoxyawabukinol, respectively, from the methanol extract of the wood. Compounds **2** and **3** are characterized by the presence of a hydroperoxy function. In this paper, we report the isolation and structural elucidation of these new compounds.



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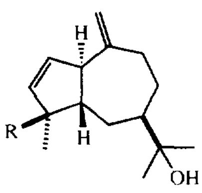

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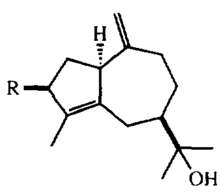

3 R = OOH
3a R = OH

RESULTS AND DISCUSSION

The wood of *V. awabuki* was extracted with methanol and the methanol extract partitioned between ethyl acetate and water. The ethyl acetate soluble portion was fractionated by repeated column chromatography on silica gel and Sephadex LH-20 and finally purified by a recycling HPLC to give three new guaiane-type sesquiterpenes, awabukinol (**1**), 3-hydroperoxyawabukinol (**2**) and 4-hydroperoxyawabukinol (**3**).

Compound **1** had a molecular formula of $C_{15}H_{24}O$, established by the HREI-mass spectrum (*m/z* 220.1826 $[M]^+$). The IR spectrum of compound **1** showed the presence of a hydroxyl group at 3395 cm^{-1} and a double bond at 1640 cm^{-1}. The NMR spectra (Tables 1

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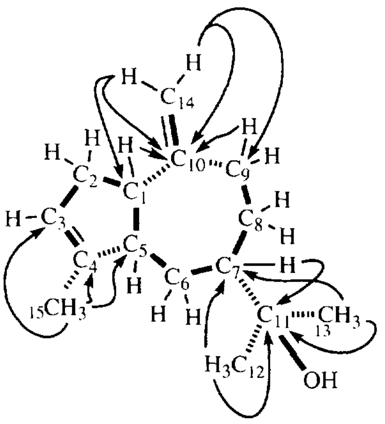
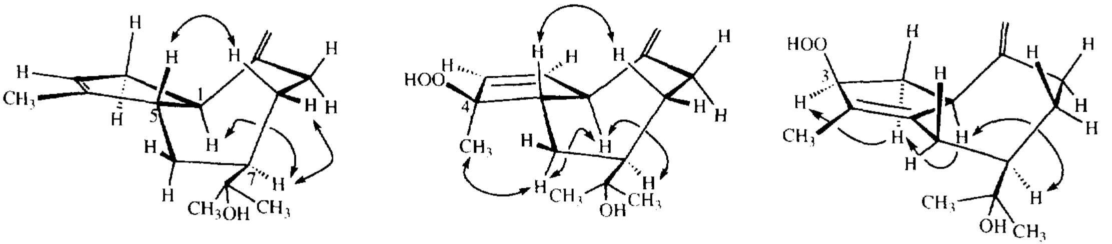


Fig. 1. Representative HMBC correlations (arrows) and partial structural fragments (bold lines).

and 2) of **1** revealed the presence of two tertiary methyl groups [δ_H 1.06 and 1.11 (each 3H, *s*); δ_C 25.7 and 28.0), an olefinic methyl group at δ_H 1.56 and an exomethylene [δ_H 4.83 (*m*) and 4.84 (*m*); δ_C 106.4 and 152.7] and also a trisubstituted double bond at δ_H 5.32 (*t*, $J = 2.0$ Hz). The analyses of two-dimensional DQF-COSY and HMQC experiments also showed the presence of the structural unit from C-4 to C-9, as shown with bold line in Fig. 1. The HMBC experiment could assemble the above structural fragments, as summarized in Fig. 1. The two methyl signals (H_3-12 and H_3-13) at δ_H 1.06 and 1.11 showed correlations with an oxygen-bearing quaternary carbon (C-11) signal at δ_C 74.1, and thus formed a dimethyl carbinol group, which should be linked to the C-7 position because of HMBC correlations of both methyl signals (H_3-12 and H_3-13) to the C-7 signal at δ_C 48.9. Furthermore, the H-1 and H-9 signals correlated to the quaternary carbon (C-10) at δ_C 152.7 of the exomethylene, which indicated that C-10 bonded to both the C-1 and C-9 positions to form a seven-membered ring containing the dimethyl carbinol group at C-7 and the exomethylene at C-10. The remaining olefinic methyl signal (H_3-15) at δ_H 1.56 correlated not only with the sp^2 C-3 and C-4 signals but also with the C-5 signal at δ_C 51.0. This suggested that the C-4 quaternary carbon appended with the methyl group (H_3-15) made a linkage with C-5 to construct a five-membered ring. The spectral evidence disclosed that the plain structure of **1** was 3,10(14)-guaiadien-11-ol. The relative stereostructure of awabukinol (**1**) was assigned as ($1\alpha,5\beta,7\beta$)-3,10(14)-guaiadien-11-ol on the basis of a NOESY experiment as shown in Fig. 2. In order to obtain the 10-oxo-derivative of compound **1** needed for measurement of the CD spectrum, selective oxidation of the $\Delta^{10(14)}$ double-bond in compound **1** was attempted. However, treatment of **1** with OsO_4–$NaIO_4$ [5] for a short period cleaved only the $\Delta^{3(4)}$ double-bond to give rise to **4**, whereas a long-term oxidation caused the cleavage of both double bonds yielding the hemi-ketal **5**. This result accounts for the $\Delta^{10(14)}$ double-bond being less reactive than the $\Delta^{3(4)}$ double-bond to dihydroxylation. Hence, at first, the $\Delta^{3(4)}$ double-bond was protected as an epoxide ring and then the $\Delta^{10(14)}$ double-bond was cleaved with O_3-Me_2S to yield the 10-oxo-derivative **6** (Fig. 3). The CD spectrum of **6** showed the negative Cotton effect at 270 nm. The conformation of **6** elucidated by the NOESY (Fig. 4) was applied to the octant rule and thereby the absolute configurations on the chiral centres in compound **1** were determined to be (1*R*), (5*S*) and (7*R*).

Compound **2** had the molecular formula of $C_{15}H_{24}O_3$, obtained from the quasi-molecular ion peak at *m/z* 275 $[M + Na]^+$ in the FAB-mass spectrum; the fifteen carbons were indicated by the ^{13}C NMR spectrum. Its IR spectrum displayed absorptions attributable to a hydroxyl group (3412 cm^{-1}) and a double bond (1625 cm^{-1}). The NMR spectra (Tables 1 and 2) of **2** showed the presence of three tertiary methyl groups (δ_H 0.97, 0.98 and 1.23; δ_C 26.4, 27.8 and 19.2), two (δ_H 0.97, 0.98) of which showed HMBC correlations with an oxygen-bearing quaternary carbon at δ_C 73.9 indicating the presence of a dimethyl carbinol group, and also they showed the presence of an exomethylene (δ_H 4.71 and 4.75; δ_C 106.9 and 153.4) and a disubstituted double bond (δ_H 5.81, *dd*, $J = 5.8$, 1.5 Hz and δ 5.76, *dd*, $J = 5.8$, 2.2 Hz; δ_C 133.6 and 136.6). These spectral data suggested that **2** was also a guaiane-type sesquiterpene having two more oxygen atoms than **1**. In fact, the ^{13}C NMR data (Table 2) of compounds **1** and **2** revealed that the chemical shifts for C-7 ~ C-14 were comparable, whereas those for C-1 ~ C-5 were not consistent. In addition, the DQFCOSY and HMQC experiments showed that **2** had the same seven-membered ring as **1** and the disubstituted double bond was placed on the C-2 and C-3 positions of the five-membered ring. A low-field signal resonance at δ_H 8.10



1 **2** **3**

Fig. 2. Relative stereochemistry for compounds **1**–**3** based on NOESY, indicated by arrows.

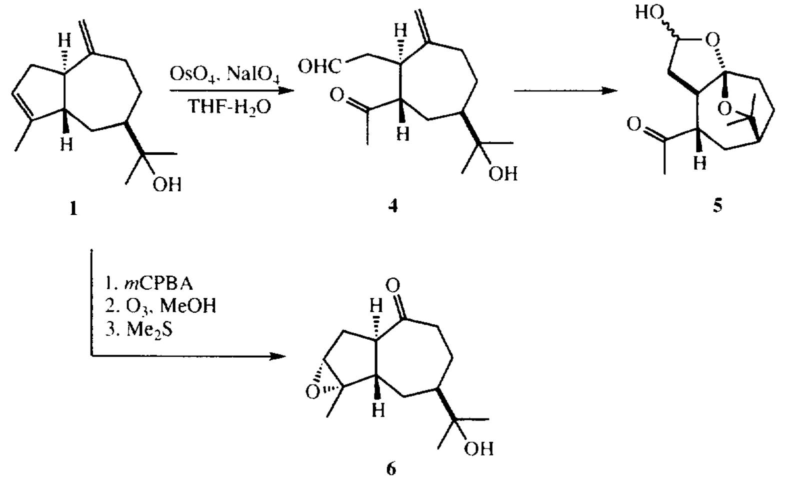


Fig. 3. Oxidative cleavage of the double bonds in **1**.

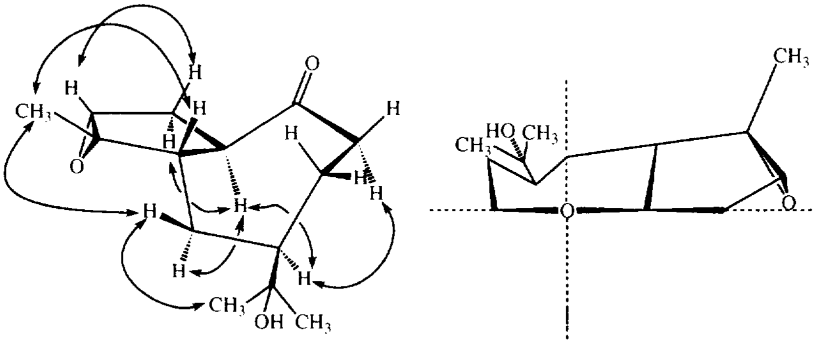


Fig. 4. Projection formula (right) of **6** based on the conformation (left) elucidated by NOESY.

implied the presence of a hydroperoxyl group in the molecule of **2**, and its presence was supported by a positive KI-starch test [7]. The hydroperoxyl group could be verified as located on the C-4 positions as follows. The C-4 quaternary carbon signal appeared abnormally low-field at δ_C 96.5 [8]. In the HMBC of **2**,

Table 1. ^{1}H NMR data of compounds **1–3** and **6**

H	**1***	**2***	**3***	**6†**
1	2.61 *brdd* (11.4, 8.5)‡	2.70 *ddd* (8.6, 2.2, 1.5)	3.13 *dd* (8.3, 7.1)	2.43 *ddd* (13.7, 9.3, 8.7)
2α	2.60 *brdd* (18.7, 2.0)	5.81 *dd* (5.8, 1.5)	1.99 *ddd* (13.6, 7.1, 5.1)	2.40 *ddd* (8.7, 8.7, 1.2)
2β	2.27 *dddd* (18.7, 11.4, 2.0, 2.0)	–	2.30 *ddd* (13.6, 8.3, 7.1)	1.86 *dd* (13.7, 8.7)
3	5.32 *t* (2.0)	5.76 *dd* (5.8, 2.2)	4.73 *dd* (8.3, 5.1)	2.93 *d* (1.2)
5	2.43 *ddd* (8.5, 7.3, 5.9)	2.41 *ddd* (12.0, 8.6, 5.3)	–	1.59 *ddd* (10.7, 9.3, 6.1)
6α	1.44 *ddd* (12.9, 7.3, 1.2)	1.58 *ddd* (13.7, 12.0, 2.0)	2.46 *dd* (13.0, 1.7)	1.41 *ddd* (10.7, 10.7, 5.9)
6β	1.79 *ddd* (12.9, 9.8, 5.9)	1.75 *ddd* (13.7, 13.7, 5.3)	1.97 *dd* (13.0, 13.0)	1.80 *ddd* (10.7, 10.7, 6.1)
7	1.70 *dddd* (12.5, 9.8, 1.2, 1.2)	1.46 *dddd* (13.7, 13.7, 2.6, 2.0)	1.65 *dddd* (13.0, 13.0, 1.7, 1.7)	1.37 *dddd* (10.7, 7.9, 5.9, 1.0)
8α	1.27 *dddd* (10.3, 10.3, 1.7, 1.2)	1.77 *ddd* (13.7, 6.6, 2.6)	1.73 *ddd* (13.0, 6.3, 1.7)	1.57 *dddd* (14.4, 5.4, 4.9, 1.0)
8β	1.94 *brddd* (12.5, 10.3, 6.1)	1.20 *dddd* (13.2, 13.2, 13.2, 1.7)	1.12 *dddd* (13.0, 13.0, 13.0, 1.0)	0.96 *dddd* (14.4, 12.9, 7.9, 2.7)
9α	2.11 *ddd* (14.6, 12.5, 1.7)	1.95 *dd* (13.2, 13.2)	1.98 *ddd* (13.0, 13.0, 1.7)	1.85 *ddd* (15.1, 12.9, 4.9)
9β	2.67 *ddd* (14.6, 6.1, 1.7)	2.48 *ddd* (13.2, 6.6, 1.7)	2.41 *ddd* (13.0, 6.3, 1.0)	2.56 *ddd* (15.1, 5.4, 2.7)
12	1.06 *s*	0.97 *s*	0.94 *s*	0.83 *s*
13	1.11 *s*	0.98 *s*	0.97 *s*	0.88 *s*
14	4.83 *m*	4.71 *m*	4.82 *d* (1.2)	–
	4.84 *m*	4.75 *m*	4.93 *d* (1.2)	–
15	1.56 *s*	1.23 *s*	1.67 *s*	1.08 *s*
OOH	–	8.10 *s*	7.60 *s*§	–

*400 MHz in C$_6$D$_6$.

†600 MHz in C$_6$D$_6$.

‡Coupling constants (*J* in Hz) are given in parentheses.

§400 MHz in CDCl$_3$.

Table 2. ^{13}C NMR data of compounds **1**, **2**, **2a**, **3**, **3a** and **6**

C	**1***	**2***	**2a**†	**3***	**3a***	**6**‡
1	49.2	54.1	55.6	51.3	51.2	50.6
2	34.0	133.6	132.0	35.8	35.1	27.9
3	123.1	136.6	139.1	92.6	78.8	63.6
4	142.0	96.5	85.3	130.1	134.9	66.1
5	51.0	48.8	52.8	143.4	139.6	42.4
6	32.3	27.4	27.0	29.0	30.5	27.8
7	48.9	48.7	49.7	45.8	46.0	47.7
8	26.2	27.3	26.6	30.4	30.5	23.1
9	41.1	39.4	40.1	34.9	35.1	45.5
10	152.7	153.4	153.6	153.1	152.9	208.4
11	74.1	73.9	74.1	72.5	72.4	72.7
12	25.7	26.4	25.5	26.4	26.4	25.5
13	28.0	27.8	27.7	27.3	27.3	28.1
14	106.4	106.9	106.8	109.6	109.3	–
15	14.8	19.2	23.3	19.1	11.2	15.9

*100 MHz in C_6D_6.
†100 MHz in $CDCl_3$.
‡150 MHz in C_6D_6.

the C-4 signal showed cross-peaks with the H-3 and H-5 signals, and the methyl signal (H_3-15) at δ_H 1.23. Moreover, reduction of the hydroperoxy function in **2** with triphenylphosphine smoothly proceeded to give the diol **2a**, in which the δ_C value of C-4 shifted up to 85.3 ppm confirming the presence of the hydroperoxyl group at the C-4 position. The above spectral and chemical evidence led to the proposal of the plane structure of 4-hydroperoxy-2,10(14)-guaiadien-11-ol for **2**. The relative stereochemistry of **2** was elucidated on the basis of NOEs as shown in Fig. 2. Thus, the structure of 4-hydroperoxyawabukinol (**2**) was represented as (1α,5β,7β)-4β-hydroperoxy-2,10(14)-guaiadien-11-ol.

Compound **3** was found to have the same molecule formula $C_{15}H_{24}O_3$ as **2** on the HRFAB-mass spectrum (*m/z* 275.1624 $[M + Na]^+$) and showed a positive KI–starch test, indicating the presence of a hydroperoxyl group. The spectral data for **3** suggested the presence of a dimethylcarbinol group [3380 cm^{-1}; δ_H 0.94 and 0.97 (each 3H, *s*); δ_C 26.4, 27.3 and 72.5], and olefinic methyl group (δ_H 1.67) and an exomethylene [1642 cm^{-1}; δ_H 4.82 and 4.93 (each 1H, *d*, $J =$ 1.2 Hz)], indicating that the structure of **3** is closely related to that of awabukinol (**1**). The NMR spectra (Tables 1 and 2) of compound **3** disclosed the presence of tetrasubstituted double bond (δ_C 130.1 and 143.4), and an oxymethine (δ_H 4.73, *dd*, $J = 8.3$, 5.1 Hz; δ_C 92.6), which should bear a hydroperoxyl group owing to the fact that its abnormally low δ_C value (92.6) was shifted to high-field at δ_C 78.8 by reduction of **3** to **3a** with triphenylphosphine. This hydroperoxylated methine (H-3) was verified to make a partial structure, $-C(1)H-C(2)H_2-C(3)HOOH-$, by analyses of DQF-COSY and HMQC. In the HMBC experiment, the H-3 signal showed cross peaks to the sp^2 quaternary carbon signals at δ_C 130.1 and 143.4, which in turn correlated to the H-1 signal at δ_H 3.13. Thereby, the tetrasubstituted double-bond must be placed at the $\Delta^{4(5)}$ position on the five-membered ring of the guaiane framework. The presence of the same seven-membered unit as **1** and **2** was also confirmed by the routine two-dimensional NMR experiments. Finally, compound **3** was found to adopt the relative stereochemistry as shown in Fig. 2 because of the observation of NEOs (H-1/H-7, and H-1/H-2α/H-3). Thus, the structure of 3-hydroperoxyawabukinol (**3**) was assigned as (1α,7β)-3β-hydroperoxy-4,10(14)-guaiadien-11-ol.

Allylic hydroperoxides are not rare among natural products, and have been often found in a group of guaianes and guainolides [9]. The compounds **2** and **3** might be rationalized to be derived from awabukinol (**1**) by a phyto-oxidative process involving activated oxygen [10]. No vibsanine-type diterpenoids that occur in the leaves of *V. awabuki* have been found in the present study on its wood. None of the compounds (**1**, **2** or **3**) exhibited antioxidant property [11].

EXPERIMENTAL

General. ^1H and ^{13}C NMR: TMS as int. standard. CC: silica gel (Merck, 230 ~ 400 mesh and Wakogel C-300) and Sephadex LH-20 (25 ~ 100 m, Pharmacia). TLC: precoated silica gel F254 (Merck). Spots were visualized by UV (254 nm) and 10% $CeSO_4$–H_2SO_4.

Plant material. Wood of *V. awabuki* was collected on October 1993 in Tokushima, Japan. A voucher specimen has been deposited in this institute.

Extraction and isolation. The MeOH extract was partitioned between EtOAc and water. The EtOAc-soluble portion (50 g) was sept by CC on silica gel (Merck) alternately with *n*-hexane, *n*-hexane–EtOAc (9:1; 7:3; 4:6), EtOAc and EtOAc–MeOH (9:1) to give 6 frs (1–6). Fr. 3 (8.6 g) was again sepd by CC on silica gel (Merck) with CH_2Cl_2–EtOAc (10:1) to give 7 frs (7–14). Fr. 9 (1.5 g) was purified by repeated CC on silica gel (C-300) with *n*-hexane–EtOAc (7:3) to give awabukinol (**1**) (42 mg) and 4-hydroperoxyawabukinol (**2**) (24 mg). Fr. 10 (1.0 g) was sepd by CC on LH-20 with EtOH followed by recycling HPLC (recycled × 5; JAIGEL-1H (20 × 600 mm i.d.), $CHCl_3$ (3.5 ml min^{-1})] to yield 3-hydroperoxyawabukinol (**3**) (15 mg).

Awabukinol (**1**). Oil. $[\alpha]_D^{24}$ +161.2° (*c* 0.74, $CHCl_3$). EI-MS *m/z* (rel. int.): 220.1826 $[M]^+$ (calc. 220.1827 for $C_{15}H_{24}O$) (8), 159 (100). IR ν_{max}^{FT} cm^{-1}: 3395 (OH), 1640 (C=C). ^1H and ^{13}C NMR: Tables 1 and 2.

Oxidation of **1**. To a soln of **1** (20 mg) in THF–H_2O (2:3; 0.8 ml) was added OsO_4 (0.7 mg) at room temp. and stirring continued for 1 min. After $NaIO_4$ (66 mg) was added, the reaction mixt. was stirred at room temp. for 2 min. The reaction mixt. was filtered and the filtrate was evapd *in vacuo*. The residue was chromatographed on silica gel (*n*-hexane–EtOAc, 4:1) to yield **4** (1.5 mg) as an oil. HREI-MS *m/z* (rel. int.): 252.1723 $[M]^+$ (calc. 252.1725 for $C_{15}H_{24}O_3$). ^1H NMR (200 MHz, $CDCl_3$): δ 1.04 (3H, *s*, H-12), 1.18 (3H, *s*, H-13), 2.21 (3H, *s*, H-15), 3.32 (1H, *ddd*, *J* = 10.0, 5.0, 5.0 Hz, H-5), 4.73 (1H, *brs*, H-14), 4.96 (1H, *brs*, H-14), 9.53 (1H, *dd*, *J* = 2.0, 1.0 Hz, H-2).

Oxidative degradation of **1**. To a soln of **1** (11 mg) in THF–H_2O (2:3; 0.5 ml) was added OsO_4 (0.7 mg) at room temp. and stirring continued for 15 min. After $NaIO_4$ (33 mg) was added, the reaction mixt. was stirred at room temp. for 45 min. The reaction mixt. was filtered and the filtrate was evapd *in vacuo*. The residue was chromatographed on silica gel (*n*-hexane–EtOAc, 1:3) to yield **5** (7.6 mg) as an oil. HREI-MS *m/z* (rel. int.): 254.1553 $[M]^+$ (calc. 254.1518 for $C_{14}H_{22}O_4$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.24 (6H, *s*, H-12, 13), 1.50 (1H, *dddd*, *J* = 12.6, 11.6, 7.1, 4.9 Hz, H-1), 1.72 (1H, *ddd*, *J* = 12.5, 11.6, 4.6 Hz, H-2), 2.09 (1H, *dd*, *J* = 12.5, 7.1 Hz, H-2), 2.19 (3H, *s*, H-15), 2.67 (1H, *m*, H-7), 2.86 (1H, *ddd*, *J* = 12.6, 6.2, 6.2 Hz, H-5), 5.59 (1H, *d*, *J* = 4.6 Hz, H-3).

Preparation of **6**. A mixt. of **1** (5 mg) and *m*-chloroperbenzoic acid (3.96 mg) in CH_2Cl_2 (1 ml) was stirred at 0° for 15 min. The reaction mixt. was diluted with CH_2Cl_2 and washed successively with 2M NaOH soln, 2M HCl soln, H_2O and satd NaCl soln. The solvent was removed *in vacuo* to give the residue, which was purified by CC on silica gel (*n*-hexane–EtOAc, 2:1) yielding the epoxide (3.9 mg). In the soln of the obtained epoxide in MeOH (2 ml) was bubbled a slow stream of O_3 at −78° for 15 min. After dimethylsulfide (0.5 ml) was added, the soln was stood at −78° for 30 min and at room temp. for 1 hr. The removal of a solvent provided residue, which was purified by CC on silica gel (*n*-hexane–EtOAc, 2:1) yielding the ketone **6** (2.0 mg). EI-MS *m/z* (rel. int.): 238.1588 $[M]^+$ (53) (calc. 238.1569 for $C_{14}H_{22}O_3$), 220 $[M-H_2O]^+$ (18), 59 (100). IR ν_{max}^{FT} cm^{-1}: 3453 (OH), 1698 (C=O). CD (EtOH); $\Delta\varepsilon$ (270 nm) − 0.35. ^1H and ^{13}C NMR: Tables 1 and 2.

4-Hydroperoxyawabukinol (**2**). Oil. $[\alpha]_D^{20}$ +73.4° (*c* 0.66, $CHCl_3$). FAB-MS *m/z* (rel. int.): 275 $[M+Na]^+$, 115 (100). HREI-MS: 234.1608 $[M-H_2O]^+$ (calc. 234.1620 for $C_{15}H_{22}O_2$). IR ν_{max}^{FT} cm^{-1}: 3412 (OH), 1625 (C=C). ^1H and ^{13}C NMR: Tables 1 and 2.

Reduction of **2**. To a soln of **2** (4.6 mg) in benzene (3 ml) was added triphenylphosphine (6 mg) at room temp. and stirring continued for 2 hr. The reaction mixture was evapd *in vacuo* to give the residue, which was chromatographed on LH-20 (*n*-hexane–$CHCl_3$, 2:3) to yield **2a** (1.5 mg) as an oil. FAB-MS *m/z* (rel. int.): 259.1688 $[M+Na]^+$ (50) (calcd 259.1674 for $C_{15}H_{24}O_2Na$), 115 $[M-144]^+$ (100). IR ν_{max}^{FT} cm^{-1}: 3399 (OH), 1642 (C=C). ^1H (400 MHz, $CDCl_3$): δ 1.18 (3H, *s*, H-12), 1.20 (3H, *s*, H-13), 1.23 (3H, *s*, H-15), 2.07 (1H, *m*, H-9), 2.59 (1H, *ddd*, *J* = 13.2, 6.1, 1.7 Hz, H-9), 2.91 (1H, *ddd*, *J* = 7.6, 1.7, 1.2 Hz, H-1), 4.60 (1H, *brs*, H-14), 4.66 (1H, *brs*, H-14), 5.77 (1H, *dd*, *J* = 5.6, 1.7 Hz, H-3), 5.80 (1H, *dd*, *J* = 5.6, 1.2 Hz, H-2). ^{13}C NMR: Tables 2.

3-Hydroperoxyawabukinol (**3**). Oil. $[\alpha]_D^{21}$ +33.0° (*c* 0.41, $CHCl_3$). FAB-MS *m/z* (rel. int.): 275 $[M+Na]^+$, 115 (100). HRFAB-MS: 275.1624 $[M+Na]^+$ (calcd 275.1624 for $C_{15}H_{24}O_3Na$). IR ν_{max}^{FT} cm^{-1}: 3380 (OH), 1642 (C=C). ^1H and ^{13}C NMR: Tables 1 and 2.

Reduction of **3**. To a soln of **3** (4.8 mg) in benzene (2.5 ml) was added triphenylphosphine (6 mg) at room temp. and stirring continued for 15 min. The reaction mixture was evapd *in vacuo* to give the residue, which was chromatographed on silica gel (*n*-hexane–EtOAc, 2:1) to yield **3a** (1.5 mg) as an oil. FAB-MS *m/z* (rel. int.): 259.1696 $[M+Na]^+$ (30) (calcd 259.1674 for $C_{15}H_{24}O_2Na$), 115 $[M-144]^+$ (100). IR ν_{max}^{FT} cm^{-1}: 3358 (OH), 1642 (C=C). ^1H (400 MHz, C_6D_6): δ 0.96 (3H, *s*, H-12), 0.97 (3H, *s*, H-13), 1.53 (1H, *ddd*, *J* = 12.9, 7.6, 6.3 Hz, H-2α), 1.62 (3H, *s*, H-15), 1.62 (1H, *dddd*, *J* = 11.5, 11.5, 3.2, 3.2 Hz, H-7), 1.77 (1H, *dddd*, *J* = 12.9, 11.5, 6.8, 6.4 Hz, H-8β), 1.96 (1H, *dd*, *J* = 16.0, 11.5 Hz, H-6β), 1.99 (1H, *ddd*, *J* = 12.7, 6.8, 6.8 Hz, H-9α), 2.35 (1H, *ddd*, *J* = 12.9, 7.3, 7.3 Hz, H-2β), 2.39 (1H, *ddd*, *J* = 12.7, 6.4, 1.0 Hz, H-9β), 2.51 (1H, *dd*, *J* = 16.0, 3.2 Hz, H-6α), 3.09 (1H, *dd*, *J* = 7.6, 7.3 Hz, H-1), 4.30 (1H, *dd*, *J* = 7.3, 6.3 Hz, H-3), 4.81 (1H, *d*, *J* = 1.7 Hz, H-14), 4.89 (1H, *d*, *J* = 1.7 Hz, H-14). ^{13}C NMR: Tables 2.

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REFERENCES

1. Makino, T. (1977) *Makino's New Illustrated Flora of Japan*. Hokuryuu-kan, Tokyo.
2. Hatsushima, S. (1975) *Flora of the Ryukyus*. Okinawa Seibutsu Kyouiku-kai, Naha, Japan.
3. Kawazu, K. (1980) *Agric. Biol. Chem.* **44**, 1367.
4. Fukuyama, K., Katsube, Y. and Kawazu, K. (1980) *J. Chem. Soc., Perkin Trans II*, 1701.
5. Minami, H., Takahahi, E., Fukuyama, Y., Kodama, M., Yoshizawa, T. and Nakagawa, K. (1995) *Chem. Pharm. Bull.* **43**, 347.

6. Pappo, R., Allen, D. S. Jr., Remieux, R. U. and Johnson, W. S. (1956) *J. Org. Chem.* **21**, 478.
7. Hashidoko, Y., Tahara, S. and Mizutani, J. (1989) *Phytochemistry* **28**, 425.
8. Kitagawa, I., Cui, Z., Son, W., Kobayashi, M. and Kyogoku, Y. (1987) *Chem. Pharm. Bull.* **35**, 124.
9. Casteel, D. A. (1992) *Nat. Prod. Rep.* **9**, 289.
10. Rustaiyan, A. and Faramarzi, S. (1988) *Phytochemistry* **27**, 479.
11. Minimi, H., Kinoshita, M., Fukuyama, Y., Kodama, M., Yoshizawa, T., Sugiura, M., Nakagawa, K. and Tago, H. (1994) *Phytochemistry* **36**, 501.