SEVEN PRENYLPHENOLS, ANTIARONES C, D, E, F, G, H, AND I FROM THE ROOT BARK OF ANTIARIS TOXICARIA LESCH.[1]

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Abstract —— Three new prenylchalcones, antiarones C, D, and E along with four new prenylflavanones, antiarones F, G, H, and I were isolated from the root bark of Antiaris toxicaria Lesch. On the basis of spectral evidence, the structures of antiarones C – I were shown to be **2** – **8**, respectively. A known compound, (±)-sigmoidin A (**1**) was also isolated.

Previously we reported the structure determination of the isoprenoid-substituted phenolic compounds isolated from the Indonesian moraceous plants, Artocarpus heterophyllus Lamk.[2,3] and Artocarpus communis Forst.[4] On the constituents of Antiaris toxicaria Lesch., many investigators reported a series of cardiac glycosides isolated from the latex and the seeds of the plant,[5] while we reported the characterization of two prenylaurones, antiarones A and B.[6] This paper deals with the characterization of three prenylchalcones along with four prenylflavanones isolated from the root bark of A. toxicaria Lesch.

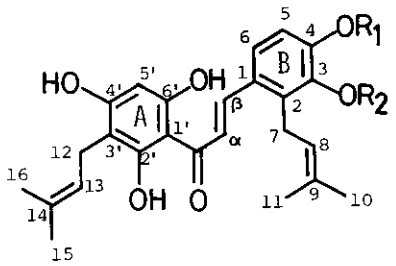
The dried root bark of A. toxicaria, collected in Indonesia, was extracted successively with n-hexane, benzene, and acetone.[6] Antiarones C (**2**) and D (**3**) were isolated from the acetone extract, and antiarones E (**4**), F (**5**), G (**6**), H (**7**) and I (**8**) along with (±)-sigmoidin A (**1**)[7] were isolated from the benzene extract as described in "EXPERIMENTAL".

Antiarone C (**2**), yellow prisms, mp 175-178°C, $C_{26}H_{30}O_6$, gave a brown color with methanolic ferric chloride. The ir spectrum disclosed absorption bands for hydroxyl and conjugated carbonyl groups, and aromatic ring. The uv spectrum exhibited maxima at 210, 261 (sh), 372 nm, and resembled those of chalcone derivatives.[8] The ^{1}H nmr spectrum showed the signals of the following protons; 1) protons in two 3,3-dimethylallyl (prenyl) groups, δ 1.64, 1.66, 1.76, 1.85 (each 3H, br s), 3.27, 3.59 (each

2H, br d, J=7 Hz), 5.14, 5.25 (each 1H, m); 2) protons in a methoxyl group, δ 3.89 (3H, s); 3) protons at C-α and C-β positions of the chalcone skeleton, δ 8.07, 8.12 (each 1H, d, J=15 Hz); 4) AB type aromatic protons, δ 6.89, 7.27 (each 1H, d, J=9 Hz); 5) an aromatic proton, δ 6.10 (1H, s); and 6) proton in a hydrogen-bonded hydroxyl group, δ 13.43 (1H, s). The ^{13}C nmr spectrum of **2** was analysed by comparing the spectrum of **2** with those of chalcone derivatives as shown in Table 1 suggesting the 3,4,2',4',6'-pentaoxygenated chalcone skeleton for **2**.[9,10] The EI-ms of **2** showed the intense fragment ions at m/z 221 ($C_{12}H_{13}O_4$, **9**), 203 ($C_{13}H_{15}O_2$, **10**), and 165 ($C_8H_5O_4$, **11**) suggesting that a prenyl group and a methoxyl group are located in the B ring while a prenyl group in the A ring. The location of the methoxyl group was supported by the following result that the uv spectrum of **2** showed a bathochromic shift (ca. +30 nm) upon addition of sodium methoxide suggesting a 4'-hydroxy-4-methoxychalcone moiety for a partial structure of **2**,[11] and that in the ^{13}C nmr spectrum of **2**, the chemical shift value of the methoxyl carbon atom (δ 56.4) suggested the methoxyl group to be mono-ortho-substituted.[12] From the above results, the formula **2** was proposed for the structure of antiarone C.

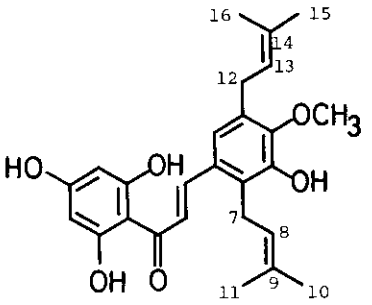
Antiarone D (**3**), yellow prisms, mp 161-164°C, $C_{26}H_{30}O_6$, gave a brown color with *methanolic ferric chloride*. The uv spectrum resembled that of **2**. The ^1H nmr spectrum showed the signals due to two prenyl groups, a methoxyl group, protons at C-α and C-β positions of the chalcone skeleton, AB type aromatic protons, an aromatic proton, and a hydrogen-bonded hydroxyl group. Comparison of the ^{13}C nmr spectra between **2** and **3** revealed that the chemical shift values of all the carbon atoms except those of the B ring and the methoxyl group of **3** were in good agreement with the values of the relevant atoms of **2** (Table 1). In the EI-ms of **3**, the fragmentation pattern of **3** resembled those of **2**. These results suggest that **3** is a structural isomer of **2**. The location of the methoxyl group was supported by the following result that the uv spectrum of **3** showed a bathochromic shift (ca. +60 nm) upon addition of sodium methoxide suggesting a 4,4'-dihydroxychalcone moiety for a partial structure of **3**,[8,11] and that in the ^{13}C nmr spectrum of **3**, the chemical shift value of the methoxyl carbon atom (δ 61.1) suggested the methoxyl group to be di-ortho-substituted.[12] From the above results, the formula **3** was proposed for the structure of antiarone D.

Antiarone E (**4**), yellow needles, mp 83-85°C, $C_{26}H_{30}O_6$, gave a brown color with methanolic ferric chloride. The uv spectrum resembled those of chalcone derivatives.[8] The ^1H nmr spectrum showed the signals due to two prenyl groups, a methoxyl group,



2 : R_1=CH_3 R_2=H

3 : R_1=H R_2=CH_3



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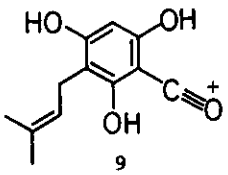

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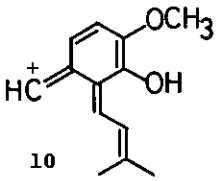

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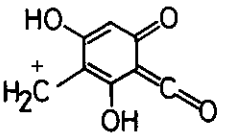

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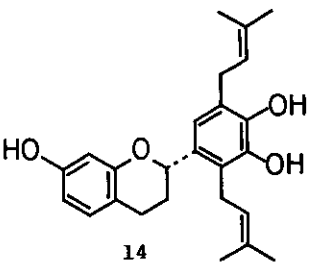

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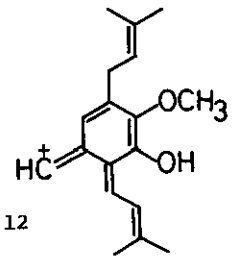

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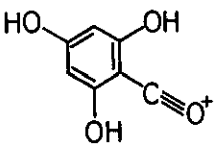

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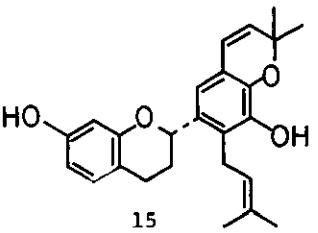

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Table 1 ^{13}C Nmr chemical shifts (ppm) of **2**, **3**, and **4**

	2	**3**	**4**		**2**	**3**	**4**
C-1	128.8*	127.8	131.6	C-7	25.6	25.8	25.7**
C-2	129.1*	137.1	128.2*	C-8	123.9	124.2*	123.7**
C-3	145.0	152.9	148.1*	C-9	131.8	132.3	131.7
C-4	149.5	146.9	148.7*	C-10	25.9	25.9	25.9
C-5	110.1	115.7	133.3	C-11	18.1	18.2	18.1
C-6	119.1	124.1	119.7	C-12	22.1	22.1	28.8
C=O	193.5	193.5	193.3	C-13	124.3	124.3*	124.0**
C-α	127.8	127.1	128.5	C-14	130.8	130.8	133.1
C-β	141.0	140.7	141.1	C-15	25.9	25.9	25.8
C-1'	105.8	105.8	105.8	C-16	17.9	17.9	18.0
C-2'	162.8	162.8	165.7	OCH_3	56.4	61.1	61.3
C-3'	108.2	108.2	96.1				
C-4'	165.9	165.9	165.6				
C-5'	95.4	95.3	96.1				
C-6'	160.2	160.2	165.7				

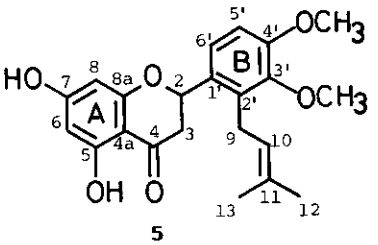
Measured in acetone-d_6 (100.4 MHz).

*, **; Assignments may be interchangeable in each column.

protons at C-α and C-β positions of the chalcone skeleton, three aromatic protons, and a hydrogen-bonded hydroxyl group. The ^{13}C nmr spectrum of **4** was analysed by comparing the spectrum with those of **2** and **3** (Table 1) indicating the 3,4,2',4',6'-pentaoxygenated chalcone structure. The EI-ms of **4** showed the fragment ions at m/z 271 (**12**) and 153 ($C_7H_5O_4$, base peak, **13**), suggesting that two prenyl groups and a methoxyl group are located in the B ring. The location of the prenyl groups was indicated to be at C-2 and C-5 positions by comparing the chemical shift values of the B ring carbon atoms of **4** with those of the relevant atoms of model compounds [**2**, **3**, kazinols A (**14**),[13] B (**15**)[13]] (Table 1). The location of the methoxyl group was supported by the bathochromic shift value (ca. +30 nm) in the uv spectrum upon addition of sodium methoxide,[11,14] and by the chemical shift value of the methoxyl carbon atom (δ 61.3).[12] From the above results, the formula **4** was proposed for the structure of antiarone E.

Antiarone F (**5**), colorless needles, mp 197-200°C, $[\alpha]_D^{27}$ 0°, $C_{22}H_{24}O_6$, gave a brown color with methanolic ferric chloride, and was positive to the magnesium-hydrochloric acid, sodium borohydride, and Gibbs test. The uv spectrum exhibited maxima at 206, 225 (sh), 289, and 325 (sh) nm, and resembled the spectra of flavanone derivatives,[8] and showed a bathochromic shift in the presence of sodium acetate. The ^1H nmr spectrum of **5** showed the signals due to a prenyl group, two methoxyl groups, ABX type protons, two aromatic protons, ortho-coupled aromatic protons, and a hydrogen-bonded hydroxyl group. The EI-ms of **5** showed the fragment ions at m/z 153 (**13**, base peak). The ^{13}C nmr spectrum of **5** was analysed by comparing the spectrum with those of model compounds [eriodictyol[9] (5,7,3',4'-tetrahydroxyflavanone), hesperetin[9] (5,7,3'-trihydroxy-4'-methoxyflavanone), homoeriodictyol[9] (5,7,4'-trihydroxy-3'-methoxyflavanone)] (Table 2). From this comparison compound **5** is assumed to be a 5,7,3',4'-tetraoxygenated flavanone derivative.[9] The chemical shift values of methoxyl carbon atoms (δ 56.1 and 60.7) indicate one of the methoxyl groups to be a di-ortho-substituted group, another to be a mono-ortho-substituted one.[12] From the above results, the formula **5** was proposed for the structure of antiarone F.

Antiarone G (**6**), colorless needles, mp 174-176°C, $[\alpha]_D^{27}$ 0°, $C_{26}H_{30}O_6$, was suggested to be a flavanone derivative by the color reaction tests. The uv spectrum resembled those of flavanone derivatives.[8] The ^1H nmr spectrum of **6** showed the signals due to two prenyl groups, a methoxyl group, ABX type protons, an aromatic proton, ortho-coupled aromatic protons, and a hydrogen-bonded hydroxyl group. The EI-ms of **6** showed the fragment ions at m/z 221 (**9**), 203 (**10**), and 165 (**11**, base peak). From



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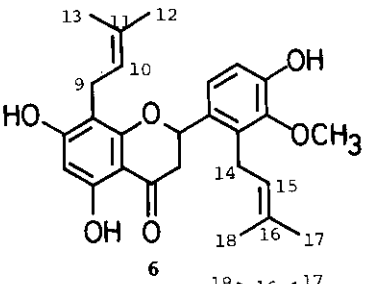

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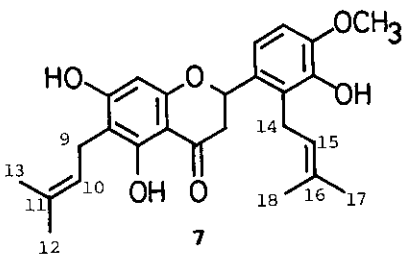

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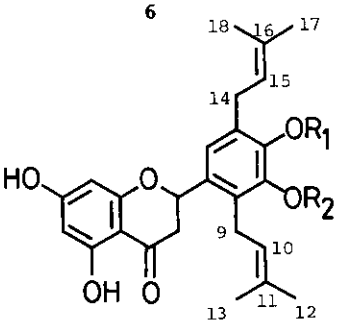

1 : $R_1=R_2=H$

8 : $R_1=CH_3$ $R_2=H$

8': $R_1=H$ $R_2=CH_3$

Table 2 ^{13}C Nmr chemical shift (ppm) of **1**, **5**, **6**, **7**, and **8**

	5	**6**	**7**	**8**	**1#**
C-2	77.0	76.9	77.1	76.7	77.2
C-3	43.2	43.2	43.4	42.9	43.2
C-4	197.5	197.9	197.6	196.9	197.5
C-4a	103.2	103.1	103.1	102.6	103.2
C-5	165.4	163.0	162.3	164.6	165.2
C-6	96.9	96.4	109.0	96.0	96.8
C-7	167.3	164.9	164.8	167.0	167.2
C-8	95.9	108.3	95.3	95.5	95.9
C-8a	164.6	161.4	162.2	164.1	164.5
C-1'	134.8	134.8	130.9	133.4	129.3
C-2'	130.6	129.9	127.0*	125.5*	125.8
C-3'	148.1*	146.7*	145.0*	146.2*	144.0
C-4'	154.1*	151.3*	148.1*	148.2*	144.0
C-5'	111.5	115.4	109.8	132.8	127.0
C-6'	124.5	123.7**	118.3	118.8	119.6
C-9	25.6	22.3	21.7**	24.9**	25.4*
C-10	123.3	123.7**	123.6***	123.5***	123.3**
C-11	131.8	131.2***	131.2***	131.1***	131.8**
C-12	25.8	25.7	25.8	25.4	25.8
C-13	18.0	17.8	17.8	17.5	18.0
C-14		25.6	25.2**	28.6**	29.1*
C-15		124.5**	124.2***	123.9***	124.3**
C-16		132.1***	131.6***	132.4***	132.9**
C-17		25.9	25.9	25.4	25.8
C-18		18.0	18.0	17.6	17.9
3'-OCH_3	60.7	60.1			
4'-OCH_3	56.1		56.4	60.8	

Measured in acetone-d_6 (100.4 MHz). # Our data.

*, **, ***; Assignments may be interchangeable in each column.

these results antiarone G is suggested to be a flavanone derivative having a prenyl group in the A ring along with a prenyl and a methoxyl group in the B ring. The ^{13}C nmr spectrum was analysed by comparing the spectrum with that of **5** (Table 2) indicating that **6** is a 5,7,3',4'-tetraoxygenated flavanone having a prenyl group at the C-2' position. The location of the methoxyl group was supported by the chemical shift value of the methoxyl carbon atom (δ 60.1).[12] In the ^{13}C nmr spectrum of **6** (gated decoupling with NOE), the signal of the carbon atom at the C-6 position was observed at δ 96.4 as a doublet of doublet (^{1}J=161.4 Hz, $^{3}J_{C6\text{-}OH5}$=7.3 Hz). This result suggests that the prenyl group is located at the C-8 position. From the above results, the formula **6** was proposed for the structure of antiarone G.

Antiarone H (**7**), *colorless needles, mp* 214-216°C, $[\alpha]_D^{27}$ 0°, $C_{26}H_{30}O_6$, was suggested to be a flavanone derivative by the color reaction tests. The uv spectrum resembled those of flavanone derivatives.[8] The ^{1}H nmr spectrum of **7** showed the signals due to two prenyl groups, a methoxyl group, ABX type protons, an aromatic proton, ortho-coupled aromatic protons, and a hydrogen-bonded hydroxyl group. The EI-ms of **7** showed the fragment ions at m/z 221 (**9**) and 165 (**11**, base peak). The ^{13}C nmr spectrum was analysed by comparing the spectrum with those of **5** and **6** (Table 2). In the ^{13}C nmr spectrum, the signal of the methoxyl carbon atom was observed at δ 56.4.[12] The above results indicate that **7** is a structural isomer of **6**. The location of the prenyl group was supported by the following results. The uv spectrum of **7** showed delayed bathochromic shift upon addition of aluminum chloride, while the spectrum of **6** showed a remarkable shift immediately after addition of aluminum chloride.[15] From the above results, the formula **7** was proposed for the structure of antiarone H.

Antiarone I (**8**), colorless needles, mp 192-195°C, $[\alpha]_D^{22}$ 0°, $C_{26}H_{30}O_6$, was suggested to be a flavanone derivative by the color reaction tests. The uv spectrum resembled those of flavanone derivatives.[8] The ^{1}H nmr spectrum of **8** showed the signals due to two prenyl groups, a methoxyl group, ABX type protons, three aromatic protons, and a hydrogen-bonded hydroxyl group. The EI-ms of **8** showed the fragment ions at m/z 271 (**12**) and 153 (**13**). *The ^{13}C nmr spectrum was analysed by comparing the* spectrum with those of (±)-sigmoidin A (**1**) and other model compounds[9] (Table 2). These results indicate that antiarone I is (±)-sigmoidin A 4'-monomethyl ether (**8**) or (±)-sigmoidin A 3'-monomethyl ether (**8'**). To discriminate the structures, antiarone I (**8**) was derived from antiarone E (**4**) by treating with silica gel. From the above results, the formula **8** was proposed for the structure of antiarone I.

On the basis of the derivation of **8** from **4**, the optical rotation value, and the

co-occurrence of chalcones (**2**, **3**, and **4**) and their relevent flavanones (**7**, **6**, and **8**), it is unlikely that antiarones F (**5**) – I (**8**) are genuine natural products.

EXPERIMENTAL

Abbreviations; s=singlet, d=doublet, t=triplet, m=multiplet, *br=broad, sh=shoulder, infl=inflection.* The general procedures followed as described in our previous paper.[3] The instruments used are described in our previous papers.[3,16]

Isolation of Antiarones C (**2**) – I (**8**) along with (±)-Sigmoidin A (**1**) from the Root Bark of A. toxicaria Lesch.

The benzene extract (10 g) of the root bark of A. toxicaria Lesch. such as reported in the previous paper,[6] was chromatographed on silica gel (250 g) with n-hexane containing increasing amount of ethyl acetate as eluent, each fraction (eluted volume of 300 ml) being monitored by tlc (fractions 1-48). The fractions eluted with n-hexane containing 15% ethyl acetate (frs. 10-18) were treated as follows. The fractions (10-13) were combined, and the mixture was evaporated to give a residue (0.1 g), which was fractionated by preparative tlc (silica gel, solvent systems, benzene:acetone=7:1, benzene:acetone=5:1, n-hexane:ethyl acetate=3:1) followed by crystallization from n-hexane-ether to give antiarones F (**5**, 13 mg) and G (**6**, 2 mg). The fraction 14 (0.3 g of residue) was fractionated by preparative tlc (benzene:acetone=10:1, n-hexane:acetone=2:1) followed by crystallization from n-hexane-ether to give antiarone H (**7**, 5 mg). The fraction 15 (0.5 g of residue) was fractionated by preparative tlc (n-hexane:acetone=3:1) followed by crystallization from n-hexane-ether to give antiarone I (**8**, 20 mg). The residue (0.2 g) of the combined fractions (frs. 16-18) was purified by crystallization from n-hexane-ether to give (±)-sigmoidin A (**1**, mp 188-191°C, $[\alpha]_D^{22}$ 0°, 120 mg). Identification of the known compound **1** was carried out by comparing the physical and spectral data of **1** with the published data.[7] The ^{13}C nmr spectrum of **1** was analysed as shown in Table 2.

The residue (0.4 g) of the fractions eluted with n-hexane containing 20% ethyl acetate (frs. 26-31) was rechromatographed on silica gel (50 g) with benzene containing 5% acetone as eluent, each fraction (eluted volume of 100 ml) being monitored by tlc (frs. 1'-10'). The residue (0.2 g) of the fractions (frs. 7'-8') was purified by preparative tlc (benzene:acetone=2:1) followed by crystallization from chloroform-ether to give antiarone E (**4**, 40 mg).

The acetone extract (16 g) as reported in the previous paper[6] was extracted with ether, and the ether solution was concentrated to afford the residue (7 g). This residue (7 g) was chromatographed on silica gel (200 g) with n-hexane containing increasing amount of ethyl acetate as eluent, each fraction (eluted volume of 100 ml) being monitored by tlc (frs. 1-36). The residue (0.2 g) of the fractions (frs. 26-31) eluted with n-hexane containing 40% ethyl acetate was fractionated by gel filtration (Sephadex LH-20, solvent system: methanol) to the fractions (frs. 1'-8', eluted volume of 100 ml each). The residue (68 mg) of the fractions (4'-5') was fractionated by preparative hplc (solvent system: n-hexane:ethyl acetate=1:1, column: Senshu Pak, SSC-Silica 4251-N, detector: uv 280 nm) to give antiarones C (**2**, 3 mg) and D (**3**, 4 mg).

Antiarone C (**2**)

Compound **2** was recrystallized from n-hexane-ether to give yellow prisms, mp 175-178°C. $FeCl_3$ test: positive (brown). EI-Ms: m/z 438 $[M]^+$ (base peak), 382, 326, 221, 203, 165. High-resolution ms (HR-Ms): m/z 438.2032 $[M]^+$ ($C_{26}H_{30}O_6$ requires: 438.2042), m/z 221.0802 ($C_{12}H_{13}O_4$ requires: 221.0814), m/z 203.1062 ($C_{13}H_{15}O_2$ requires: 203.1072), m/z 165.0208 ($C_8H_5O_4$ requires: 165.0188). Uv λ_{max}^{MeOH} nm (log ε): 210 (4.71), 261 (sh 4.02), 372 (4.43). Uv $\lambda_{max}^{MeOH+AlCl_3}$: 211 (4.70), 267 (sh 3.97), 412 (4.44). Uv $\lambda_{max}^{MeOH+NaOMe}$: 211 (4.95), 268 (sh 4.02), 340 (sh 4.14), 398 (4.38). Uv $\lambda_{max}^{MeOH+AcONa}$: 217 (4.97), 258 (sh 4.04), 374 (4.38). Ir ν_{max}^{KBr} cm^{-1} : 3550, 3375, 1620, 1600, 1560, 1490, 1440.

^{1}H Nmr (acetone-d_6): δ 1.64, 1.66 (each 3H, br s, C-9-CH_3), 1.76, 1.85 (each 3H, br s, C-14-CH_3), 3.27 (2H, br d, J=7 Hz, C-12-H x 2), 3.59 (2H, br d, J=7 Hz, C-7-H x 2), 3.89 (3H, s, C-4-OCH_3), 5.14 (1H, m, C-8-H), 5.25 (1H, m, C-13-H), 6.10 (1H, s, C-5'-H), 6.89 (1H, d, J=9 Hz, C-5-H), 7.27 (1H, d, J=9 Hz, C-6-H), 8.07 (1H, d, J=15 Hz, C-α-H), 8.12 (1H, d, J=15 Hz, C-β-H), 13.43 (1H, s, C-2'-OH).

Antiarone D (**3**)

Compound **3** was recrystallized from n-hexane-ether to give yellow prisms, mp 161-164°C. $FeCl_3$ test: positive (brown). EI-Ms: m/z 438 $[M]^+$, 382, 326, 221, 203, 165 (base peak). HR-Ms: m/z 438.2028 $[M]^+$ ($C_{26}H_{30}O_6$ requires: 438.2042). Uv λ_{max}^{EtOH} nm (log ε): 205 (4.30), 260 (sh 3.59), 373 (4.06). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 205 (4.34), 260 (sh 3.61), 322 (sh 3.60), 404 (4.06). Uv $\lambda_{max}^{EtOH+NaOMe}$: 216 (5.06), 266 (sh 3.61), 342 (sh 3.64), 434 (4.03). Uv $\lambda_{max}^{EtOH+AcONa}$: 212 (5.04), 260 (sh 3.62), 375 (3.97). Ir ν_{max}^{KBr} cm^{-1} : 3470, 3300, 1620, 1600, 1560, 1485, 1430. ^{1}H Nmr (acetone-d_6): δ 1.63, 1.68 (each 3H, br s, C-9-CH_3), 1.76, 1.87 (each 3H, br s, C-14-CH_3), 3.27 (2H, br d, J=7 Hz, C-12-H x 2), 3.57 (2H, br d, J=7 Hz, C-7-H x 2), 3.78 (3H, s, C-3-OCH_3), 5.11 (1H, m, C-8-H), 5.25 (1H, m, C-13-H), 6.09 (1H, s, C-5'-H), 6.83 (1H, d, J=9 Hz, C-5-H), 7.43 (1H, d, J=9 Hz, C-6-H), 8.07 (2H, s, C-α- and C-β-H), 14.45 (1H, s, C-2'-OH).

Antiarone E (**4**)

Compound **4** was recrystallized from chloroform-ether to give yellow needles, mp 83-85°C. $FeCl_3$ test: positive (brown). EI-Ms: m/z 438 $[M]^+$, 382, 369, 271, 270, 153 (base peak). HR-Ms: m/z 438.2050 $[M]^+$ ($C_{26}H_{30}O_6$ requires: 438.2042), m/z 153.0184 ($C_7H_5O_4$ requires: 153.0188). Uv λ_{max}^{MeOH} nm (log ε): 212 (4.70), 250 (sh 3.83), 360 (4.42). Uv $\lambda_{max}^{MeOH+AlCl_3}$: 211 (4.67), 256 (sh 3.81), 397 (4.49). Uv $\lambda_{max}^{MeOH+NaOMe}$: 272 (3.99), 391 (4.41). Uv $\lambda_{max}^{MeOH+AcONa}$: 215 (4.92), 250 (sh 3.97), 373 (4.38). Ir ν_{max}^{KBr} cm^{-1} : 3300 (br), 1625, 1600, 1560, 1540, 1500, 1480, 1450, 1420. ^{1}H Nmr (acetone-d_6): δ 1.66, 1.73 (each 3H, br s, C-9-CH_3), 1.75, 1.84 (each 3H, br s, C-14-CH_3), 3.35 (2H, br d, J=7 Hz, C-12-H x 2), 3.55 (2H, br d, J=7 Hz, C-7-H x 2), 3.77 (3H, s, C-4-OCH_3), 5.14 (1H, m, C-8-H), 5.30 (1H, m, C-13-H), 5.98 (2H, s, C-3'- and C-5'-H), 7.11 (1H, s, C-6-H), 8.09 (2H, s, C-α- and C-β-H), 12.04 (2H, br s, C-2'- and C-6'-OH).

Antiarone F (**5**)

Compound **5** was recrystallized from n-hexane-ether to give colorless needles, mp 197-200°C, $[\alpha]_D^{27}$ 0° (MeOH). $FeCl_3$ test: positive (brown). Mg-HCl test: positive (violet). $NaBH_4$ test: positive (red). Gibbs test: positive (blue). EI-Ms: m/z 384 $[M]^+$, 328, 217, 153 (base peak). HR-Ms: m/z 384.1560 $[M]^+$ ($C_{22}H_{24}O_6$ requires: 384.1572). Uv λ_{max}^{MeOH} nm (log): 206 (4.38), 225 (sh 4.03), 289 (3.84), 325 (sh 3.23). Uv $\lambda_{max}^{MeOH+AlCl_3}$: 206 (4.40), 220 (sh 4.17), 311 (4.01), 377 (3.23). Uv $\lambda_{max}^{MeOH+AcONa}$: 215 (4.83), 242 (sh 3.63), 323 (4.05). Ir ν_{max}^{KBr} cm^{-1} : 3200, 1645, 1620, 1600, 1495, 1455, 1425. ^{1}H Nmr (acetone-d_6): δ 1.65, 1.69 (each 3H, br s, C-11-CH_3), 2.68 (1H, dd, J=3 and 17 Hz, C-3-H), 3.22 (1H, dd, J=13 and 17 Hz, C-3-H), 3.55 (2H, br d, J=8 Hz, C-9-H x 2), 3.78, 3.88 (each 3H, s, C-3'- and C-4'-OCH_3), 5.07 (1H, m, C-10-H), 5.63 (1H, dd, J=3 and 13 Hz, C-2-H), 5.96 (2H, s, C-6- and C-8-H), 7.00 (1H, d, J=8 Hz, C-5'-H), 7.33 (1H, d, J=8 Hz, C-6'-H), 12.17 (1H, s, C-5-OH).

Antiarone G (**6**)

Compound **6** was recrystallized from n-hexane-ether to give colorless needles, mp 174-176°C, $[\alpha]_D^{27}$ 0° (MeOH). $FeCl_3$ test: positive (brown). Mg-HCl test: positive (violet). $NaBH_4$ test: positive (red). Gibbs test: negative. EI-Ms: m/z 438 $[M]^+$, 382, 339, 326, 221, 203, 165 (base peak). HR-Ms: m/z 438.2050 $[M]^+$ ($C_{26}H_{30}O_6$ requires: 438.2042). Uv λ_{max}^{EtOH} nm (log ε): 205 (4.58), 294 (3.99), 333 (sh 3.43). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 205 (4.63), 220 (infl 4.39), 314 (4.18), 373 (sh 3.50). Uv $\lambda_{max}^{EtOH+AcONa}$: 295 (3.86), 336 (3.89). Ir ν_{max}^{KBr} cm^{-1} : 3420, 1640, 1620, 1590, 1500, 1480, 1435. ^{1}H Nmr (acetone-d_6): δ 1.55, 1.60 (each 3H, br s, C-11-CH_3), 1.65, 1.67 (each 3H, br s, C-16-CH_3), 2.65 (1H, dd,

J=3 and 17 Hz, C-3-H), 3.14 (2H, br d, J=7 Hz, C-9-H x 2), 3.17 (1H, dd, J=13 and 17 Hz, C-3-H), 3.53 (2H, br d, J=7 Hz, C-14-H x 2), 3.79 (3H, s, C-3'-OCH_3), 5.15 (2H, m, C-10- and C-15-H), 5.56 (1H, dd, J=3 and 13 Hz, C-2-H), 6.03 (1H, s, C-6-H), 6.88 (1H, d, J=9 Hz, C-5'-H), 7.27 (1H, d, J= C-6'-H), 12.14 (1H, s, C-5-OH).

Antiarone H (7)

Compound **7** was recrystallized from n-hexane-ether to give colorless needles, mp 214-216°C, $[\alpha]_D^{27}$ 0° (MeOH). $FeCl_3$ test: positive (brown). Mg-HCl test: positive (violet). $NaBH_4$ test: positive (orange). Gibbs test: positive (blue). EI-Ms: m/z 438 $[M]^+$, 382, 339, 326, 221, 203, 165 (base peak). HR-Ms: m/z 438.2032 $[M]^+$ ($C_{26}H_{30}O_6$ requires: 438.2042). Uv λ_{max}^{EtOH} nm (log ε): 206 (4.55), 294 (4.00), 340 (sh 3.26). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 206 (4.58), 299 (3.93), 340 (sh 3.24). Uv $\lambda_{max}^{EtOH+AcONa}$: 211 (5.06), 294 (3.88), 334 (3.84). Ir ν_{max}^{KBr} cm^{-1} : 3450, 3370, 1640, 1610, 1500, 1440. ^1H Nmr (acetone-d_6): δ 1.64, 1.68 (each 3H, br s, C-16-CH_3), 1.75, 1.89 (each 3H, br s, C-11-CH_3), 2.66 (1H, dd, J=3 and 17 Hz, C-3-H), 3.16 (1H, dd, J=13 and 17 Hz, C-3-H), 3.25 (2H, br d, J=7 Hz, C-9-H x 2), 3.52 (2H, br d, J=7 Hz, C-14-H x 2), 3.88 (3H, s, C-4'-OCH_3), 5.14 (1H, m, C-15-H), 5.24 (1H, m, C-10-H), 5.62 (1H, dd, J=3 and 13 Hz, C-2-H), 6.03 (1H, s, C-8-H), 6.92 (1H, d, J=9 Hz, C-5'-H), 7.07 (1H, d, J=9 Hz, C-6'-H), 12.47 (1H, s, C-5-OH).

Antiarone I (8)

Compound **8** was recrystallized from n-hexane-ether to give colorless needles, mp 192-195°C, $[\alpha]_D^{22}$ 0° (EtOH). $FeCl_3$ test: positive (brown). Mg-HCl test: positive (violet). $NaBH_4$ test: positive (orange). EI-Ms: m/z 438 $[M]^+$, 382, 369, 271, 270, 153 (base peak). HR-Ms: m/z 438.2037 $[M]^+$ ($C_{26}H_{30}O_6$ requires: 438.2042). Uv λ_{max}^{EtOH} nm (log ε): 212 (4.67), 226 (infl 4.42), 288 (4.21), 325 (sh 3.45). Uv $\lambda_{max}^{EtOH+AlCl_3}$: 213 (4.66), 311 (4.33), 377 (3.53). Uv $\lambda_{max}^{EtOH+AcONa}$: 215 (4.70), 248 (sh 3.71), 290 (3.88), 324 (4.31). Ir ν_{max}^{KBr} cm^{-1} : 3400, 3120, 1635, 1600, 1580, 1490, 1450, 1420. ^1H Nmr (acetone-d_6): δ 1.65, 1.71 (each 3H, br s, C-11-CH_3), 1.68, 1.74 (each 3H, br s, C-16-CH_3), 2.67 (1H, dd, J=3 and 17 Hz, C-3-H), 3.15 (1H, dd, J=13 and 17 Hz, C-3-H), 3.37 (2H, br d, J=7 Hz, C-14-H x 2), 3.50 (2H, br d, J=7 Hz, C-9-H x 2), 3.77 (3H, s, C-4'-OCH_3), 5.15 (1H, m, C-10-H), 5.31 (1H, m, C-15-H), 5.65 (1H, dd, J=3 and 17 Hz, C-2-H), 5.96 (2H, s, C-6- and C-8-H), 6.96 (1H, s, C-6'-H), 12.17 (1H, s, C-5-OH).

Formation of Antiarone I (8) from Antiarone E (4)

Antiarone E (**4**, 10 mg) dissolved in acetone was absorbed on the two sheets of silica gel plate (Wakogel B-5F, 20 cm x 20 cm x 0.5 mm). After the plates were left for 1 h at room temperature, the plates were developed by the solvent (benzene:acetone=2:1). After usual treatment, antiarones I (**8**, 2 mg) and E (**4**, 7 mg) were obtained. Identification of antiarone I (**8**) thus obtained was carried out by mixed melting point determination with authentic sample and by comparison of the ir and ^1H nmr spectra with those of authentic sample.

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