

TWO NEW PRENYLAURONES, ANTIARONES A AND B, FROM THE ROOT BARK OF
ANTIARIS TOXICARIA LESCH.^{#,1}

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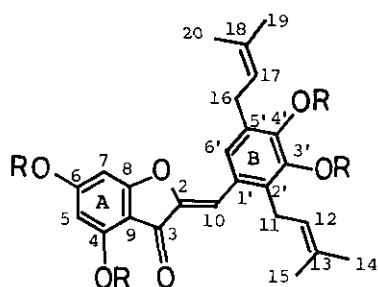
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Abstract — Two new prenylated aurones, antiarones A and B, were isolated from the root bark of Antiaris toxicaria Lesch. On the basis of spectral evidence, the structures of antiarones A and B were shown to be **1** and **2**, respectively. These two compounds are the first examples of prenylaurones.

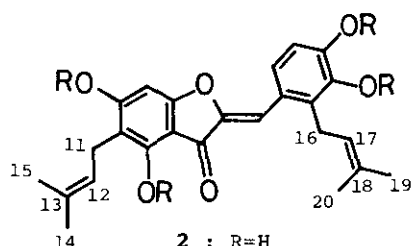
Previously we reported a series of isoprenoid-substituted phenolic compounds isolated from the mulberry tree and related plants.² Some of these compounds are regarded biogenetically as natural Diels-Alder type adducts of dehydroprenylphenols and chalcones. In continuation of our studies on the isoprenoid-substituted phenols from the Moraceae plants, we examined the phenolic constituents of the root bark of Artocarpus heterophyllus Lamk., Indonesian Moraceous plant, and reported the characterization of two prenylflavones, artonins A and B,³ along with two Diels-Alder type adducts, artonins C and D.⁴ On the other hand, Antiaris toxicaria Lesch., an Indonesian Moraceous plant, is a big tree grown in forest and known as "upas tree", of which latex from wood has been used for an arrow poison. On the constituents of the plant, many investigators reported a series of cardiac glycosides isolated from the latex and the seeds.⁵ This paper describes the characterization of two new prenylaurones 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. Antiarones A (**1**) and B (**2**) were isolated from the acetone extract as described in "EXPERIMENTAL".

Antiarone A (**1**) is yellow needles, mp 220-223 °C, exhibited positive ferric chloride reaction. The molecular formula of **1** was determined by HR-ms to be C₂₅H₂₆O₆. Treatment of **1** with acetic anhydride in pyridine gave the tetraacetate (**1a**). The ir spectrum of **1** disclosed absorption bands due to hydroxyl, conjugated



1 : R=H
1a : R=COCH₃



2 : R=H
2a : R=COCH₃

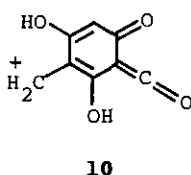
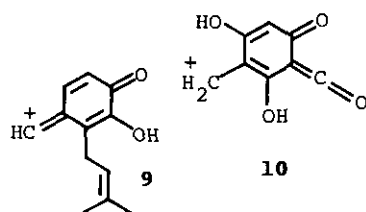
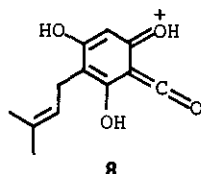
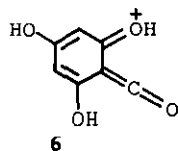
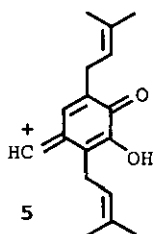
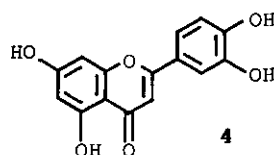
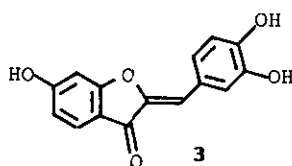
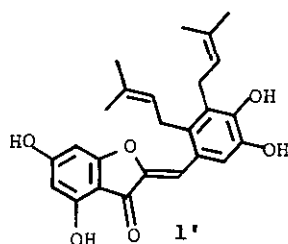


Table 1 ¹³C Nmr chemical shifts (ppm)

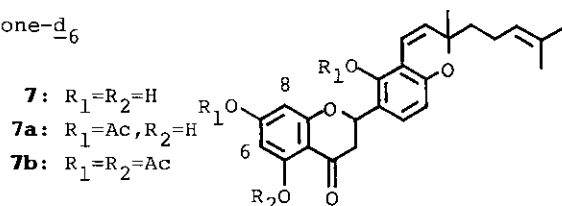
	1*	2*	3**	11*		1*	2*		4***
C-2	147.7	147.6	145.6	147.6	C-11	25.8	21.8	C-2	164.5
C-3	182.0	183.4	180.9	181.7	C-12	124.0	123.4	C-3	103.3
C-4	158.9	155.9	125.3	158.8	C-13	132.0	131.6	C-4	182.2
C-5	98.5	110.9	115.9	98.6	C-14	26.0	25.9	C-5	162.1
C-6	168.3	166.2	167.3	168.4	C-15	18.2	17.9	C-6	99.2
C-7	91.9	91.8	98.2	92.1	C-16	28.7	25.8	C-7	164.7
C-8	168.2	165.4	165.9	168.3	C-17	123.1	123.9	C-8	94.2
C-9	104.4	104.1	113.7	104.3	C-18	133.5	131.9	C-8a	157.9
C-10	108.8	109.1	112.6	110.4	C-19	26.0	25.9	C-4a	104.2
C-1'	123.6	124.0	123.3	126.1	C-20	17.9	18.2	C-1'	122.1
C-2'	128.9	130.5	111.5	133.6				C-2'	113.8
C-3'	143.8	144.1	145.3	115.3				C-3'	146.2
C-4'	145.9	147.2	147.7	161.8				C-4'	150.1
C-5'	127.0	113.9	117.9	115.3				C-5'	116.4
C-6'	125.5	124.6	124.2	133.6				C-6'	119.3
			OCH ₃	55.8					

Solvent: *; acetone-d₆ **; DMSO-d₆ at 60 °C ***; DMSO-d₆

carbonyl, and benzene ring moieties, and the uv spectrum exhibited maxima at 205, 267, 340, and 402 nm and was similar to those of aurone derivatives.⁶ Moreover the uv spectrum of **1** showed remarkable bathochromic shift upon addition of aluminum chloride, while the spectrum in the presence of aluminum chloride showed the hypsochromic shift on addition of acid. These results suggest the presence of ortho-dihydroxy groups in the structure.⁶ The ¹H nmr spectrum showed the signals of the following protons: 1) protons in two 3,3-dimethylallyl (prenyl) groups, δ 1.66, 1.78, 1.81, 1.86 (each 3H, br s), 3.39 (2H, br d, $J=7.3$ Hz), 3.57 (2H, br d, $J=6.8$ Hz), 5.10, 5.40 (each 1H, m), 2) a pair of meta coupled aromatic protons, δ 6.13 (1H, d, $J=1.8$ Hz), 6.28 (1H, d, $J=1.8$ Hz), 3) two aromatic and/or olefinic protons, δ 6.83, 7.71 (each 1H, s). In the ¹³C nmr studies, the carbon atoms of **1** were assigned by the off-resonance decoupling technique as well as by comparing the ¹³C nmr spectrum of **1** with those of sulfuretin (**3**)⁷, luteolin (**4**)⁷, and other flavonoids⁷ (Table 1). The chemical shifts of the carbon atoms at the C-3' and C-4' positions were similar to those of the corresponding carbon atoms of **3** and other 3',4'-dioxxygenated flavonoids.⁷ The phloroglucinol type oxygenated pattern for the A ring was suggested by comparison between the chemical shifts of the carbon atoms in the A ring of **1** and those of the relevant carbon atoms of **4** and other 5,7-dioxxygenated flavonoids.⁷ The HR-ms of **1** showed the fragment ions at m/z 257 (**5**, C₁₇H₂₁O₂) and 153 (**6**, C₇H₅O₄). From these results, antiarone A seems to be a 4,6,3',4'-tetrahydroxyaurone having two prenyl groups in the B ring. Presence of 4,6-dihydroxyl groups in the A ring was confirmed by the acetylation shift values of the meta coupled protons in the A rings of **1a** and model compound, sang-genon N acetates (**7a**, **b**) (Table 2).⁸ The proton signals at δ 7.71 and 6.83 ppm of **1** were assigned to the B ring proton and the proton at the C-10 position,⁶ respectively, and this assignment was supported by the acetylation shift values of the relevant protons (Table 2). The signal at δ 7.71 ppm was assigned to the proton at the C-2' or C-6' positions on the basis of the chemical shifts of the B ring protons of aurone derivatives.⁶ From these results, two possible structures (**1** and **1'**) were proposed. Discrimination between these structures was carried out as follows: In the ¹³C nmr spectrum of **1** (off-resonance decoupling spectrum), the chemical shift of the doublet signal at δ 125.5 ppm was similar to that of the carbon atom at the C-6' position of **3**⁷ rather than to that of the carbon atom at the C-2' position (Table 1). From above results, formula **1** was proposed for the structure of antiarone A.

Table 2 Acetylation shift values (Δ ppm)

	5-H	7-H	6'-H	10-H		6-H	8-H		6-H	8-H
1	6.13	6.28	7.71	6.83	7	6.00	6.00	7	6.00	6.00
1a	6.84	7.17	8.05	6.95	7a	6.22	6.25	7b	6.55	6.70
Δ	-0.71	-0.89	-0.34	-0.12	Δ	-0.22	-0.25	Δ	-0.55	-0.70

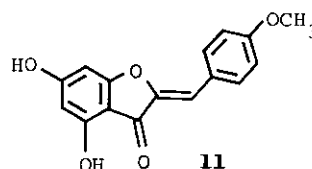
Measured in acetone- d_6 

Antiarone B (**2**) is yellow needles, mp 217-220 °C, exhibited positive ferric chloride reaction. The molecular formula of **2** was determined by HR-ms to be $C_{25}H_{26}O_6$. Treatment of **2** with acetic anhydride in pyridine gave the tetraacetate (**2a**). The uv spectrum was similar to those of **1** and other aurone derivatives.⁶ Furthermore the uv spectrum of **2** showed a similar bathochromic shift upon addition of aluminum chloride as in **1**, while the spectrum in the presence of aluminum chloride showed a hypsochromic shift on addition of acid to the solution.⁶ From these results, antiarone B seems to be an aurone derivative having the ortho-dihydroxyl groups in the structure⁶ and a structural isomer of **1**. The 1H nmr spectrum showed the signals of the following protons: 1) protons in two prenyl groups, δ 1.65, 1.67, 1.76, 1.88 (each 3H, br s), 3.31 (2H, br d, $J=7.1$ Hz), 3.60 (2H, br d, $J=6.8$ Hz), 5.13, 5.25 (each 1H, m), 2) a pair of ortho coupled aromatic protons, δ 6.85, 7.67 (each 1H, d, $J=8.6$ Hz), 3) two aromatic and/or olefinic protons, δ 6.39, 6.87 (each 1H, s). The HR-ms of **2** showed the fragment ions at m/z 221 (**8**, $C_{12}H_{13}O_4$), 189 (**9**, $C_{12}H_{13}O_2$), and 165 (**10**, $C_8H_5O_4$). Comparison of the ^{13}C nmr spectrum of **2** with those of **1** and **4** suggests that **2** is a 4,6,3',4'-tetrahydroxyaurone derivative (Table 1). From above results, the 2'-prenyl-3',4'-dihydroxyphenyl partial structure for the B ring was confirmed and the location of the prenyl group in the A ring was suggested to be at the C-5 or C-7 position. On comparison of the chemical shifts of the carbon atoms in the A ring of **2** with those of the relevant carbon atoms of **1**, 6- or 8-prenylflavonoids,² and 2- or 4-prenylxanthenes,² the carbon signal at δ 91.8 ppm observed as a doublet signal in the off-resonance decoupling spectrum was assigned to the carbon atom at the C-7 position. Accordingly the location of the prenyl group was supported to be at the C-5 position. From above results, formula **2** was

proposed for the structure of antiarone B.

On the structures of antiarones A (**1**) and B (**2**), the stereochemistry of the double bond at the C-10 position was suggested to be *Z*-form from the chemical shifts of the carbon atoms at the C-10 positions⁹ as follows: **1**, δ 108.8 ppm; **2**, δ 109.1 ppm. To our knowledge, antiarones A (**1**) and B (**2**) are the first examples of prenylaurones. On the other hand, the signals due to hydrogen-bonding between 4-hydroxyl group and C-3 carbonyl group were not observed in the ^1H nmr spectra of antiarones A (**1**) and B (**2**). This fact coincided with the results from ir and uv spectroscopic studies.^{10, 11} In this point of view 4,6-dihydroxy-4'-methoxyaurone (**11**) was synthesized in order to corroborate the absence of hydrogen-bonded hydroxyl group in the 4-hydroxyaurone derivative.

The compound **11** showed no any signal due to hydrogen-bonded hydroxyl group in the ^1H nmr spectrum. The ^{13}C nmr spectral data of **11** were summarized in Table 1.



EXPERIMENTAL

Abbreviations: s=singlet, d=doublet, t=triplet, m=multiplet, br=broad, sh=shoulder, inf=inflection. The general procedures followed as described in our previous paper.¹² The instruments used are described in our previous paper.¹³

Isolation of Antiarones A (**1**) and B (**2**) from the Root Bark of *A. toxicaria* Lesch.

The dried root bark of *A. toxicaria* Lesch. (750 g) collected in Botanical Garden of Bogor, Indonesia in February 1988, and identified by members of the botanical garden, was extracted with *n*-hexane (5 l) at room temperature for 3 days, and such was repeated two more times. The residue was extracted successively with benzene (5 l x 3) and acetone (5 l x 3) as described above. Evaporation of the *n*-hexane, benzene, and acetone solutions to dryness yielded 8 g, 10 g, and 16 g of the residue, respectively. The acetone extract (16 g) was extracted with ether. 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 being monitored by tlc. The fraction eluted with *n*-hexane containing 33% ethyl acetate was evaporated to give a residue (0.6 g), which was fractionated by gel filtration (Sephadex LH-20, solvent system: methanol) and by preparative hplc (solvent system: acetonitrile:water=7:3, column: Senshu Pak, C-8-4301-P) to give antiarones A (**1**, 5 mg) and B (**2**, 3.5 mg).

Antiarone A (**1**)

Compound **1** was recrystallized from chloroform-ether to give yellow needles, mp 220-223 °C. FeCl_3 test: brown. EI-MS: m/z 422 $[\text{M}]^+$, 407, 353, 270, 257, 243, 201, 153 (base peak). High-resolution ms (HR-ms), m/z 422.1732 $[\text{M}]^+$ ($\text{C}_{25}\text{H}_{26}\text{O}_6$ requires: 422.1729), 353.1010 ($\text{C}_{20}\text{H}_{17}\text{O}_6$ requires: 353.1025), 257.1525 ($\text{C}_{17}\text{H}_{21}\text{O}_2$ requires: 257.1542), 153.0189 ($\text{C}_7\text{H}_5\text{O}_4$ requires: 153.0188). Uv $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 205 (4.61), 267 (3.87), 340 (4.02), 402 (4.35). Uv $\lambda_{\text{max}}^{\text{MeOH}+\text{AlCl}_3}$: 205 (4.61), 290 (3.81), 351 (3.89), 542 (4.50). Uv $\lambda_{\text{max}}^{\text{MeOH}+\text{AlCl}_3+\text{HCl}}$: 272, 356, 410, 466 nm. Ir $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3540, 3480, 1660 (sh), 1640, 1620 (sh), 1600, 1580 (sh), 1520, 1450. ^1H Nmr (acetone- d_6): δ 1.66, 1.78, 1.81, 1.86 (each 3H, br s, C-13- and C-18- CH_3), 3.39 (2H, br d, $J=7.3$ Hz, C-11- or C-16-H x 2), 3.57 (2H, br d, $J=$

6.8 Hz, C-16- or C-11-H x 2), 5.10, 5.40 (each 1H, m, C-12- and C-17-H), 6.13 (1H, d, $J=1.8$ Hz, C-5-H), 6.28 (1H, d, $J=1.8$ Hz, C-7-H), 6.83 (1H, s, C-10-H), 7.71 (1H, s, C-6'-H).

Antiarone A Tetraacetate (1a)

A mixture of **1** (5 mg), acetic anhydride (0.1 ml), and pyridine (0.1 ml) was kept at room temperature for 30 min and treated as usual. Antiarone A tetraacetate (**1a**) was crystallized from *n*-hexane-ether to give pale yellow needles, (3 mg), mp 150-152 °C. EI-MS, m/z 590 $[M]^+$. 1H Nmr (acetone- d_6): δ 1.66, 1.76, 1.78, 1.83 (each 3H, br s, C-13- and C-18-CH₃), 2.33 (6H, s, COCH₃ x 2), 2.35, 2.36 (each 3H, s, COCH₃), 3.29 (2H, br d, $J=7.0$ Hz, C-11- or C-16-H x 2), 3.40 (2H, br d, $J=6.8$ Hz, C-16- or C-11-H x 2), 5.00, 5.30 (each 1H, m, C-12- and C-17-H), 6.84 (1H, d, $J=2.0$ Hz, C-5-H), 6.95 (1H, s, C-10-H), 7.17 (1H, d, $J=2.0$ Hz, C-7-H), 8.05 (1H, s, C-6'-H).

Antiarone B (2)

Compound **2** was recrystallized from chloroform to give yellow needles, mp 217-220 °C. FeCl₃ test: brown. EI-MS, m/z 422 $[M]^+$, 323, 247, 234, 221, 189, 165 (base peak). HR-MS, m/z : 422.1726 $[M]^+$ (C₂₅H₂₆O₆ requires: 422.1729), 221.0795 (C₁₂H₁₃O₄ requires: 221.0813), 189.0900 (C₁₂H₁₃O₂ requires: 189.0915), 165.0202 (C₈H₅O₄ requires: 165.0188). Uv λ_{max}^{MeOH} nm (log ϵ): 206 (4.45), 269 (3.76), 344 (3.58), 401 (4.19). Uv $\lambda_{max}^{MeOH+AlCl_3}$: 207 (4.46), 289 (3.65), 355 (3.83), 396 (3.90), 522 (4.26). Uv $\lambda_{max}^{MeOH+AlCl_3+HCl}$: 234, 319, 362, 410 (sh), 464 nm. Ir ν_{max}^{KBr} cm⁻¹: 3420, 1660, 1642, 1610, 1580. 1H Nmr (acetone- d_6): δ 1.65, 1.67, 1.76, 1.88 (each 3H, br s, C-13- and C-18-CH₃), 3.31 (2H, br d, $J=7.1$ Hz, C-11- or C-16-H x 2), 3.60 (2H, br d, $J=6.8$ Hz, C-16- or C-11-H x 2), 5.13, 5.25 (each 1H, m, C-12- and C-17-H), 6.39 (1H, s, C-7-H), 6.85 (1H, d, $J=8.6$ Hz, C-5'-H), 6.87 (1H, s, C-10-H), 7.67 (1H, d, $J=8.6$ Hz, C-6'-H).

Antiarone B Tetraacetate (2a)

A mixture of **2** (4 mg), acetic anhydride (0.1 ml) and pyridine (0.1 ml) was kept at room temperature for 30 min and treated as usual. Antiarone B tetraacetate (**2a**) was crystallized from *n*-hexane-ether to give pale yellow needles, (2 mg), mp 170-173 °C. EI-MS, m/z 590 $[M]^+$. 1H Nmr (acetone- d_6): δ 1.65 (6H, br s, C-13- and C-18-CH₃), 1.77, 1.85 (each 3H, br s, C-13- and C-18-CH₃), 2.05, 2.29, 2.36, 2.37 (each 3H, s, COCH₃), 3.28, 3.49 (each 2H, br d, $J=7.0$ Hz, C-11- and C-16-H x 2), 5.01 (2H, m, C-12- and C-17-H), 6.95 (1H, s, C-10-H), 7.23 (1H, s, C-7-H), 7.28 (1H, d, $J=8.8$ Hz, C-5'-H), 8.14 (1H, d, $J=8.8$ Hz, C-6'-H).

Synthesis of 4,6-Dihydroxy-4'-methoxyaurone (11)

To a mixture of 2,4,6-trimethoxymethoxyacetophenone (1 g) and *p*-anisaldehyde (650 mg) in ethanol (20 ml) was added 25% aqueous potassium hydroxide (5 ml). The mixture was stirred at room temperature for 6 h, and then the reaction mixture was treated as usual. The product was purified by preparative tlc (*n*-hexane:ether=1:1) to give 4-methoxy-2',4',6'-trimethoxymethoxychalcone (**12**, 500 mg). The compound **12** showed the following data: pale yellow needles, mp 68-69 °C. EI-MS, m/z 418 $[M]^+$. Anal. Calcd for C₂₂H₂₆O₈: C, 63.16; H, 6.22. Found: C, 62.98; H, 6.29. Ir ν_{max}^{KBr} cm⁻¹: 1650, 1605, 1515. 1H Nmr (CDCl₃, 90 MHz): δ 3.37 (6H, s, CH₂OCH₃ x 2), 3.48 (3H, s, CH₂OCH₃), 3.81 (3H, s, OCH₃), 5.11 (4H, s, CH₂OCH₃ x 2), 5.17 (2H, s, CH₂OCH₃), 6.57 (2H, s, C-3'- and C-5'-H), 6.77 (1H, d, $J=17$ Hz, C- α -H), 6.88 (2H, d, $J=9$ Hz, C-3- and C-5-H), 7.35 (1H, d, $J=17$ Hz, C- β -H), 7.46 (2H, d, $J=9$ Hz, C-2- and C-6-H).

To a solution of **12** (450 mg) in methanol (20 ml) was added 3N HCl (3 ml). The solution was stirred at room temperature for 1 h. The reaction mixture was treated as usual and the product was purified by preparative tlc (*n*-hexane:ether=1:1) to give 2'-hydroxy-4-methoxy-4',6'-dimethoxymethoxychalcone (**13**, 130 mg). The compound **13** showed the following data: yellow needles, mp 100 °C. EI-MS, m/z 374 $[M]^+$. Anal. Calcd for C₂₀H₂₂O₇: C, 64.17; H, 5.88. Found: C, 64.14; H, 5.97. Ir ν_{max}^{KBr} cm⁻¹: 3450, 1620, 1605, 1580, 1550, 1515. 1H Nmr (CDCl₃, 90 MHz): δ 3.48, 3.54 (each 3H, s, CH₂OCH₃), 3.85 (3H,

s, OCH_3), 5.20, 5.30 (each 2H, s, CH_2OCH_3), 6.26, 6.32 (each 1H, d, $J=2$ Hz, C-3'- and C-5'-H), 6.93 (2H, d, $J=9$ Hz, C-3- and C-5-H), 7.55 (2H, d, $J=9$ Hz, C-2- and C-6-H), 7.80 (2H, s, C- α - and C- β -H), 13.79 (1H, s, C-2'-OH).

To a solution of **13** (100 mg) in methanol (20 ml) was added 25% aqueous potassium hydroxide (2 ml) and 35% hydrogen peroxide (2 ml).¹⁴ The reaction mixture was stirred at room temperature for 7 h. After treated as usual, the product was purified by preparative tlc (n-hexane:ether=1:2) to give 4'-methoxy-4,6-dimethoxymethoxyaurone (**14**, 30 mg). The compound **14** showed the following data: pale yellow needles, mp 117-118 °C. EI-MS, m/z 372 $[M]^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_7$: C, 64.52; H, 5.38. Found: C, 63.84; H, 5.44. $\text{Ir } \nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1695, 1655, 1600 (sh), 1590, 1510, 1490. $^1\text{H Nmr}$ (CDCl_3 , 90 MHz): δ 3.51, 3.54 (each 3H, s, CH_2OCH_3), 3.86 (3H, s, OCH_3), 5.26, 5.37 (each 2H, s, CH_2OCH_3), 6.50, 6.63 (each 1H, d, $J=2$ Hz, C-5- and C-7-H), 6.75 (1H, s, C-10-H), 6.95 (2H, d, $J=9$ Hz, C-3'- and C-5'-H), 7.83 (2H, d, $J=9$ Hz, C-2'- and C-6'-H).

To a solution of **14** (25 mg) in methanol (15 ml) was added 3N HCl (3 ml). The reaction mixture was refluxed for 20 min. After treated as usual, the product was purified by preparative tlc (ether only) to give 4,6-dihydroxy-4'-methoxyaurone (**11**, 8 mg). The compound **11** showed the following data: yellow needles, mp 240-243 °C. EI-MS, m/z 284 $[M]^+$. HR-MS, m/z 284.0710 $[M]^+$ ($\text{C}_{16}\text{H}_{12}\text{O}_5$ requires: 284.0684). $\text{Uv } \lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 205 (4.24), 220 (sh 4.15), 245 (sh 3.91), 335 (sh 4.12), 388 (4.33). $\text{Uv } \lambda_{\text{max}}^{\text{EtOH+AlCl}_3}$: 206 (4.26), 224 (4.24), 260 (sh 3.75), 350 (4.09), 387 (4.18), 445 (4.28). $\text{Ir } \nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3430, 3150, 1670, 1645, 1605 (sh), 1590, 1515, 1465. $^1\text{H Nmr}$ (acetone- d_6 , 400 MHz): δ 3.88 (3H, s, 4'- OCH_3), 6.15, 6.36 (each 1H, d, $J=1.8$ Hz, C-5- and C-7-H), 6.63 (1H, s, C-10-H), 7.05 (2H, d, $J=9.0$ Hz, C-3'- and C-5'-H), 7.91 (2H, d, $J=9.0$ Hz, C-2'- and C-6'-H), 9.5-10.0 (2H, br, C-4- and C-6-OH).

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