Two New Dihydrochalcone Derivatives, Antiarones J and K, from the Root Bark of Antiaris toxicaria

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TWO NEW DIHYDROCHALCONE DERIVATIVES, ANTIARONES J AND K, FROM THE ROOT BARK OF *ANTIARIS TOXICARIA*[1]

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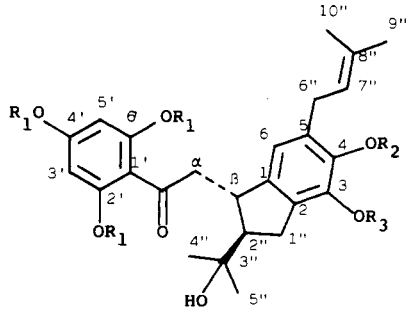
ABSTRACT.—Two new dihydrochalcone derivatives, antiarones J [**1**] and K [**2**], were isolated from the MeOH extract of the root bark of *Antiaris toxicaria*. The structure of antiarone J was identified on the basis of spectroscopic data, and the structure of antiarone K was determined on the basis of X-ray crystallographic analysis and spectroscopic data. Antiarones J and K are regarded as chalcone derivatives having an isoprenoid moiety at the C-2 position.

In the course of our studies on the phenolic compounds isolated from the mulberry tree and related plants (1), we reported the structure determination of the isoprenoid-substituted phenolic compounds isolated from the Indonesian moraceous plants, *Artocarpus heterophyllus* Lamk. (2,3), *Artocarpus communis* Forst. (4), and *Artocarpus rigida* Bl. (5). On the other hand, *Antiaris toxicaria* Lesch. (Moraceae), an Indonesian plant, is known as "upas tree," latex from the wood of which has been used for an arrow poison (6). Many investigators reported a series of cardiac glycosides isolated from the latex and the seeds (6), while we reported the characterization of two prenylaurones (7) and three prenylchalcones along with four prenylflavanones (8). This paper describes the characterization of two new isoprenoid-substituted dihydrochalcone derivatives isolated from the root bark.

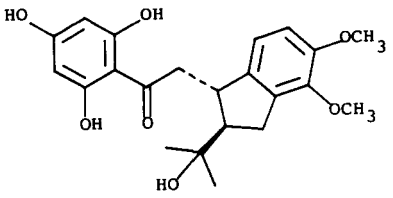
The root bark of *An. toxicaria*, collected in Indonesia, was extracted with MeOH. Antiarones J [**1**] and K [**2**] were isolated from the extract.

Antiarone J [**1**], colorless prisms, mp 120–122°, $[\alpha]^{25}D$ 0°, gave a violet color with $FeCl_3$. The molecular formula was determined by hrms to be $C_{26}H_{32}O_7$ ($[M]^+$ 456.2157, calcd 456.2148). The ir spectrum disclosed absorption bands due to hydroxyl, conjugated carbonyl, and benzene ring moieties. Treatment of **1** with Ac_2O in



1 $R_1=R_3=H$, $R_2=Me$
1A $R_1=R_2=H$, $R_3=Me$

[1]Part 13 in the series, "Constituents of the Moraceae Plants." For Part 12, see Hano *et al.* (5).



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pyridine gave the tetraacetate. While the tetraacetate was negative to the $FeCl_3$ test, the ir spectrum disclosed an absorption band for a hydroxyl group. The uv spectrum of **1** exhibited maxima at 208, 223, 289, and 327 (sh) nm and was similar to that of phloroacetophenone. The uv spectrum showed a red shift upon addition of $AlCl_3$.

From these data, antiarone J seemed to be a phloroacetophenone derivative. The ^{1}H-nmr spectrum showed protons in a 3,3-dimethylallyl (prenyl) group, δ 1.67 (6H, br s), 3.24 (2H, br d, J = 7.1 Hz), 5.21 (1H, m); three aromatic protons, δ 5.95 (2H, s), 6.49 (1H, s); a methoxyl group, δ 3.70 (3H, s); and two hydroxyl groups, δ 11.82 (2H, br s). Furthermore, the following proton signals were observed: two methyl groups, δ 1.10 (6H, s); two pairs of methylene protons, δ 2.87 (1H, dd, J = 4.7 and 16.8 Hz), 2.99 (1H, dd, J = 9.1 and 16.8 Hz), 3.33 (1H, dd, J = 7.1 and 16.8 Hz), 3.48 (1H, dd, J = 6.5 and 16.8 Hz); two methine protons, δ 2.35 (1H, dt, J = 9.1 and 4.7 Hz), 3.83 (1H, ddd, J = 4.7, 6.8 and 7.1 Hz). These aliphatic protons were correlated as shown in Figure 1 by decoupling experiments. The ^{13}C-nmr spectrum indicated the presence of twenty-six carbons, and the assignments between the carbons and the relevant protons were carried out by ^{13}C-^{1}H shift correlation spectroscopy (^{13}C-^{1}H COSY) as shown in Table 1 and Figure 1. The ^{13}C-^{1}H COSY spectrum as well as the chemical shifts of the carbons being considered, **1** is suggested to have a 2,4,6-trihydroxyacetophenone moiety and a 1,2,3,4,5-pentasubstituted benzene ring. Comparison of the ^{13}C-nmr spectrum with those of antiarone E [**3**] (8) and 2′,4′,6′-trihydroxydihydrochalcone [**4**] (9) suggests that **1** is a dihydrochalcone derivative having the same substitution pattern as **3**.

To clarify the connectivities of the carbon atoms, the following long-range selective ^{1}H decoupling (LSPD) (Figure 2) and ^{13}C-^{1}H long-range COSY (LRCOSY, J = 4 Hz) experiments were carried out. When the signal at δ 3.83 (β-H) was irradiated, the signal at δ 205.8 (C=O, dt, ^2J = 5.5 Hz, ^3J = 3.7 Hz) changed to a triplet (^2J = 5.5 Hz), and the signal at δ 52.6 (C-α, t, ^2J = 5.1 Hz, ^3J = 5.1 Hz) to a doublet (^3J = 5.1 Hz). Furthermore, the methylene carbon signal at δ 31.1 (C-1″), as well as the two aromatic carbon signals at δ 116.3 (C-6) and 144.8 (C-1), showed remarkable changes upon irradiation. When the signal at δ 3.24 (H_2-6″) was irradiated, the doublet of broad trip-

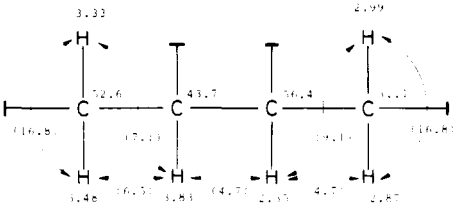


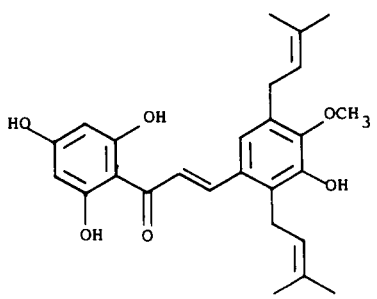
FIGURE 1. ^{1}H-^{1}H and ^{13}C-^{1}H connectivities in aliphatic region of **1**. Values in parentheses are J in Hz.

TABLE 1. ^{13}C-nmr Data of Compounds **1**, **2**, **3**, and **4**.

Carbon	Compound				
	1	^{1}H Chemical Shifts[b]	**3**	**4**	**2**
C-1	144.8		131.6	142.9	142.1
C-2	128.5		128.2	129.1	137.0
C-3	146.2		148.1	129.2	145.8
C-4	145.1		148.7	126.5	152.1
C-5	133.9		133.3	129.2	112.8
C-6	116.3	6.49 s	119.7	129.1	119.7
C=O	205.8		193.3	205.2	205.6
C-α	52.6	3.33 dd (7.1, 16.8), 3.48 dd (6.5, 16.8)	128.5	46.3	52.6
C-β	43.7	3.83 dt (6.8, 4.7)	141.1	31.1	43.3
C-1′	105.9		105.8	105.1	105.7
C-2′	165.4		165.7	165.4	165.4
C-3′	96.0	5.95 s	96.1	95.8	95.9
C-4′	165.3		165.6	165.4	165.4
C-5′	96.0	5.95 s	96.1	95.8	95.9
C-6′	165.4		165.7	165.4	165.4
C-1″	31.1	2.87 dd (4.7, 16.8), 2.99 dd (9.1, 16.8)	25.7 (C-7)		31.1
C-2″	56.4	2.35 dt (9.1, 4.7)	123.7 (C-8)		56.2
C-3″	72.7		131.7 (C-9)		72.7
C-4″	27.1	1.10 s	25.8 (C-10)		27.1
C-5″	28.3	1.10 s	18.0 (C-11)		28.0
C-6″	29.2	3.24 brd (7.1)	28.8 (C-12)		
C-7″	124.5	5.21 m	124.0 (C-13)		
C-8″	132.1		133.1 (C-14)		
C-9″	25.8	1.67 s	25.9 (C-15)		
C-10″	17.8	1.67 s	18.1 (C-16)		
3-OMe					59.9
4-OMe	60.9	3.70 s	61.3		56.4

[a]Measured in Me_2CO-d_6.
[b]These assignments were made with the aid of ^{13}C-^{1}H correlation spectroscopy.

let signal at δ 116.3 (C-6) changed to a broad doublet (^{1}J = 157.0 Hz). In the LRCOSY spectrum of **1**, the methyl proton signal at δ 1.10 (6H, s) showed the cross peaks due to long-range coupling with the oxygen-bearing quarternary sp^{3} carbon at δ 72.3 (C-3″) and with the methine carbon at δ 56.4 (C-2″). This result indicated the 1-hydroxy-1-methylethyl group to be connected to the methine carbon at δ 56.4 (C-2″). Furthermore, the methine proton at δ 2.35 (H-2″) showed long-range correlations with both the methylene carbons at 31.1 (C-1″) and 52.6 (C-α), and the methylene protons at



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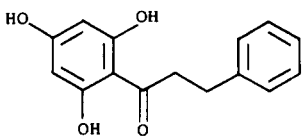

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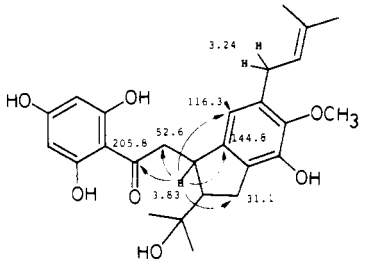

FIGURE 2. Results of LSPD experiments with **1**.

2.88 and 2.99 (H-1″) exhibited correlations with the carbons at δ 144.8 (C-1) and 146.2 (C-3). In the ^{13}C-nmr spectrum of **1**, the chemical shift of the methoxyl carbon (δ 60.9) indicated the methoxyl group to be di-ortho-substituted (10).

From the above results two possible structures (**1** and **1A**) were suggested. Discrimination between the structures was based on the following evidence. In the LR-COSY spectrum of **1**, the proton signal of the methoxyl group (δ 3.70) showed long-range correlation with the carbon at δ 145.1 (C-4), which showed correlation with the aromatic proton at δ 6.49 (H-6). Comparison of the ^{1}H-nmr spectra of **1** and its tetraacetate indicates the acetylation of the phenolic hydroxyl group at the C-3 position caused higher field shifts of the methylene protons at the C-1″ position located at the peri-position to the hydroxyl group (H-1″a: Δ +0.16 ppm, H-1″b: Δ +0.09 ppm) (11,12). The relative configuration between H-2″ and H-β was determined to be trans based on nOe experiments, in which irradiation at δ 1.10 (3″-Me × 2) caused enhancement of the signal at δ 3.83 (12%). From the above results, the formula **1** was proposed for the structure of antiarone J.

Antiarone K [**2**], colorless prisms, mp 117–119°, $[\alpha]^{25}$D 0°, gave a violet color with $FeCl_3$. The molecular formula was determined by hrms to be $C_{22}H_{26}O_7$ ($[M]^+$ 402.1644, calcd 402.1679). The ir spectrum disclosed absorption bands due to hydroxyl, conjugated carbonyl, and benzene ring moieties. The uv spectrum exhibited maxima at 206, 223, and 287 nm, and was similar to that of **1**. From these data, antiarone K seemed to be a phloroacetophenone derivative such as **1**. The ^{1}H-nmr spectrum of **2** showed the signals of the following protons: four aromatic protons, δ 5.94 (2H, s), 6.76 (1H, d, J = 8.2 Hz), 6.83 (1H, d, J = 8.2 Hz); two methyoxyl groups, δ 3.78 (6H, s); and two hydroxyl groups, δ 11.78 (2H, br s). Furthermore, the following aliphatic proton signals were observed: two methyl groups, δ 1.06, 1.08 (each 3H, s); two pairs of methylene protons, δ 2.95 (1H, dd, J = 8.8 and 17.2 Hz), 3.06 (1H, dd, J = 4.4 and 17.2 Hz), 3.32 (1H, dd, J = 6.8 and 16.7 Hz), 3.48 (1H, dd, J = 6.8 and 16.7 Hz); and two methine protons, δ 2.35 (1H, dt, J = 8.8 and 4.4 Hz), 3.82 (1H, dt, J = 4.4 and 6.8 Hz). The chemical shifts and coupling patterns of the aliphatic protons were similar to relevant proton signals of **1**. Comparison between the ^{13}C-nmr spectrum of **2** and that of **1** showed that the chemical shifts of all the carbon signals except those of the B ring of the framework of **2** were similar to the relevant carbon signals of **1**. In the ^{13}C-nmr spectrum of **2**, the chemical shifts of the methoxyl carbons (δ 56.4 and 59.9) indicated that one of the methoxyl groups is di-ortho-substituted and another is mono-ortho-substituted (10). The same relative configuration (trans) as **1** between H-2″ and H-β was indicated by comparison of ^{1}H- and ^{13}C-nmr data of **2** with those of **1**. From the above results, the formula **2** was suggested for the structure of antiarone K. To confirm the structure, the X-ray crystallographic analysis of **2** was carried out, and the crystal structure of **2** was determined as shown in Figure 3. As antiarone E

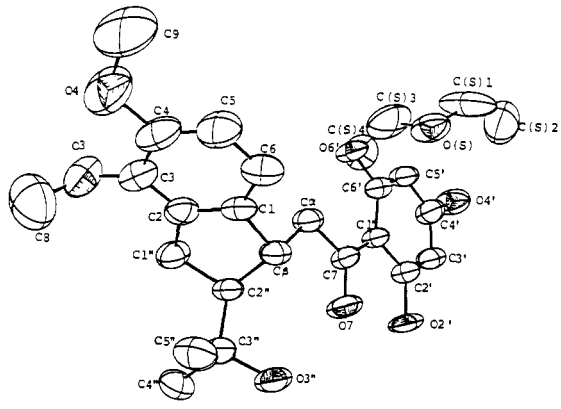

FIGURE 3. Crystal structure of antiarone K [**2**].

[**3**] was isolated from the same source (8), antiarones J [**1**] and K [**2**] are assumed to be derivatives from chalcone derivatives having an isoprenoid moiety at the C-2 position of the chalcone framework.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were measured with a Yazawa micro-melting point apparatus (hot-stage type) and are uncorrected. Uv spectra were measured with a Shimadzu UV-265 spectrophotometer and the ir spectra with a Hitachi 260-30 IR spectrophotometer. ^{1}H-nmr and ^{13}C-nmr spectra were recorded with a JEOL GX-400 FTNMR spectrometer. TMS was used as an internal standard, and chemical shifts are reported on the δ (ppm) scale. Optical rotations were measured with a JASCO DIP-4 Digital Polarimeter. Eims and hrms were obtained with JEOL JMS D-300 and DX-303 instruments. Hplc analyses were carried out with an SSC (Senshu Scientific, Tokyo, Japan) high pressure liquid chromatograph with an uv detector. Wakogel C-200 (Si gel, Wako Pure Chemical Industries, Osaka, Japan) was used for cc. Analytical tlc was performed on Wakogel B-5 FM (Si gel, Wako), and the spots were visualized under uv light. Preparative tlc was run on Wakogel B-5F (Si gel, Wako).

PLANT MATERIAL.—Root bark of *An. toxicaria* was collected in the Botanical Garden of Bogor, Indonesia, in March 1989, and was identified by staff members at the Botanical Garden of Bogor. A voucher specimen is deposited in the Herbarium of Toho University.

ISOLATION OF ANTIARONES J [**1**] AND K [**2**].—The fresh root bark of *An. toxicaria* (10 kg) was extracted with MeOH at room temperature. Evaporation of the MeOH solution yielded an emulsion from which the precipitate was separated. Evaporation of the filtrate to dryness yielded 150 g of residue, which was chromatographed on Amberlite XAD-2 (350 g) with *n*-hexane (4 liters), C_6H_6 (4 liters), Et_2O (4 liters), and Me_2CO (4 liters), which were evaporated to give 40 g, 50 g, 25 g, and 5 g of residues, respectively. The residue (25 g) obtained from the Et_2O solution was chromatographed on Si gel (300 g) with *n*-hexane–EtOAc (2:1) as an eluent (fractions 1–22), each fraction monitored by tlc (eluted volume of 100 ml). Fractions 16–22 were evaporated to give a residue (4 g), which was rechromatographed on Si gel (150 g) with C_6H_6-Me_2CO (12:1→8:1→5:1) as an eluent. The fractions eluted with C_6H_6-Me_2CO (12:1) were evaporated to give a residue (1.13 g). From the residue, antiarone J [**1**] (270 mg) was obtained sequentially by preparative tlc [solvent system *n*-hexane–Me_2CO (3:2) and $CHCl_3$-MeOH (10:1)] and by recrystallization from C_6H_6/Me_2CO. Fractions 1 and 2 were evaporated to give a residue (0.18 g). From the residue, antiarone K [**2**] (29 mg) was obtained sequentially by preparative tlc [solvent system *n*-hexane–Me_2CO (3:2)] and by preparative hplc [column Senshu Pak SSC-Silica 4251-N, solvent system *n*-hexane–EtOAc (1:1), detector uv 280 nm] followed by recrystallization from *n*-hexane/Et_2O.

ANTIARONE J [**1**].—Compound **1** was obtained as colorless prisms: mp 120–122°, $[\alpha]^{25}D$ 0° (c = 0.89, MeOH); $FeCl_3$ test positive (violet); eims (70 eV) *m/z* (rel. int.) $[M]^+$ 456 (2), 438 (100), 330 (12), 271 (70), 270 (98), 153 (67), 126 (4); hrms *m/z* $[M]^+$ 456.2157 (calcd for $C_{26}H_{32}O_7$, 456.2148), 438.3036 (calcd for $C_{26}H_{30}O_6$, 438.2043), 330.1884 (calcd for $C_{20}H_{26}O_4$, 330.1832), 153.0191 (calcd for $C_7H_5O_4$, 153.0188), 126.0305 (calcd for $C_6H_6O_3$, 126.0317); uv λ max (EtOH) (log ε) 208 (4.78), 223 (infl 4.47), 289 (4.34), 327 (sh 3.56); uv λ max (EtOH + $AlCl_3$) (log ε) 209 (4.80), 220 (infl 4.58),

3.11 (4.48), 369 (sh 3.59); uv λ max (EtOH + NaOAc) (log ε) 215 (4.92), 300 (4.20), 321 (4.28); uv λ max (EtOH + MeONa) (log ε) 240 (infl 4.24), 322 (4.51); ir ν max (KBr) 3500, 3400, 3200 (br), 1640, 1600, 1570, 1520, 1460.

ANTIARONE J TETRAACETATE.—A mixture of **1** (6 mg) and Ac_2O (0.2 ml) in pyridine (0.2 ml) was kept at room temperature for 3 h and treated as usual. The product was purified by preparative hplc [column SSC-Silica 4251-N, solvent system *n*-hexane–EtOAc (2:1), detector uv 280 nm] to give antiarone J tetraacetate (4 mg): $FeCl_3$ test negative; eims (70 eV) *m/z* (rel. int.) $[M]^+$ 624 (1), 606 (24), 564 (20), 521 (6), 312 (51), 279 (45); ir ν max (KBr) 3540 (br), 1780, 1700, 1620, 1580, 1480, 1455, 1425, 1380, 1180; ^{1}H-nmr [$(CD_3)_2CO$] δ 1.14, 1.15 (each 3H, s), 1.68, 1.70 (each 3H, br s), 2.13 (6H, s, Ac × 2), 2.28, 2.31 (each 3H, s Ac), 2.28–2.32 (1H, overlapping with the signals of acetyl groups), 2.71 (1H, dd, J = 5.5 and 16.8 Hz), 2.90 (1H, dd, J = 9.1 and 16.8 Hz), 3.16 (1H, dd, J = 8.2 and 18.8 Hz), 3.28 (2H, br d, J = 6.5 Hz), 3.32 (1H, dd, J = 4.4 and 18.8 Hz), 3.71 (3H, s, OMe), 3.85 (1H, dt, J = 8.2 and 4.4 Hz), 5.24 (1H, m), 6.93 (1H, br s), 7.00 (2H, s).

ANTIARONE K [**2**].—Compound **2** was obtained as colorless prisms, mp 117–119°, $[\alpha]^{25}D$ 0° (c = 0.066, MeOH), $FeCl_3$ test positive (violet); eims (70 eV) *m/z* (rel. int.) $[M]^+$ 402 (5), 384 (40), 277 (18), 276 (100), 217 (99), 216 (68), 190 (44), 153 (82), 126 (67); hrms *m/z* $[M]^+$ 402.1644 (calcd for

TABLE 2. Positional Parameters and Their Standard Deviations for **2**.[a]

Atom	*x*	*y*	*z*	B(A2)
O-3	0.4088(4)	−0.417(1)	0.0315(6)	6.8(3)
O-4	0.4838(4)	−0.290(1)	0.0782(8)	9.5(4)
O-7	0.2445(3)	0.0242(9)	−0.1141(4)	5.5(2)
O-2′	0.1745(3)	0.140(1)	−0.1168(5)	6.0(2)
O-4′	0.1316(3)	0.289(1)	0.1108(6)	6.6(3)
O-6′	0.2704(3)	0.0816(9)	0.1226(4)	4.7(2)
O-3″	0.2758(3)	−0.1249(9)	−0.2210(5)	5.2(2)
C-1	0.3702(4)	−0.124(1)	−0.0258(7)	4.4(3)
C-2	0.3713(5)	−0.242(1)	−0.0144(7)	4.3(3)
C-3	0.4092(5)	−0.299(1)	0.0186(8)	5.3(3)
C-4	0.4461(5)	−0.226(2)	0.0404(9)	6.3(4)
C-5	0.4455(5)	−0.108(2)	0.0306(9)	6.3(4)
C-6	0.4070(5)	−0.051(1)	−0.0045(8)	5.6(4)
C-7	0.2537(4)	0.038(1)	−0.0430(7)	4.2(3)
C-α	0.2974(4)	−0.019(1)	−0.0043(7)	4.2(3)
C-β	0.3226(4)	−0.081(1)	−0.0649(7)	4.1(3)
C-1′	0.2254(4)	0.103(1)	0.0007(6)	4.0(3)
C-2′	0.2325(4)	0.125(1)	0.0809(7)	4.0(3)
C-3′	0.2025(4)	0.183(1)	0.1188(7)	4.7(3)
C-4′	0.1626(5)	0.231(1)	0.0757(8)	5.3(3)
C-5′	0.1537(5)	0.215(1)	−0.0024(7)	5.2(3)
C-6′	0.1845(5)	0.155(1)	−0.0390(7)	4.8(3)
C-1″	0.3248(5)	−0.300(1)	−0.0423(7)	4.7(3)
C-2″	0.2979(4)	−0.201(1)	−0.0919(6)	4.1(3)
C-3″	0.2984(4)	−0.224(1)	−0.1796(7)	4.4(3)
C-4″	0.2715(5)	−0.335(1)	−0.2040(8)	5.7(4)
C-5″	0.3474(5)	−0.232(2)	−0.2036(8)	5.8(4)
C-8	0.4314(7)	−0.489(2)	−0.013(1)	10.4(7)
C-9	0.5224(7)	−0.221(3)	0.115(2)	14.2(8)
O(S)	0.1365(5)	0.260(1)	0.2630(7)	9.8(4)
C(S)-1	0.131(1)	0.147(3)	0.296(1)	13.9(9)
C(S)-2	0.116(1)	0.057(2)	0.254(2)	15(1)
C(S)-3	0.1330(8)	0.371(3)	0.303(1)	15.1(8)
C(S)-4	0.109(1)	0.454(3)	0.275(2)	15(1)

[a]Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)*[a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

$C_{22}H_{26}O_7$, 402.1679), 384.1561 (calcd for $C_{22}H_{24}O_6$, 384.1573), 153.0192 (calcd for $C_7H_5O_4$, 153.0188); uv λ max (MeOH) (log ε) 206 (4.61), 223 (4.36), 287 (4.32); uv λ max (MeOH + $AlCl_3$) (log ε) 206 (4.62), 219 (4.46), 311 (4.44); uv λ max (MeOH + NaOAc) (log ε) 213 (4.75), 224 (4.37), 295 (4.16), 321 (4.21); uv λ max (MeOH + MeONa) (log ε) 240 (infl 3.09), 323 (3.46); ir ν max (KBr) 3400, 3150 (br), 1650, 1600, 1570, 1525, 1490, 1460.

X-RAY DATA FOR ANTIARONE K [**2**][2].—A colorless block of antiarone K [**2**], approximate dimensions 0.43 × 0.23 × 0.23 mm, was used. All measurements were carried out on an Enraf-Nonius CAD-4 Diffractometer System by the ω-2θ scan technique (θ max 60°) with CuKα radiation (λ = 1.54184 Å). Cell constants and an orientation matrix for data collection were obtained by least-square refinement of 20 reflections, which yielded $a = 29.955$ (9) Å, $b = 11.399$ (4) Å, $c = 17.351$ (3) Å, $\beta = 97.87$ (2), and $V = 5930.0$ Å^3. For $Z = 8$ and formula wt = 476.57 ($C_{22}H_{26}O_7 \cdot C_4H_{10}O$) the calculated density is 1.07 g/cm^3. Examination of systematic extinction indicated that the monoclinic crystal belonged to the space group *C2/c* (no. 15). Data collection gave 3337 independent reflections with $I > 1\sigma(I)$. Lorentz and polarization corrections were applied to the data. No correction was applied for absorption. The structure was solved by the direct method. Hydrogen atoms were not included in the calculation. The refinement by a full-matrix least-square method gave $R = 0.17$. All calculations were performed on a VAX11/750 computer with SDP/VAX. Final atomic coordinates are listed in Table 2.

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[2]Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.