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Five New Xanthones from *Garcinia dulcis*

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From the bark of *Garcinia dulcis*, a new xanthone, dulciol A (**1**), was isolated in addition to two known xanthones [12b-hydroxydes-D-garcigerin (**2**) and toxyloxanthone B (**3**)]. Furthermore, from the roots of this plant, four novel xanthones with a 1,1-dimethylallyl group, dulciols B−E (**4**−**7**), were obtained, besides eight known xanthones [**2**; garciniaxanthones A (**8**), B (**9**), and D (**14**); globuxanthone (**10**); and subelliptenones C (**11**), D (**12**), and F (**13**)]. The structures of these xanthones were determined by spectroscopic analysis, including 2D NMR.

The sub-woody plant *Garcinia dulcis* Kurz. (Guttiferae) grows mainly in Southeast Asia, and its leaves and seeds have been used in traditional medicine against lymphatitis, parotitis, struma, and other disease conditions.[1] Despite much previous phytochemical research on *Garcinia* species, little attention has been paid thus far to the chemical constituents of *G. dulcis*.[2] In the continuing phytochemical studies on the plants of the Guttiferae in search of bioactive principles,[3−6] we have examined the chemical constituents of *G. dulcis*. We report herein the isolation and characterization of five new xanthones, along with nine known xanthones, from the bark and the root of this species.

Results and Discussion

The bark of *G. dulcis*, collected in Indonesia, was extracted successively with *n*-hexane, C_6H_6, Me_2CO, and 70% MeOH. The C_6H_6 extract was repeatedly chromatographed to isolate dulciol A (**1**), 12b-hydroxydes-D-garcigerin (**2**), and toxyloxanthone B (**3**). The roots of *G. dulcis* were also extracted in a similar manner, and the C_6H_6 and Me_2CO extracts were purified by column chromatography, VLC, and preparative TLC to give 12 xanthones: **2**; dulciols B (**4**) and D (**6**); garciniaxanthones A (**8**) and B (**9**) (from the C_6H_6 extract) and dulciols C (**5**) and E (**7**); globuxanthone (**10**); subelliptenones C (**11**), D (**12**), and F (**13**); and garciniaxanthone D (**14**) (from the Me_2CO extract).

Compound **1**, dulciol A, was obtained as a pale yellow amorphous powder that reacted positively with $FeCl_3$ and Gibbs reagents. The $[M]^+$ at m/z 464.2187 in the HREIMS corresponded to the molecular formula $C_{28}H_{32}O_6$. The UV and IR absorption data suggested that **1** was a xanthone derivative. In the ^{1}H-NMR spectrum, four hydroxyl groups [δ 8.68, 8.80, 9.55 (1H each, br s), and 13.62 (1H, s, chelated)] and two meta-coupled protons [δ 6.19 and 6.35 (1H each, J = 2.2 Hz)] were exhibited, in addition to a C_5- and a C_{10}-alkyl chain. In the ^{13}C-NMR spectrum, the signals of vinyl methyl groups were observed at δ 16.9, 18.1, 18.7, 26.1, and 26.2, which indicated that the C_5- and C_{10}-alkyl chains were an isoprenyl and a geranyl group, respectively. Analysis of the ^{1}H−^{1}H long-range COSY NMR spectrum (Figure 1) indicated that the methylene protons at δ 3.48 exhibited a cross-peak with the methylene protons (δ 2.02) on the geranyl group, suggesting that the methylene protons at δ 4.12 were attributable to the isoprenyl group. The chemical shift of a methylene observed at a lower field showed that the isoprenyl group was located at a peri position (C-8) to a carbonyl group. All carbons bearing protons were assigned from the ^{1}H-^{13}C COSY NMR spectrum (Table 1). In the HMBC NMR spectrum (Figure 1), the chelated hydroxyl group was correlated to an aromatic carbon at δ 99.1, which in turn correlated to a meta-coupled proton (δ 6.19) in the ^{1}H−^{13}C COSY NMR spectrum. These results led to a partial structure of **1** as 1,3-dihydroxy-8-isoprenylxanthone. The locations of the other substituents were determined as follows. In the ^{13}C-NMR spectrum, the aromatic carbons with an oxygen function were observed at δ 135.5, 146.8, and 150.5, which suggested the presence of a 1,3,4-trioxygenated benzene ring. Another partial structure of **1** was put forth as 5-geranyl-6,7-dihydroxy-8-isoprenylxanthone, which was supported by correlations observed in the HMBC NMR spectrum (Figure 1). Thus, the structure of dulciol A was characterized as **1**.

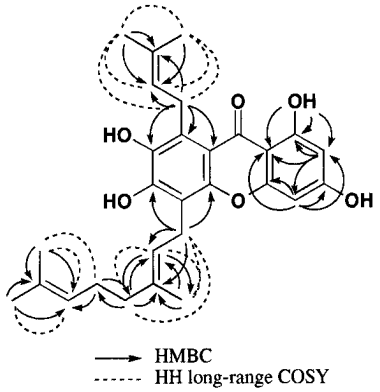

Figure 1. HMBC (J = 8 Hz) and ^{1}H−^{1}H long-range COSY NMR spectral interactions of **1**.

Compound **4**, dulciol B, obtained as yellow needles, gave a positive response to $FeCl_3$ reagent. The $[M]^+$ at m/z 464.2219 in the HREIMS exhibited the molecular formula $C_{28}H_{32}O_6$. The UV and IR spectra indicated that **4** was also a xanthone. The ^{1}H-NMR spectrum

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Table 1. 13C-NMR Spectral Data of 1 and 4−7[a]

	compound				
carbon	**1**	**4**	**5**	**6**	**7**
1	165.5[b]	153.8	153.7	153.5	151.0
2	99.1	129.1	129.0	129.8	133.7
3	165.6[b]	122.1	122.0	123.8	120.8
4	94.2	135.9	136.5	137.0	140.1
5	126.6	126.5	126.1	142.8	146.9
6	146.8	150.2	150.5	135.8	117.0
7	135.5	135.1	136.0	117.9	124.6
8	131.0[c]	130.9[b]	132.8[b]	120.7	116.2
9	183.8	185.1	185.1	183.4	175.9
4a	158.0	141.3	141.4	142.7	143.8
8a	112.4	112.1	112.1	117.6	124.0
9a	104.3	109.5	109.5	109.8	109.3
10a	150.5	145.8	146.0	143.7	145.1
11	25.5	41.0	41.0	41.0	55.5
12	124.3	27.0	27.0	26.9	26.3[b]
13	136.1	27.0	27.0	26.9	26.4[b]
14	40.8	148.2	148.2	147.9	90.9
15	18.7[d]	110.8	110.8	110.0	14.8
16	27.7	25.3	25.6[c]	109.0	
17	125.8	123.8	124.1	150.4	
18	132.0	130.8[b]	130.9[b]		
19	26.2[e]	25.9[f]	25.2[c]		
20	18.1	18.2	18.3		
21	29.4	29.2	25.9[c]		
22	125.5	125.2	45.6		
23	131.1[c]	132.0	70.4		
24	26.1[e]	25.9[f]	29.3		
25	16.9[d]	18.4	29.3		

[a] Measured in Me_2CO-d_6. [b−e] Signals with the same superscript are interchangeable. [f] Overlapping signals.

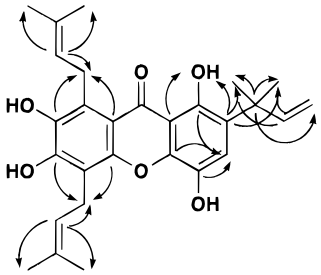


Figure 2. COLOC (J = 8 Hz) spectral interactions of **4**.

showed the presence of four hydroxyl groups [δ 8.70 (2H, br s), 9.65 (1H, br s), and 13.58 (1H, s, chelated)], an aromatic proton [δ 7.24 (1H, s)], and a 1,1-dimethylallyl group [δ 1.53 (6H, s, Me × 2)], 5.00 (1H, dd, J = 10.7, 1.5 Hz, −CH=CH_2), 5.07 (1H, dd, J = 17.0, 1.5 Hz, −CH=CH_2), and 6.31 (1H, dd, J = 17.0, 10.7 Hz, −CH=CH_2)], in addition to two isoprenyl groups [δ 1.68 (6H, s, vinyl Me × 2), 1.79, 1.81 (3H each, s, vinyl Me × 2), 3.48, 4.10 (2H each, d, J = 6.4 Hz, −CH_2−CH=), 5.11 (2H, t-like m, −CH_2=CH−)]. All carbons with protons assigned by the ^{1}H−^{13}C COSY spectrum are shown in Table 1. In the COLOC NMR spectrum (Figure 2), the chelated hydroxyl group was correlated to an aromatic carbon at δ 129.1, which was further correlated to the methyl groups (δ 1.53) of the 1,1-dimethylallyl moiety. These results showed that the 1,1-dimethylallyl group was located at the ortho-position of the chelated hydroxyl group. In the ^{1}H-NMR spectrum, a NOE was observed between the methyl groups (δ 1.53) of the 1,1-dimethylallyl unit and the aromatic proton at δ 7.24. Furthermore, in the COLOC spectrum, the aromatic proton (δ 7.24) gave cross-peaks to three aromatic carbons with an oxygen function at δ 135.9, 141.3, and 153.8, which indicated the presence of a 1,3,4-trioxygenated benzene ring in **4**. A plausible

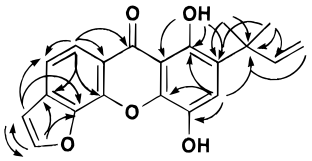


Figure 3. HMBC (J = 10 Hz) spectral interactions of **6**.

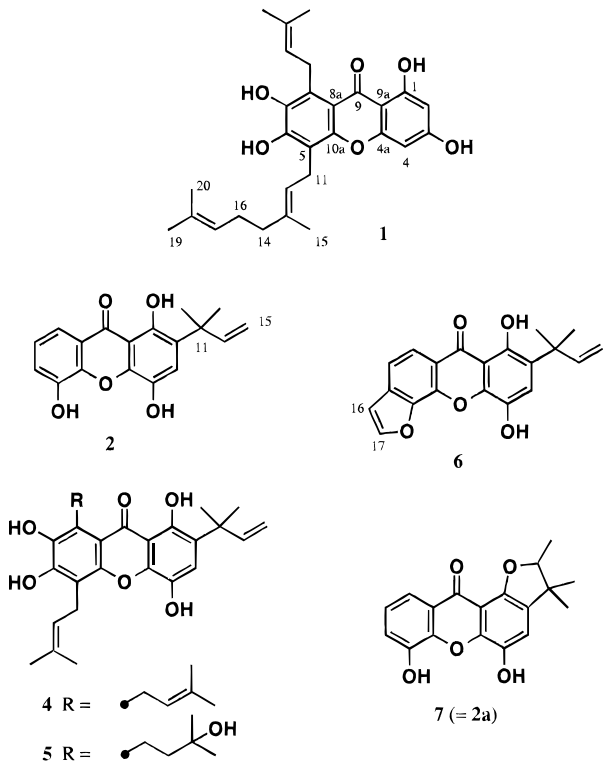
partial structure was, therefore, 1,4-dihydroxy-2-(1,1-dimethylallyl)xanthone. On the other hand, the methylene protons of the isoprenyl groups were observed at a low field (δ 4.10) in the ^{1}H-NMR spectrum, which indicated that one of the isoprenyl groups was located at the peri position to the carbonyl group. The positions of the remaining substituents were determined as follows. In the ^{13}C-NMR spectrum, the aromatic carbons with an oxygen-function were observed at δ 135.1, 145.8, and 150.2, which suggested the presence of a 1,3,4-trioxygenated benzene ring. Therefore, another isoprenyl group was located at C-5, which was further substantiated by correlations in the COLOC spectrum. The structure of dulciol B was concluded to be **4**.

Compound **5**, dulciol C, was positive to $FeCl_3$ and had a molecular formula $C_{28}H_{34}O_7$ supported by the HREIMS (m/z 482.2318). The ^{1}H-NMR spectrum closely resembled that of **4** except for disappearance of an isoprenyl group at C-8 and appearance of a new 3-hydroxy-3-methylbutanyl chain [δ 1.32 (6H, s, Me × 2), 1.74, 3.40 (2H each, m, −CH_2− × 2)]. The resonances for the 3-hydroxy-3-methylbutanyl moiety in the ^{1}H- and ^{13}C-NMR spectra were compared with those of subelliptenone E, a xanthone isolated from *Garcinia subelliptica*;[3] and the spectral data were superimposable. Thus, the structure of dulciol C was characterized as **5**.

Compound **6**, dulciol D, reacted positively to $FeCl_3$. The $[M]^+$ at m/z 336.0986 in the HREIMS gave the molecular formula $C_{20}H_{16}O_5$. In the ^{1}H-NMR spectrum, the presence of a fused furan ring [δ 7.16 and 8.21 (1H each, d, J = 2.0 Hz)] and two ortho-coupled protons [δ 7.68 and 8.07 (1H each, d, J = 8.3 Hz)] was confirmed in addition to two hydroxyls, a 1,1-dimethylallyl group and an aromatic proton. The presence of the furan ring was substantiated by the methine carbons (δ 109.0 and 150.4) in the ^{13}C-NMR spectrum.[7] A partial structure of **6**, 1,4-dihydroxy-2-(1,1-dimethylallyl)xanthone, was deduced by comparison of the ^{1}H- and ^{13}C-NMR spectral data with those of **4**, and supported by a HMBC experiment (Figure 3). The position of the furan ring was determined as follows. In the HMBC spectrum, the ortho-coupled proton at δ 8.07 was correlated to the carbonyl carbon. The aromatic carbons with an oxygen function were observed at δ 142.8 and 143.7 in the ^{13}C-NMR spectrum, which indicated the presence of a 1,2-dioxygenated benzene ring in **6**. Therefore, the furan ring was fused at C-7 through an oxygen at C-8. The structure of dulciol D was thus elucidated as **6**, and was further supported by an HMBC experiment.

Compound **7**, dulciol E, had the molecular formula $C_{18}H_{16}O_5$. The ^{1}H-NMR spectrum showed the presence of two hydroxyl groups, a 1,2,3-trisubstituted benzene ring [δ 7.23 (1H, t, J = 8.3 Hz), 7.26 (1H, dd, J = 8.3, 2.4 Hz), and 7.65 (1H, dd, J = 8.3, 2.4 Hz)], an isolated aromatic proton (δ 7.12), and a 1,1,2-trimethyldihydrofuran ring [δ 1.13 and 1.36 (3H each, s, Me × 2), 1.41 (3H, d, J = 6.6 Hz, Me), and 4.51 (1H, q, J = 6.6 Hz)]. The chemical shift of the 1,2,3-trisubstituted benzene

ring in the ^{1}H-NMR spectrum implied the presence of a 5-hydroxyxanthone moiety, the partial structure of which was supported by comparison of the ^{1}H- and ^{13}C-NMR spectra of compounds **7** and **2** [1,4,5-trihydroxy-2-(1,1-dimethylallyl)xanthone]. The positions of the 1,1,2-trimethyldihydrofuran ring and another hydroxyl group were assigned as follows. In the ^{13}C-NMR spectrum (Table 1), the aromatic carbons with an oxygen function were observed at δ 140.1, 143.8, and 151.0, which gave evidence for the presence of a 1,3,4-trioxygenated benzene ring. The carbonyl carbon observed at δ 175.9 showed that **7** had no chelated hydroxyl group.[8] A NOE was observed between the methyl protons (δ 1.36) on the 1,1,2-trimethyldihydrofuran ring and the isolated aromatic proton (δ 7.12). Therefore, the 1,1,2-trimethyldihydrofuran ring was fused at C-2 through an oxygen at C-1, and another hydroxyl group was located at C-4. The structure of dulciol E was thus determined as **7**. When **2** was treated with MeOH/HCl, a cyclized compound (**2a**) was obtained. The ^{1}H-NMR spectral data of **2a** were similar to those of **7**, supporting the structure assigned to **7**.



The structures of **2**, **3**, and **8**−**14** were characterized as 12b-hydroxydes-D-garcigerin (**2**)[4] and toxyloxanthone B (**3**);[9] garciniaxanthones A (**8**) and B (**9**);[10] globuxanthone (**10**); subelliptenones C (**11**), D (**12**);[4] and F (**13**);[3] and garciniaxanthone D (**14**),[11] respectively, by comparison with their spectral data cited in the literature.

Experimental Section

General Experimental Procedures. The following instruments were used: melting points (uncorrected), Büchi melting point apparatus; MS, JEOL JMS-D300 (70 eV) instrument; ^{1}H- and ^{13}C-NMR spectra, JEOL JNM EX-400 (TMS as internal standard, all compounds were measured in Me_2CO-d_6), IR spectra (on KBr pellets), JASCO IR-AI spectrometer; UV spectra (MeOH solution), Shimadzu UV-2200 spectrometer. The following adsorbents were used for purification: analytical TLC, Merck Kieselgel 60 F_{254}; column chromatography, Merck Kieselgel 60, Fuji Davison Silica gel BW-300, and Pharmacia Fine Chemicals AB Sephadex LH-20.

Plant Material. The bark and roots of *G. dulcis* were collected at Pasoeroean (Jawa Timur) in Indonesia, in September 1995, and were identified by one of the authors (S. R.). Voucher specimens are deposited in the Herbarium of Gifu Pharmaceutical University.

Extraction and Isolation. The dried and ground bark of *G. dulcis* (900 g) was extracted successively under reflux with *n*-hexane (2 L × 12 h × 3) (weight of extractive after removal of solvent: 10 g), C_6H_6 (2 L × 12 × 3) (5 g), Me_2CO (2 L × 12 h × 3) (60 g), and 70% MeOH (2 L × 12 h × 3) (50 g). The C_6H_6 extract (4 g) was chromatographed on Si gel eluted with an *n*-hexane−EtOAc system. From *n*-hexane−EtOAc (3:1), **1** (25 mg) was obtained. A fraction eluted with *n*-hexane−EtOAc (5:1) was further chromatographed on Sephadex LH-20 to give four fractions. The third of the fractions was purified using preparative TLC with *n*-hexane−EtOAc−MeOH (8:2:1) to give **2** (3 mg) and **3** (1 mg).

The dried and ground roots (950 g) of *G. dulcis* were extracted successively under reflux with C_6H_6 (2 L × 12 h × 3) (27 g), Me_2CO (2 L × 12 h × 3) (68 g), and 70% MeOH (2 L × 12 h × 3) (70 g). The C_6H_6 extract (18 g) was chromatographed on Si gel eluted with a C_6H_6-Me_2CO system to give eight fractions (1−8). Fraction 3 [C_6H_6−Me_2CO (25:1)] was recrystallized from C_6H_6 to give **2** (160 mg). Fraction 2 (25:1) was subjected to VLC on Si gel eluted with an *n*-hexane-Me_2CO system. A fraction eluted with *n*-hexane-Me_2CO (20:1) was further purified by Sephadex LH-20 (Me_2CO) to afford **8** (18 mg), and the fraction eluted with *n*-hexane−Me_2CO (10:1) was further chromatographed on Sephadex LH-20 (Me_2CO) to give three fractions. The second fraction was purified by preparative TLC [*n*-hexane-Me_2CO (5:1)] to give **6** (8 mg). Fraction 5 [*n*-hexane−Me_2CO (25:1)] was chromatographed over Sephadex LH-20 (Me_2CO) to give **4** (190 mg). Fraction 7 (10:1) was chromatographed on Sephadex LH-20 to give four fractions. The third fraction was subjected to VLC eluted with a C_6H_6−EtOAc system. A fraction eluted with C_6H_6−EtOAc (10:1) was further purified by preparative TLC [*n*-hexane−EtOAc (5:1)] to give **9** (8 mg). The Me_2CO extract (50 g) was chromatographed on Si gel eluted with a C_6H_6−Me_2CO system to give 11 fractions (fractions A-K). Fraction F [(C_6H_6−Me_2CO (5:1)] was subjected to VLC on Si gel eluted with C_6H_6−Me_2CO (20:1) to give eight fractions. From the third fraction, **11** (10 mg) was obtained. After purification with Sephadex LH-20 (Me_2CO), the second fraction was subjected to preparative TLC [*n*-hexane−EtOAc−MeOH (8:2:1)] to give **10** (2 mg) and **12** (5 mg). The sixth fraction was repeatedly subjected to Sephadex LH-20 (Me_2CO) and preparative TLC [$CHCl_3$−MeOH (20:1)] to give **5** (6 mg) and **13** (3 mg). Fraction G [$CHCl_3$−MeOH (2:1)] was chromatographed on Si gel eluted with a $CHCl_3$−MeOH system. A fraction eluted with $CHCl_3$−MeOH (10:1) was further purified by Sephadex LH-20 (MeOH) to give **14** (7 mg).

Dulciol A (1): yellow amorphous solid; UV (MeOH) λ max 209, 240 sh, 253, 280, 328 nm; IR ν max 3450, 2920, 1650, 1605, 1595 cm^{-1}; ^{1}H NMR δ 1.57 (3H, s, H_3-20), 1.62 (3H, s, H_3-19), 1.68 (3H, s, H_3-24), 1.80 (6H,

s, H_3-15, H_3-25), 2.02 (2H, m, H_2-14), 2.06 (2H, m, H_2-16), 3.48 (2H, d, J = 6.4 Hz, H_2-11), 4.12 (2H, d, J = 6.8 Hz, H_2-21), 5.10 (3H, m, H-12, H-17, H-22), 6.19 (1H, d, J = 2.2 Hz, H-2), 6.35 (1H, d, J = 2.2 Hz, H-4), 8.68, 8.80, 9.55 (1H each, br s, OH × 3), 13.62 (1H, s, OH-1); ^{13}C-NMR spectral data, see Table 1; EIMS *m/z*: 464 $[M]^+$ (55), 421 (48), 395 (32), 379 (16), 365 (10), 353 (26), 339 (100), 325 (76), 301 (21), 299 (42), 297 (25), 153 (8); HREIMS $[M]^+$ *m/z* 464.2187 (calcd 464.2199 for $C_{28}H_{32}O_6$).

Dulciol B (4): yellow needles (MeOH); mp 109 °C; UV λ max 206, 231, 260, 285, 342, 380 sh nm; IR ν max 3485, 3400, 2960, 2920, 1690, 1595 cm^{-1}; ^{1}H NMR δ 1.53 (6H, s, H_3-12, H_3-13), 1.68 (6H, s, H_3-20, H_3-25), 1.79, 1.81 (3H each, s, H_3-19, H_3-24), 3.48 (2H, d, J = 6.4 Hz, H_2-16), 4.10 (2H, d, J = 6.4 Hz, H_2-21), 5.00 (1H, dd, J = 10.7, 1.5 Hz, H-15*Z*), 5.07 (1H, dd, J = 17.0, 1.5, H-15*E*), 5.11 (2H, m, H-17, H-22), 6.31 (1H, dd, J = 17.0, 10.7 Hz, H-14), 7.24 (1H, s, H-3), 8.70 (2H, br s, OH × 2), 9.65 (1H, br s, OH), 13.52 (1H, s, OH-1); ^{13}C-NMR spectral data, see Table 1; EIMS *m/z*: 464 $[M]^+$ (58), 449 (20), 421 (60), 393 (46), 367 (100), 365 (26), 337 (13), 311 (11), 91 (12); HREIMS $[M]^+$ *m/z* 464.2219 (calcd 464.2199 for $C_{28}H_{32}O_6$).

Dulciol C (5): yellow amorphous solid; UV λ max 206, 230, 261, 285, 308, 342 nm; IR ν max 3400, 2970, 2920, 1704, 1642, 1605, 1585 cm^{-1}; ^{1}H NMR δ 1.32 (6H, s, H_3-24, H_3-25), 1.53 (6H, s, H_3-12, H_3-13), 1.67 (3H, s, H_3-20), 1.74 (2H, m, H_2-22), 1.83 (3H, s, H_3-19), 3.40 (2H, m, H_2-21), 3.55 (2H, d, J = 6.3 Hz, H_2-16), 4.99 (1H, dd, J = 10.7, 1.5 Hz, H-15*Z*), 5.05 (1H, dd, J = 17.6, 1.5 Hz, H-15*E*), 5.13 (1H, m, H-17), 6.31 (1H, dd, J = 17.6, 10.7 Hz, H-14), 7.24 (1H, s, H-3), 13.58 (1H, s, OH-1); ^{13}C-NMR spectral data, see Table 1; EIMS *m/z* 482 $[M]^+$ (92), 480 (67), 464 (37), 421 (87), 419 (33), 393 (55), 391 (20), 367 (91), 365 (34), 325 (13), 218 (52), 164 (40), 135 (100); HREIMS $[M]^+$ *m/z* 482.2318 (calcd 482.2304 for $C_{28}H_{34}O_7$).

Dulciol D (6): yellow amorphous solid; UV λ max 206, 240, 247, 268, 289, 395 nm; IR ν max 3530, 3350, 1630, 1595; ^{1}H NMR δ 1.55 (6H, s, H_3-12, H_3-13), 5.02 (1H, dd, J = 10.7, 1.5 Hz, H-15*Z*), 5.07 (1H, dd, J = 17.6, 1.5, H-15*E*), 6.32 (1H, dd, J = 17.6, 10.7 Hz, H-14), 7.16 (1H, d, J = 2.0 Hz, H-16), 7.42 (1H, s, H-3), 7.68 (1H, d, J = 8.3 Hz, H-7), 8.07 (1H, d, J = 8.3 Hz, H-8), 8.21 (1H, d, J = 2.0 Hz, H-17), 8.52 (1H, br s, OH), 13.06 (1H, s, OH-1); ^{13}C-NMR spectral data, see Table 1; EIMS *m/z*: 336 $[M]^+$ (83), 321 (100), 295 (26), 281 (21), 161 (7); HREIMS $[M]^+$ *m/z* 336.0986 (calcd 336.0998 for $C_{20}H_{16}O_5$).

Dulciol E (7): yellow amorphous solid; $[\alpha]^{24}_D$ 0° (*c* 0.1, MeOH); UV λ max 207, 230 sh, 248, 265 sh, 317, 396 nm; IR ν max 3300, 2970, 1640, 1605 cm^{-1}; ^{1}H NMR δ 1.13, 1.36 (3H each, s, H_3-12, H_3-13), 1.41 (3H, d, J = 6.6 Hz, H_3-15), 4.51 (1H, q, J = 6.6 Hz, H-14), 7.12 (1H, s, H-3), 7.23 (1H, t, J = 8.3 Hz, H-7), 7.26 (1H, dd, J = 8.3, 2.4 Hz, H-6), 7.65 (1H, dd, J = 8.3, 2.4 Hz, H-8), 9.15 (2H, br s, OH × 2); ^{13}C-NMR spectral data, see Table 1; EIMS *m/z*: 312 $[M]^+$ (51), 297 (100), 269 (15); HREIMS $[M]^+$ *m/z* 312.1004 (calcd 312.0998 for $C_{18}H_{16}O_5$).

Acid Transformation of 2. Compound **2** (20 mg) was heated with 10% HCl−MeOH (10 mL) under reflux for 24 h. The reaction mixture was diluted with H_2O and extracted with EtOAc. After the EtOAc was evaporated, the residue was subjected to preparativeTLC [*n*-hexane−EtOAc−MeOH (8:2:1)] to yield **2a** (8 mg).

References and Notes

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