Three Xanthones and a Benzophenone from *Garcinia mangostana*

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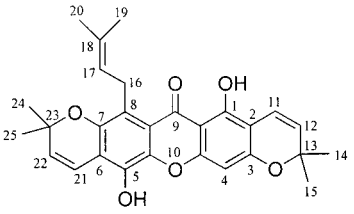
Investigation of the constituents of *Garcinia mangostana* has led to the isolation of four new compounds: three minor xanthones, garcimangosone A (**1**), garcimangosone B (**2**), and garcimangosone C (**3**), and a benzophenone glucoside, garcimangosone D (**4**). The structures of these four compounds were established by spectral (NMR and MS) and chemical methods.

The fruit hulls of *Garcinia mangostana* L. (Guttiferae) are reported to be used as an antiinflammatory agent and an astringent or used against diarrhea.[1] They contain the abundant xanthones such as 8-desoxygartanin, α-mangostin, and γ-mangostin.[1−6] We have isolated four new compounds, three minor xanthones, garcimangosone A (**1**), garcimangosone B (**2**), and garcimangosone C (**3**), and a benzophenone glucoside, garcimangosone D (**4**), from the EtOAc portion of the fruit hulls of this plant. Twenty-three known compounds were also obtained (listed in the Extraction and Isolation section), and their structures were identified by comparison of their spectral data with those in the literature. Among these known compounds, tovophyllin A[7] and B[7,8] and 1,3,6,7-tetrahydroxy-8-(3-methyl-2-butenyl)-9*H*-xanthen-9-one[9] were first isolated from this plant. The present paper reports the isolation and structure elucidation of **1**−**4**.



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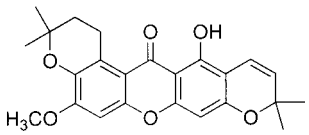

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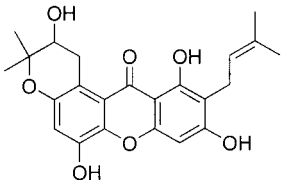

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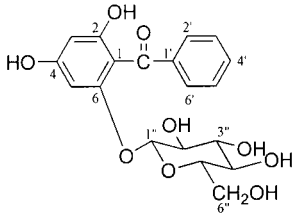

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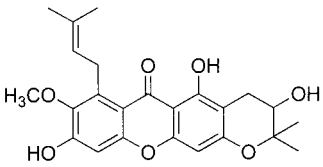

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Results and Discussion

EtOH extraction of the dried and pieced fruit hulls of *G. mangostana* followed by column chromatographic separation afforded four new compounds. Compounds **1**−**3** were obtained as yellow powders. The UV and IR spectral characteristics suggested these three compounds were xanthone derivatives.[3,5]

Compound **1** had a molecular ion peak at *m*/*z* 460 in EIMS corresponding to $C_{28}H_{28}O_6$. In the ^{1}H NMR spectrum of **1**, a singlet at δ 13.97 indicated the presence of a chelated hydroxyl substituted at C-1 of the xanthone ring. On the basis of the 2D (^{1}H−^{1}H COSY, HMQC, HMBC) spectral data, one set of characteristic signals for an isoprenyl group adjacent to the carbonyl group [δ 1.63 (3H, s), 1.82 (3H, s), 4.16 (2H, d, J = 6.0 Hz), 5.30 (1H, br t)][5] and two sets of signals for a pair of 6′,6′-dimethylpyrano groups [δ 1.44 (6H, s), 5.67 (1H, d, J = 10.0 Hz), 6.66 (1H, d, J = 10.0 Hz); δ 1.51 (s, 6H), 5.88 (1H, d, J = 10.0 Hz), 6.93 (1H, d, J = 10.0 Hz)] were observed. The remaining one-proton singlet at δ 6.20 was attributed to an aromatic proton. In the HMBC spectrum of **1** (Figure 1, Supporting Information), one vinyl proton signal at δ 6.66 (H-11) of one chromene ring showed key cross-peaks with a quaternary aromatic carbon signal at δ 105.0 (C-2) and two *O*-linked carbon signals at δ 158.6 and 160.6. The signals at δ 105.0 (C-2) and 160.6 also correlated with the aromatic proton signal at δ 6.35. Thus, the 6′,6′-dimethylpyrano group containing the above vinyl proton was linked with the chromene double bond *ortho* to the C-1 hydroxyl, the aromatic proton signal at δ 6.35 was assigned to H-4, and

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the carbon signals at δ 158.6 and 160.6 were assigned to C-1 and C-3, respectively. Moreover, the methylene proton signal at δ 4.13 (H-16) showed key cross-peaks with the carbon signals at δ 113.0 (C-8a), 128.9 (C-8), and *O*-linked carbon signal at δ 141.5 (C-7) that also correlated with one vinyl proton signal at δ 6.93 (H-21) of the other chromene ring. Therefore, the 6,′6′-dimethylpyrano group containing this vinyl proton was linked with the chromene double bond *ortho* to the C-5 hydroxyl. Accordingly, the structure of **1** was determined to be 1,5-dihydroxy-8-isoprenyl-6′,6′-dimethylpyrano(2′,3′:3,2)-6″,6″-dimethylpyrano(2″,3″:7,6)xanthone and named garcimangosone A.

Compound **2** had a molecular ion peak at *m*/*z* 408 in EIMS corresponding to $C_{24}H_{24}O_6$. ^{1}H NMR and HMBC data indicated that **2** also was a 1-hydroxy-6′,6′-dimethylpyrano-(2′,3′:3,2)-substituted xanthone. The ^{1}H NMR spectrum of **2** showed a set of signals for a dihydropyrano with a methylene at C-8 [δ 1.28 (6H, s), 1.75 (2H, br t), 3.42 (2H, br t)],[10] a methoxyl signal at δ 3.88 (3H, s), and an aromatic proton signal at δ 6.65 (1H, s). In the HMBC spectrum of **2** (Supporting Information), the higher-field methylene proton signal at δ 1.75 (H-17) showed a cross-peak with an aromatic carbon signal at δ 138.7 (C-8), and the lower-field methylene proton signal at δ 3.42 (H-16) showed cross-peaks with the carbon signals at δ 109.3 (C-8a), 138.7 (C-8), and 146.1 (C-7). Moreover, the aromatic proton signal at δ 6.65 showed cross-peaks with the carbon signals at δ 109.3 (C-8a), 157.1 (C-10a), and 146.1 (C-6, overlapped with C-7) that correlated with the methoxyl proton signal at δ 3.88. Thus, this methoxyl group was linked to C-6 and the aromatic proton signal was assigned to H-5. Accordingly, **2** was determined to be 1-hydroxy-6-methoxy-6′,6′-dimethylpyrano(2′,3′:3,2)-6″,6″-dimethyldihydropyrano(2″,3″:7,8)-xanthone and named garcimangosone B.

Compound **3** had a molecular ion peak at *m*/*z* 412 in EIMS corresponding to $C_{23}H_{24}O_7$. The spectra (^{1}H and ^{13}C NMR) of compound **3** were similar to those of mangostanol (**5**), a xanthone isolated from *Garcinia mangostana*,[1] except for the absence of the methoxyl moiety. In the ^{1}H NMR spectrum of **3**, the signals at 1.62, 1.72, 3.26, and 5.13 were due to an isoprenyl group. The signals of two methyls at δ 1.25 and 1.34, a pair of downfield-shifted methylene signals at δ 2.75 and 3.12, as well as a methine at δ 4.41 were due to a pyranone ring including a methylene at C-8. The remaining signals at δ 6.14 and 6.53 were due to two aromatic protons.

In the HMBC spectrum of **3** (Figure 1, Supporting Information), the methylene proton signal at δ 3.26 (H-11) showed cross-peaks with a quaternary aromatic carbon signal at δ 112.3 (C-2) and two *O*-linked carbon signals at δ 153.1 (C-3) and 161.4 (C-1). One aromatic proton signal at δ 6.53 (H-4) showed cross-peaks with the carbon signals at δ 96.6 (C-9a), 112.3 (C-2), 153.0 (C-4a), and 161.4 (C-3). Furthermore, the methyl proton signals at δ 1.25 and 1.34 showed key cross-peak with a tertiary carbinol signal at δ 86.5 (C-17). The methylene proton signals at δ 2.75 and 3.14 (H_2-16) showed key cross-peaks with three aromatic carbon signals at δ 99.1 (q), 106.2 (q), and 144.7 (*O*-linked, C-7). The other aromatic proton signal (δ 6.14) showed cross-peaks with three carbon signals at δ 99.1, 144.7 (C-7), and 158.9 (*O*-linked). In this experiment, correlation between H-17 and C-8 was not observed. Nevertheless, from our experiences in spectral assignments of all xanthones isolated from this plant, the aromatic protons usually showed significant cross-peaks by two-bond coupling with *ortho O*-linked aromatic carbons. Accordingly, the proton signal at δ 6.14 was assigned to H-6, and the carbon signals at δ 99.1, 106.2, and 158.9 were assigned to C-8, C-8a, and C-5, respectively. Thus, compound **3** was determined to be 1,3,5,22-tetrahydroxy-2-isoprenyl-6′,6′-dimethyldihydropyrano(2′,3′:7,8)xanthone and named garcimangosone C.

Compound **4** was obtained as a yellow powder and was a benzophenone glucoside based on the spectral analysis. The positive FABMS displayed an ion peak at *m*/*z* 393 [M + H]$^+$ corresponding to $C_{19}H_{20}O_9$. The ^{13}C and DEPT NMR spectra of **4** showed 19 carbons including one methylene, 12 methine, five quaternary, and one carbonyl carbon. In the ^{1}H NMR spectrum of **4**, the appearance of the signals at δ 2.68, 3.25, 3.36, 3.40, 3.66, 3.84, 4.82, correlating with the carbon signals at δ 62.5 (C-6″), 71.0 (C-4″), 74.2 (C-2″), 77.4 (C-3″), 77.7 (C-5″), and 101.0 (C-1″) in the HETCOR spectrum, suggested the presence a six-membered sugar in the structure of **4**. The remaining signals were attributed to two *m*-coupled aromatic protons at δ 6.12 and 6.26 and five protons of a phenyl group at δ 7.40 (2H), 7.49 (1H), 7.62 (2H). Acid hydrolysis of **4** gave a sugar moiety that was identified as glucose through use of high-performance anion-exchange chromatography.[11]

In the HMBC spectrum of **4** (Figure 1, Supporting Information), the aromatic proton signal at δ 7.62 (H-2′, 6′) showed cross-peaks with the carbonyl carbon signal at δ 198.9. Both aromatic protons at δ 6.12 (H-3) and 6.26 (H-5) correlated with each other and showed cross-peaks with a quaternary carbon signal at δ 107.4 (C-1) and a *O*-linked carbon signal at δ 164.8 (C-4). The former (H-3) showed a cross-peak with an *O*-linked carbon signal at δ 163.9 (C-2), and the latter (H-5) showed a cross-peak with another *O*-linked carbon signal at δ 160.0 (C-6) that correlated with the anomeric proton signal of glucose at δ 4.82 (H-1″). Thus, glucose was determined to be at C-2, and **4** was determined to be 2,4-dihydroxy-6-*O*-β-D-glucoside-benzophenone and named garcimangosone D. In the ^{1}H NMR spectrum of **4**, the glucosyl proton signal at C-2″ shifted upfield and appeared at δ 2.68, which was considered to be due to the shielding effect from the phenyl group.

Experimental Section

General Experimental Procedures. IR spectra were taken on an Avatar 320 FT-IR spectrometer. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. UV spectra were recorded on a JASCO model 7800 UV/vis spectrometer. EIMS spectra were obtained using a JEOL JMS-D100 or Finnigan MAT GCQ spectrometer. LCMS spectra were taken on a Finnigan LCQ. ^{1}H NMR and ^{13}C NMR spectra were measured with a Varian Gemini-500 spectrometer.

Plant Material. The fruit hulls of *G. mangostana* were collected at a local market in Taipei, Taiwan, in July, 1998.

Extraction and Isolation. The air-dried fruit hulls of *G. mangostana* (3 kg) were extracted with EtOH. After evaporation of the solvent, the concentrated EtOH extract was partioned between EtOAc and H_2O, and the EtOAc fraction was chromatographed on a silica gel column eluting with gradient solvent systems of *n*-hexanes−EtOAc (20:1 to 5:1), CH_2Cl_2−Me_2CO (10:1 to 0:1), and CH_2Cl_2−MeOH (10:1 to 0:1) to yield 22 fractions. Fractions 5−9 belonged to the portion eluted with *n*-hexanes−EtOAc (10:1 to 5:1), and each fraction was further separated by a silica gel column (*n*-hexanes−EtOAc = 15:1), Sephadex LH-20 (MeOH−H_2O = 3:1), and preparative silica-TLC (*n*-hexanes−EtOAc = 15:1) to afford tovophyllin A (12 mg),[7] tovophyllin B (10 mg),[7,8] garcimangosone A (**1**, 8 mg), 5,9-dihydroxy-8-methoxy-2,2-dimethyl-7-(3-methylbut-2-enyl)-2*H*,6*H*-pyrano-[3,2-*b*]xanthone-6-one (20 mg),[12] 8-desoxygartanin (180 mg),[13] gartanin (240 mg),[13] β-mangostin (18 mg),[14] garcinone E (16 mg),[5] 1,7-dihydroxy-2-isoprenyl-3-methoxyxanthone (12 mg),[14] and 1,5-dihydroxy-

2-isoprenyl-3-methoxyxanthone (4 mg).[14] Fractions 10−14 belonged to the portion eluted with CH_2Cl_2−Me_2CO (10:1), of which fraction 10 was repeatedly rechromatographed over a silica gel column eluting with *n*-hexanes−EtOAc (5:1) to give α-mangostin (54 mg).[14] From fraction 11, the Me_2CO-undissolved precipitate was obtained, which was determined to be garcimangosone C (**3**, 8 mg), and the filtrate was further purified by Sephadex LH-20 (MeOH−H_2O = 5:1) and preparative silica-TLC (CH_2Cl_2−Me_2CO = 15:1) to afford γ-mangostin (120 mg)[5] and 1-isomangostin (6 mg).[15] Moreover, fractions 12 and 14 were separated on a silica gel column eluting with CH_2Cl_2−Me_2CO (20:1 to 5:1) and Sephadex LH-20 (MeOH−H_2O = 3:1) to give garcinone B (5 mg),[9] garcimangosone B (**2**, 7 mg), garcinone-D (16 mg),[3] 3-isomangostin (4 mg),[15] and mangostanol (**5**, 7 mg).[1] Fraction 15, CH_2Cl_2−Me_2CO = 5:1 eluate, was purified through a silica gel column eluting with CH_2Cl_2−Me_2CO (15:1), Sephadex LH-20 (MeOH−H_2O = 3:1), and preparative silica-TLC (CH_2Cl_2−Me_2CO = 10:1) to give 1,3,6,7-tetrahydroxy-8-(3-methyl-2-butenyl)-9*H*-xanthen-9-one (22 mg).[9] Fraction 18, eluting with CH_2Cl_2−MeOH (10:1), was further separated by a silica gel column eluting with CH_2Cl_2−MeOH (20:1 to 10:1) and Sephadex LH-20 (MeOH−H_2O = 3:1) to afford (−)-epicatechin (220 mg).[16] Fractions 19 and 20, eluting with CH_2Cl_2−MeOH (5:1), were purified by a silica gel column eluting with CH_2Cl_2−MeOH (20:1 to 5:1) and Sephadex LH-20 (MeOH−H_2O = 2:1 to 5:1) to obtain garcimangosone D (**4**, 12 mg), taxifolin-3-*O*-α-L-rhamnoside (30 mg),[17] and proanthocyanidin A_2 (18 mg).[18] Furthermore, the H_2O fraction was separated by elution from Diaion HP-20 with aqueous MeOH (25%, 50%, 100%). The 25% eluate was further separated using Sephadex LH-20 (MeOH−H_2O = 2:1) to give 11 fractions. Fraction 4 was purified by a silica gel column eluting with EtOAc−MeOH (30:1 to 20:1), Sephadex LH-20 (MeOH−H_2O = 2:1), and preparative silica-TLC (EtOAc−MeOH = 25:1) to give procyandin B_2 (12 mg).[18,19] Fraction 9 was repeatedly rechromatographed over Sephadex LH-20 (MeOH−H_2O = 2:1) to obtain procyanidin B_5 (27 mg).[18,19] Fraction 11 was further separated by Sephadex LH-20 (MeOH−H_2O = 2:1) and preparative silica-TLC (EtOAc−MeOH−H_2O = 5:1:1) to afford proanthocyanidin A_1 (13 mg).[20]

Garcimangosone A (1): yellow powder; mp 143−145°; UV (MeOH) λ_{max} (log ϵ) 342 (4.25), 285 (4.69) nm; IR (KBr) ν_{max} 3449 (OH), 2923, 1647, 1614, 1441, 1366, 1177, 1116 cm^{-1}; ^1H NMR (Me_2CO-d_6, 500 MHz) δ 13.97 (1H, s, 1-OH), 6.93 (1H, d, J = 10.0 Hz, H-21), 6.68 (1H, d, J = 10.5 Hz, H-11), 6.35 (1H, s, H-4), 5.88 (1H, d, J = 10.0 Hz, H-22), 5.69 (1H, d, J = 10.5 Hz, H-12), 5.30 (1H, br t, J = 6.6 Hz, H-17), 4.13 (2H, d, J = 7.0 Hz, H-16), 1.81, 1.63 (each 3H, s, H-19, H-20), 1.51 (6H, s, H-24, H-25), 1.45 (6H, s, H-14, H-15); ^{13}C NMR (Me_2CO-d_6, 125 MHz), Table 1; EIMS *m*/*z* 460 $[M]^+$ (83), 445 (100), 418 (85), 389 (19); HREIMS *m*/*z* 460.1883 (calcd for $C_{28}H_{28}O_6$, 460.1887).

Garcimangosone B (2): yellow powder; mp 136−138°; UV (MeOH) λ_{max} (log ϵ) 330 (3.92), 288 (4.25) nm; IR (KBr) ν_{max} 3456 (OH), 2972, 1649, 1604, 1466, 1290, 1177, 1123 cm^{-1}; ^1H NMR (Me_2CO-d_6, 500 MHz) δ 14.24 (1H, s, 1-OH), 6.77 (1H, s, H-5), 6.65 (1H, d, J = 9.5 Hz, H-11), 6.17 (1H, s, H-4), 5.65 (1H, d, J = 9.5 Hz, H-12), 3.88 (3H, s, OCH_3), 3.42 (2H, m, H-16), 1.75 (2H, m, H-17), 1.42 (6H, s, H-14, H-15), 1.28 (6H, s, H-19, H-20); ^{13}C NMR (Me_2CO-d_6, 125 MHz), Table 1; EIMS *m*/*z* 408 $[M]^+$ (38), 393 (100), 379 (19), 365 (32), 342 (23), 327 (25), 313 (36), 299 (47); HREIMS *m*/*z* 408.1575 (calcd for $C_{24}H_{24}O_6$, 408.1574).

Garcimangosone C (3): yellow powder; mp 260−262°; UV (MeOH) λ_{max} (log ϵ) 442 (4.11), 261 (4.03), 242 (4.18) nm; IR (KBr) ν_{max} 3388 (OH), 2923, 1621, 1552, 1464, 1384,1202, 1065 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 6.53 (1H, s, H-4), 6.14 (1H, s, H-6), 5.13 (1H, br t, J = 6.6 Hz, H-12), 4.41 (1H, dd, J = 12.7, 3.0 Hz, H-17), 3.26 (2H, d, J = 6.6 Hz, H-11), 3.14 (1H, dd, J = 16.6, 3.0 Hz, H-16a), 2.75 (1H, dd, J = 16.6, 12.7 Hz, H-16b), 1.72, 1.62 (each 3H, s, H-14, H-15), 1.34, 1.25 (each 3H, s, H-19, H-20); ^{13}C NMR (DMSO-d_6, 125 MHz), Table 1; EIMS *m*/*z* 412 $[M]^+$ (46), 394 (96), 379 (69), 357 (47), 339 (100), 323 (50), 297 (26); HREIMS *m*/*z* 412.1519 (calcd for $C_{23}H_{24}O_7$, 412.1523).

Table 1. ^{13}C NMR Data (δ) for **1**, **2**, and **3**

no.	**1**[a]	**2**[a]	**3**[b]
1	158.6	158.5	153.3
2	105.0	104.7	112.3
3	160.6	160.1	161.4
4	94.6	94.5	94.9
4a	157.0	157.1	153.0
5	146.9	102.9	158.9
6	108.0	146.1	99.9
7	141.5	146.1	144.7
8	128.9	138.7	99.1
8a	113.0	109.3	106.2
9	183.4	182.3	175.2
9a	104.3	104.0	96.6
10a	147.9	157.1	156.3
11	116.0	116.1	21.4
12	128.4	128.0	122.2
13	78.7	78.4	130.8
14	28.4	28.4	17.7
15	28.4	28.4	25.5
16	26.3	23.2	21.3
17	124.2	45.7	86.5
18	131.5	70.4	70.0
19	18.2	29.4	24.4
20	26.0	29.4	26.3
21	115.8		
22	130.8		
23	79.6		
24	28.2		
25	28.2		
OCH_3		60.9	

[a] Measured in Me_2CO-d_6. [b] Measured in DMSO-d_6.

Garcimangosone D (4): yellow powder; mp 136−138°; $[\alpha]^{25}_D$ −64° (*c* 0.5, MeOH); UV (MeOH) λ_{max} (log ϵ) 258 (4.37), 204 (4.80) nm; IR (KBr) ν_{max} 3362 (OH), 2917, 1600, 1450, 1277, 1074 cm^{-1}; ^1H NMR (Me_2CO-d_6, 500 MHz) δ 7.62 (2H, m, H-2′, 6′), 7.49 (1H, m, H-4′), 7.40 (2H, m, H-3′, 5′), 6.26 (1H, d, J = 2.0 Hz, H-5), 6.12 (1H, d, J = 2.0 Hz, H-3), 4.82 (1H, d, J = 8.0 Hz, H-1″), 3.84 (1H, dd, J = 12.0, 3.0 Hz, H-6″), 3.66 (1H, dd, J = 12.0, 6.0 Hz, H-6″), 3.40 (1H, m, H-5″), 3.36 (1H, br t, J = 8.5 Hz, H-3″), 3.25 (1H, br t, J = 8.5 Hz, H-4″), 2.68 (1H, br t, J = 8.0 Hz, H-2″); ^{13}C NMR (Me_2CO-d_6, 125 MHz) δ 198.9 (C=O), 164.8 (C-4), 163.9 (C-2), 160.0 (C-6), 142.2 (C-1′), 132.1 (C-4′), 129.3 (C-2′, 6′), 128.5 (C-3′, 5′), 107.4 (C-1), 101.0 (C-1″), 97.9 (C-3), 95.6 (C-5), 77.7 (C-5″), 77.4 (C-3″), 74.2 (C-2″), 71.0 (C-4″), 62.5 (C-6″); positive FABMS *m*/*z* 393 $[M + H]^+$ (64); HRFABMS 393.1172 $[M + H]^+$ (calcd for $C_{19}H_{21}O_9$, 393.1186).

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Supporting Information Available: HMBC data of compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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