Chemical Constituents from the Bark of *Garcinia xanthochymus* and Their 1,1-Diphenyl-2-picrylhydrazyl (DPPH) Radical-Scavenging Activities

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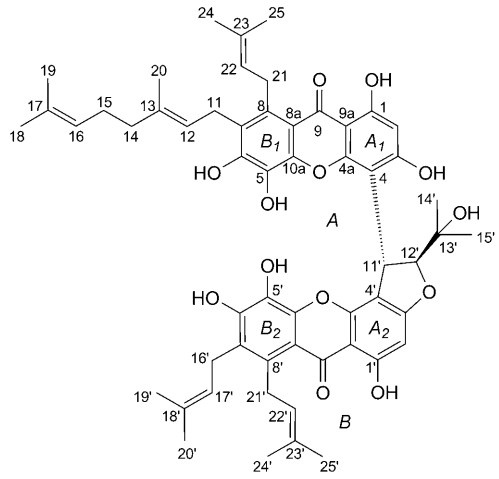
A new bis-xanthone (xanthone = 9*H*-xanthen-9-one), named bigarcinenone A (**1**) which is the first example of a bis-xanthone with the xanthone–xanthone linkage between an aromatic C-atom and a C_5 side chain from a guttiferae plant, a new phloroglucinol (= benzene-1,3,5-triol) derivative, named garcinenone F (**2**), together with seven known xanthones were isolated from the bark of *Garcinia xanthochymus*. Their structures were elucidated by spectroscopic methods, especially 2D-NMR techniques. Bigarcinenone A (**1**) exhibited potent antioxidant activity in the 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical-scavenging test with a IC_{50} value of 9.2 μM, compared to the positive control, the well-known antioxidant butylated hydroxytoluene (BHT) with a IC_{50} of 20 μM (*Table 3*).

Introduction. – The genus *Garcinia* belongs to the Guttiferae family, which comprises 200 species confined to the tropics as trees or shrubs, and rarely subshrubs, and there are 21 species in China [1][2]. It is well known to be a rich source of oxygenated and prenylated xanthones (= 9*H*-xanthon-9-ones) [2]. Xanthone constituents have been reported to possess several biological activities, such as cytotoxic [3], antimalarial [4], antimicrobial [5], antioxidant [6], trypanocidal [7], and antiplasmodial activities [8].

Garcinia xanthochymus is a traditional Dai medicine native to the south and southwest of Yunnan Province, P. R. China, which can grow up to 10–20 m. It is widely used as a traditional medicine for dispelling worms and removing food toxin [9]. Previous phytochemical studies of the leaves, seeds, fruits, twig bark, and wood have shown the presence of benzophenones [10], flavonoids [11], triterpenes [12], and xanthones [13]. In the course of our ongoing research project on bioactive natural products from *G. xanthochymus*, an AcOEt-soluble part of the EtOH extract of the bark of *G. xanthochymus* was found to have significant antioxidant activity (IC_{50} = 4.6 μg/ml) as determined by a 1,1-diphenyl-2-picrylhydrazyl (= 1,1-diphenyl-2-(2,4,6-trinitrophenyl)hydrazyl; DPPH) scavenging bioassay in our preliminary test. This prompted us to perform a detailed bioassay-guided isolation on this plant. As a result, a new bis-xanthone, named bigarcinenone A (**1**), which is the first example of a bis-xanthone with the xanthone–xanthone linkage between an aromatic C-atom and a C_5 side chain from a guttiferae plant, a new phloroglucinol (= benzene-1,3,5-triol) derivative, named garcinenone F (**2**), together with seven known xanthones were

isolated from the bark of *Garcinia xanthochymus*. Their structures were elucidated by spectroscopic methods, especially 2D-NMR techniques. This paper deals with the structural investigation of these natural products and their DPPH-radical-scavenging activities.



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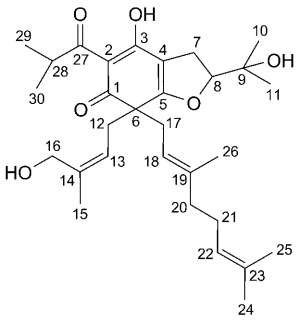

2[1])

Result and Discussion. – Compound **1** was obtained as yellow, optically active powder. The UV spectrum of **1** suggested the presence of a xanthone structure [14], while the complexity of the ^{1}H- and ^{13}C-NMR spectra pointed to the structure of a bis-xanthone. This was supported by the HR-ESI-MS, which showed a pseudomolecular ion peak $[M+\mathrm{Na}]^+$ at m/z 965.4112 corresponding to $C_{56}H_{62}NaO_{13}^+$. The ^{1}H- and ^{13}C-NMR data (*Table 1*) suggested that **1** possessed two similar prenylated xanthone moieties. ^{1}H,^{1}H-COSY, HMBC (*Fig.*) and ROESY experiments and comparison with known compounds established the structure of **1** as *rel*-(11′*R*,12′*R*)-4-[11′,12′-dihydro-1′,5′,6′-trihydroxy-12′-(1-hydroxy-1-methylethyl)-7′,8′-bis(3-methylbut-2-en-1-yl)-9-oxo-9*H*-furo[2,3-*c*]xanthene-11′-yl]-7-geranyl-1,3,5,6-tetrahydroxy-8-(3-methylbut-2-en-1-yl)-9*H*-xanthen-9-one[1]) which was named bigarcinenone A.

The ^{1}H- and ^{13}C-NMR data revealed that part *A* of **1** resembled those of the known compound garciniaxanthone E [15]. The ^{1}H-NMR spectrum (*Table 1*) showed a chelated OH group (δ(H) 13.7 (*s*)), a geranyl group (δ(H) 3.38–3.44 (*m*, 2 H), 4.99–5.04 (*m*, 1 H), 1.74 (*s*, 3 H), 1.96–1.99 (*m*, 2 H), 2.04–2.08 (*m*, 2 H), 4.99–5.04 (*m*, 1 H), 1.54 (*s*, 3 H), and 1.63 (*s*, 3 H)), a 3-methylbut-2-en-1-yl group (δ(H) 1.60 (*s*, 3 H), 1.74 (*s*, 3 H), 4.02–4.03 (*m*, 2 H), and 4.99–5.04 (*m*, 1 H)), and an isolated aromatic H-atom (δ(H) 6.27 (*s*)). Comparison of the ^{1}H-NMR data of garciniaxanthone E with those of part *A* of **1** suggested that the pair of *meta*-coupled aromatic H-atoms at δ(H) 6.11 (*d*, $J = 1.5$) and 6.36 (*d*, $J = 1.5$) of garciniaxanthone E were replaced in **1** by the isolated aromatic H-atom at δ(H) 6.27 (*s*). The only difference of the ^{13}C-NMR data of part *A* of **1** and garciniaxanthone E was that the CH signal at δ(C) 93.0 (*d*) of garciniaxanthone E was replaced in **1** by the quaternary C-atom at δ(C) 106.8 (*s*). Thus, these data suggested that the structure of part *A* of **1** was the same as that of garciniaxanthone E, except for the

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part.*

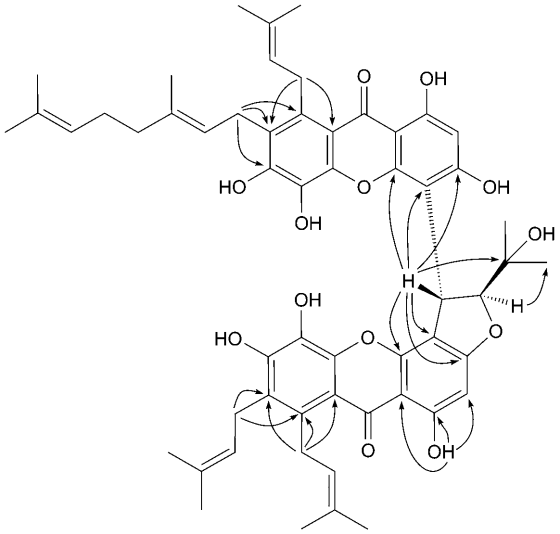

Figure. *Significant HMBCs for compound* **1**

presence of one more substituent group at C(4). This was further confirmed by HMBC experiments (*Fig.*). The correlations δ(H) 3.38–3.44/δ(C) 148.6 (C(6)), 125.8 (C(7)), and 134.2 (C(8)) and δ(H) 4.02–4.03/δ(C) 110.9 (C(8a)), 125.8 (C(7)), and 134.2 (C(8)) indicated that the geranyl and 3-methylbut-2-en-1-yl group were located at C(7) and C(8), respectively[1]). The correlations OH–C(1) (13.7 (*s*))/δ(C) 104.0 (C(9a)), 164.8 (C(1)), and 93.0 (*d*), and δ(H) 6.27/δ(C) 104.0 (C(9a)), 164.8 (C(1)), and 106.8(*s*) allowed us to establish an unequivocal assignment of δ(C) 93.0 (*d*) to C(2) and 106.8 (*s*) to C(4). Furthermore, the structure of part *A* was in agreement with its EI-MS (*m*/*z* 464).

Except for the ^{1}H-NMR signals of part *A* mentioned above, the signals of two additional 3-methylbut-2-en-1-yl groups, of an isolated aromatic H-atom (δ(H) 6.48 (*s*)), and of a chelated OH group (δ(H) 13.6 (*s*)) appeared in the ^{1}H-NMR spectrum of part *B* of **1**. The ^{13}C-NMR data of ring B_2 of part *B* of **1** were similar to those of 1,3,5,6-tetrahydroxy-4,7,8-tris(3-methylbut-2-en-1-yl)xanthone [13b], suggesting that the substituent pattern of ring B_2 of part *B* was identical to that of 1,3,5,6-tetrahydroxy-4,7,8-tris(3-methylbut-2-en-1-yl)xanthone. This was further confirmed by HMBC experiments (*Fig.*). Combining the DEPT and 2D-NMR, the signals at δ(H) 5.77 (*d*, J = 3.6, 1 H), 5.47 (*d*, J = 3.6, 1 H), and 1.35 and 1.43 (2*s*, each 3 H) and δ(C) at 35.1 (*d*), 96.9 (*d*), 72.1 (*s*), and 24.9 (2*q*) indicated the presence of a 2,3-dihydro-2-(1-hydroxy-1-methylethyl)furan-3-yl moiety. A *trans*-configuration of the H-atoms of the dihydrofuranyl moiety was inferred from their coupling constant (J(11′,12′) = 3.6 Hz) [16]. This assumption was further supported by the NOEs Me(14′) (δ(H) 1.35 (*s*)) and Me(15′) (δ(H) 1.43 (*s*))/H–C(11′) (δ(H) 5.77 (*d*, J = 3.6)) in the ROESY plot. The correlations δ(H) 5.77/δ(C) 154.9 (C(4′a)), 107.0 (C(4′)), and 165.6 (C(3′)), and δ(H) 5.47/δ(C) 107.0 (C(4′)) and 165.6 (C(3′)) in the HMBC plot established the location of the dihydrofuran ring at C(3′) and C(4′) of the xanthone moiety with an ether linkage at C(3′). The correlation δ(H) 5.77/δ(C) 150.6 (C(4a)), 154.9 (C(4′a)), 106.8 (C(4)), 107.0 (C(4′)), 160.6 (C(3)), and 165.6 (C(3′)) in the HMBC plot and the correlation δ(H) 5.77/δ(C) 35.1 (C(11′)) in the HSQC plot indicated that C(4) of part *A* was connected to C(11′) of part *B*. Therefore, the structure of bigarcinenone A was deduced as shown for **1**. However, the absolute configuration of **1** was not determined.

Naturally occurring bis-xanthones from guttiferae plants are rare; they include ether-linked ones such as mesuabixanthone A and B linked through a dioxane ring

Table 1. *^{1}H- and ^{13}C-NMR Data* ((D_6)acetone) of **1**[1]). δ in ppm, J in Hz.

Part *A*			Part *B*		
	δ(H)	δ(C)		δ(H)	δ(C)
C(1)		164.8	C(1′)		162.8
H–C(2)	6.27 (*s*)	93.0	H–C(2′)	6.48 (*s*)	99.2
C(3)		160.6	C(3′)		165.6
C(4)		106.8	C(4′)		107.0
C(4a)		150.6	C(4′a)		154.9
C(5)		131.0	C(5′)		131.3
C(6)		148.6	C(6′)		156.1
C(7)		125.8	C(7′)		125.9
C(8)		134.2	C(8′)		134.3
C(8a)		110.9	C(8′a)		111.0
C(9)		182.6	C(9′)		182.6
C(9a)		104.0	C(9′a)		104.1
C(10a)		144.6	C(10′a)		144.6
CH_2(11)	3.38–3.44 (*m*)	24.3	H–C(11′)	5.77 (*d*, J = 3.6)	35.1
H–C(12)	4.99–5.04 (*m*)	123.1	H–C(12′)	5.47 (*d*, J = 3.6)	96.9
C(13)		135.0	C(13′)		72.1
CH_2(14)	1.96–1.99 (*m*)	39.7	Me(14′)	1.35 (*s*)	24.9
CH_2(15)	2.04–2.08 (*m*)	26.6	Me(15′)	1.43 (*s*)	24.9
H–C(16)	4.99–5.04 (*m*)	124.4	CH_2(16′)	3.38–3.44 (*m*)	24.5
C(17)		131.0	H–C(17′)	4.99–5.04 (*m*)	123.1
Me(18)	1.63 (*s*)	25.2	C(18)		131.3
Me(19)	1.54 (*s*)	17.1	Me(19′)	1.60 (*s*)	25.2
Me(20)	1.74 (*s*)	15.9	Me(20′)	1.76 (*s*)	17.5
CH_2(21)	4.02–4.03 (*m*)	28.2	CH_2(21′)	4.02–4.03 (*m*)	28.2
H–C(22)	4.99–5.04 (*m*)	124.7	H–C(22′)	4.99–5.04 (*m*)	124.7
C(23)		130.0	C(23′)		130.1
Me(24)	1.60 (*s*)	25.2	Me(24′)	1.60 (*s*)	25.2
Me(25)	1.74 (*s*)	17.6	Me(25′)	1.74 (*s*)	17.6
OH–C(1)	13.7 (*s*)		OH–C(1)	13.6	

system (isolated from *Mesua ferrea*) [17], bijaponicaxanthone [11], bijaponicaxanthone C [18], and jacarelhyperol D [19] linked through the dehydrogenation between a phenol-like OH group and a CH group of the side chain (from *Hypericum japonicun*), and C–C linked bis-xanthones such as garcilivins A–C [20] linked through 3-methylbut-2-en-1-yl side chains (from *G. livingstonei*) and griffipavixanthone [21] with cyclized prenyl groups providing the linkage (from *G. pavifolia*). To the best of our knowledge, bigarcinenone A (**1**) is the first example of a bis-xanthone with the xanthone–xanthone linkage between an aromatic C-atom and a C_5 side chain from guttiferae plants.

Compound **2** was isolated as a colorless, optically active oil. The molecular formula of **2** was determined as $C_{30}H_{44}O_6$ by HR-EI-MS (M^+ at m/z 500.3132). The ^{1}H- and ^{13}C-NMR, and HMBC data (*Table 2*) suggested that **2** was a phloroglucinol derivative. Further confirmation of the structure was provided by the 2D-NMR data and comparison with known compounds. From these data, the structure of **2** was identified as 7-geranyl-3,7-dihydro-4-hydroxy-7-(4-hydroxy-3-methylbut-2-en-1-yl)-2-(1-hy-

Table 2. *^{1}H- and ^{13}C-NMR, and HMBC Data* ((D$_6$)acetone) *of* **2**[1]). δ in ppm, J in Hz.

	δ(H)	δ(C)	HMBC (H → C)
C(1)		196.3 (*s*)	
C(2)		107.5 (*s*)	
C(3)		188.6 (*s*)	
C(4)		110.4 (*s*)	
C(5)		178.6 (3)	
C(6)		55.7 (*s*)	
CH_2(7)	2.95–3.00 (*m*)	27.1 (*t*)	C(4), C(5), C(8), C(9)
H–C(8)	4.91–4.95 (*m*)	93.6 (*d*)	C(10), C(11)
C(9)		71.0 (*s*)	
Me(10)	1.26 (*s*)	25.5 (*q*)	C(8), C(9)
Me(11)	1.31 (*s*)	25.5 (*q*)	C(8), C(9)
CH_2(12)	2.47 (*dd*, J = 13.2, 8.7), 2.68–2.78 (*m*)	36.3 (*t*)	C(1), C(5), C(6), C(13), C(14)
H–C(13)	4.95–5.05 (*m*)	120.4 (*d*)	
C(14)		139.6 (*s*)	
Me(15)	1.65 (*s*)	21.3 (*q*)	C(13), C(14), C(16)
CH_2(16)	4.05 (br. *s*)	60.6 (*t*)	C(13), C(14), C(15)
CH_2(17)	2.43 (*dd*, J = 13.8, 6), 2.68–2.78 (*m*)	37.6 (*t*)	C(1), C(5), C(6), C(18), C(19)
H–C(18)	4.95–5.05 (*m*)	118.7 (*d*)	
C(19)		138.5 (*s*)	
CH_2(20)	1.86–1.90 (*m*)	40.0 (*t*)	
CH_2(21)	1.92–1.96 (*m*)	27.0 (*t*)	C(22), C(23)
H–C(22)	4.95–5.05 (*m*)	124.5 (*d*)	
C(23)		131.5 (*s*)	
Me(24)	1.47 (*s*)	17.3 (*q*)	C(22), C(23)
Me(25)	1.61 (*s*)	25.1 (*q*)	C(22), C(23)
Me(26)	1.52 (*s*)	16.2 (*q*)	C(18), C(19), C(20)
C(27)		207.9 (*s*)	
H–C(28)	3.93–4.01 (*m*)	34.8 (*d*)	
Me(29)	1.07 (*d*, J = 7.5)	18.7 (*q*)	C(28)
Me(30)	1.09 (*d*, J = 7.5)	19.0 (*q*)	C(28)
OH–C(3)	19.2 (*s*)		

droxy-1-methylethyl)-5-(2-methylpropanoyl)benzofuran-6(2*H*)-one, which was named garcinenone F.

The ^{13}C-NMR spectrum showed 30 C-atoms: eight Me groups, six CH_2 groups including an oxygenated one, five CH groups, and eleven quaternary C-atoms. Comparison of the ^{13}C-NMR data of **2** with those of hyperalin C, isolated from *Hypericum calycinum* L. [22], revealed that **2** contained two enolic C-atoms at δ(C) 188.6 (C(3)) and 178.6 (C(5)), one C=O group at δ(C) 196.3 (C(1)), and three quaternary C-atoms at δ(C) 107.5 (C(2)), 110.4 (C(4)), and 55.7 (C(6))[1]), which was the same as for hyperalin C. Thus, **2** was characterized as having a cyclohexa-2,4-dien-1-one moiety. Extensive analysis of the ^{1}H- and ^{13}C-NMR spectra, together with HMBC spectra, indicated the presence of an enolic H-atom (δ(H) 19.2 (*s*, 1 H)), a 4-hydroxy-3-methylbut-2-en-1-yl group (δ(H) 2.47 (*dd*, J = 13.2, 8.7, 1 H), 2.68–2.78 (*m*, 1 H), 4.95–5.05 (*m*, 1 H), 1.65 (*s*, 3 H), and 4.05 (br. *s*, 2 H); δ(C) 36.3 (*t*), 120.4 (*d*), 139.6 (*s*), 21.3 (*q*), and 60.6 (*t*)), a geranyl group (δ(H) 2.43 (*dd*, J = 13.8, 6, 1 H), 2.68–2.78 (*m*, 1 H), 4.95–5.05 (*m*, 1 H), 1.86–1.90 (*m*, 2 H), 1.92–1.96 (*m*, 2 H), 4.95–5.05 (*m*, 1 H), 1.47 (*s*, 3 H), 1.61 (*s*, 3 H), and 1.52 (*s*); δ(C) 37.6 (*t*), 118.7 (*d*), 138.5 (*s*), 40.0 (*t*), 27.0 (*t*), 124.5 (*d*), 131.5 (*s*), 17.3 (*q*) 25.1 (*q*), and 16.2 (*q*)), a 2-methylpropanoyl group (δ(H) 3.93–4.01 (*m*), 1.07 (*d*, J = 7.5), and 1.09 (*d*, J = 7.5); δ(C) 207.9

(*s*), 34.8 (*d*), 18.7 (*q*), and 19.0 (*q*)), and a 2,3-dioxygenated 3-methylbutyl moiety (δ(H) 2.95–3.00 (*m*, 2 H), 4.91–4.95 (*m*, 1 H), 1.26 (*s*, 3 H), and 1.31 (*s*, 3 H); δ(C) 27.1 (*t*), 93.6, (*d*), 71.0 (*s*), and 25.5 (2*q*)). The positions of the substituents were deduced by analysis of the HMBC data (*Table 2*). The HMBC cross-peaks CH_2(12) and CH_2(17)/δ(C) 196.3 (C(1)), 178.6 (C(5)), and 55.7(C(6)), established that a 4-hydroxy-3-methylbut-2-en-1-yl and a geranyl group were linked to C(6). The HMBCs CH_2(7)/δ(C) 110.4 (C(4)), 178.6 (C(5)), 93.6 (C(8)), and 71.0 (C(9)), and comparison of the ^{13}C-NMR data of **2** with those of the known compound garcinielliptones HE [23d] revealed that the 2,3-dioxygenated 3-methylbutyl moiety was part of a 2,3-dihydro-2-(1-hydroxy-1-methylethyl)furan moiety fused at C(4) and C(5). The remaining 2-methylpropanoyl group was attached at C(2) based on NOEs between Me(29) and Me(30) and CH_2(16). Thus, the enolic OH groups should be located at C(3). The chemical shifts of H_α–C(7) and H_β–C(7) were overlapped in the ^{1}H-NMR. Thus, the relative configurations at C(6) and C(8) were not deduced from the ROESY data, and the absolute configuration of **2** remains undetermined.

A number of polyisoprenylated phloroglucinol derivatives have been isolated from *G. subelliptica* and other *Garcinia* species [23]. Most of them bear a bicyclononane ring system as in the case of hyperforin, whereas garcinenone F, having a cyclohexa-2,4-dien-1-one C-moiety is considered to be closely related to the lupulone derivatives occurring in *Humulus lupulus*. Lupulone derivatives possess one or more stereogenic centers, but these compounds were racemic ($[\alpha]_D = O$) [24]. However, **2** was optically active. Compound **2** was an unstable transparent oil, and crystals suitable for X-ray-analysis were not obtained. Therefore, the configuration of **2** was not determined. It should be noted that a phloroglucinol derivative of the type of garcinenone F was isolated for the first time from this plant, which is rich in xanthones.

The seven known compounds were identified as 1,4,5-trihydroxyxanthone [25], 1,2,5-trihydroxyxanthone [26], 1,2-dihydroxy-5,6-dimethoxyxanthone [26], 5-hydroxy-1,3-dimethoxyxanthone [27], 5-hydroxy-1,2-dimethoxyxanthone [27], 1,3,7-trihydroxy-5-methoxyxanthone [28], and 1,3,7-trihydroxyxanthone [29] by comparison of their spectroscopic data with those reported in the literature. Notably, all these simple oxygenated xanthones were isolated from *G. xanthochymus* for the first time.

Eight of the isolated xanthones were evaluated for their antioxidant activities by the DPPH-radical-scavenging method (*Table 3*) [30]. Most of the isolated compounds showed considerable radical-scavenging activity in the DPPH assay. The most active compound was **1** with an IC_{50} value of 9.2 μM, *i.e.*, **1** was 2-fold more potent than the well-known synthetic antioxidant butylated hydroxytoluene (BHT; $IC_{50} = 20.0$ μM). The DPPH-radical-scavenging activities of these compounds seemed to be related to the number of phenol like OH groups at the xanthone skeleton. It has been shown that the radical-scavenging activity was increased in the presence of an increasing number of phenol-like OH groups in a molecule [30]. However, 1,2-dihydroxy-5,6-dimethoxy-

Table 3. *DPPH-Radical-Scavenging Activity of* **1** *and Simple Oxygenated Xanthones*

	IC_{50} [μM]		IC_{50} [μM]
1	9.2	5-Hydroxy-1,3-dimethoxyxanthone	250.0
1,4,5-Trihydroxyxanthone	16.3	5-Hydroxy-1,2-dimethoxyxanthone	239.7
1,2,5-Trihydroxyxanthone	17.6	1,3,7-Trihydroxy-5-methoxyxanthone	23.3
1,2-Dihydroxy-5,6-dimethoxyxanthone	18.4	1,3,7-Trihydroxyxanthone	23.3
BHT	20.0		

xanthone having two OH groups showed a stronger radical-scavenging activity compared to 1,3,7-trihydroxy-5-methoxy- and 1,3,7-trihydroxyxanthenone which had three phenol-like OH groups. This was explained by the known strong antioxidant capacity of phenol-like *para*- and *ortho*-dihydroxy moieties, which confer a high stability to the formed radical and participate in the electron delocalization [32]. From the above data, it can be deduced that the main components responsible for the antioxidant activities of *Garcinia xanthochymus* are the xanthones derivatives.

We gratefully acknowledge financial support of this work by the *National Natural Science Foundation of China* (No. 30670215).

Experimental Part

General. Thin-layer chromatography (TLC): Pre-coated silica gel GF_{254} plates (*Qingdao Haiyang Chemical Co., Ltd.*, P. R. China). Column chromatography (CC): silica gel (SiO_2, 200–300 mesh; *Qingdao Haiyang Chemical Co., Ltd.*, P. R. China) and C_{18} reversed-phase silica gel (*YMC Co., Ltd.*, Japan). HPLC: *UltiMate-3000* HPLC system; *UltiMate-3000* pump; *UltiMate-3000* variable-wavelength detector; column *Waters* $5C_{18}$*-MS-II* (10 × 250 mm). Optical rotation: *Perkin-Elmer-341* polarimeter. UV Spectra: *SP-2102UVPC* spectrometer; λ_{max} (log ε) in nm. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-AM-400* instrument; δ in ppm rel. to Me_4Si as internal standard (= 0 ppm), *J* in Hz. EI- and HR-EI-MS: *Finnigan-MAT-95* mass spectrometer (70 eV); in *m*/*z* (rel. %). ESI- and HR-ESI-MS: *Finnigan-LCQ-Deca* and *Waters*/*Micromass-Q-Tof-Ultima* mass spectrometers, resp.; in *m*/*z* (rel. int.).

Plant Material. The barks of *Garcinia xanthochymus* were collected from the Xishuangbanna Prefecture, Yunnan Province, P. R. China, and the plant was identified by the Xishuangbanna Prefecture National Medicine Research Institute. The voucher specimen (06061201) was deposited in the herbarium of the College of Life Sciences, South Central University for Nationalities, P. R. China.

Extraction and Isolation. The milled, air-dried barks of *Garcinia xanthochymus* (6.5 kg) were powdered and then extracted with 95% EtOH (3 × 25 l) at r.t. The dried EtOH extract (1.5 kg) was suspended in 90% MeOH/H_2O and then successively partitioned with petroleum ether (3 × 3.0 l), AcOEt (3 × 3.0 l), and BuOH (3 × 3.0 l). The AcOEt extract (590 g) was subjected to CC (SiO_2, petroleum ether/Me_2CO 9:1, 8:2, 7:3, 1:1, 3:7, and 0:1): *Fractions 1–13*). *Fr. 5* (10.7 g) was subjected to CC (SiO_2, cyclohexane/Me_2CO 95:5 → 0:1): *Fr. 5.1–5.16*. The 1,3,7-trihydroxy-5-methoxyxanthone (1.2 mg) was crystallized from *Fr. 5.2*. *Fr. 5.5* (796.2 mg) was subjected to CC (SiO_2, cyclohexane/CH_2Cl_2 1:1 → 0:1): 1,2,5-trihydroxyxanthone (3.2 mg). *Fr. 6* (17.0 g) was subjected to CC (SiO_2, toluene/Me_2CO 95:5 → 3:7): *Fr. 6.1–6.16*. *Fr. 6.7* (6.54 g) was was subjected to CC (SiO_2, $CHCl_3$/Me_2CO 95:5 → 3:7): *Fr. 6.7.1–6.7.18*. *Fr. 6.7.8* (2.8 g) was purified by CC (SiO_2, CH_2Cl_2/MeOH 95:5 → 1:1) followed by semi-prep. HPLC (MeOH/H_2O 85:15, 3 ml/min; t_R 20.5 min): **2** (1.6 mg). *Fr. 6.8* (2.2 g) was subjected to CC (*ODS*, H_2O/MeOH 7:3 → 3:7) and then further purified by semi-prep. HPLC (MeOH/H_2O 88:12; t_R 30.6 min): **1** (5.6 mg). *Fr. 7* (33.8 g) was subjected to CC (SiO_2, toluene/Me_2CO 95:5 → 7:3): *Fr. 7.1–7.15*. *Fr. 7.4* (952.4 mg) was purified by CC (SiO_2, cyclohexane/CH_2Cl_2 1:1 → 0:1): 1,2-dihydroxy-5,6-dimethoxyxanthone (2.7 mg). *Fr. 7.5* (2.3 g) was subjected to CC (*ODS*, H_2O/MeOH 7:3 → 3:7): 1,3,7-trihydroxyxanthone (2.1 mg). *Fr. 8* (12.8 g) was subjected to CC (SiO_2, toluene/Me_2CO 9:1 → 3:7): *Fr. 8.1–8.9*). *Fr. 8.7* (856.8 mg) was then subjected to CC (*ODS*, H_2O/MeOH 7:3 → 3:7): 1,4,5-trihydroxyxanthone (6.2 mg). *Fr. 8.6* (573.8 mg) was subjected to CC (*ODS*, H_2O/MeOH 7:3 → 3:7): 5-hydroxy-1,3-dimethoxyxanthone (1.2 mg) and 5-hydroxy-1,2-dimethoxyxanthone (3.6 mg).

Bigarcinenone A (= rel-*(1*R*,2*R*)-1-{7-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-1,3,5,6-tetrahydroxy-8-(3-methylbut-2-en-1-yl)-9-oxo-9*H*-xanthen-4-yl}-1,2-dihydro-5,9,10-trihydroxy-2-(1-hydroxy-1-methylethyl)-7,8-bis(3-methylbut-2-en-1-yl)-6*H*-furo[2,3-c]xanthen-6-one*; **1**): Yellow amorphous powder. $[\alpha]_D = -1.3$ (*c* = 0.3, Me_2CO). UV (MeOH): 238 (4.38), 281 (4.09), 324 (4.12), 343 (4.14). ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS: 464 (34), 460 (60), 421 (50), 392 (100), 339 (72). HR-ESI-MS: 965.4112 ($[M + Na]^+$, $C_{56}H_{62}NaO_{13}^+$; calc. 965.4088).

Garcinenone F (= *7-[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]-3,7-dihydro-4-hydroxy-7-[(2*Z*)-4-hydroxy-3-methylbut-2-en-1-yl]-2-(1-hydroxy-1-methylethyl)-5-(2-methyl-1-oxopropyl)benzofuran-6-(2*H*)-one*; **2**): Colorless oil. $[\alpha]_D = +23.8$ ($c = 0.37$, Me_2CO). UV (MeOH): 211 (4.66), 268 (4.15), 286 (4.15), 309 (4.04). ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 499 (75, $[M-H]^+$). EI-MS: 500 (8, M^+), 415 (40), 364 (28), 346 (52), 303 (100), 293 (56), 69 (44). HR-EI-MS: 500.3132 ($C_{30}H_{44}O_6^+$; calc. 500.3138).

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Received March 17, 2008