

## Xanthenes from *Garcinia parvifolia*

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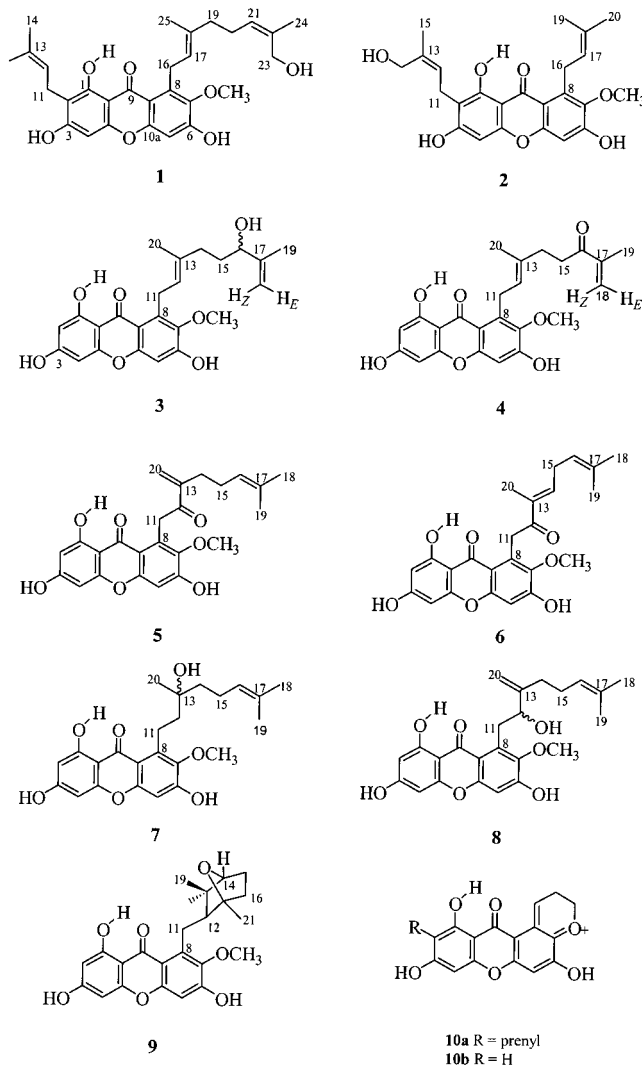
Nine new xanthenes, parvixanthenes A–I (**1–9**), isolated from the dried bark of *Garcinia parvifolia*, were found to have a common 1,3,6,7-oxygenated pattern for their xanthone nucleus, but various oxygenated isoprenyl or geranyl substituent groups. The structures were determined by spectroscopic methods.

The tropical family Guttiferae is well known to be a rich source of isoprenylated xanthenes and biflavonoids.<sup>1–4</sup> In particular, the genus *Garcinia* has also provided many bioactive isoprenylated and rearranged xanthenoids and biflavonoids.<sup>5–10</sup> In continuation of our search for bioactive natural products from Malaysian plants, we have examined the bark extracts of *G. parvifolia* Miq. (syn. *G. dioica* Bl.). The fruit of this tree is edible, and the young leaves are sometimes eaten as a vegetable.<sup>8</sup> Some known xanthenes, such as rubraxanthone, cowinin, and the novel cytotoxic griffiparvixanthone, have previously been isolated from this species.<sup>1,8</sup> In the present study, we report the isolation and structure determination of nine minor xanthenes (**1–9**) from the bark of *G. parvifolia*.

### Results and Discussion

The dried and ground bark of *G. parvifolia*, collected from Sabah (Malaysia), was extracted with *n*-hexane, chloroform, and methanol, successively. The chloroform extract was repeatedly chromatographed over Si gel and Sephadex LH-20 to give nine xanthenes (**1–9**).

Parvixanthone A (**1**) was isolated as a yellow gum. Its molecular formula C<sub>29</sub>H<sub>34</sub>O<sub>7</sub> was deduced by HREIMS [ $m/z$  494.2309 [M]<sup>+</sup> (calcd 494.2305)]. The <sup>1</sup>H NMR data of **1** showed characteristic peaks for a prenyl group [ $\delta$  3.55 (2H, d), 5.36 (1H, t), 1.52 (3H, s), 1.73 (3H, s)] and a geranyl group [ $\delta$  1.96–2.09 (4H, m), 4.13 (2H, d), 5.05 (1H, t), 5.29 (1H, t), 1.56 (3H, s), 1.83 (3H, s)] (Table 1). However, one of the methyl groups was hydroxylated to a hydroxymethylene group, which was confirmed by a methylene carbon at  $\delta$  62.3 that correlated with the two-proton resonance at  $\delta$  4.39 (HMQC). The UV, IR, and <sup>13</sup>C NMR spectra of **1** were quite similar to data published for cowanol,<sup>4</sup> which has a 1,3,6,7-tetrahydroxyxanthone nucleus. Only two such xanthenes have been reported, namely, cowanol and isocowanol, both isolated from the bark of *G. cowa*. Although many of the <sup>1</sup>H and <sup>13</sup>C NMR signals of **1** showed similarities to those of cowanol and isocowanol,<sup>4</sup> some distinguishable features were observed. For example, three olefinic protons of **1** were well separated ( $\delta$  5.05, 5.29, 5.36), while two of the three olefinic protons of isocowanol were overlapped at 5.29 ppm. Furthermore, the EIMS of **1** was quite different from those of cowanol and isocowanol; for example, the fragment ion **10a** ( $m/z$  355) of **1** was missing in cowanol.<sup>4</sup>



The methylene group at  $\delta$  4.13 indicated a deshielding by the adjacent carbonyl group and allowed the assignment of the geranyl group to position C-8. The hydroxymethylene group was deduced to be at the geranyl group from the important fragment at  $m/z$  355, which was formed from the loss of the hydroxylated geranyl side chain, and the fragment **10a**, which is quite common in 7-methoxy-8-geranyl-xanthenes.<sup>11</sup> This was confirmed by the long-range coupling (1.0 Hz) between the high-field olefinic proton (H-6 of the geranyl group) and the hydroxymethylene proton, which allowed the hydroxyl group to be placed at C-23

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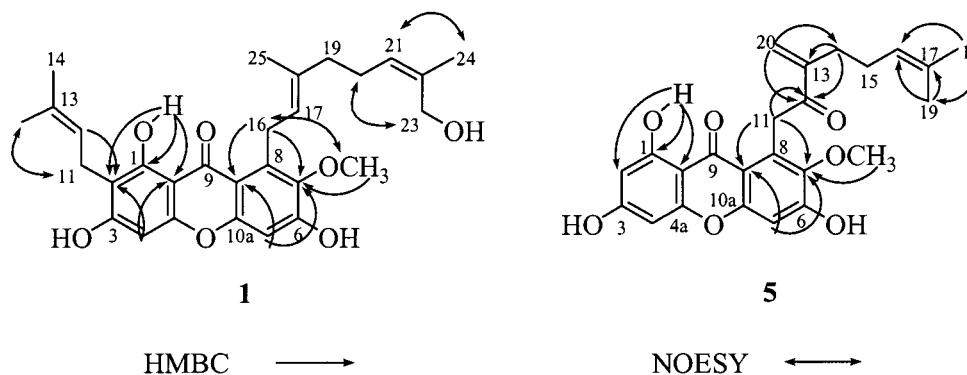
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**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR Data of **1** and **2** in Acetone- $d_6$ 

position	$\delta_{\text{H}}^a$		$\delta_{\text{C}}^b$	
	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>
1	13.80 (s, OH)	13.89 (s, OH)	162.9	162.9
2			106.2	111.7
3			163.6	163.8
4	6.25 (s)	6.37 (s)	99.1	94.4
4a			157.1	157.1
5	6.98 (s)	6.83 (s)	103.7	103.2
6			158.4	157.8
7			145.3	145.5
8			138.7	139.4
8a			112.3	113.2
9			183.7	183.5
9a			104.4	104.8
10a			155.7	155.9
11	3.55 (2H, d, $J = 7.6$ Hz)	3.43 (2H, d, $J = 7.1$ Hz)	27.9	21.8
12	5.36 (brt, $J = 7.6$ Hz)	5.35 (brt, $J = 7.1$ Hz)	125.9	125.8
13			132.2	136.9
14	1.73 (3H, s)	4.29 (2H, s)	18.3	61.6
15	1.52 (3H, s)	1.73 (3H, s)	26.4	21.5
16	4.13 (2H, d, $J = 6.4$ Hz)	4.12 (d, $J = 6.4$ Hz)	27.4	26.5
17	5.29 (brt, $J = 6.4$ Hz)	5.26 (brt, $J = 6.4$ Hz)	125.6	125.4
18			136.6	139.1
19	1.96–2.09 (2H, m)	1.82 (3H, s)	41.1	17.4
20	1.96–2.09 (2H, m)	1.65 (3H, s)	22.4	25.3
21	5.05 (brtt, $J = 6.8, 1.0$ Hz)		125.8	
22			135.7	
23	4.39 (d, $J = 1.0$ Hz)		62.3	
24	1.56 (3H, s)		17.3	
25	1.83 (3H, s)		22.5	
MeO-7	3.81 (3H, s)	3.85 (3H, s)	62.0	60.9

<sup>a</sup> 500 MHz, chemical shifts ( $\delta$ ) in ppm; integrated for one proton unless otherwise stated; coupling constant ( $J$ ) in Hz; s: singlet, d: doublet, m: multiplet. <sup>b</sup> 125 MHz, chemical shifts ( $\delta$ ) in ppm.

**Figure 1.** Structure and selected HMBC and NOESY correlations of compounds **1** and **5**.

rather than C-24 (Figure 1). The HMBC correlation C-7/H-16, OMe-7 and NOESY correlation H-16/OMe-7 indicated the methoxyl group was at C-7 adjacent to the 8-hydroxygeranyl group (Figure 1). The 2-prenyl group was determined by comparing the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data with related compounds<sup>4,11</sup> and confirmed by the HMBC correlations between C-2/H-4, H-12, OH-1 (Figure 1). The structure of compound **1** was determined as 1,3,6-trihydroxy-8-(8-hydroxy-3,7-dimethylocta-2,6-dienyl)-7-methoxy-2-(3-methylbut-2-enyl)xanthen-9-one and was given the trivial name parvixanthone A.

Compound **2** was isolated as a yellow powder, from which the molecular formula was determined as  $\text{C}_{24}\text{H}_{26}\text{O}_7$  by HREIMS ( $m/z$  426.1683, calcd 426.1679). The UV and IR spectra showed characteristic peaks for a 1,3,6,7-tetrahydroxylated xanthone.<sup>9</sup> Similar to **1**, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Table 1) spectra of **2** showed characteristic peaks for one chelated hydroxyl group, two isoprenyl groups, and one hydroxymethylene group. One of the isoprenyl groups was substituted at position C-8, which was deduced from the relatively low-field resonance of H-16 ( $\delta$  4.12) and confirmed by HMBC cross-peaks between H-16/C-7, 9a and H-5/C-7, 9a. A 14-hydroxylated isoprenyl group, deduced

from the HMBC correlations H-14/C-12, 13, 15 and H-15/C-12, 13, 14, was placed at position C-2 by the observed HMBC correlations at H-11/C-1, 3; OH-1/C-1, 2; and H-4/C-2. The NOESY correlations between H-14/H-11 and H-15/H-12 indicated that the double bond of this isoprenyl group has the *Z*-configuration. The 7-methoxyl group was deduced from the HMBC correlations of C-7/H-16, OMe-7 and the NOESY correlation of H-16/OMe-7. Thus, compound **2** was determined to be 1,3,6-trihydroxy-2-(4-hydroxy-3-methylbut-2-enyl)-7-methoxy-8-(3-methylbut-2-enyl)xanthen-9-one and given the trivial name parvixanthone B.

The new compound parvixanthone C (**3**) was isolated as a yellowish gum. The HREIMS indicated its molecular formula as  $\text{C}_{24}\text{H}_{26}\text{O}_7$ . Comparing the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data (Tables 2 and 3) with related compounds<sup>4</sup> (compounds **1** and **2**) revealed that **3** is a 1,3,6-tetraoxygenated xanthone including one methoxyl group and substituted by one 10-carbon unit. The  $^1\text{H}$  NMR data of **3** showed a downfield hydroxyl resonance at  $\delta$  13.50, two *meta*-coupled aromatic protons ( $\delta$  6.18, d,  $J = 1.4$  Hz; 6.29, d,  $J = 1.4$  Hz), a singlet aromatic proton ( $\delta$  6.83, H-5), and a methoxyl proton ( $\delta$  3.79, 3H, s). Similar to xanthonoids **1** and **2**, the attachment

**Table 2.**  $^1\text{H}$  NMR Data of Compounds **3–8** in Acetone- $d_6^a$ 

proton	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
1	13.50 (s, OH)	13.48 (s, OH)	13.17 (s, OH)	13.17 (s, OH)	13.48 (s, OH)	13.38 (s, OH)
2	6.18 (d, 1.4)	6.21 (d, 2.0)	6.18 (d, 2.0)	6.18 (d, 2.0)	6.20 (d, 1.6)	6.22 (d, 1.7)
4	6.29 (d, 1.4)	6.33 (d, 2.0)	6.34 (d, 2.0)	6.34 (d, 2.0)	6.31 (d, 1.6)	6.34 (d, 1.7)
5	6.84 (s)	6.86 (s)	6.92 (s)	6.92 (s)	6.84 (s)	6.88 (s)
11	4.11 (2H, d, 6.3)	4.13 (2H, d, 6.5)	4.79 (2H, s)	4.81 (2H, s)	3.43 (2H, brdd, 6.3, 10.3)	A: 3.69 (dd, 12.5, 3.6) B: 3.56 (dd, 12.5, 9.6)
12	5.30 (brt, 6.3)	5.31 (dt, 1.3, 6.5)			1.76 (2H, m)	4.42 (dd, 9.6, 3.6)
14	1.97 (2H, m)	2.26 (2H, t, 7.3)	2.35 (2H, t, 7.5)	5.93 (brt)	1.56 (2H, m)	2.18 (2H, m)
15	1.58 (2H, m)	2.79 (2H, t, 7.3)	2.18 (2H, m)	2.28–2.48 (2H, m)	2.19 (2H, m)	2.29 (2H, m)
16	3.95 (brdt, 1.4, 6.3)		5.18 (brt)	5.17 (brt)	5.18 (brt, 7.0)	5.23 (brt, 7.0)
18	4.83 (s, $\text{H}_\beta$ ) 4.68 (brd, 1.4, $\text{H}_\beta$ )	5.99 (s, $\text{H}_\beta$ ) 5.73 (s, $\text{H}_\beta$ )	1.68 (3H, s)	1.67 (3H, s)	1.67 (3H, s)	1.64 (3H, s)
19	1.63 (3H, s)	1.74 (3H, s)	1.60 (3H, s)	1.60 (3H, s)	1.30 (3H, s)	1.69 (3H, s)
20	1.83 (3H, s)	1.86 (3H, s)	6.32 (s, $\text{H}_\beta$ ) 5.88 (s, $\text{H}_\beta$ )	1.29 (3H, s)	1.64 (3H, s)	5.12 (s, $\text{H}_\beta$ ) 4.83 (s, $\text{H}_\beta$ )
MeO-7	3.80 (3H, s)	3.79 (3H, s)	3.73 (3H, s)	3.73 (3H, s)	3.85 (3H, s)	3.85 (3H, s)

<sup>a</sup> 500 MHz, chemical shifts ( $\delta$ ) in ppm; integrated for one proton unless otherwise stated; s: singlet, d: doublet, m: multiplet; coupling constants (numbers in parentheses) in Hz.

**Table 3.**  $^{13}\text{C}$  NMR Data of Compounds **3–8** in Acetone- $d_6^a$ 

carbon	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
1	165.1	164.9	164.7	164.6	164.6	165.0
2	98.9	98.8	98.8	98.8	98.5	98.7
3	165.6	165.6	165.6	165.5	165.1	165.8
4	94.0	93.8	94.0	94.0	93.6	93.9
4a	158.2	158.2	158.2	158.1	157.8	158.2
5	103.0	102.9	103.4	103.3	102.4	103.1
6	157.7	158.0	157.5	157.3	157.3	157.8
7	144.8	145.1	145.5	145.3	144.3	144.8
8	138.4	138.0	137.8	137.9	139.9	138.4
8a	110.4	109.4	110.4	110.2	111.8	110.4
9	182.9	182.8	182.3	182.3	182.5	183.2
9a	103.9	103.8	103.5	103.6	103.5	103.9
10a	156.4	156.0	156.0	156.0	156.1	156.3
11	27.0	26.8	38.2	38.2	22.7	34.7
12	124.8	124.9	198.8	197.2	43.2	75.5
13	149.5	134.6	149.6	137.9	72.0	131.7
14	36.7	35.2	32.3	32.1	42.3	32.7
15	34.8	36.7	27.9	28.5	23.2	27.8
16	75.4	201.8	124.8	125.9	126.0	125.4
17	135.5	144.9	132.1	132.3	131.0	136.2
18	112.1	124.6	25.8	25.8	25.7	25.8
19	16.9	17.7	17.8	17.8	27.2	27.8
20	18.0	16.7	123.7	24.9	17.6	108.6
MeO-7	61.5	61.6	61.6	61.6	61.4	61.0

<sup>a</sup> 125 MHz, chemical shifts ( $\delta$ ) in ppm.

of the geranyl unit in **3** was deduced from the two-proton resonance at  $\delta$  4.12, which was supported by the HMBC cross-peaks H-11/C-7,8a and H-5/C-7,8a. In addition, the placement of the 7-methoxyl group was established from the EIMS fragment **10b**, the HMBC correlations C-7/H-11, OMe-7, and the NOESY correlation H-11/OMe-7.

The olefinic proton at  $\delta$  5.29 (t) and the methylene protons at  $\delta$  4.12 were typical resonances for H-12 and H<sub>2</sub>-11 of a geranyl group attached at position C-8. The  $^1\text{H}$  NMR resonance at  $\delta$  3.95 indicated the C<sub>10</sub> side chain of **3** has one hydroxyl group (OH-16). Two olefinic protons at  $\delta$  4.83 (s) and 4.68 (d, br,  $J$  = 1.4 Hz) and two carbons at  $\delta$  112.6 and 150.0 revealed the presence of an exomethylene group. The above groups were determined to be linked from HMBC (H-16/C-18,19) and NOESY (H-16/H-18E,19) data. The H<sub>2</sub>-15 protons resonated at relatively high field (1.56–1.59), but the chemical shift of the adjacent H<sub>2</sub>-14 methylene was as expected for a geranyl group. On the basis of this information, the side chain was determined as a 3,7-dimethyl-2,7-dien-6-hydroxyoctyl group. Compound **3** (parvixanthone C) was determined as 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-2,7-dien-6-hydroxyoctyl)xanthen-9-one. The chiral center of parvixanthone C at position C-16 was not further studied.

Compound **4**, isolated as a yellow powder, had the molecular formula C<sub>24</sub>H<sub>24</sub>O<sub>7</sub>, as deduced from HREIMS ( $m/z$  424.1528, calcd 424.1522). The  $^{13}\text{C}$  NMR data of **4** showed 13 carbons for a 1,3,6,7-oxygenated xanthone unit and a 7-methoxyl substituent similar to compounds **1–3** (Table 3). The remaining 10 carbons were accounted for by a geranyl side chain having two double bonds and a conjugated carbonyl carbon (Table 2). Two singlet protons at  $\delta$  5.73 and 5.79 attached to the carbon at  $\delta$  124.6 (HMBC) indicated the presence of an exomethylene group, which was conjugated with the carbonyl group, as deduced from HMBC data (H-18/C-16). This conjugated system was determined to be at the end of the geranyl group since there was also a HMBC correlation of H<sub>2</sub>-18 to the C-19 methyl. The C<sub>10</sub> substituent was deduced from detailed HMBC and  $^1\text{H}$ – $^1\text{H}$  COSY analysis to be a 3,7-dimethyl-6-oxoocta-2,7-dienyl unit. This substituent was determined to be at position C-8 and adjacent to the 7-methoxyl group by the observation of similar HMBC and NOESY correlation data as described for compounds **1–3**. Compound **4**, given the trivial name parvixanthone D, was assigned as 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-6-oxoocta-2,7-dienyl)-xanthen-9-one.

Parvixanthone E (**5**) was isolated as a brown amorphous powder. The UV, IR, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR (Tables 2 and 3) data were quite similar to **4** and other 1,3,5,6-oxygenated xanthonenes. The presence of a conjugated carbonyl ( $\delta_{\text{C}}$  198.8) and an exomethylene [ $\delta_{\text{H}}$  5.88 (s, 1H); 6.32 (s, 1H)] revealed that compound **5** has a side chain similar to **4**. The olefinic protons ( $\delta_{\text{H}}$  5.88, 6.32) indicated conjugation to the carbonyl was confirmed by the HMBC cross-peaks H-20/C-12, C-14 (Figure 1). The isoprenyl group linked to C-14 could be established by the  $^1\text{H}$ – $^1\text{H}$  COSY correlations between H-14/H-15 and H-15/H-16 and the HMBC correlations between Me-18/C-16, C-17, C-19 and Me-19/C-16, C-17, C-18. The side chain was placed at position 8 of the xanthone nucleus based on the HMBC correlations between H-11/C-7,8a,12. The methylene protons H<sub>2</sub>-11 resonated at relatively low field ( $\delta_{\text{H}}$  4.79) because they were deshielded by both the C-9 and the C-12 carbonyls. The C-7 methoxyl group was determined as described for compounds **3** and **4**. In this manner, the structure of compound **5**, parvixanthone E, was deduced to have the structure 1,3,6-trihydroxy-7-methoxy-8-(7-methyl-3-methylene-2-oxooct-6-enyl)xanthen-9-one.

Parvixanthone F was isolated as a yellow gum. The  $^1\text{H}$  NMR data of **6** were similar to those of **5** except for the replacement of the exomethylene by a methyl group. The  $^{13}\text{C}$  NMR data of **6** were also quite similar to those of **5**

**Table 4.**  $^1\text{H}$ ,  $^{13}\text{C}$ , HMBC, NOESY, and  $^1\text{H}$ - $^1\text{H}$  COSY NMR Data of **9** in Acetone- $d_6$ 

position	$\delta_{\text{H}}^a$	$\delta_{\text{C}}^b$	HMBC <sup>c</sup>		NOESY	COSY
			$^2J$	$^3J$		
1	13.48 (s, OH)	161.0	1	2, 9a		
2	6.21 (d, 1.9)	98.7	3	4, 9a		4
3		157.8				
4	6.33 (d, 1.9)	93.8	2	3, 9a		2
4a		157.3				
5	6.85 (s)	102.4	6, 10a	7, 8a		
6		155.4				
7		144.3				
8		139.8				
8a		113.2				
9		176.3				
9a		103.8				
10a		154.3				
11	A: 3.27 (dd, 13.3, 6.7) B: 3.40 (dd, 13.3, 7.3)	25.8	12	8a	19, 11B 21, 11A	11B, 12 11A, 12
12	1.86 (m, overlap with H <sub>15<math>\alpha</math></sub> )	57.9	11		11A, 11B, 16 $\alpha$ , 20	11A, 11B
13		46.5				
14	3.66 (d, 4.8 Hz)	86.4		17	15 $\beta$ , 19	15 $\beta$
15	<i>endo</i> ( $\alpha$ ): 1.80 (m) <i>exo</i> ( $\beta$ ): 1.52 (m)	26.4			15 $\beta$ , 16 $\alpha$ , 20 14, 15 $\alpha$ , 16 $\beta$	15 $\beta$ , 16 $\alpha$ , 14, 15 $\alpha$ , 16 $\beta$
16	<i>endo</i> ( $\alpha$ ): 1.43 (m) <i>exo</i> ( $\beta$ ): 1.30 (m)	39.8			12, 15 $\alpha$ , 16 $\beta$ 15 $\beta$ , 16 $\alpha$	15 $\alpha$ , 16 $\beta$ 15 $\beta$ , 16 $\alpha$
17		87.5				
19	1.11 (3H, s)	24.6	13	12, 17, 20	11A, 14, 20	
20	0.91 (3H, s)	25.6	13	12, 17, 19	12, 15 $\alpha$ , 19	
21	1.28 (3H, s)	18.8	17	12, 16	11B	
MeO-7	3.80 (3H, s)	69.3		7		

<sup>a</sup> 500 MHz, chemical shifts ( $\delta$ ) in ppm; integrated for 1H unless otherwise stated; s: singlet, d: doublet, m: multiplet; coupling constant (numbers in parentheses) in Hz. <sup>b</sup> 125 MHz, chemical shifts ( $\delta$ ) in ppm. <sup>c</sup> Carbons correlated with proton.

except that **6** had one more methyl carbon and different resonances for the olefinic bonds (Table 3). These data indicated that **5** and **6** differed only by a double bond isomerization. This was confirmed by the HMBC correlations: Me-20/C-12,14 and H-14/C-12. Analogous to **4** and **5**, the side chain of **6** was determined to be at position 8 of the xanthone nucleus adjacent to a 7-methoxyl group. Compound **6** (parvixanthone F) has the structure 1,3,6-trihydroxy-7-methoxy-8-(3,7-dimethyl-2-oxoocta-3,6-dienyl)-xanthen-9-one.

An optically active compound **7**,  $[\alpha]_{\text{D}}^{28} -8.0^\circ$ , was isolated as a yellow oil, with the molecular formula  $\text{C}_{24}\text{H}_{28}\text{O}_7$ , as deduced by HREIMS ( $m/z$  428.1839 [M]<sup>+</sup>; calcd 428.1835). The similarity of the UV, IR, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **7** to analogous values for xanthenes **1**–**6** indicated that **7** has a structurally similar 1,3,6-trihydroxy-7-methoxyxanthone nucleus with a  $\text{C}_{10}$  substituent at position C-8 (Tables 2 and 3). Four methylene carbons ( $\delta$  21.5, 22.0, 42.0, 44.1) and one oxygenated quaternary carbon ( $\delta$  70.8) indicated that one of double bonds of the geranyl unit was hydrated. This was confirmed by COSY correlations between H-11/H-12, H-14/H-15, and H-15/H-16 and HMBC correlations between Me-20/C-12,13,14. The COSY correlation between H<sub>2</sub>-12 and H<sub>2</sub>-11, which was deshielded by the xanthone carbonyl, indicated that the double bond at position C-2 of a geranyl group was hydrated. Thus, compound **7** was determined as 1,3,6-trihydroxy-7-methoxy-8-(3-hydroxy-3,7-dimethyloct-6-enyl)xanthen-9-one and was assigned the trivial name parvixanthone G. The chiral center of parvixanthone G at position C-13 was not determined.

Parvixanthone H (**8**) was isolated as a yellow oil. The HREIMS suggested its molecular formula as  $\text{C}_{24}\text{H}_{26}\text{O}_7$ . The similarity of its UV, IR, and  $^{13}\text{C}$  NMR spectra to those of compounds **1**–**7** indicated that it had a similar 1,3,6-hydroxy-7-methoxyxanthone nucleus (Table 3). The protons at  $\delta$  5.12 (s, 1H) and 4.83 (s, 1H) and the corresponding carbon that resonated at  $\delta$  108.6 showed the presence of

an exomethylene group, which was connected to a hydroxymethine group ( $\delta_{\text{H}}$  4.42,  $\delta_{\text{C}}$  75.5), as deduced from the HMBC correlations between C-13/H-12,20 and C-12/H-11,20. The isomerized geranyl group containing an exomethylene group could be determined from certain HMBC (H-14/C-12,13,20; C-16/H-18,19) and  $^1\text{H}$ - $^1\text{H}$  COSY (H-14/H-15, H-15/H-16) correlations. Thus, the side chain of parvixanthone H was deduced as a 2-hydroxy-7-methyl-3-methyleneoct-6-enyl substituent, which was placed at position C-8 adjacent to the 7-methoxyl group, as evidenced from the HMBC correlations of H-11/C-7,8a and a NOESY correlation H-11/OMe-7. The structure of **8**, parvixanthone H, was assigned as 1,3,6-trihydroxy-7-methoxy-8-(2-hydroxy-7-methyl-3-methyleneoct-6-enyl)xanthen-9-one. The absolute stereochemistry of parvixanthone H at position C-12 was not determined.

A final new compound, parvixanthone I (**9**), was isolated as a brown amorphous powder. The HREIMS determined its molecular formula as  $\text{C}_{24}\text{H}_{26}\text{O}_7$ . The UV, IR, and  $^{13}\text{C}$  NMR spectrum suggested it was a 1,3,6,7-polyoxygenated xanthone (Table 4). With the absence of carbon resonances appearing at field lower than 90 ppm, the  $\text{C}_{10}$  side chain of **9** was deduced to be saturated. The degrees of unsaturation, calculated from the formula of **9**, were 12, of which ten were attributed to the xanthone nucleus and the other two due to the side chain. Hence, there are two rings in the side chain of **9**, which was determined as a [2.2.1]-bicyclic system by  $^1\text{H}$ - $^1\text{H}$  COSY and HMBC spectroscopy (Table 4). The C-14/C-15/C-16 connectivity was deduced from the  $^1\text{H}$ - $^1\text{H}$  COSY cross-peaks between H-14/H-15 and H-15/H-16. From this partial structure, the six-membered ring from C-12 to C-17 could be confirmed from the following HMBC correlations: Me-19/C-12,13,17,20; Me-20/C-12,13,17,19; and Me-21/C-12,16,17. The C-14 and C-17 positions were further deduced to be connected by an oxygen bridge (O-18) by the important HMBC correlation of H-14/C-17 and the fact that both C-14 ( $\delta_{\text{C}}$  86.4) and C-17 ( $\delta_{\text{C}}$  87.5) were oxygenated. Thus, a monoterpenoid substitution

in **9** was determined as a 7-oxo-[2.2.1]-system, which was linked to position C-8 of the xanthone nucleus, as indicated by the HMBC correlations between H-11/C-7,8a,12. The structure of the bicyclic system was further confirmed by comparison of the NMR data of analogous partial structures in two known sesquiterpenes.<sup>12</sup> The structure of compound **9** was determined as 1,3,6-trihydroxy-7-methoxy-8-(1,3,3-trimethyl-7-oxabicyclo[2.2.1]hept-2-ylmethyl)-xanthen-9-one.

## Experimental Section

**General Experimental Procedures.** Optical rotations were measured in CHCl<sub>3</sub> at 25 °C using a digital polarimeter (JASCO, DIP-1000). UV spectra were recorded on a Hewlett-Packard 8452A diode array spectrometer, and IR spectra were recorded on a Bio-Rad FT-IR spectrometer. NMR spectra were recorded by Bruker ACF 300 [300 MHz (<sup>1</sup>H) and 75 MHz (<sup>13</sup>C)], AMX 500 [500 MHz (<sup>1</sup>H) and 125 MHz (<sup>13</sup>C)], or DRX 500 [500 MHz (<sup>1</sup>H) and 125 MHz (<sup>13</sup>C)] instruments using acetone-*d*<sub>6</sub> as solvent with TMS as an internal standard unless otherwise stated. EIMS were run on a Micromass VG 7035 mass spectrometer at 70 eV. Column chromatography was performed on Si gel (Kieselgel 60, particle size 0.040–0.063 mm) and Sephadex LH-20. TLC was run on Si gel precoated glass plates (Merck Silica gel 60 F<sub>254</sub>).

**Plant Material.** The specimen of *Garcinia parvifolia* (Guttiferae) was collected from Mt. Tawai, Kinabatangan, Sabah, Malaysia, in July 1997 and identified by L. Madani. A voucher specimen (SAN142683) was deposited at the herbarium of the Forest Research Centre, Sepilok, Sandakan, Sabah, Malaysia.

**Extraction and Isolation.** Dried and powdered bark (480 g) of *Garcinia parvifolia* was successively and exhaustively extracted with *n*-hexane, chloroform, and methanol. Evaporation in vacuo concentrated the extracts to dried residues (6.3 g from *n*-hexane and 6.0 g from chloroform). The methanol fraction was diluted with water and re-extracted with *n*-butanol, affording 10 g of extract after evaporation in vacuo. The chloroform-soluble fraction was then subjected to Si gel column chromatography and eluted with solvent mixtures of increasing polarity (100% chloroform to 50% methanol in chloroform) to give 10 fractions. Further separation of fractions 6–8 was carried out by Si gel flash chromatography, column chromatography on Sephadex LH-20 with CHCl<sub>3</sub>–MeOH (1:1), and preparative TLC. Compounds **1–8** were eluted from Si gel in the following order: **9** (1.2 mg, 0.00025%), **4** (1.8 mg, 0.00038%), **1** (0.5 mg, 0.00010%), **5** (1.0 mg, 0.00021%), **6** (0.4 mg, 0.000083%), **2** (0.9 mg, 0.00019%), **8** (0.8 mg, 0.00017%), **7** (1.2 mg, 0.00025%), and **3** (1.4 mg, 0.00029%).

**Parvixanthone A (1):** yellow gum; UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 204 (4.30), 243 (4.25), 314 (3.80), 353 (3.50) nm; IR (KBr)  $\nu_{\max}$  3400, 3185, 2950, 2866, 1651, 1606, 1580, 1504, 1460, 1436, 1280, 1168, 1048, 1035, 901, 836, 816 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data, see Table 1; EIMS  $m/z$  494 [M]<sup>+</sup> 494 (8), 476 (35), 460 (20), 423 (35), 407 (100), 378 (35), 367 (48), 355 (28); HREIMS  $m/z$  494.2309 (calcd for C<sub>29</sub>H<sub>34</sub>O<sub>7</sub>, 494.2305).

**Parvixanthone B (2):** yellow powder; UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 206 (4.35), 242 (4.21), 314 (3.84), 353 (3.55) nm; IR (KBr)  $\nu_{\max}$  3410 (br), 2964, 2931, 1648, 1507, 1463, 1369, 1281, 1243, 984, 836, 726, 627 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data, see Table 1; EIMS  $m/z$  426 [M]<sup>+</sup> (5), 408 (12), 393 (20), 365 (25), 339 (15), 299 (12), 256 (25); HREIMS  $m/z$  426.1683 (calcd for C<sub>24</sub>H<sub>26</sub>O<sub>7</sub>, 426.1679).

**Parvixanthone C (3):** yellow gum; [ $\alpha$ ]<sub>D</sub><sup>25</sup> -125.9° (*c* 0.27, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 208 (4.39), 242 (4.41), 310 (4.20), 347 (3.96) nm; IR (KBr)  $\nu_{\max}$  3407, 3188, 2947, 2866, 1650, 1604, 1581, 1506, 1464, 1436, 1275, 1168, 1053, 1033, 906, 836, 818 cm<sup>-1</sup>; <sup>1</sup>H NMR data, see Table 2; <sup>13</sup>C NMR data, see Table 3; EIMS  $m/z$  426 [M]<sup>+</sup> (5), 408 (5), 365 (25), 341 (8), 325 (10), 309 (50), 299 (100), 284 (20); HREIMS  $m/z$  426.1676 (calcd for C<sub>24</sub>H<sub>26</sub>O<sub>7</sub>, 426.1679).

**Parvixanthone D (4):** yellow powder; UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 208 (4.19), 240 (4.10), 312 (3.85), 346 (3.68) nm; IR (KBr)  $\nu_{\max}$  3410, 3190, 2959, 2920, 1649, 1603, 1509, 1462, 1435,

1276, 1190, 1167, 838 cm<sup>-1</sup>; <sup>1</sup>H NMR data, see Table 2; <sup>13</sup>C NMR data, see Table 3; EIMS  $m/z$  424 [M]<sup>+</sup> (5), 341 (18), 299 (100), 284 (40), 273 (50), 245 (45); HREIMS  $m/z$  424.1528 (calcd for C<sub>24</sub>H<sub>24</sub>O<sub>7</sub>, 424.1522).

**Parvixanthone E (5):** brown powder; UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 210 (4.32), 240 (4.34), 312 (4.14), 348 (3.86) nm; IR (KBr)  $\nu_{\max}$  3301, 2965, 2934, 2859, 1650, 1608, 1583, 1507, 1472, 1432, 1281, 1188, 1164, 1125, 1080, 829 cm<sup>-1</sup>; <sup>1</sup>H NMR data, see Table 2; <sup>13</sup>C NMR data, see Table 3; EIMS  $m/z$  424 [M]<sup>+</sup> (10), 299 (100), 284 (40), 273 (40), 245 (50); HREIMS  $m/z$  424.1526 (calcd for C<sub>24</sub>H<sub>24</sub>O<sub>7</sub>, 424.1522).

**Parvixanthone F (6):** yellow powder; UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 209 (4.38), 240 (4.36), 313 (4.18), 350 (3.85) nm; IR (KBr)  $\nu_{\max}$  3295, 2964, 2935, 2859, 1648, 1610, 1585, 1507, 1472, 1432, 1280, 1188, 1158, 1120, 1087, 826 cm<sup>-1</sup>; <sup>1</sup>H NMR data, see Table 2; <sup>13</sup>C NMR data, see Table 3; EIMS  $m/z$  424 [M]<sup>+</sup> (20), 299 (100), 284 (45), 273 (50); HREIMS  $m/z$  424.1519 (calcd for C<sub>24</sub>H<sub>24</sub>O<sub>7</sub>, 424.1522).

**Parvixanthone G (7):** yellow oil; [ $\alpha$ ]<sub>D</sub><sup>28</sup> -8.0° (*c* 0.45, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 206 (4.16), 242 (4.20), 312 (4.05), 348 (3.83) nm; IR (KBr)  $\nu_{\max}$  3412, 3189, 2972, 2939, 2861, 1648, 1604, 1577, 1507, 1459, 1432, 1376, 1274, 1192, 1167, 1124, 1082, 1050, 834, 812 cm<sup>-1</sup>; <sup>1</sup>H NMR data, see Table 2; <sup>13</sup>C NMR data, see Table 3; EIMS  $m/z$  428 [M]<sup>+</sup> (7), 410 (30), 365 (20), 345 (25), 341 (35), 299 (60), 288 (100), 273 (45); HREIMS  $m/z$  428.1839 (calcd for C<sub>24</sub>H<sub>28</sub>O<sub>7</sub>, 428.1835).

**Parvixanthone H (8):** yellow oil; [ $\alpha$ ]<sub>D</sub><sup>28</sup> +33.3° (*c* 0.03, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 207 (4.22), 240 (4.18), 314 (3.80), 352 (3.58) nm; IR (KBr)  $\nu_{\max}$  3413, 3190, 2971, 2937, 2859, 1650, 1603, 1578, 1458, 1275, 1190, 1169, 1125, 1082, 1050, 833, 815 cm<sup>-1</sup>; <sup>1</sup>H NMR data, see Table 2; <sup>13</sup>C NMR data, see Table 3; EIMS  $m/z$  426 [M]<sup>+</sup> (25), 408 (40), 299 (100), 287 (50); HREIMS  $m/z$  426.1685 (calcd for C<sub>24</sub>H<sub>26</sub>O<sub>7</sub>, 426.1679).

**Parvixanthone I (9):** yellow powder; [ $\alpha$ ]<sub>D</sub><sup>28</sup> +103.6° (*c* 0.11, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 208 (4.42), 240 (4.38), 314 (4.00), 352 (3.78) nm; IR (KBr)  $\nu_{\max}$  3423, 3192, 2966, 2927, 2859, 1651, 1603, 1581, 1460, 1275, 1186, 1169, 1121, 1082, 1034 833, 816 cm<sup>-1</sup>; <sup>1</sup>H and <sup>13</sup>C NMR data, see Table 4; EIMS  $m/z$  426 [M]<sup>+</sup> (35), 408 (30), 393 (40), 383 (30), 369 (25), 355 (35), 299 (100), 285 (65); HREIMS  $m/z$  426.1689 (calcd for C<sub>24</sub>H<sub>26</sub>O<sub>7</sub>, 426.1679).

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**Supporting Information Available:** Three tables of 2D NMR data of **1–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

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