Caged-Triprenylated and -Tetraprenylated Xanthones from the Latex of *Garcinia scortechinii*

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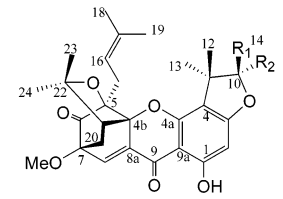
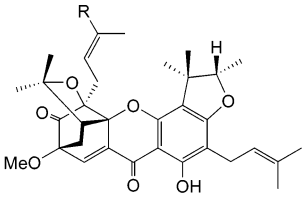
The latex of *Garcinia scortechinii* has yielded eight new caged-polyprenylated xanthones: two triprenylated (**1** and **2**) and five tetraprenylated xanthones (**3**−**7**) and one degraded caged-tetraprenylated xanthone (**8**), together with the known scortechinones A (**9**) and B (**10**). Their structures were elucidated by analysis of spectroscopic data and comparison of the NMR data with those reported previously.

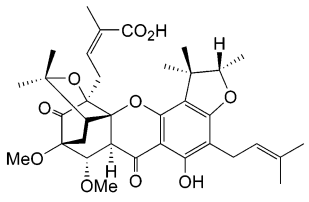
Many caged-prenylated xanthones have been isolated from several *Garcinia* species, e.g., *G. bracteata*,[1] *G. gaudichaudii*,[2−5] *G. forbesii*,[6] *G. hanburyi*,[7,8] and *G. morella*.[9−14] Of these compounds, only one, gaudichaudione H,[3] is a bridgehead-methoxylated triprenylated xanthone. In contrast, our preliminary investigation on twigs of *G. scortechinii*, a small slender tree distributed throughout Malaysia and Southern Thailand, resulted in the isolation of three caged-tetraprenylated xanthones: scortechinones A, B, and C, having a characteristic structure with a C-7 bridgehead methoxyl group and a 2,3,3-trimethylhydrofuran unit linked at C-3 and C-4 of the aromatic ring.[15] The present study deals with the isolation and structural elucidation of seven new caged-polyprenylated xanthones of this same type and one new degraded caged-xanthone from *Garcinia scortechinii* (Guttiferae) latex.



1: R_1 = Me, R_2 = H
2: R_1 = H, R_2 = Me



3: R = CO_2H
4: R = CO_2Me
5: R = CHO



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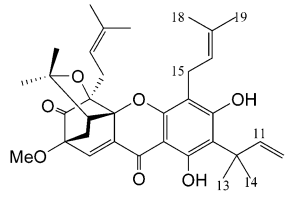

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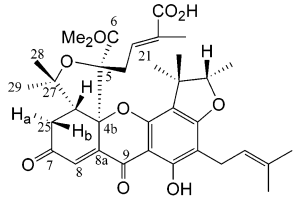

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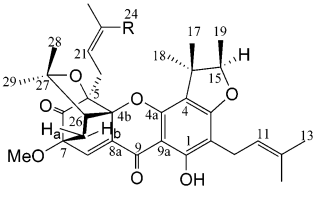

9: R = Me
10: R = CO_2H

Results and Discussion

The latex of *G. scortechinii* was subjected successively to silica gel column chromatography and preparative TLC to yield two caged-triprenylated xanthones (**1** and **2**), five caged-tetraprenylated xanthones (**3**−**7**), and one degraded caged-tetraprenylated xanthone (**8**), along with the known scortechinones A (**9**) and B (**10**) (relative stereochemistry). Some of the compounds are diastereomers with respect to the substituted hydrofuran ring. The ^{13}C chemical shifts were assigned using ^{13}C NMR, 2D HMQC, and 2D HMBC data, while carbon types were classified by DEPT spectra.

Compounds isolated from the latex of *G. scortechinii* were 7-methoxy caged-polyprenylated xanthones with a 2,2,3-trimethylhydrofuran moiety attached at C-3 and C-4 by forming an ether linkage at C-3. They showed typical UV and IR spetroscopic data as follows. An absorption band in the UV spectrum in the range of 360−368 nm was due to a conjugated carbonyl chromophore. Absorption bands of a ketone carbonyl and a chelated *ortho*-hydroxyl carbonyl group, in the IR spectrum, were in the range of 1742−1753 and 1634−1644 cm^{-1}, respectively. Compounds of this type showed common signals in the ^1H NMR spectrum (Table 1) for a chelated hydroxy proton (1-OH), an olefinic proton (H-8) of a cisoid α,β-unsaturated carbonyl moiety, and characteristic signals for a −OC(Me)$_2$−CHCH$_2$−C− unit of a caged-prenylated moiety (H-25, H-26, Me-28, and Me-29). This cage moiety was placed at C-4b, C-5, and C-7 due to the ^3J HMBC correlations of the methylene H_a-25 and H_b-25 with C-4b, C-6, C-8, and C-27; the methine H-26 with C-5, C-7, and C-28; and Me-28 and Me-29 with C-26 (see Supporting Information). The chemical shift values of Me-28 and Me-29 were assigned by the NOEDIFF data observed between Me-28 and H-26 and between Me-29 and H_a-25 as well as the methoxy protons (7-OCH_3). Furthermore, the ^1H NMR spectrum of caged-polyprenylated xanthones showed characteristic signals for a 2,3,3-trimethylhydrofuran unit: two singlets of Me-17 and Me-18, one doublet of Me-19, and a quartet of H-15. This unit was fused to the aromatic ring by linkage of its *gem*-dimethyl carbon and ring oxygen atom with C-4 and C-3, respectively, according to the ^3J HMBC correlations of Me-17 and

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Table 1. ^{1}H NMR Data of Scortechinones A (**9**), B (**10**), and D−K (**1**−**8**)

H	1	2	3	4	5	6	7	8	9	10
1-OH	13.03 (s)	13.09 (s)	13.10 (s)	13.13 (s)	13.08 (s)	12.08 (s)	13.62 (s)	12.69 (s)	13.15 (s)	13.10 (s)
H-2	6.04 (s)	6.03 (s)								
3-OH							7.70 (s)			
6-OMe								3.63 (s)		
7-OMe	3.64 (s)	3.64 (s)	3.63 (s)	3.63 (s)	3.63 (s)	3.50 (s)	3.63 (s)		3.62 (s)	3.52 (s)
H-8	7.52 (d, 1.5)	7.52 (d, 1.0)	7.61 (d, 1.0)	7.58 (brs)	7.60 (brs)	4.46 (s)	7.48 (d, 1.0)	6.62 (s)	7.49 (d, 1.4)	7.56 (d, 1.2)
8-OMe						3.36 (s)				
H-8a						3.16 (s)				
H_a-10	4.40 (q, 6.5)	4.55 (q, 6.5)	3.20 (d, 7.0)	3.21 (d, 7.0)	3.20 (d, 6.5)	3.21 (m)		3.22 (d, 7.5)	3.22 (d, 7.2)	3.17 (mdd, 14.4, 7.2)
H_b-10										3.11 (mdd, 14.4, 7.2)
H-11			5.22 (mt, 7.0)	5.22 (mt, 7.0)	5.21 (t, 6.5)	5.25 (mt, 7.0)	6.43 (dd, 17.5, 10.5)	5.21 (mt, 7.5)	5.22 (ht, 7.2, 1.4)	5.20 (ht, 7.2, 1.5)
H_a-12							5.46 (d, 17.5)			
H_b-12							5.37 (dd, 10.5, 1.0)			
Me-12	1.17 (s)	1.42 (s)								
Me-13	1.59 (s)	1.49 (s)	1.67 (s)	1.69 (s)	1.69 (s)	1.69 (s)	1.60 (s)	1.69 (s)	1.68 (brs)	1.65 (q, 1.5)
Me-14	1.41 (d, 6.5)	1.30 (d, 6.5)	1.74 (s)	1.75 (s)	1.75 (s)	1.76 (s)	1.59 (s)	1.75 (s)	1.75 (brs)	1.72 (s)
H_a-15	2.71 (md, 14.5)	2.68 (md, 14.5)	4.54 (q, 6.5)	4.55 (q, 6.5)	4.56 (q, 6.5)	4.40 (q, 6.8)	3.30 (d, 6.5)	4.37 (q, 6.5)	4.37 (q, 6.4)	4.46 (q, 6.6)
H_b-15	2.58 (dd, 14.5, 10.5)	2.55 (dd, 14.5, 11.0)								
H-16	4.38 (md, 10.5)	4.36 (md, 11.0)					5.14 (mt, 6.5)			
Me-17			1.41 (s)	1.41 (s)	1.42 (s)	1.43 (s)		1.42 (s)	1.16 (s)	1.37 (s)
Me-18	1.38 (brs)	1.38 (brs)	1.46 (s)	1.47 (s)	1.45 (s)	1.10 (s)	1.66 (d,1.0)	1.27 (s)	1.58 (s)	1.37 (s)
Me-19	1.09 (brs)	1.07 (brs)	1.30 (d, 6.5)	1.30 (d, 6.5)	1.30 (d, 6.5)	1.34 (d, 6.8)	1.70 (s)	1.41 (d, 6.5)	1.41 (d, 6.4)	1.23 (d, 6.6)
H_a-20	2.36 (d, 13.0)	2.36 (dd, 13.0, 1.0)	2.79 (mdd, 15.0, 5.5)	2.83 (dd, 15.5, 6.0)	2.89 (dd, 15.5, 5.5)	3.23 (m)	2.59 (m)	2.79 (dd, 15.0, 7.5)	2.79 (ddh, 14.4, 4.5, 1.5)	3.27 (brdd, 16.0, 9.6)
H_b-20	1.66 (dd, 13.0, 9.5)	1.67 (dd, 13.0, 9.5)	2.56 (dd, 15.0, 10.0)	2.56 (dd, 15.5, 10.0)	2.62 (dd, 15.5, 8.0)		2.54 (d, 10.0)	2.69 (dd, 15.0, 7.5)	2.55 (dd, 14.4, 10.5)	2.83 (ddq, 16.0, 4.5, 2.0)
H-21	2.59 (d, 9.5)	2.61 (d, 9.5)	6.41 (ddq, 10.0, 5.5, 1.5)	6.20 (mdd, 10.0, 6.0)	6.23 (mdd, 8.0, 5.5)	6.62 (qt, 6.8, 1.5)	4.43 (mdd, 10.0, 5.5)	6.67 (mt, 7.5)	4.39 (m)	5.67 (ddq, 9.6, 4.5, 1.5)
Me-23	1.72 (s)	1.72 (s)	1.38 (s)	1.38 (s)	1.36 (s)	1.98 (d, 1.5)	1.37 (s)	1.67 (s)	1.36 (brt, 1.5)	1.72 (s)
Me-24	1.30 (s)	1.29 (s)					1.01 (s)		1.07 (brt, 1.4)	
24-OMe				3.64 (s)						
24-CHO					9.23 (s)					
H_a-25			2.33 (d, 13.0)	2.35 (d, 13.0)	2.38 (d, 13.0)	2.02 (d, 14.2)	2.33 (d, 13.0)	2.94 (dd, 16.5, 13.0)	2.33 (dd, 12.8, 1.4)	2.33 (dd, 13.2, 1.2)
H_b-25			1.69 (dd, 13.0, 9.5)	1.69 (dd, 13.0, 9.5)	1.69 (dd, 13.0, 9.5)	1.63 (dd, 14.2, 8.8)	1.61 (dd, 13.0, 10.0)	2.62 (dd, 16.5, 7.0)	1.65 (dd, 12.8, 9.6)	1.68 (dd, 13.2, 9.2)
H-26			2.61 (d, 9.5)	2.61 (d, 9.5)	2.66 (d, 9.5)	2.70 (d, 8.8)	2.50 (d, 10.0)	3.17 (dd, 13.0, 7.0)	2.55 (d, 9.6)	2.60 (d, 9.2)
Me-28			1.72 (s)	1.73 (s)	1.74 (s)	1.41 (s)	1.65 (s)	1.76 (s)	1.71 (s)	1.72 (s)
Me-29			1.29 (s)	1.30 (s)	1.31 (s)	1.20 (s)	1.28 (s)	1.45 (s)	1.29 (s)	1.28 (s)

Me-18 with C-4 and the methine H-15 with C-3 and C-4 together with the chemical shift values of C-3 and C-4. Caged-polyprenylated xanthones with the 2,3,3-trimethylhydrofuran ring were classified into two types according to the spatial arrangement of H-15 at either the α- or *β*-position (relative stereochemistry). In the case of scortechinone A (**9**), Me-18 gave enhancement with H-15 and one methylene proton (H_a-20) and Me-24 of a C-5 prenyl group in the NOEDIFF spectrum. This indicated that Me-18, H-15, and the C-5 prenyl group were located on the same side of the molecule. In contrast, H-15 in scortechinone C[15] was assigned to the *β*-position since irradiation of Me-17 enhanced only the signals of H-15 and Me-18 of the tetrahydrofuran unit, while irradiation of Me-18 affected H_a-20 of the C-5 α,*β*-unsaturated carboxylic acid unit as well as Me-19. In the case of caged-polyprenylated xanthones with 3-methylbut-2-enyl units, such as **9**, the chemical shift values of Me-13 and Me-23 were assigned by their NOE enhancements with olefinic protons, H-11 and H-21, respectively.

Scortechinone D (**1**), with a molecular formula of $C_{28}H_{34}O_6$ for $[M - CO]^+$ by HREIMS, exhibited UV and IR spectra similar to those of **9**. The ^{1}H NMR spectrum (Table 1) also showed signals similar to those of **9**, but with only one prenyl unit present. An aromatic proton at *δ* 6.04 replaced signals of the absent prenyl unit. The HMBC correlations (see Supporting Information) established the same location of a prenyl unit as **9**. The relative stereochemistry was established by NOEDIFF results. The methyl protons (Me-13) of the trimethylhydrofuran ring gave NOE enhance-

Table 2. ^{13}C NMR Data of Scortechinones A (**9**), B (**10**), and D−K (**1**−**8**)[a]

C	C-type	1	2	3	4	5	6	7	8	9	10
1	C	166.2	166.4	163.5	163.5	163.6	161.6	162.9	162.9	163.3	163.5
2	C			106.2	106.1	106.4	105.4	111.6	106.4	105.8	105.8
	CH	92.8	92.8								
3	C	168.7	168.5	166.9	166.9	167.3	166.8	163.3	167.9	166.9	167.1
4	C	113.7	112.6	112.0	112.0	112.2	113.7	108.2	112.7	113.0	112.3
4a	C	155.8	156.3	154.0	154.0	154.1	152.2	156.3	152.9	153.8	154.1
4b	C	89.5	89.6	89.4	89.4	89.6	86.3	88.7	90.6	89.3	89.4
5	C	84.2	84.4	83.3	83.6	83.2	87.1	84.2	93.8	84.2	83.8
6	C=O	202.1	202.1	202.0	201.8	202.1	205.7	202.0	171.3	202.3	202.3
6-OMe	CH_3								52.3		
7	C	84.9	84.9	85.0	84.9	84.9	81.4	84.8		84.9	84.9
	C=O								197.0		
7-OMe	CH_3	54.0	54.0	54.1	54.0	54.0	52.4	54.0		54.9	53.9
8	CH	134.4	134.4	135.4	135.3	135.9	75.2	134.0	128.6	134.0	135.1
8-OMe	CH_3						57.4				
8a	C	132.0	132.1	132.1	132.1	132.4		132.6	145.9	132.4	132.4
	CH						48.8				
9	C=O	178.3	178.1	177.5	177.6	177.4	195.0	179.1	182.1	178.2	177.6
9a	C	101.4	101.4	101.3	101.4	101.3	102.4	101.0	102.8	101.4	101.3
10	C							41.0			
	CH	91.1	91.7								
	CH_2			21.4	21.4	21.4	21.4		21.5	21.4	21.4
11	C	43.2	43.4								
	CH			121.5	121.6	121.4	121.6	149.5	121.3	121.8	121.7
12	C			132.0	132.1	132.1	132.1		132.4	132.0	132.1
	CH_2							113.7			
	CH_3	21.0	28.2								
13	CH_3	23.9	20.0	25.7	25.7	25.8	25.8	27.2 **	25.8	25.7	25.7
14	CH_3	13.5	16.3	17.8	17.8	17.8	17.7	26.9 **	17.7	17.7	17.7
15	CH			91.3	91.3	91.4	90.2		90.6	90.6	91.4
	CH_2	29.0	29.0					22.2			
16	C			43.7	43.7	43.7	43.9		43.5	43.5	43.5
	CH	117.3	117.3					122.4			
17	C	135.7	135.6					132.3			
	CH_3			28.2	28.2	28.2	26.1		24.4	21.1	28.1*
18	CH_3	25.6	25.5	20.3	20.3	20.5	22.1	25.7	21.1	24.1	20.0*
19	CH_3	16.9	16.8	16.3	16.4	16.3	13.8	18.1	13.7	13.6	15.8
20	CH_2	30.8	30.7	29.3	29.1	29.4	28.6	28.8	35.9	28.9	29.9
21	CH	49.9	50.0	135.9	133.3	145.5	139.3	117.5	137.1	117.2	137.0
22	C	83.3	83.2	129.3	130.2	140.9	127.4	135.3	130.3	135.6	128.7
23	CH_3	30.8	31.0	11.4	11.8	8.8	20.7	25.5	12.5	25.5	20.6
24	C=O			171.0	167.5	194.5	172.3		170.6		170.7
	CH_3	29.0	29.0					16.7		16.9	
24-OMe	CH_3				51.8						
25	CH_2			30.9	30.8	30.6	24.0	30.2	38.3	30.9	30.5
26	CH			49.8	49.9	49.8	45.3	49.7	55.9	49.9	49.8
27	C			83.7	83.6	84.0	82.4	83.5	85.1	83.2	83.7
28	CH_3			30.9	30.9	31.0	30.5	30.1	31.2	30.8	30.9
29	CH_3			28.9	29.0	28.9	27.2	29.0	25.4	29.0	28.8

[a] *reassigned (see text). **interchangeable.

ment with the H-10 methine, one of the methylene protons (H_b-15), and Me-12. These results indicated that the C-5 prenyl group was located on the same side, the α side of the molecule, as Me-13 and H-10. Thus, scortechinone D (**1**) is a new caged-triprenylated xanthone lacking a C-2 prenyl substituent.

Scortechinone E (**2**) had the same molecular formula as **1**. Its IR and UV spectra were almost identical to those of **1**. In addition, their ^1H NMR (Table 1) and ^{13}C NMR (Table 2) signals were alike except for chemical shift values of the methyl groups of the 2,3,3-trimethylhydrofuran unit. The attachment of the C-5 prenyl group was identical to **1** according to the HMBC data (see Supporting Information). However, NOE enhancements observed between the methine H-10 (δ 4.55) and Me-12 (δ 1.42) and between Me-13 (δ 1.49) and one of the methylene protons (H_b-15, δ 2.55) of the C-5 prenyl group suggested that H-10 was β, not α as in **1**. Therefore, scortechinone E (**2**) is a diastereomer of **1** differing only in the stereochemistry at C-10.

Scortechinone F (**3**), with a molecular formula of $C_{34}H_{40}O_9$ by HREIMS, exhibited IR and UV spectra almost identical to those of **10**. Its ^1H NMR signals (Table 1) were also similar to those of **10**. Differences in chemical shift values of protons of the C-5 prenyl substituent, especially the olefinic H-21 (δ 6.41) and Me-23 (δ 1.38), which were shifted to lower and higher field than in **10**, respectively, suggested that H-21 lay in the deshielding zone of the carboxyl group. The HMBC data (see Supporting Information) established attachment of 3-methylbut-2-enyl and 3-carboxybut-2-enyl groups at C-2 and C-5, respectively, identical to that of **10**. Consequently, **3** differed from **10** in the configuration of the double bond of the C-5 side chain, which was confirmed to be *E* since irradiation of H-21 enhanced the signal of methylene H_a-20 but not Me-23, in a NOEDIFF experiment. Furthermore, the oxymethine (H-15) of the 2,3,3-trimethylhydrofuran was assigned *cis* to Me-17 and *trans* to Me-18 because it gave NOEDIFF results similar to that of scortechinone C[15]. Irradiation of H-15 enhanced Me-17, whereas selective irradiation of Me-18 enhanced H-21 as well as H_a-20 and H_b-20 of the C-5 3-carboxybut-2-enyl group. Thus, scortechinone F (**3**) is a new naturally occurring caged-tetraprenylated xanthone

that differs from **10** in the stereochemistry at C-15 and the configuration of the double bond of the C-5 substituent.

Scortechinone G (**4**), with a molecular formula of $C_{35}H_{42}O_9$ (HREIMS), showed UV and IR spectra typical of a caged-polyprenylated xanthone with an additional IR absorption band at 1718 cm^{-1} due to an α,β-unsaturated ester-carbonyl group. Its ^1H NMR spectrum (Table 1) was similar to that of **3** except for one additional methoxyl singlet at δ 3.64. The presence of the methoxyl group was confirmed by an oxymethyl carbon signal at δ 51.8 in the ^{13}C NMR spectrum (Table 2). The HMBC data (see Supporting Information) established the C-5 substituent to be an α,β-unsaturated methyl ester. NOEDIFF experiments confirmed the stereochemistry of the ester and of the hydrofuran ring, as shown in **4**. Therefore, scortechinone G (**4**) is the methyl ester derivative of **3**.

Scortechinone H (**5**) was found to have a molecular formula of $C_{33}H_{40}O_7$ for $[M - CO]^+$ from HREIMS. The IR spectrum exhibited characteristic absorption bands of a caged xanthone with an extra carbonyl band at 1690 cm^{-1}. The ^1H NMR spectrum (Table 1) was almost identical to that of **3** except for an additional signal of an aldehyde proton at δ 9.23. The HMBC correlations (see Supporting Information) between the aldehyde H-24 and olefinic C-21 (δ 145.5), C-22 (δ 140.9), and the methyl C-23 (δ 8.8) suggested that the C-5 3-carboxybut-2-enyl substituent in **3** was replaced by a 2-butenyl-3-carboxaldehyde unit. This was in agreement with the molecular formula, which contained one less oxygen atom than that of **3**. A NOE enhancement of the aldehyde H-24 after irradiation of the olefinic H-21 (δ 6.23) established an *E* configuration for the C-21/C-22 double bond. The HMBC data established locations of 3-methylbut-2-enyl and 2-butenyl-3-carboxaldehyde groups identical to that of **3** according to the HMBC data. Irradiation of the methine H-15 (δ 4.56) enhanced signals of Me-17 (δ 1.42) and Me-19 (δ 1.30), whereas irradiation of Me-18 (δ 1.45) enhanced signals of Me-19 and the methylene protons [δ 2.89 (H_a-20) and 2.62 (H_b-20)] of the C-5 unsaturated aldehyde unit. This suggested that **5** had the same relative configuration of C-5 and C-15 as **3**. Thus, scortechinone H (**5**) is a new naturally occurring caged-tetraprenylated xanthone having a C-5 2-butenyl-3-carboxaldehyde unit.

Scortechinone I (**6**), $C_{35}H_{44}O_{10}$ as determined by HREIMS, exhibited IR absorption bands similar to those of **3**. However the UV spectrum had an absorption maximum at shorter wavelength (λ_{max} 304 nm), as found for gaudichaudic acid H.[4] The ^1H NMR spectrum (Table 1) showed signals characteristic of a caged-prenylated moiety, but a signal at low field (δ 7.61, H-8 in **3**) was absent, being replaced by two methine proton signals [δ 4.46 (H-8) and 3.16 (H-8a)] and one methoxy proton signal (δ 3.36, 8-OCH_3). The methoxyl group was assigned to be at C-8 due to a HMBC correlation (see Supporting Information) between the methoxy protons (8-OCH_3) and an oxymethine C-8 (δ 75.2). The methine protons at δ 4.46 and 3.16 were attributed to H-8 and H-8a, respectively, since H-8 showed ^3J correlations in the HMBC spectrum with C-4b, C-6, and C-9, while H-8a gave correlations with C-5, C-7, and C-26. Irradiation of H_b-25 (δ 1.63), in a NOE experiment, enhanced signals of the methine H_a-25 (δ 2.02), H-26 (δ 2.70) and the oxymethine H-8 (δ 4.46) but did not affect the signals of 8-OCH_3 (δ 3.36) and the methine H-8a (δ 3.16). In addition, irradiation of H-8a enhanced signals of H-8, 8-OCH_3, and H-21 of the α-C-5 3-carboxybut-2-enyl substituent. These results indicated that H-8 and H-8a had *trans*, β and α configurations, respectively. The location of 3-methylbut-2-enyl and 3-carboxybut-2-enyl groups as in **3** was based on the HMBC data. The relative stereochemistry was provided by NOEDIFF experiments. When the oxymethine H-15 (δ 4.40) of the trimethylhydrofuran ring was irradiated, the singlet signal of Me-17 (δ 1.43) and the doublet signal of Me-19 (δ 1.34) were enhanced, indicating that H-15 was *cis* to Me-17. Irradiation of Me-18 (δ 1.10) enhanced signals of Me-19, Me-17, one of the methylene protons (δ 3.23, H-20), the olefinic H-21 (δ 6.62), and Me-23 (δ 1.98) of the C-5 α,β-unsaturated carboxylic acid unit. This suggested that Me-18, Me-19, and the C-5 α,β-unsaturated carboxylic acid unit were located on the same side of the molecule, the α-position. Therefore, H-15 was β as in **3**. The configuration of the C-21/C-22 double bond was assigned to be *Z* by enhancement of H-21 after irradiation of Me-23. Therefore, scortechinone I (**6**) is a new caged-tetraprenylated xanthone lacking a C-8a−C8 double bond.

Scortechinone J (**7**), with a molecular formula of $C_{33}H_{42}O_6$ for $[M - CO]^+$ (HREIMS), showed UV and IR spectra similar to those of **9**. Comparison of its ^1H NMR spectrum (Table 1) with that of **9** revealed similar spectral data, except for the absence of an oxymethine proton and methyl groups of a trimethylhydrofuran ring. New signals were observed: a singlet signal at δ 7.70 of a hydroxyl group and characteristic signals of a 1,1-dimethylallyl group. The hydroxyl group was assigned at C-3 (δ 163.3) by its HMBC correlations (see Supporting Information) with C-2 (δ 111.6), C-3 and C-4 (δ 108.2), and 1-OH, Me-13, and Me-14 of the 1,1-dimethylallyl group showed ^3J correlations with C-2, suggesting attachment of this group at C-2. Irradiation of the olefinic proton (H-11) of the 1,1-dimethylallyl group caused a NOE enhancement of the olefinic H_b-12 at δ 5.37, indicating that H-11 was *cis* to H_b-12. One of two prenyl groups was assigned at C-4 by ^3J HMBC correlations of its methylene (H-15) with C-3 and C-4a. Furthermore, HMBC data established the identical attachment of the C-5 prenyl group and 7-OCH_3 as in **9**. Thus, scortechinone J (**7**) is a new caged-tetraprenylated xanthone with an uncyclized prenyl unit at C-4.

Scortechinone K (**8**), $C_{34}H_{40}O_{10}$, showed UV and IR absorption bands almost identical to those of **3**. However, one additional carbonyl signal was detected at δ 171.3 in the ^{13}C NMR spectrum (Table 2). The ^1H NMR spectrum (Table 1) was similar to that of **3** with significant differences in the chemical shift values of an olefinic H-8, H_a-25, H_b-25, H-26, and Me-29 of the left-handed ring. The ^{13}C NMR, DEPT, and HMQC spectra showed resonances for 17 quaternary carbons, five methine carbons, three methylene carbons, and nine methyl carbons. The HMBC data (see Supporting Information) confirmed the positions of 3-methylbut-2-enyl and 3-carboxybut-2-enyl groups identical to that of **3**. However, a correlation between the methoxy protons (δ 3.63) and a carbonyl C-6 (δ 171.3) indicated the presence of the methyl ester group. Furthermore, the methyl carboxylate unit was located on the same oxyquaternary C-5 (δ 93.8) as the C-5 3-carboxybut-2-enyl group due to a HMBC correlation of the methylene proton (H_b-20) of the side chain with C-5 and C-6. A ^2J HMBC correlation of the methylene protons (H-25) with the carbonyl carbon at δ 197.0 revealed that C-7 was a carbonyl carbon. One of the methylene protons (H_b-25) also showed a ^3J correlation only with an oxyquaternary C-4b (δ 90.6) but did not correlate with C-6 as normally observed in caged-xanthones. These suggested a bond cleavage between C-6 and C-7 in the structure of **3**. Both C-6 and C-7 in **3** became carbonyl carbons in **8**. The remaining

olefinic proton (δ 6.62) was attributed to H-8 according to its ^3J HMBC correlations with a quaternary C-4b and a carbonyl C-9 (δ 182.1). NOE enhancements between the oxymethine H-15 and Me-17 and Me-19 of the 2,3,3-trimethylhydrofuran ring and between Me-18 and Me-19 and the methylene proton (H_b-20) of the C-5 3-carboxybut-2-enyl unit suggested that H-15 and the C-5 side chain had β and α dispositions, respectively, as in **3**. The configuration of the C-21/C-22 double bond of the C-5 substituent was found to be *E* since irradiation of the olefinic H-21 showed a NOE enhancement with the methylene H_a-20 but not Me-23. In addition, enhancement of H-26 (δ 3.17) and H_b-20 (δ 2.69) upon irradiation of Me-28 (δ 1.76) indicated that H-26, Me-28, and the C-5 substituent were on the same side of the tetrahydrofuran ring. Me-28 was β disposed since irradiation of H-26 enhanced only the signal of H_b-25 (δ 2.62). Thus, scortechinone K (**8**) is the second rearranged tetraprenylated xanthone after gaudispirolactone, which was isolated from *Garcinia gaudichaudii*.[5]

In our previous investigation, the relative stereochemistry at C-15 of scortechinone B (**10**) was not determined because of accidental equivalence of the ^{1}H resonances of Me-17 and Me-18.[15] Comparison of the ^{1}H and ^{13}C NMR signals of the 2,3,3-trimethylhydrofuran unit with those of other caged-polyprenylated xanthones (Tables 1 and 2) now suggests in **10** H-15 has β stereochemistry too. In caged compounds with the β-methine proton of the hydrofuran ring (**2**, **3**, **4**, **5**, and **6**) the geminal methyl groups have similar δ_H values, but distinctly different δ_C values ($\Delta\delta_C$ ca. 8 ppm).

Experimental Section

General Experimental Procedures. Melting points were determined on an electrothermal melting point apparatus (Electrothermal 9100) and are reported without correction. Infrared spectra (IR) were obtained on a FTS165 FT-IR spectometer and Perkin-Elmer Spectrum GX FT-IR system and are recorded in wavenumber (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 500 MHz or Bruker AMX 400 MHz spectrometer using deuteriochloroform solutions with tetramethylsilane (TMS) as internal standard. Ultraviolet spectra (UV) were measured with a Specord S100 spectrophotometer (Analytik Jena Ag). Optical rotations were measured in methanol solution with sodium D line (590 nm) on an AUTOPOL II automatic polarimeter. EIMS, FABMS, and HREIMS data were determined on a VG ZAB 2SEQ mass spectrometer. Thin-layer chromatography (TLC) and precoated TLC were performed on silica gel 60 GF_{254} (Merck). Column chromatography was performed on silica gel (Merck) type 100 (70−230 Mesh ASTM) and eluted with a gradient of $CHCl_3$/MeOH.

Plant Material. Latex of *G. scortechinii* was collected at the Ton Nga Chang Wildlife Sanctuary, Hat Yai, Songkla, Thailand, in June 2000. The plant was identified by Ajarn Prakart Sawangchote, Department of Biology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, where a voucher specimen has been deposited.

Isolation. The latex (8.36 g) was divided in two parts by dissolving with $CHCl_3$. The $CHCl_3$-soluble part was evaporated to dryness under reduced pressure to give a yellow solid (8.18 g). This was further fractionated by column chromatography to yield nine fractions. Fraction 2 (188 mg, eluted with $CHCl_3$−0.5% MeOH/$CHCl_3$) was separated on preparative TLC using 5% EtOAc/petroleum ether as a mobile phase (2 runs) to afford **9** (28.3 mg), **7** (10.6 mg), **1** (7.1 mg), and **2** (11.7 mg). Fraction 4 (1.10 g, eluted with 1% MeOH/$CHCl_3$) was subjected to column chromatography to yield three subfractions. The first subfraction, upon repeated column chromatography, gave **4** (3.9 mg) and **5** (3.1 mg). Fraction 5, eluted with 1−1.5% MeOH/$CHCl_3$, yielded **10** (2.96 g). Compound **6** (10.2 mg) was obtained from fraction 6 (51.3 mg, eluted with 1.5−12% MeOH/$CHCl_3$) after purification on preparative TLC using 4% MeOH/$CHCl_3$ as a mobile phase. Fraction 7 (557 mg, eluted with 12−40% MeOH/$CHCl_3$) was subjected to column chromatography to yield three subfractions. The second subfraction was further purified by preparative TLC using 3% MeOH/$CHCl_3$ as a mobile phase to afford **3** (12.8 mg) and **8** (2.8 mg).

Scortechinone D (1): yellow solid, mp 176.8−177.9 °C; $[\alpha]^{29}_D$ +222 (*c* 0.018); UV (MeOH) λ_{max} (log ϵ) 360 (4.01); IR (neat) ν_{max} 3461, 1744, 1640 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), Table 1; ^{13}C NMR (125 MHz, $CDCl_3$), Table 2; FABMS *m/z* 495 $[M + 1]^+$ (60), 467 (100), 399 (19), 223 (17), 195 (21), 127 (29), 113 (71); HREIMS *m/z* 466.2354 $[M - CO]^+$ (calcd for $C_{28}H_{34}O_6$, 466.2355).

Scortechinone E (2): yellow solid, mp 188.9−190.0 °C; $[\alpha]^{29}_D$ −240 (*c* 0.025); UV (MeOH) λ_{max} (log ϵ) 361 (4.02); IR (neat) ν_{max} 3461, 1742, 1635 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), Table 1; ^{13}C NMR (125 MHz, $CDCl_3$), Table 2; FABMS *m/z* 495 $[M + 1]^+$ (70), 467 (100), 399 (29), 223 (38), 195 (45), 179 (36), 169 (57), 155 (74), 141 (76); HREIMS *m/z* 466.2356 $[M - CO]^+$ (calcd for $C_{28}H_{34}O_6$, 466.2355).

Scortechinone F (3): yellow gum; $[\alpha]^{29}_D$ −333 (*c* 0.015); UV (MeOH) λ_{max} (log ϵ) 362 (4.06); IR (neat) ν_{max} 3500−2500, 1746, 1691, 1635 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), Table 1; ^{13}C NMR (125 MHz, $CDCl_3$), Table 2; EIMS *m/z* 592 $[M]^+$(10), 564 (100), 495 (21), 437 (50), 381 (51), 289 (30), 277 (32); HREIMS *m/z* 592.2663 (calcd for $C_{34}H_{40}O_9$, 592.2672).

Scortechinone G (4): yellow gum; $[\alpha]^{29}_D$ −95 (*c* 0.021); UV (MeOH) λ_{max} (log ϵ) 364 (3.90); IR (neat) ν_{max} 3461, 1742, 1718, 1634 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), Table 1; ^{13}C NMR (125 MHz, $CDCl_3$), Table 2; FABMS *m/z* 607 $[M + 1]^+$(76), 579 (44), 553 (29), 525 (25), 467 (97), 439 (22), 391 (100); HREIMS *m/z* 606.2806 (calcd for $C_{35}H_{42}O_9$, 606.2829).

Scortechinone H (5): yellow gum; $[\alpha]^{29}_D$ −120 (*c* 0.025); UV (MeOH) λ_{max} (log ϵ) 360 (3.96); IR (neat) ν_{max} 3469, 1743, 1690, 1634 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), Table 1; ^{13}C NMR (125 MHz, $CDCl_3$), Table 2; FABMS *m/z* 577 $[M + 1]^+$(13), 549 (38), 437 (35), 391 (52), 381 (82), 367 (23), 351 (29), 339 (49), 323 (26), 309 (22), 297 (23), 279 (100), 259 (100), 245 (42), 233 (100), 217 (88), 203 (83); HREIMS *m/z* 548.2783 $[M - CO]^+$ (calcd for $C_{33}H_{40}O_7$, 548.2774).

Scortechinone I (6): yellow gum; $[\alpha]^{29}_D$ +43 (*c* 0.023); UV (MeOH) λ_{max} (log ϵ) 304 (4.22); IR (neat) ν_{max} 3600−2500, 1751, 1687, 1634 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$), Table 1; ^{13}C NMR (100 MHz, $CDCl_3$), Table 2; FABMS *m/z* 625 $[M + 1]^+$(100), 607 (33), 289 (35), 233 (47), 153 (81), 135 (91); HREIMS *m/z* 624.2933 (calcd for $C_{35}H_{44}O_{10}$, 624.2934).

Scortechinone J (7): yellow gum; $[\alpha]^{29}_D$ −200 (*c* 0.015); UV (MeOH) λ_{max} (log ϵ) 361 (3.81); IR (neat) ν_{max} 3397, 1746, 1634 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), Table 1; ^{13}C NMR (125 MHz, $CDCl_3$), Table 2; EIMS *m/z* 534 $[M - CO]^+$ (100), 465 (45), 437 (38), 247 (46), 203 (12), 149 (40), 69 (44); HREIMS *m/z* 534.2983 $[M - CO]^+$ (calcd for $C_{33}H_{42}O_6$, 534.2981).

Scortechinone K (8): yellow gum; $[\alpha]^{29}_D$ +48 (*c* 0.021); UV (MeOH) λ_{max} (log ϵ) 368 (4.11); IR (neat) ν_{max} 3600−2500, 1753, 1690, 1640 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$), Table 1; ^{13}C NMR (125 MHz, $CDCl_3$), Table 2; EIMS *m/z* 608 $[M]^+$ (100), 553 (36), 509 (62), 422 (69), 407 (32), 379 (68), 367 (90), 249 (21), 178 (26), 69 (40), 57 (52); HREIMS *m/z* 608.2624 (calcd for $C_{34}H_{40}O_{10}$, 608.2622).

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Supporting Information Available: Tables of major HMBC correlations of **1**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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