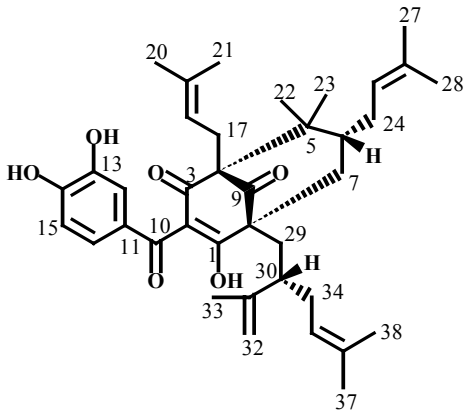
3 RESULTS AND DISCUSSION

3.1 Structural determination of compounds isolated from the green fruits, ripe fruits, flowers and seeds of G. dulcis

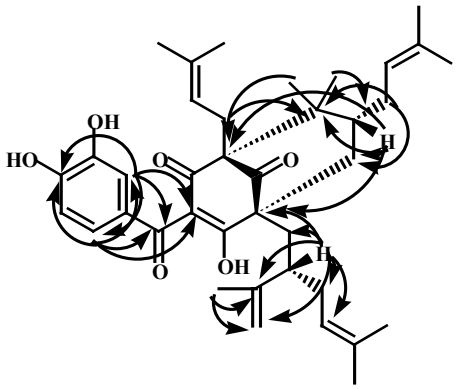
The green fruits, ripe fruits and flowers of *Garcinia dulcis* Kurz. collected from Songkhla province in the southern part of Thailand. The extracts obtained from the green fruits, ripe fruits, flowers and seeds. Isolation and purification of acetone and methanolic extracts of the green fruits gave twenty compounds and six compounds, respectively. Twenty-five compounds were obtained from acetone extract of the ripe fruits. From the flowers, twenty-seven compounds were given from the acetone extract and three compounds were obtained from the methanolic extract. The dichloromethane and methanolic extracts of the seeds gave three and twelve compounds, respectively. The structures of all compounds were elucidated by analysis of spectroscopy.

GD1 : (4*R*,6*R*,8*R*)-2-(3,4-dihydroxybenzoyl)-1-hydroxy-8-[(2*S*)-2-isopropenyl-5-methyl-4-hexenyl]-5,5-dimethyl-4,6-bis(3-methyl-2-butenyl)bicyclo[3.3.1] non-1-ene-3,9-dione (camboginol or garcinol)



GD1 is a yellow solid, m.p. 125-128 °C. Its molecular formula was $C_{38}H_{50}O_6$ as indicated by mass spectrum ($[M]^+$ *m/z* 602). The optical rotation was $[\alpha]_D^{29}$ -128.5 ° (c = 0.02 in CH_3OH). The ^1H NMR spectrum (**Table 24**) showed the resonances of aromatic protons H-15 (δ 6.61, *d*, *J* = 8.4 Hz), H-16 (δ 7.00, *dd*, *J* = 8.4, 2.0 Hz) and H-12 (δ 6.97, *d*, *J* = 2.0 Hz) which referred to the presence of 3,4-dihydroxybenzoyl group. The presence of three prenyl groups were observed. The signals at δ 5.10 (*br t*, H-18), 2.39 (*br d*, H-17), 1.68 (*s*, H-20), 1.57 (*s*, H-21) were due to a prenyl group at C-4. Whereas those at δ 4.95 (*br t*, H-25), 1.75 (*s*, H-28), 1.71 (*s*, H-27), 1.38 (*br s*, H-24) and δ 5.08 (*br t*, H-35), 1.89 (*m*, H-34), 1.82 (*s*, H-37), 1.56 (*s*, H-38) belonged to the prenyl group attached to CH-carbon. HMBC correlations showed the correlations of H-17 to C-5; H-24 to C-5, C-7 and H-34 to C-29, C-30, C-31 indicated that the prenyl groups were at C-4, C-6 and C-30, respectively. The spectrum further showed the signals of isopropenyl group at δ 4.43 (2H, *br s*, H-32) and 1.70 (3H, *s*, H-33) of which this group was located at C-30 according to the correlations of H-30 to C-31 and C-32. In addition, two methyl groups on a saturated carbon were observed at δ 1.05

(3H, *s*, H-22) and 1.61 (3H, *s*, H-23) and were placed at C-5 from the HMBC correlations of H-22 to C-4, C-5, C-6 and H-23 to C-22. Two groups of methylene protons were assigned from the resonances at δ 2.17 (1H, *m*, H-7), 1.90 (1H, *m*, H-7) and 2.74 (1H, *m*, H-29), 1.73 (1H, *m*, H-29) whereas two methine protons were indicated from the signals at δ 1.49 (1H, *m*, H-6) and 2.08 (1H, *m*, H-30). Four signals of carbonyl carbons were shown in the ^{13}C NMR spectrum which corresponded to a non-enolisable carbonyl carbon (δ 209.17) and three enolisable carbonyl carbons (δ 194.01, 195.10 and 198.73). The remaining signals were assigned for eleven quaternary carbons, eight methine carbons, six methylene carbons and nine methyl carbons. The HMBC confirmed the above assignment, **GD1** was then identified as (4*R*,6*R*,8*R*)-2-(3,4-dihydroxybenzoyl)-1-hydroxy-8-[(2*S*)-2-isopropenyl-5-methyl-4-hexenyl]-5,5-dimethyl-4,6-bis(3-methyl-2-butenyl)bicyclo[3.3.1]non-1-ene-3,9-dione. The proposed structure, the spectral data, melting point and optical rotation were agreed with the structure of camboginol (Rama Rao, *et al*., 1980; Krishnamurthy, *et al*., 1981).



Major HMBC correlations of **GD1**

Table 24 The NMR spectral data of **GD1**

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	GD1	**camboginol**	**GD1**	**camboginol**	
1	194.01 (C=O)	194.1	-	-	-
2	115.88 (C)	116.0	-	-	-
3	195.10 (C=O)	195.1	-	-	-
4	69.77 (C)	69.8	-	-	-
5	49.66 (C)	49.6	-	-	-
6	46.83 (CH)	47.0	1.49 (1H, *m*)	1.40-2.90 (*m*)	C-4, C-5, C-7, C-8, C-25
7	28.94 (CH_2)	29.0	1.90 (1H, *m*)	1.40-2.90 (*m*)	C-24, C-29
			2.17 (1H, *m*)		C-24, C-29
8	57.96 (C)	58.0	-	-	-
9	209.17 (C=O)	209.1	-	-	-
10	198.73 (C=O)	198.9	-	-	-
11	127.70 (C)	127.8	-	-	-
12	116.44 (CH)	116.6	6.97 (1H, *d*, 2.0)	6.95 (*d*, 2.0)	C-2, C-10, C-14, C-16
13	143.70 (C)	143.8	-	-	-
14	149.83 (C)	150.0	-	-	-
15	114.37 (CH)	114.4	6.61 (1H, *d*, 8.4)	6.58 (*d*, 9.0)	C-11, C-13, C-14
16	124.03 (CH)	120.2	7.00 (1H, *dd*, 8.4, 2.0)	7.05 (*q*)	C-2, C-10, C-12, C-14
17	42.64 (CH_2)	42.8[b]	2.39 (2H, *br d*)	1.40-2.90 (*m*)	C-5, C-19
18	122.64 (CH)	122.7[a]	5.10 (1H, *br t*)	4.90 (*br t*)	C-20, C-21
19	132.03 (C)	132.0	-	-	-
20	26.98 (CH_3)	26.0[c]	1.68 (3H, *s*)	1.70	C-18, C-19, C-21
21	17.87 (CH_3)	17.9[d]	1.57 (3H, *s*)	1.56	C-18, C-19, C-20
22	27.01 (CH_3)	26.5	1.05 (3H, *s*)	1.04 (*s*)	C-4, C-5, C-6
23	17.20 (CH_3)	17.3	1.16 (3H, *s*)	1.16 (*s*)	C-6, C-22
24	32.61 (CH_2)	32.7[b]	1.38 (2H, *br s*)	1.40-2.90 (*m*)	C-5, C-7, C-26
25	123.76 (CH)	124.2[a]	4.95 (1H, *br t*)	4.90 (*br t*)	C-27, C-28
26	132.98 (C)	132.9	-	-	-
27	26.03 (CH_3)	25.8[c]	1.71 (3H, *s*)	1.70	C-25, C-26, C-28
28	18.18 (CH_3)	18.2[d]	1.75 (3H, *s*)	1.56	C-25, C-26, C-27

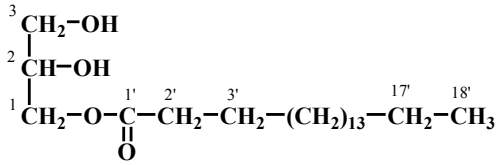
Table 24 (Continued)

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	GD1	**camboginol**	**GD1**	**camboginol**	
29	26.36 (CH_2)	27.0[b]	2.74 (1H, *m*)	1.40-2.90 (*m*)	C-1, C-8, C-9, C-30
			1.73 (1H, *m*)		C-1, C-8, C-9, C-30
30	43.57 (CH)	43.7	2.08 (1H, *m*)	1.40-2.90 (*m*)	C-8, C-29, C-31, C-32, C-33, C-34, C-35
31	148.06 (C)	148.1	-	-	-
32	113.28 (CH_2)	112.7	4.43 (2H, *br s*)	4.36 (*br s*)	C-31, C-33
33	22.58 (CH_3)	22.7	1.70 (3H, *s*)	1.70	C-30, C-31, C-32
34	35.51 (CH_2)	36.3[b]	1.89 (2H, *m*)	1.70	C-29, C-30, C-31, C-35, C-36
35	120.02 (CH)	124.0[a]	5.08 (1H, *br t*)	4.9 (*br t*)	C-37, C-38
36	135.34 (C)	135.3	-	-	-
37	25.71 (CH_3)	25.8[c]	1.82 (3H, *s*)	1.70	C-35, C-36, C-38
38	17.64 (CH_3)	17.7[d]	1.56 (3H, *s*)	1.56	C-36, C-37

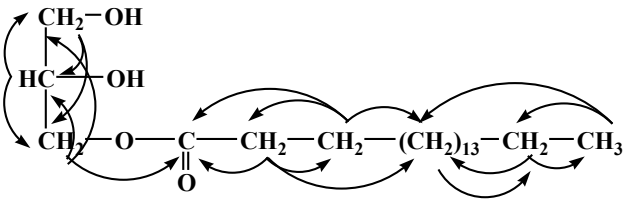
* Carbon type was deduced from DEPT experiments.

[a] Olefinic methine carbons, [b] Methylene carbons, [c, d] Methyl carbons: Assignment maybe interchangeable.

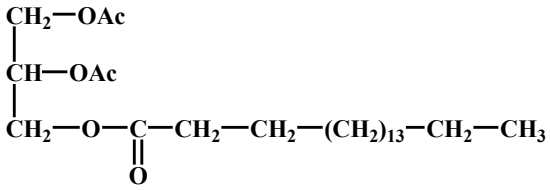
GD2 : Octadecanoic acid-2,3-dihydroxypropyl ester



GD2 is a white solid, m.p. 63-65 °C. The ^{1}H NMR spectrum (**Table 25**) exhibited two sharp *triplet* signals of H-2′ at δ 2.35 (2H, J = 6.6 Hz) and H-18′ at δ 0.88 (3H, J = 6.6 Hz), a *quintet* signal of H-3′ at δ 1.63 (2H, J = 6.6 Hz) and a *multiplet* signal of H-4′ - H-17′ at δ 1.32-1.25 (28H). These assignments were supported by the HMBC correlations of H-2′ to C-1′, C-3′, C-4′; H-3′ to C-1′, C-2′, C-4′; H-17′ to C-16′, C-18′ and H-18′ to C-16′, C-17′. The ^{1}H NMR spectra further showed two *doublet of doublet* signals of non equivalent methylene protons H-1 at δ 4.21 (1H, J = 11.2 and 4.2 Hz) and 4.15 (1H, J = 11.2 and 5.6 Hz), two *doublet of doublet* signals of non equivalent methylene protons H-3 at δ 3.70 (1H, J = 11.2 and 4.2 Hz) and 3.61 (1H, J = 11.2 and 5.6 Hz) and a *multiplet* signal of methine proton H-2 at δ 3.94. These signals were supported by the correlations of H-1 to C-2, C-3, C-1′; H-2 to C-1, C-3 and H-3 to C-1, C-2 in HMBC. The presence of hydroxy groups at C-2 and C-3 were confirmed by the appearance of two signals of acetyl protons (δ 2.05, 3H and 2.06, 3H) and the down field shifts of H-2 (δ 5.23, 1H, *m*) and H-3 (δ 4.27, 1H, *dd*, J = 8.4, 4.2 Hz and 4.29, 1H, *dd*, J = 8.4, 4.2 Hz) of its acetylated product (**Table 26**). Thus **GD2** was assigned to be octadecanoic acid-2,3-dihydroxypropyl ester (Chupin, *et al.*, 2001).



Major HMBC correlations of **GD2**



Structure of **GD2(A)**

Table 25 The NMR spectral data of **GD2**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	COSY	HMBC
1	65.16 (CH_2)	4.21 (1H, *dd*, 11.2, 4.2)	H-2	C-2, C-3, C-1′
		4.15 (1H, *dd*, 11.2, 5.6)	H-2	C-2, C-3, C-1′
2	70.25 (CH)	3.94 (1H, *m*)	H-1, H-3	C-1, C-3
3	63.30 (CH_2)	3.70 (1H, *dd*, 11.2, 4.2)	H-2	C-1, C-2
		3.61 (1H, *dd*, 11.2, 5.6)	H-2	C-1, C-2
1′	174.36 (C=O)	-	-	-
2′	34.14 (CH_2)	2.35 (2H, *t*, 6.6)	H-3′	C-1′, C-3′, C-4′
3′	24.90 (CH_2)	1.63 (2H, *qn*, 6.6)	H-2′, H-4′	C-1′, C-2′, C-4′
4′	29.11 (CH_2)		H-3′	C-16′, C-(5′-15′), C-17′
	29.70 (CH_2)			
	29.69 (CH_2)			
	29.68 (CH_2)			
	29.67 (CH_2)			
	29.66 (CH_2)			
5′-15′	29.64 (CH_2)	1.32-1.25 (28H, *m*)		
	29.63 (CH_2)			
	29.58 (CH_2)			
	29.43 (CH_2)			
	29.35 (CH_2)			
	29.23 (CH_2)			
16′	31.91 (CH_2)		H-17′	
17′	22.68 (CH_2)		H-16′,H-18′	C-16′, C-(5′-15′), C-18′
18′	14.12 (CH_3)	0.88 (3H, *t*, 6.6)	H-17′	C-16′, C-17′
2-OH	-	2.46 (1H, *d*, 5.0)	-	-
3-OH	-	2.02 (1H, *br t*, 5.8)	-	-

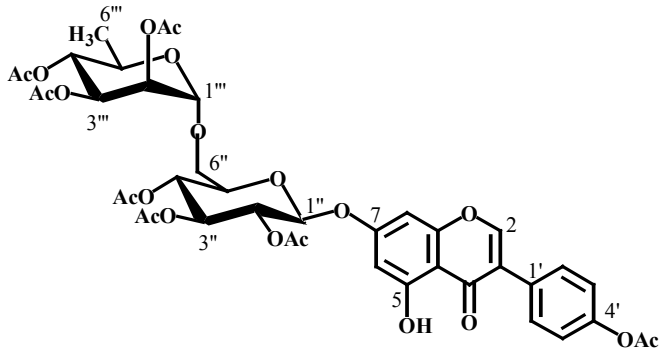
* Carbon type was deduced from DEPT experiments.

Table 26 The ^{1}H NMR spectral data of **GD2** and **GD2(A)**

Position	**GD2** δ_H (*multiplicity*, J_{Hz})	**GD2(A)** δ_H (*multiplicity*, J_{Hz})
1	4.21 (1H, *dd*, 11.2, 4.2)	4.15 (1H, *dd*, 7.8, 5.4)
	4.15 (1H, *dd*, 11.2, 5.6)	4.12 (1H, *dd*, 7.8, 5.4)
2	3.94 (1H, *m*)	5.23 (1H, *m*)
3	3.70 (1H, *dd*, 11.2, 4.2)	4.29 (1H, *dd*, 8.4, 4.2)
	3.61 (1H, *dd*, 11.2, 5.6)	4.27 (1H, *dd*, 8.4, 4.2)
2′	2.35 (2H, *t*, 6.6)	2.29 (2H, *t*, 7.0)
3′	1.63 (2H, *qn*, 6.6)	1.58 (2H, *qn*, 6.4)
4′-17′	1.32-1.25 (28H, *m*)	1.23 (28H, *m*)
18′	0.88 (3H, *t*, 6.6)	0.85 (3H, *t*, 6.4)
2-$OCOCH_3$	-	2.05 (3H, *s*)*
3-$OCOCH_3$	-	2.06 (3H, *s*)*

* Assignment maybe interchangeable.

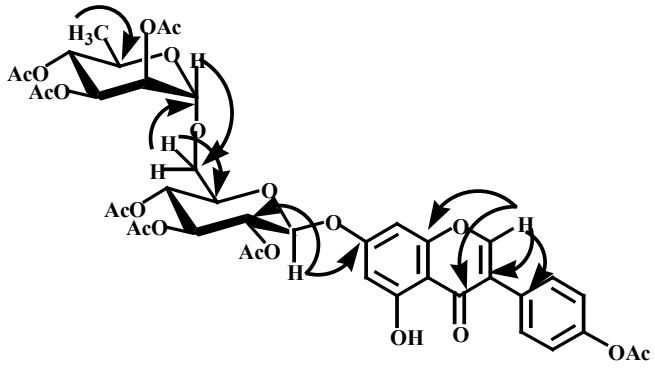
GD3 : 5-Hydroxy-4′, 2″, 3″, 4″, 2‴, 3‴, 4‴-heptaacetateisoflavone 7-*O*-[*α*-rhamnopyranosyl-(1→6)]-*β*-glucopyranoside



GD3 is yellow needles. EIMS showed the molecular ion of 872 which corresponded to $C_{41}H_{44}O_{21}$. The UV spectra (λ_{max} 323.0, 257.2 and 215.8 nm) indicated an isoflavone nucleus. IR absorption bands at 3410 cm^{-1} and 1646 cm^{-1} suggested the presence of hydroxyl group and carbonyl group, respectively.

The ^{1}H NMR spectrum (**Table 27**) revealed a *singlet* of a chelated hydroxyl group (5-OH) at δ 12.72 and a *singlet* of isoflavone type vinylic proton (H-2) at δ 7.97. The 4′-oxysubstituted pattern of B-ring was readily deduced from the proton signals forming an AA′BB′ system at δ 7.58 (J = 8.3 Hz, H-2′, H-6′) and 7.19 (J = 8.3 Hz, H-3′, H-5′). Two *doublets* at δ 6.42 and 6.55 with coupling constant of 2.5 Hz, represented the H-6 and H-8, respectively. The correlations of H-6 to C-4a, C-5, C-8 and H-8 to C-4, C-4a, C-6, C-7, C-8a confirmed the assignment of H-6 and H-8. A *doublet* at δ 5.18 (J = 6.8 Hz) was assigned for the anomeric proton H-1″ of *β*-glucose unit. A *doublet* at δ 4.73 (J = 2.3 Hz) and a *doublet* at δ 1.18 (J = 5.0 Hz) were attributed to the anomeric proton H-1‴ and a methyl group of *α*-rhamnose unit, respectively. A (1→6)-glycosidic linkage of rhamnose to glucose was proposed from the downfield shift of C-6″. In addition, the linkage was confirmed by the HMBC correlation of the anomeric proton H-1‴ to C-6″ (δ 66.27). The correlation of H-1″

to C-7 (δ 161.98) of the aglycone suggested that the glucose moiety was attached to the 7-hydroxyl of the aglycone. Moreover the sugar moieties were assigned to be acetyl derivatives according to the resonances of seven acetyl groups (δ 2.33, 2.09, 2.08, 2.07, 2.05 (6H) and 1.98). These data permitted the identification of **GD3** as 5-hydroxy-4′, 2″, 3″, 4″, 2‴, 3‴, 4‴-heptaacetateisoflavone 7-*O*-[α-rhamnopyranosyl-(1→6)]-β-glucopyranoside. This compound was a new naturally occurring but synthetically known isoflavone glycoside (Roesler, *et al*., 1965).



Major HMBC correlations of **GD3**

Table 27 The NMR spectral data of **GD3**

Position	δ_C *	δ_H (*multiplicity*, J_{Hz})	HMBC
2	154.02 (CH)	7.97 (1H, *s*)	C-3, C-4, C-8a, C-1′
3	123.05 (C)	-	-
4	180.61 (C=O)	-	-
4a	107.53 (C)	-	-
5	162.58 (C)	-	-
6	100.51 (CH)	6.42 (1H, *d*, 2.5)	C-4a, C-5, C-8
7	161.98 (C)	-	-
8	94.67 (CH)	6.55 (1H, *d*, 2.5)	C-4, C-4a, C-6, C-7, C-8a
8a	157.59 (C)	-	-
1′	128.29 (C)	-	-
2′, 6′	129.96 (CH)	7.58 (2H, *d*, 8.3)	C-3, C-2′,6′, C-3′,5′, C-4′
3′, 5′	121.79 (CH)	7.19 (2H, *d*, 8.3)	C-1′, C-3′,5′, C-4′
4′	150.75 (C)	-	-
Glc-1″	97.94 (CH)	5.18 (1H, *d*, 6.8)	C-7, C-2″, C-3″
2″	73.57 (CH)	3.89 (1H, *m*)	C-3″
3″	69.18 (CH)	5.27 (1H, *m*)	C-1″, C-4″, 3″-O<u>C</u>OCH$_3$
4″	70.81 (CH)	5.33 (1H, *t*, 8.0)	C-3″, C-6″
5″	72.50 (CH)	5.31 (1H, *m*)	C-1″, C-3″, C-4″, C-6″
6″	66.27 (CH_2)	3.63 (2H, *dd*, 11.5, 6.9)	C-5″, C-1‴
Rha-1‴	98.20 (CH)	4.73 (1H, *d*, 2.3)	C-6″, C-2‴, C-3‴
2‴	69.08 (CH)	5.27 (1H, *m*)	C-1‴, C-4‴
3‴	68.70 (CH)	5.09 (1H, *t*, 8.0)	C-1‴, C-4‴
4‴	70.74 (CH)	5.04 (1H, *t*, 8.0)	C-3‴, C-6‴
5‴	66.61 (CH)	3.85 (1H, *m*)	C-3‴, C-4‴
6‴	17.27 (CH_3)	1.18 (3H, *d*, 5.0)	C-4‴, C-5‴

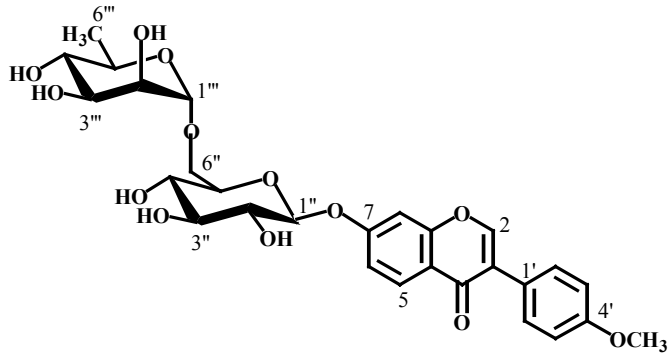
Table 27 (Continued)

Position	δ_C *	δ_H (*multiplicity*, J_{Hz})	HMBC
5-OH	-	12.72 (1H, *s*)	-
4′-$OCOCH_3$	169.20 (C=O)[a], 20.56 (CH_3)[b]	1.98 (3H, *s*)[c]	C-4′
2″-$OCOCH_3$	170.41 (C=O)[a], 20.57 (CH_3)[b]	2.09 (3H, *s*)[c]	C-2″
3″- $OCOCH_3$	169.90 (C=O)[a], 20.73 (CH_3)[b]	2.05 (3H, *s*)[c]	C-3″
4″- $OCOCH_3$	169.88 (C=O)[a], 20.74 (CH_3)[b]	2.07 (3H, *s*)[c]	C-4″
2‴- $OCOCH_3$	169.70 (C=O)[a], 20.57 (CH_3)[b]	2.08 (3H, *s*)[c]	C-2‴
3‴- $OCOCH_3$	169.41 (C=O)[a], 20.76 (CH_3)[b]	2.05 (3H, *s*)[c]	C-3‴
4‴- $OCOCH_3$	169.38 (C=O)[a], 21.11 (CH_3)[b]	2.33 (3H, *s*)[c]	C-4″

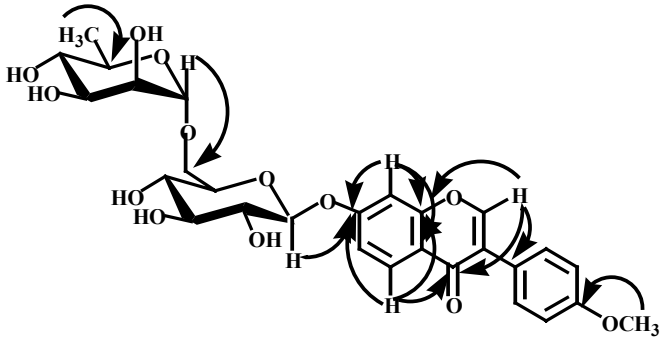
* Carbon type was deduced from DEPT experiments.

[a, b, c] Assignment maybe interchangeable.

GD4 : 7-*O*-[α-Rhamnopyranosyl(1→6)]-β-glucopyranoside-4′-methoxyisoflavone (derriscannoside A)



GD4 was isolated as brown needles. It is an isoflavone of which the characteristic resonance of the methine proton H-2 appeared as a *singlet* signal at δ 8.25. The AA′BB′ resonances of aromatic protons H-2′, H-6′ and H-3′, H-5′ were displayed at δ 7.51 (*d*, *J* = 8.7 Hz) and 6.95 (*d*, *J* = 8.7 Hz), respectively. The signals of ABX type at δ 8.10 (*d*, *J* = 8.7 Hz), 7.11 (*dd*, *J* = 8.7 and 2.5 Hz) and 7.23 (*d*, *J* = 2.5 Hz) were proposed for the signals of H-5, H-6 and H-8, respectively. A *singlet* signal at δ 3.83 was assigned for 4′-OCH_3. The ^{1}H NMR spectrum (**Table 28**) further indicated the presence of two sugar moieties. A *doublet* signal at δ 4.96 with *J* = 7.0 Hz was assigned for the anomeric proton of glucose (H-1′′). A *singlet* resonance at δ 4.67 (H-1′′′) and a *doublet* resonance at δ 1.22 (*J* = 5.6 Hz, H-6′′′) implied the presence of a rhamnose. The other proton signals of sugars appeared at δ 3.85-3.35. HMBC correlations of H-1′′ to C-7 (δ 161.30) and H-1′′′ to C-6′′ (δ 61.98) suggested that glucose was directly connected to isoflavone nucleus at C-7 and rhamnose was formed (1→6) a glycosidic bond to glucose. The ^{13}C NMR and the DEPT spectra were shown in **Table 28**. The assignment suggested that **GD4** was 7-*O*-[α-rhamnopyranosyl (1→6)]-β-glucopyranoside-4′-methoxyisoflavone (derriscannoside A, Dianpeng, *et al*., 1999).



Major HMBC correlations of **GD4**

Table 28 The NMR spectral data of **GD4**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	153.21 (CH)	8.25 (1H, *s*)	C-4, C-8a, C-1′
3	123.65 (C)	-	-
4	175.14 (C=O)	-	-
4a	118.81 (C)	-	-
5	126.77 (CH)	8.10 (1H, *d*, 8.7)	C-4, C-7, C-8a
6	115.60 (CH)	7.11 (1H, *dd*, 8.7, 2.5)	C-4a, C-7
7	161.30 (C)	-	-
8	103.78 (CH)	7.23 (1H, *d*, 2.5)	C-4, C-4a, C-6, C-7, C-8a
8a	157.19 (C)	-	-
1′	124.09 (C)	-	-
2′, 6′	129.84 (CH)	7.51 (2H, *d*, 8.7)	C-3, C-2′,6′, C-4′
3′, 5′	113.45 (CH)	6.95 (2H, *d*, 8.7)	C-1′, C-3′,5′, C-4′
4′	159.50 (C)	-	-
4′-OCH_3	54.96 (CH_3)	3.83 (3H, *s*)	C-4′

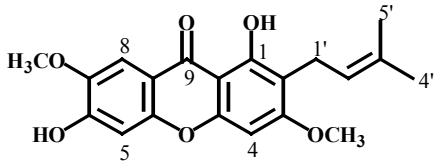
Table 28 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
Glc-1″	100.63 (CH)	4.96 (1H, *d*, 7.0)	C-7, C-3″, C-5″
2″	83.24 (CH)	3.30-3.20 (1H, *m*)	C-3″
3″	76.97 (CH)	3.50-3.44 (1H, *m*)	C-2″, C-4″
4″	73.02 (CH)	3.52-3.50 (1H, *m*)	C-3″, C-5″, C-6″
5″	75.82 (CH)	3.62-3.59 (1H, *m*)	C-3″, C-4″, C-5″, C-6″
6″	61.98 (CH_2)	3.54 (2H, *br s*)	C-4″, C-5″, C-1‴
2″-OH	-	5.37 (1H, *br s*)[a]	-
3″-OH	-	5.07 (1H, *br s*)[a]	-
4″-OH	-	5.11 (1H, *br s*)[a]	-
Rha-1‴	100.53 (CH)	4.67 (1H, *br s*)	C-6″, C-2‴, C-3‴, C-5‴
2‴	70.29 (CH)	3.85 (1H, *m*)	C-2‴, C-4‴
3‴	71.21 (CH)	3.80-3.65 (1H, *m*)	C-1‴, C-4‴
4‴	72.56 (CH)	3.45-3.35 (1H, *m*)	C-3‴, C-5‴
5‴	68.16 (CH)	3.65-3.60 (1H, *m*)	C-3‴, C-4‴
6‴	17.61 (CH_3)	1.22 (3H, *d*, 5.6)	C-4‴, C-5‴
2‴-OH	-	4.45 (1H, *br s*)[b]	-
3‴-OH	-	4.36 (1H, *br s*)[b]	-
4‴-OH	-	4.55 (1H, *br s*)[b]	-

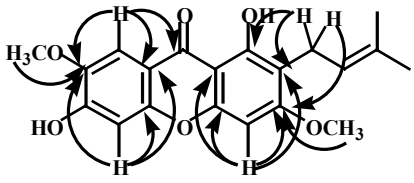
* Carbon type was deduced from DEPT experiments.

[a, b] Assignment maybe interchangeable.

GD5 : 1,6-Dihydroxy-3,7-dimethoxy-2-(3-methyl-2-butenyl)xanthone



GD5 is a pale yellow solid, m.p. 250-251 °C. The ^{1}H NMR spectrum (**Table 29**) showed two *singlet* signals of a chelated hydroxy proton (1-OH) at δ 13.10 and a non chealated hydroxy proton (6-OH) at δ 8.17. Three *singlet* signals were observed at δ 6.40, 6.92 and 7.56. These signals were assigned for aromatic protons H-4, H-5 and H-8, respectively. The deshielded aromatic proton at δ 7.56 was assigned to be at C-8 due to an anisotropic effect of the carbonyl group. Two *singlet* signals at δ 3.90 and 3.98 were assigned for two methoxy groups of 3-OCH_3 and 7-OCH_3, respectively. In addition, a set of signals of a prenyl side chain were shown in the spectrum, of which the methylene protons resonated at δ 3.34 (*d*, H-1′), olefinic proton resonated at δ 5.21 (*t*, H-2′) and two methyl groups resonated at δ 1.66 (*s*, H-4′) and 1.78 (*s*, H-5′). The ^{13}C NMR and DEPT experiments indicated the presence of a carbonyl carbon, ten quaternary carbons, four methine carbons, a methylene carbon and four methyl carbons. The location of the prenyl side chain at C-2 was determined from HMBC correlations; H-1′(δ 3.34) correlated to C-1, C-2 and C-3. The location of aromatic protons H-4, H-5 and H-8 were indicated by correlations of H-4 to C-2, C-3, C-4a, C-9a; H-5 to C-7, C-8a, C-10a and H-8 to C-7, C-9, C-10a. Therefore **GD5** was proposed to be 1,6-dihydroxy-3,7-dimethoxy-2-(3-methyl-2-butenyl)xanthone or known as cowagarcinone B (Chairerk, 2001).



Major HMBC correlations of **GD5**

Table 29 The NMR spectral data of **GD5**

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	GD5	**	**GD5**	**	
1	159.25 (C)	159.36	-	-	-
2	111.51 (C)	111.76	-	-	-
3	163.67 (C)	163.85	-	-	-
4	89.51 (CH)	89.58	6.40 (1H, *s*)	6.43 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	156.30 (C)	156.24	-	-	-
5	102.76(CH)	102.49	6.92 (1H, *s*)	6.94 (1H, *s*)	C-7, C-8a, C-10a
6	152.20 (C)	152.37	-	-	-
7	145.14 (C)	144.32	-	-	-
8	104.68(CH)	104.62	7.56 (1H, *s*)	7.61 (1H, *s*)	C-7, C-9, C-10a
8a	113.50 (C)	113.63	-	-	-
9	179.85(C=O)	179.86	-	-	-
9a	103.20 (C)	104.62	-	-	-
10a	153.24 (C)	152.54	-	-	-
1′	21.30 (CH_2)	21.36	3.34 (2H,*d*,6.6)	3.37 (2H,*d*,6.5)	C-1, C-2, C-3, C-2′, C-3′
2′	122.20(CH)	122.21	5.21 (1H,*t*, 6.9)	5.24 (1H,*t*,7.0)	C-1′, C-5′
3′	131.90 (C)	131.83	-	-	-
4′	25.79 (CH_3)	25.80	1.66 (3H, *s*)	1.68 (3H, *s*)	C-2′, C-3′, C-5′

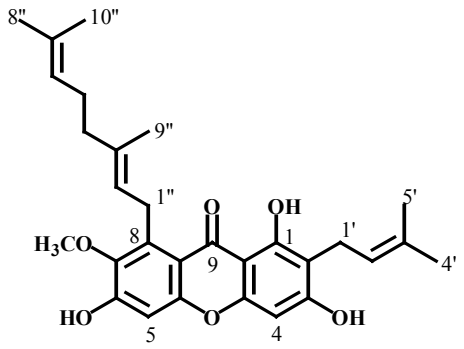
Table 29 (Continued)

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	GD5	**	**GD5**	**	
5′	17.78 (CH_3)	17.80	1.78 (3H, *s*)	1.80 (3H, *s*)	C-2′, C-3′, C-4′
1-OH	-	-	13.10 (1H, *s*)	13.00 (3H, *s*)	-
6-OH	-	-	8.17 (1H, *s*)	6.34 (1H, *s*)	-
3-OCH_3	55.87 (CH_3)	55.90	3.90 (3H, *s*)	3.92 (3H, *s*)	C-3
7-OCH_3	56.38 (CH_3)	56.53	3.98 (3H, *s*)	4.01 (3H, *s*)	C-7

* Carbon type was deduced from DEPT experiments.

** PGC8 (Chairerk, 2001)

GD6 : 1,3,6-Trihydroxy-7-methoxy-2-(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone (cowanin)



GD6 is a yellow solid, m.p. 137-138 °C. The ^{1}H NMR spectrum (**Table 30**) demonstrated the resonances of a chelated hydroxy group (1-OH) at δ 13.80 and two *singlet* signals of H-4 and H-5 at δ 6.29 and 6.81, respectively. A signal of methoxy group was shown at δ 3.81 and the methoxyl was located at C-7. The ^{1}H NMR spectrum also showed a characteristic signals of a prenyl unit at δ 5.31(1H, *br t*, H-2′), 3.46 (2H, *d*, H-1′), 1.84 (3H, *s*, H-5′) and 1.78 (3H, *s*, H-4′). The remaining signals were assigned for a geranyl side chain. A *doublet* at δ 4.10 and a *broad triplet* at δ 5.28 were assigned for the signals of methylene protons H-1″ and an olefinic proton H-2″, respectively. A *broad triplet* at δ 5.04 and a *multiplet* at δ 2.06 were the signals of an olefinic proton H-6″ and two groups of methylene protons H-4″ and H-5″, respectively whereas three *singlet* signals at δ 1.85 (3H, *s*, H-9″), 1.61 (3H, *s*, H-10″) and 1.56 (3H, *s*, H-8″) were those of three methyl groups. Since the chemical shift of methylene protons H-1″ of the geranyl side chain was appeared at lower field than that of H-1′ of the prenyl side chain, the geranyl group thus was placed nearby the carbonyl group and the prenyl moiety was placed at C-2. Thus **GD6** was assigned to be 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl) xanthone or known as cowanin (Na Pattalung, *et al.*, 1994).

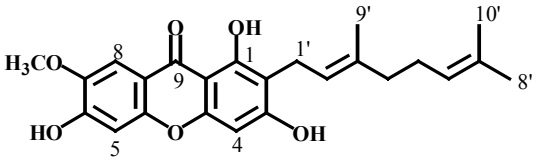
Table 30 The ^{1}H NMR spectral data of **GD6**

Position	δ_H (*multiplicity*, J_{Hz})	
	GD6*	**cowanin****
4	6.29 (1H, *s*)	6.30 (1H, *s*)
5	6.81 (1H, *s*)	6.86 (1H, *s*)
1′	3.46 (2H, *d*, 7.0)	3.45 (2H, *br d*, 7.0)
2′	5.31 (1H, *br t*, 7.0)	5.28 (1H, *br t*, 7.0)
4′	1.78 (3H, *s*)	1.76 (3H, *s*)
5′	1.84 (3H, *s*)	1.82 (3H, *s*)
1″	4.10 (2H, *d*, 7.0)	4.09 (2H, *br d*, 7.0)
2″	5.28 (1H, *br t*, 7.0)	5.28 (1H, *br t*, 7.0)
4″	2.06 (1H, *m*)	2.03 (1H, *m*)
5″	2.06 (1H, *m*)	2.03 (1H, *m*)
6″	5.04 (1H, *br t*, 7.0)	5.03 (1H, *br t*)
8″	1.56 (3H, *s*)	1.59 (3H, *s*)
9″	1.85 (3H, *s*)	1.84 (3H, *s*)
10″	1.61 (3H, *s*)	1.61 (3H, *s*)
1-OH	13.80 (1H, *s*)	13.80 (1H, *s*)
7-OCH_3	3.81 (3H, *s*)	3.80 (3H, *s*)

* 500 MHz, in $CDCl_3$

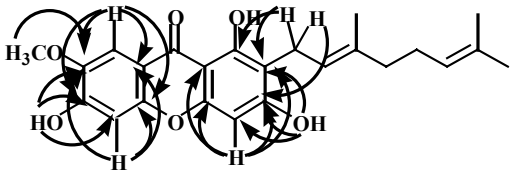
** 400 MHz, in $CDCl_3$

GD7 : 1,3,6-Trihydroxy-7-methoxy-2-(3,7-dimethyl-2,6-octadienyl)xanthone (cowaxanthone)



GD7 is a yellow solid, m.p. 197-199 °C. EIMS showed the molecular ion of 410 which corresponded to $C_{24}H_{26}O_6$. A xanthone nucleus was elucidated from the UV spectra (λ_{max} 361.4, 320.5, 258.3 and 241.8 nm). IR absorption bands at 3369 cm^{-1} and 1646 cm^{-1} indicated the presence of hydroxyl stretching and conjugated carbonyl stretching, respectively. The ^1H NMR spectrum (**Table 31**) showed the resonances of a hydrogen-bonded phenolic hydroxy group at δ 13.35 (*s*, 1-OH), two free hydroxy protons at δ 6.39 (*s*, 3-OH) and 6.43 (*s*, 6-OH) and three *singlet* signals of three isolated aromatic protons at δ 7.58 (H-8), 6.92 (H-5) and 6.48 (H-4). The most deshielded aromatic proton signal, δ 7.58, was assigned for H-8 according to an anisotropic effect by the carbonyl group. The sharp *singlet* resonance at δ 4.00 belonged to the methoxy group which was located at C-7 according to HMBC correlation of OCH_3 protons to C-7. The remaining proton signals were assigned for the geranyl side chain which was located at C-2. Those signals were assigned as follow; three *singlet* signals at δ 1.84, 1.68 and 1.67 were of three vinylic methyl groups, a *doublet* signal at δ 3.48 was assigned for benzylic methylene protons H-1′, a *multiplet* signal at δ 2.10 (4H) was the signal of two groups of methylene protons H-4′ and H-5′ and two sets of *broad triplet* signals at δ 5.31 and 5.06 were the signals of two olefinic methine protons H-2′ and H-6′. HMBC correlations between H-4 to C-2, C-3, C-4a, C-9a and 3-OH to C-2, C-3, C-4 confirmed the connection of isolated aromatic proton at C-4. The HMBC correlation of H-1′ to C-1, C-2 and C-3 confirmed

the presence of the geranyl unit at C-2. The ^{13}C NMR spectral data deduced from DEPT and HMQC experiments showed the signals of a carbonyl carbon, eleven quaternary carbons, five methine carbons, three methylene carbons and four methyl carbons. Accordingly, **GD7** was confirmed to be 1,3,6-trihydroxy-7-methoxy-2-(3,7-dimethyl-2,6-octadienyl)xanthone or cowaxanthone (Likhitwitayawuid, *et al*., 1997).



Major HMBC correlations of **GD7**

Table 31 The NMR spectral data of **GD7**

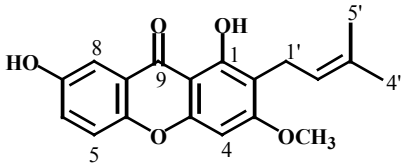
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.11 (C)	-	-
2	108.72 (C)	-	-
3	162.24 (C)	-	-
4	94.18 (CH)	6.48 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	156.01 (C)	-	-
5	102.60 (CH)	6.92 (1H, *s*)	C-7, C-8a, C-9, C-10a
6	152.60 (C)	-	-
7	144.30 (C)	-	-
8	104.54 (CH)	7.58 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
8a	113.30 (C)	-	-
9	179.96 (C=O)	-	-
9a	103.04 (C)	-	-
10a	152.52 (C)	-	-

Table 31 (Continued)

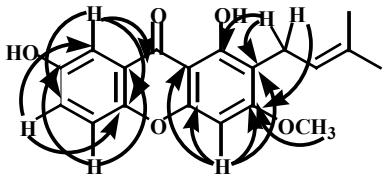
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1′	21.39 (CH_2)	3.48 (2H, *d*, 7.2)	C-1, C-2, C-3, C-2′, C-3′
2′	121.25 (CH)	5.31 (1H, *br t*, 7.2)	C-2, C-1′, C-4′, C-9′
3′	139.56 (C)	-	-
4′	39.73 (CH_2)	2.10 (2H, *m*)	C-2′, C-3′, C-5′, C-6′, C-9′
5′	26.36 (CH_2)	2.10 (2H, *m*)	C-3′, C-4′, C-6′, C-7′
6′	123.73 (CH)	5.06 (1H, *br t*, 7.2)	C-4′, C-10′
7′	132.12 (C)	-	-
8′	25.69 (CH_3)	1.68 (3H, *s*)	C-6′, C-7′, C-10′
9′	16.27 (CH_3)	1.84 (3H, *s*)	C-2′, C-3′, C-4′
10′	17.72 (CH_3)	1.67 (3H, *s*)	C-6′, C-7′, C-8′
1-OH	-	13.35 (1H, *s*)	C-1, C-2, C-9a
3-OH	-	6.39 (1H, *s*)	C-2, C-3, C-4
6-OH	-	6.43 (1H, *s*)	C-5, C-6, C-7
7-OCH_3	56.49 (CH_3)	4.00 (3H, *s*)	C-7

* Carbon type was deduced from DEPT experiments.

GD8 : 1,7-Dihydroxy-3-methoxy-2-(3-methyl-2-butenyl)xanthone



GD8 is a yellow solid, m.p. 228-230 °C. The ^{1}H NMR spectrum (**Table 32**) showed two *singlet* signals, which disappeared upon addition of D_2O, of a chelated hydroxy group (1-OH) at δ 12.90 and a non chelated hydroxy group (7-OH) at δ 9.25. The signals in aromatic region, δ 7.50 (*d*), 7.28 (*d*) and 7.16 (*dd*) appearing as ABX type were proposed for the signals of H-8, H-5 and H-6, respectively. These assignment were supported by ^{3}J correlations of H-8 to C-6, C-10a, C-9; H-5 to C-7a, C-8a and H-6 to C-8, C-10a on HMBC experiment. A *singlet* signal of the aromatic proton H-4 was at δ 6.31 according to the correlation to C-2, C-3, C-9, C-4a and C-9a from the HMBC experiment. The spectrum further showed the typical signals of a prenyl side chain which appeared at δ 1.57 (3H, *s*, H-4′) and 1.69 (3H, *s*, H-5′), 3.23 (2H, *d*, H-1′) and 5.11 (1H, *br t*, H-2′). This prenyl unit was assigned to be at C-2 and was supported by the correlation of H-1′ to C-1, C-2 and C-3. A signal of a methoxy group appearing as a *singlet* at δ 3.82 was indicated to be at C-3 by the ^{3}J correlation of methoxy protons to C-3. The ^{13}C NMR spectral data (**Table 32**) suggested that **GD8** contained two methyl carbons, a methylene carbon, five methine carbons, nine quaternary carbons, a methoxy carbon and a carbonyl carbon. The proposed structure, the spectral data and the melting point were found to be corresponded to 1,7-dihydroxy-3-methoxy-2-(3-methyl-2-butenyl)xanthone (Mahabusarakam, *et al.*, 1987).



Major HMBC correlations of **GD8**

Table 32 The NMR spectral data of **GD8**

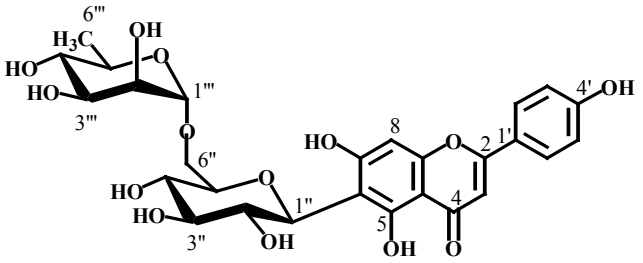
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.00 (C)	-	-
2	111.00 (C)	-	-
3	164.00 (C)	-	-
4	89.47 (CH)	6.31 (1H, *s*)	C-2, C-3, C-4a, C-9, C-9a
4a	156.00 (C)	-	-
5	118.44 (CH)	7.28 (1H, *d*, 9.0)	C-7, C-8a, C-10a
6	124.24 (CH)	7.16 (1H, *dd*, 9.0, 2.5)	C-7, C-8, C-10a
7	149.50 (C)	-	-
8	108.85 (CH)	7.50 (1H, *d*, 2.5)	C-6, C-7, C-9, C-10a
8a	121.00 (C)	-	-
9	180.50 (C=O)	-	-
9a	103.00 (C)	-	-
10a	153.50 (C)	-	-
1′	21.20 (CH_2)	3.23 (2H, *d*, 7.0)	C-1, C-2, C-3, C-2′, C-3′
2′	122.10 (CH)	5.11 (1H, *br t*, 7.0)	C-1′, C-4′, C-5′
3′	131.50 (C)	-	-
4′	25.75 (CH_3)	1.57 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.50 (CH_3)	1.69 (3H, *s*)	C-2′, C-3′, C-4′

Table 32 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1-OH	-	12.90 (1H, *s*)	-
3-OCH_3	55.88 (CH_3)	3.82 (3H, *s*)	C-3
7-OH	-	9.25 (1H, *s*)	C-6, C-7, C-8

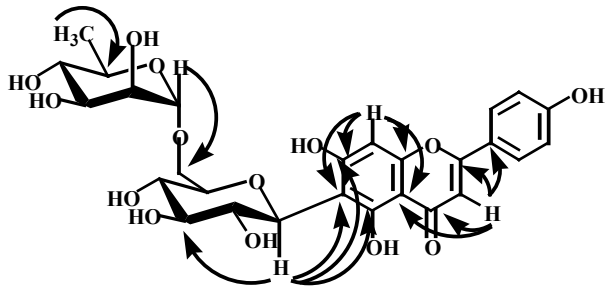
* Carbon type was deduced from DEPT experiments.

GD9 : 5,7,4′-Trihydroxyflavone 6-*C*-[*α*-rhamnopyranosyl-(1→6)]-*β*-glucopyranoside



GD9 is a yellow solid, m.p. 200-202 °C. The HRMS showed the $[M+H]^+$ of 579.1742 corresponded to $C_{27}H_{31}O_{14}$. This compound exhibited UV absorption bands at 333.6, 271.7, 238.0 and 215.8 nm, a characteristic of a flavone nucleus and IR absorption bands at 3402 cm^{-1} (a hydroxyl group), 1650 cm^{-1} (a carbonyl group of an flavone). The ^{1}H NMR spectrum showed the characteristic resonances of a flavone proton at δ 6.63 (*s*, H-3), a hydrogen-bonded hydroxy proton at δ 13.31 (*s*, 5-OH) and an aromatic proton at δ 6.51 (*s*, H-8). Two *doublet* resonances (J = 9.3 Hz) at δ 7.83 (2H) and δ 6.90 (2H) were in agreement with the A_2B_2 type of aromatic protons H-2′, H-6′ and H-3′, H-5′. The ^{1}H NMR (**Table 33**) further indicated the presence of two sugar moieties. The resonances of an anomeric proton H-1″ and an anomeric carbon C-1″ of a *β*-glucose were observed at δ 4.58 (*d*, J= 9.3 Hz) and δ 74.11 whereas the resonances of an anomeric proton H-1‴, an anomeric carbon C-1‴ and methyl protons (H-6‴) of an *α*-rhamnose were shown at δ 4.51 (*br s*), 101.52 and 1.06 (*d*, J= 6.0 Hz). The proton signals of sugar moieties appeared at δ 3.42-3.40 (*m*, H-2″, H-5″), 3.24 (*t*, H-3″), 3.16 (*t*, H-4″), 3.80 (*d*, H-6″), 4.51 (*br s*, H-1‴), 4.10-4.02 (*m*, H-2‴), 3.34 (*t*, H-3‴), 3.14 (*t*, H-4‴), 3.92-3.90 (*m*, H-5‴) and 1.06 (*d*, H-6‴). The identification of 6-*C*-*β*-glucopyranoside was indicated by the HMBC correlation of H-1″ to C-5, C-6 and C-7. The (1→6)-*C*-glucosidic bond was assigned from the downfield shift of C-6″ of glucose unit (δ 68.54) and the cross peak of H-1‴ to C-6″.

The complete HMBC data confirmed the structure. 5,7,4′-Trihydroxyflavone 6-*C*-[α-rhamnopyranosyl-(1→6)]-β-glucopyranoside was then assigned for **GD9**, a novel compound.



Major HMBC correlations of **GD9**

Table 33 The NMR spectral data of **GD9**

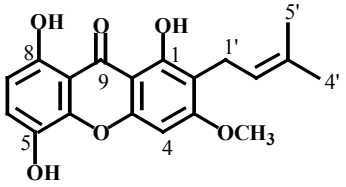
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
2	165.19 (C)	-	-
3	103.77 (CH)	6.63 (1H, *s*)	C-2, C-4, C-4a, C-1′
4	183.24 (C=O)	-	-
4a	104.55 (C)	-	-
5	161.98 (C)	-	-
6	109.32 (C)	-	-
7	164.34 (C)	-	-
8	94.60 (CH)	6.51 (1H, *s*)	C-4, C-4a, C-6, C-7, C-8a
8a	157.65 (C)	-	-
1′	122.35 (C)	-	-
2′, 6′	129.67 (CH)	7.83 (2H, *d*, 9.3)	C-2, C-2′,6′, C-4′
3′, 5′	117.28 (CH)	6.90 (2H, *d*, 9.3)	C-1′, C-3′,5′, C-4′
4′	161.55 (C)	-	-

Table 33 (Continued)

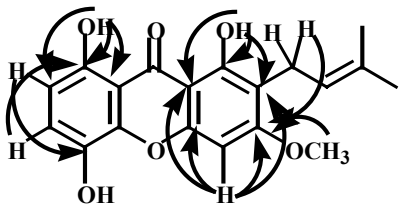
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
Glc-1″	74.11 (CH)	4.58 (1H, *d*, 9.3)	C-5, C-6, C-7, C-3″, C-5″
2″	71.31 (CH)	3.42-3.40 (1H, *m*)	C-3″
3″	79.60 (CH)	3.24 (1H, *t*, 9.3)	C-2″, C-4″
4″	71.47 (CH)	3.16 (1H, *t*, 9.3)	C-3″, C-5″, C-6″
5″	73.06 (CH)	3.42-3.40 (1H, *m*)	C-6″
6″	68.54 (CH_2)	3.80 (1H, *d*, 9.3)	C-4″, C-5‴, C-1‴
Rha-1‴	101.52 (CH)	4.51 (1H, *br s*)	C-6″, C-2‴, C-3‴, C-5‴
2‴	71.56 (CH)	4.10-4.02 (1H, *m*)	C-4‴
3‴	70.71 (CH)	3.34 (1H, *t*, 9.3)	C-1‴, C-4‴
4‴	71.33 (CH)	3.14 (1H, *t*, 9.3)	C-3‴, C-5‴
5‴	69.40 (CH)	3.92-3.90 (1H, *m*)	C-3‴, C-4‴
6‴	18.61 (CH_3)	1.06 (3H, *d*, 6.0)	C-4‴, C-5‴
5-OH	-	13.31 (1H, *s*)	C-4a, C-5, C-6, C-1″

* Carbon type was deduced from DEPT experiments.

GD10 : 1,5,8-Trihydroxy-3-methoxy-2-(3-methyl-2-butenyl)xanthone



GD10 is a yellow solid, m.p. 195-197 °C. The ^{1}H NMR spectrum (**Table 34**) exhibited the resonances of H-4 (δ 6.49, *s*), H-6 (δ 7.25, *d*, *J* = 9.0 Hz), H-7 (δ 6.70, *d*, *J* = 9.0 Hz), 3-OCH_3 (δ 3.95) and two chelated hydroxy protons 1-OH (δ 12.12) and 8-OH and (δ 11.32). The characteristic signals of a prenyl side chain were observed at δ 5.22 (*br t*, H-2′), 3.36 (*d*, *J* = 7.0 Hz, H-1′), 1.69 (*s*, H-4′) and 1.80 (*s*, H-5′). HMBC correlation of H-1′ to C-2 indicated that the prenyl side chain was at C-2. The assignment of H-4 was confirmed by the correlation of H-4 to C-2, C-3, C-4a and C-9a. The NOE effect of H-4 to the methoxy proton resonances confirmed the location of 3-OCH_3. These assignment indicated that **GD10** was 1,5,8-trihydroxy-3-methoxy-2-(3-methyl-2-butenyl)xanthone which was first isolated from *Garcinia mangostana* (Parveen and Khan, 1988).



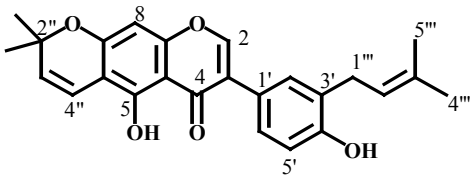
Major HMBC correlations of **GD10**

Table 34 The NMR spectral data of **GD10**

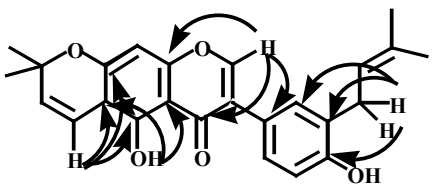
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.26 (C)	-	-
2	112.83 (C)	-	-
3	165.05 (C)	-	-
4	89.96 (CH)	6.49 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	155.66 (C)	-	-
5	135.51 (C)	-	-
6	122.97 (CH)	7.25 (1H, *d*, 9.0)	C-5, C-8
7	109.95 (CH)	6.70 (1H, *d*, 9.0)	C-5, C-8
8	153.96 (C)	-	-
8a	107.57 (C)	-	-
9	184.40 (C=O)	-	-
9a	102.60 (C)	-	-
10a	142.78 (C)	-	-
1′	21.31 (CH_2)	3.36 (2H, *d*, 7.0)	C-2, C-2′
2′	121.63 (CH)	5.22 (1H, *br t*, 7.5)	C-2, C-4′, C-5′
3′	132.26 (C)	-	-
4′	25.82 (CH_3)	1.69 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.80 (CH_3)	1.80 (3H, *s*)	C-2′, C-3′, C-4′
1-OH	-	12.12 (1H, *s*)	C-1, C-2, C-9a
8-OH	-	11.32 (1H, *s*)	C-7, C-8, C-8a
3-OCH_3	56.13 (CH_3)	3.95 (3H, *s*)	C-3

* Carbon type was deduced from DEPT experiments.

GD11 : 5,4′-Dihydroxy-3′-(3-methyl-2-butenyl)-2″,2″-dimethylchromeno (5″,6″:6,7)isoflavone (chandalone)



GD11 is a pale yellow solid, m.p. 65-66 °C. The ^{1}H NMR spectrum (**Table 35**) demonstrated the *singlet* resonance of a chelated hydroxy group (5-OH) at δ 13.19 and two *singlet* signals of H-2 and H-8 at δ 7.82 and 6.34, respectively. The ABX pattern of aromatic protons H-2′, H-5′ and H-6′were shown at δ 7.25 (*d*, *J* = 2.5 Hz), 6.87 (*d*, *J* = 10.0 Hz) and 7.26 (*d*, *J* = 10.0 and 2.5 Hz), respectively. Two *doublet* signals of the vicinal olefinic protons at δ 5.64 and 6.74 and a *singlet* resonance of two methyl groups at δ 1.49 (6H) indicated the presence of a chromene ring. Correlations of H-4″ to C-5, C-6, C-7 and H-8 to C-4a, C-6, C-7, C-8a, C-4 identified the position of the dimethylchromene ring to be at C-6 and C-7. In addition, a set of signal of a prenyl side chain was shown in the spectrum at δ 3.41 (*d*, H-1‴), 5.36 (*br t*, H-2‴), 1.79 (*s*, H-4‴) and 1.80 (*s*, H-5‴). The HMBC correlation of H-1‴ to C-2′ , C-3′ and C-4′ suggested the position of the prenyl side chain at C-3′. 5,4′-Dihydroxy-3′-(3-methyl-2-butenyl)-2″,2″-dimethylchromeno(5″,6″:6,7)isoflavone (Falshaw, *et al*., 1969) then was proposed for **GD11**.



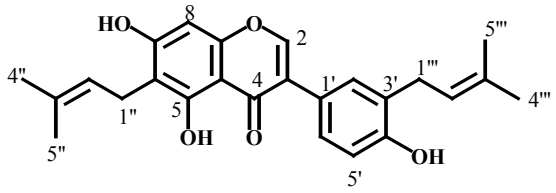
Major HMBC correlations of **GD11**

Table 35 The NMR spectral data of **GD11**

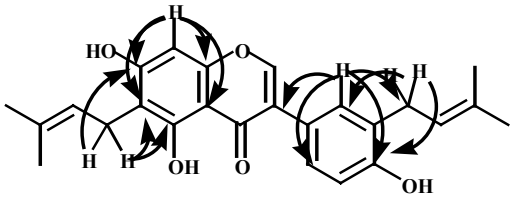
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	152.52 (CH)	7.82 (1H, *s*)	C-4, C-8a, C-1′
3	123.68 (C)	-	-
4	180.96 (C=O)	-	-
4a	106.09 (C)	-	-
5	159.45 (C)	-	-
6	156.89 (C)	-	-
7	105.53 (C)	-	-
8	94.83 (CH)	6.34 (1H, *s*)	C-4, C-4a, C-6, C-7, C-8a
8a	157.27 (C)	-	-
1′	122.93 (C)	-	-
2′	130.53 (CH)	7.25 (1H, *d*, 2.5)	C-3, C-4′, C-6′, C-1′′′
3′	127.10 (C)	-	-
4′	154.74 (C)	-	-
5′	115.90 (CH)	6.87 (1H, *d*, 10.0)	C-1′, C-3′, C-4′, C-6′
6′	128.18 (CH)	7.26 (1H, *dd*, 10.0, 2.5)	C-3, C-2′, C-4′
2′′	78.01 (C)	-	-
3′′	128.13 (CH)	5.64 (1H, *d*, 10.0)	C-6, C-7, C-2′′, C-4′′, C-5′′
4′′	115.48 (CH)	6.74 (1H, *d*, 10.0)	C-5, C-6, C-7
1′′′	29.82 (CH_2)	3.41 (2H, *d*, 6.0)	C-2′, C-3′, C-4′, C-2′′′, C-3′′′
2′′′	121.53 (CH)	5.36 (1H, *br t*, 6.0)	C-3′, C-1′′′, C-4′′′, C-5′′′
3′′′	134.99 (C)	-	-
4′′′	25.84 (CH_3)	1.79 (3H, *s*)	C-2′′′, C-3′′′, C-5′′′
5′′′	17.97 (CH_3)	1.80 (3H, *s*)	C-2′′′, C-3′′′, C-4′′′
5-OH	-	13.19 (1H, *s*)	C-4a, C-6
2′′-$(CH_3)_2$	28.27 (CH_3)	1.49 (6H, *s*)	2′′-$(CH_3)_2$, C-2′′, C-3′′

* Carbon type was deduced from DEPT experiments.

GD12 : 5,7,4′-Trihydroxy-6,3′-bis(3-methyl-2-butenyl)isoflavone (lupalbigenin)



GD12 was isolated as a yellow solid, m.p. 122-125 °C. The ^{1}H NMR spectrum (**Table 36**) showed a sharp *singlet* signal of a chelated hydroxy group 5-OH at δ 13.17, a *singlet* signal of a vinylic proton H-2 at δ 7.80 and a *singlet* signal of an isolated aromatic proton H-8 at δ 6.40. The resonances of aromatic protons H-2′, H-6′ and H-5′ were shown as ABX pattern at δ 7.23, 6.83 and 6.86, respectively. The signals of two prenyl side chains were observed. The first set resonated at δ 1.74 (*s*, H-4″), 1.83 (*s*, H-5″), 3.43 (*d*, H-1″) and 5.29 (*s*, H-2″) whereas the second appeared at δ 1.78 (6H, *s*, H-4‴ and H-5‴), 3.39 (*d*, H-1‴) and 5.35 (*br t*, H-2‴). HMBC correlations (**Table 36**) showed the correlation of H-1″ to C-5, C-6 and C-7. It's therefore confirmed that one prenyl side chain was at C-6. In addition, the correlation of H-1‴ to C-2′ and C-4′ supported that another prenyl group was at C-3′. **GD12** was therefore assigned to be 5,7,4′-trihydroxy-6,3′-bis(3-methyl-2-butenyl)isoflavone which was known as lupalbigenin (Pistelli, *et al*., 1996).



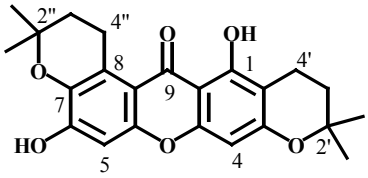
Major HMBC correlations of **GD12**

Table 36 The NMR spectral data of **GD12**

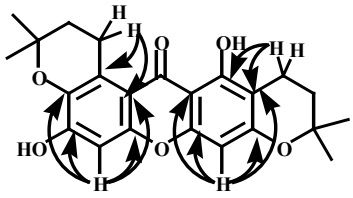
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	152.40 (CH)	7.80 (1H, *s*)	C-3, C-4, C-8a, C-1′, C-2′, C-6′
3	123.60 (C)	-	-
4	180.92 (C=O)	-	-
4a	105.61 (C)	-	-
5	159.57 (C)	-	-
6	110.82 (C)	-	-
7	161.61 (C)	-	-
8	93.70 (CH)	6.40 (1H, *s*)	C-4a, C-6, C-7, C-8a, C-1″
8a	156.02 (C)	-	-
1′	122.89 (C)	-	-
2′	130.44 (CH)	7.23 (1H, *d*, 2.3)	C-3, C-4′, C-6′, C-1‴
3′	127.33 (C)	-	-
4′	154.75 (C)	-	-
5′	115.75 (CH)	6.86 (1H, *d*, 9.2)	C-1′, C-3′, C-4′, C-6′
6′	128.04 (CH)	6.83 (1H, *dd*, 9.2, 2.3)	C-3, C-2′, C-4′, C-5′
1″	21.46 (CH_2)	3.43 (2H, *d*, 8.0)	C-5, C-6, C-7, C-2″, C-3″, C-4″, C-5″
2″	121.59 (CH)	5.29 (1H, *br t*, 8.0)	C-6, C-1″, C-4″, C-5″
3″	134.11 (C)	-	-
4″	25.78 (CH_3)	1.74 (3H, *s*)	C-3″, C-5″
5″	17.89 (CH_3)	1.83 (3H, *s*)	C-3″, C-4″
1‴	29.50 (CH_2)	3.39 (2H, *d*, 8.0)	C-2′, C-4′, C-2‴, C-3‴, C-4‴, C-5‴
2‴	121.76 (CH)	5.35 (1H, *br t*, 8.0)	C-3′, C-1‴, C-4‴, C-5‴
3‴	134.41 (C)	-	-
4‴	25.80 (CH_3)	1.78 (3H, *s*)	C-3‴, C-5‴
5‴	17.87 (CH_3)	1.78 (3H, *s*)	C-3‴, C-4‴
5-OH	-	13.17 (1H, *s*)	C-4, C-4a, C-5, C-6

* Carbon type was deduced from DEPT experiments.

GD13 : 1,6-Dihydroxy-2′,2′-dimethylchromano(5′,6′:2,3)-2′′,2′′-dimethylchromano(5′′,6′′:8,7)xanthone (BR-xanthone A)



GD13 is a yellow solid, m.p. 182-183 °C. The ^{1}H NMR spectrum (**Table 37**) exhibited four *singlet* signals of 1-OH (δ 13.76), 6-OH (δ 6.39), H-4 (δ 6.25) and H-5 (δ 6.80). ^{1}H NMR spectrum revealed a characteristic signals of two dimethylchromane rings. The first set of resonances of a dimethylchromane ring with *gem*-dimethyl protons at δ 1.37 (6H, *s*) and two methylene protons at δ 1.84 (2H, *t*, H-3′) and 2.72 (2H, *t*, H-4′) was assigned to be at C-3 and C-2 by the correlation of H-4′ to C-1 and C-2 in HMBC. The second set of signals of another dimethylchromane ring with *gem*-dimethyl protons and two methylene protons at δ 1.39 (*s*, 6H), 1.88 (*t*, H-3′′) and 3.51 (*t*, H-4′′) was suggested to be fused to the xanthone nucleus at C-7 and C-8 by the HMBC correlation of H-4′′ to C-8, C-8a and C-10a. The ^{13}C NMR and HMBC experiment corresponded to the assigned structure. Thus, **GD13** was 1,6-dihydroxy-2′,2′-dimethylchromano(5′,6′:2,3)-2′′,2′′-dimethylchromano(5′′,6′′:8,7)xanthone or BR-xanthone A (Bulasubramanian, *et al.*, 1988).



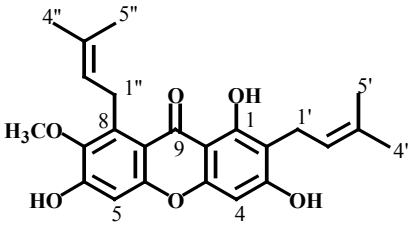
Major HMBC correlations of **GD13**

Table 37 The NMR spectral data of **GD13**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.98 (C)	-	-
2	102.94 (C)	-	-
3	154.31 (C)	-	-
4	93.36 (CH)	6.25 (1H, *s*)	C-2, C-3, C-9, C-9a
4a	159.95 (C)	-	-
5	100.65 (CH)	6.80 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	152.67 (C)	-	-
7	153.06 (C)	-	-
8	121.08 (C)	-	-
8a	110.00 (C)	-	-
9	182.06 (C=O)	-	-
9a	103.48 (C)	-	-
10a	138.98 (C)	-	-
2′	75.57 (C)	-	-
3′	31.45 (CH_2)	1.84 (2H, *t*, 6.6)	C-2, C-2′, C-4′, 2′-(CH_3)$_2$
4′	15.70 (CH_2)	2.72 (2H, *t*, 6.6)	C-1, C-2, C-2′, C-3′
2″	73.81 (C)	-	-
3″	32.40 (CH_2)	1.88 (2H, *t*, 6.6)	C-8, C-2″, C-4″, 2″-(CH_3)$_2$
4″	22.26 (CH_2)	3.51 (2H, *t*, 6.6)	C-8, C-8a, C-10a, C-2″, C-3″
1-OH	-	13.76 (1H, *s*)	-
6-OH	-	6.39 (1H, *s*)	-
2′-(CH_3)$_2$	26.08 (CH_3)	1.37 (6H, *s*)	C-2′, C-3′, 2′-(CH_3)$_2$
2″-(CH_3)$_2$	26.42 (CH_3)	1.39 (6H, *s*)	C-2″, C-3″, 2″-(CH_3)$_2$

* Carbon type was deduced from DEPT experiments.

GD14 : 1,3,6-Trihydroxy-7-methoxy-2,8-bis(3-methyl-2-butenyl)xanthone (mangostin)



GD14 was isolated as a yellow solid, m.p. 182-183 °C. The ^{1}H NMR (**Table 38**) revealed the presence of four sharp *singlet* signals at δ 13.80 (1-OH), 6.82 (H-5), 6.29 (H-4) and 3.81 (7-OCH_3). The signals of two prenyl side chains were observed. Those signals were two *broad triplet* signals of two olefinic protons (δ 5.29 and 5.27), two *doublet* signals of benzylic methylene protons (δ 4.06 and 3.46) and three *singlet* signals of four methyl groups (δ 1.85 (6H), 1.77 and 1.70). **GD14** was then identified to be 1,3,6-trihydroxy-7-methoxy-2,8-bis(3-methyl-2-butenyl)xanthone. The ^{1}H NMR spectral data and melting point were identical with mangostin, authentic sample, which was previously isolated from *Garcinia mangostana* (Mahabusarakam, *et al.*, 1987).

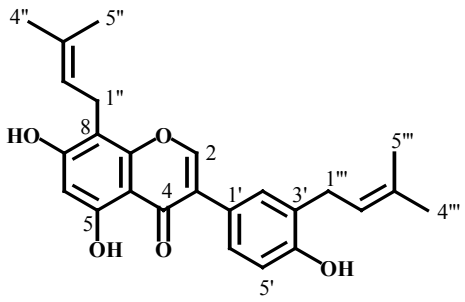
Table 38 The ^{1}H NMR spectral data of **GD14**

δ_H (*multiplicity*, J_{Hz})	
GD14*	**mangostin****
13.80 (1H, *s*)	13.80 (*s*)
6.82 (1H, *s*)	6.30 (*s*)
6.29 (1H, *s*)	6.28 (*s*)
5.29 (1H, *br t*)	5.28 (*t*, 7.0)
5.27 (1H, *br t*)	5.28 (*br s*, 7.0)
4.06 (2H, *br d*, 5.7)	4.11 (*d*, 7.0)
3.81 (3H, *s*)	3.81 (*s*)
3.46 (2H, *br d*, 6.9)	3.47-3.40 (*d*, 7.0)
1.85 (6H, *s*)	1.84 (*s*), 1.85 (*s*)
1.77 (3H, *s*)	1.78 (*s*)
1.70 (3H, *s*)	1.70 (*s*)

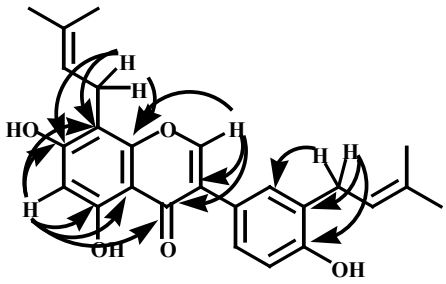
* 300 MHz in $CDCl_3$

** 400 MHz in $CDCl_3$

GD15 : 5,7,4′-Trihydroxy-8,3′-bis(3-methyl-2-butenyl)isoflavone (isolupalbigenin)



GD15 is yellow needles, m.p. 164-166 °C. The ^{1}H NMR spectrum (**Table 39**) showed three *singlet* signals of 5-OH (δ 13.10), H-2 (δ 7.72) and H-6 (δ 6.37). The spectrum also showed the resonances of aromatic protons H-2′, H-5′ and H-6′ which appeared as an ABX pattern at δ 7.13, 7.12 and 6.82, respectively. In addition, two sets of signals due to two prenyl side chains were present and were assigned to attach to the parent structure at C-8 and C-3′. The first showed the signals at δ 5.22 (H-2′′), 3.30 (H-1′′), 1.74 (H-5′′) and 1.63 (H-4′′) whereas the second showed the signals at δ 5.30 (H-2′′′), 3.30 (H-1′′′) and 1.67 (H-4′′′, H-5′′′). The ^{13}C NMR and the DEPT spectra suggested that **GD15** contained four methyl carbons, two methylene carbons, seven methine carbons, eleven quaternary carbons and a carbonyl carbon. The HMBC (**Table 39**) also showed the correlations of H-1′′′ to C-2′, C-3′, C-4′ and H-1′′ to C-7, C-8, C-8a suggested that the prenyl groups were at C-3′ and C-8. **GD15** was therefore assigned to be 5,7,4′-trihydroxy-8,3′-bis(3-methyl-2-butenyl)isoflavone which was known as isolupalbigenin (Tahara, *et al*., 1994).



Major HMBC correlations of **GD15**

Table 39 The NMR spectral data of **GD15**

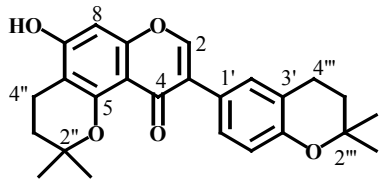
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	152.19 (CH)	7.72 (1H, *s*)	C-3, C-4, C-8a
3	123.62 (C)	-	-
4	180.87 (C=O)	-	-
4a	105.26 (C)	-	-
5	161.92 (C)	-	-
6	93.35 (CH)	6.37 (1H, *s*)	C-4, C-4a, C-5, C-7, C-8
7	159.49 (C)	-	-
8	111.72 (C)	-	-
8a	155.89 (C)	-	-
1′	122.16 (C)	-	-
2′	130.10 (CH)	7.13 (1H, *br d*, 1.2)	C-3, C-1′, C-3′, C-4′, C-1‴
3′	128.10 (C)	-	-
4′	155.04 (C)	-	-
5′	127.59 (CH)	7.12 (1H, *br d*, 6.9)	C-4′, C-6′
6′	115.27 (CH)	6.82 (1H, *br dd*, 6.9, 1.2)	C-1′, C-2′, C-4′, C-5′
1″	21.43 (CH_2)	3.30 (2H, *br d*, 6.6)	C-7, C-8, C-8a, C-2″, C-3″
2″	122.28 (CH)	5.22 (1H, *br t*, 6.0)	C-8, C-1″, C-4″, C-5″

Table 39 (Continued)

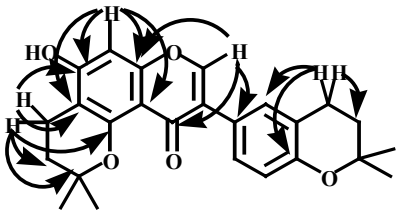
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
3′′	132.64 (C)	-	-
4′′	25.77 (CH_3)	1.63 (3H, *s*)	C-3′′, C-5′′
5′′	17.85 (CH_3)	1.74 (3H, *s*)	C-2′′, C-3′′, C-4′′
1′′′	29.60 (CH_2)	3.30 (2H, *br d*, 6.6)	C-2′, C-3′, C-4′, C-2′′′, C-3′′′
2′′′	122.40 (CH)	5.30 (1H, *br t*, 6.0)	C-2′′′, C-4′′′, C-5′′′
3′′′	131.73 (C)	-	-
4′′′	25.77 (CH_3)	1.67 (3H, *s*)	C-2′′′, C-3′′′, C-4′′′, C-5′′′
5′′′	17.82 (CH_3)	1.67 (3H, *s*)	C-2′′′, C-3′′′, C-4′′′, C-5′′′
5-OH	-	13.10 (1H, *s*)	C-4a, C-5

* Carbon type was deduced from DEPT experiments.

GD16 : 7-Hydroxy-2″,2″-dimethylchromano(5″,6″:6,5)-2‴,2‴-dimethylchromano(5‴,6‴:3′,4′)isoflavone



GD16 is a yellow solid, m.p. 178-180 °C. Its molecular formula of $C_{25}H_{26}O_5$ were established on the basis of HRMS ($[M]^+$ *m/z* 406.1733). The UV spectrum showed maxima absorptions of an isoflavone type at 328.4 and 263.4 nm. The IR spectrum showed the stretchings of a hydroxyl group at 3375 cm^{-1} and a carbonyl group at 1652 cm^{-1}. The ^1H NMR spectrum (**Table 40**) showed signals of a characteristic isoflavone proton at δ 7.67 (*s*, H-2). An ABX pattern of aromatic protons H-2′, H-5′ and H-6′ was present at δ 7.27 (*d*, *J* = 1.7 Hz), 6.73 (*d*, *J* = 8.5 Hz) and 7.15 (*dd*, *J* = 8.5 and 1.7 Hz), respectively whereas an isolated aromatic proton H-8 was at δ 6.42. The presence of two dimethylchroman rings were suggested from the resonances of four methyl groups at δ 1.33 (*s*, 2‴-Me_2), 1.39 (*s*, 2″-Me_2) and four methylene groups at δ 1.80 (*t*, *J* = 3.3 Hz, H-3‴), 1.82 (*t*, *J* = 3.3 Hz, H-3″), 2.66 (*t*, *J* = 6.6 Hz, H-4″), 2.80 (*t*, *J* = 6.6 Hz, H-4‴). The HMBC correlations of H-4″ to C-5, C-6, C-7, C-2″, C-3″ and H-4‴ to C-2′, C-3′, C-4′, C-2‴, C-3‴ indicated that the dimethylchroman rings were fused to the isoflavone nucleus at C-5, C-6 and C-3′, C-4′, respectively. A carbonyl group was indicated from a carbon resonance at δ 177.50 and a stretching band in the IR spectrum at 1652 cm^{-1}. The complete HMBC data confirmed the structure of **GD16** as 7-hydroxy-2″,2″-dimethylchromano(5″,6″:6,5)-2‴,2‴-dimethylchromano(5‴,6‴:3′,4′)isoflavone. This compound appears to be novel.



Major HMBC correlations of **GD16**

Table 40 The NMR spectral data of **GD16**

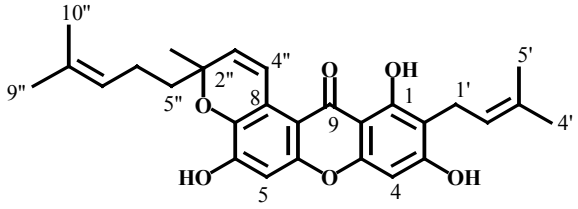
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	149.63 (CH)	7.67 (1H, *s*)	C-4, C-8a, C-1′
3	117.42 (C)	-	-
4	177.50 (C=O)	-	-
4a	107.38 (C)	-	-
5	157.00 (C)	-	-
6	105.50 (C)	-	-
7	161.90 (C)	-	-
8	93.89 (CH)	6.42 (1H, *s*)	C-4, C-4a, C-6, C-7, C-8a
8a	159.88 (C)	-	-
1′	122.50 (C)	-	-
2′	130.80 (CH)	7.27 (1H, *d*, 1.7)	C-4′, C-6′, C-4‴
3′	120.50 (C)	-	-
4′	154.90 (C)	-	-
5′	116.87 (CH)	6.73 (1H, *d*, 8.5)	C-1′, C-3′, C-4′
6′	128.20 (CH)	7.15 (1H, *dd*, 8.5, 1.7)	C-2′, C-4′
2″	75.25 (C)	-	-
3″	31.40 (CH_2)	1.82 (2H, *t*, 3.3)	C-6, C-2″, C-4″, 2″-$(CH_3)_2$
4″	17.12 (CH_2)	2.66 (2H, *t*, 6.6)	C-5, C-6, C-7, C-2″, C-3″

Table 40 (Continued)

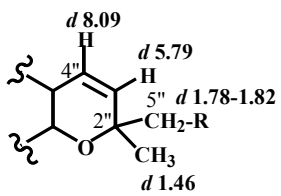
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2′′′	74.27 (C)	-	-
3′′′	32.82 (CH_2)	1.80 (2H, *t*, 3.3)	C-3′, C-2′′′, C-4′′′, 2′′′-$(CH_3)_2$
4′′′	22.47 (CH_2)	2.80 (2H, *t*, 6.6)	C-2′, C-3′, C-4′, C-2′′′, C-3′′′
2′′-$(CH_3)_2$	26.56 (CH_3)	1.39 (6H, *s*)	C-2′′, 2′′-$(CH_3)_2$, C-3′′
2′′′-$(CH_3)_2$	26.86 (CH_3)	1.33 (6H, *s*)	C-2′′′, 2′′′-$(CH_3)_2$, C-3′′′

* Carbon type was deduced from DEPT experiments.

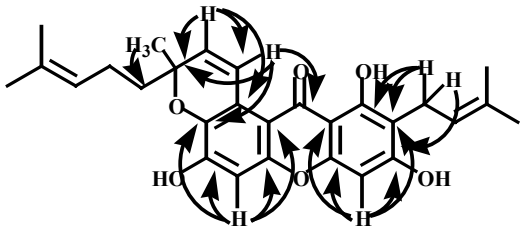
GD17 : 1,3,6-Trihydroxy-2-(3-methyl-2-butenyl)-2″-methyl-2″-(4-methyl-3-pentenyl)chromeno(5″,6″:8,7)xanthone



GD17 is a yellow solid, m.p. 93-95 °C. The ^{1}H NMR spectrum (**Table 41**) exhibited three *singlet* signals of a hydrogen bonded hydroxy group 1-OH (δ 13.70) and two non chelated hydroxy groups (δ 6.41 and 6.26). The spectrum also showed two sharp *singlet* signals of two isolated aromatic protons H-4 and H-5 (δ 6.31 and 6.82). The placement of H-4 and H-5 were supported by the cross peaks of H-4 to C-2, C-3, C-4a, C-9a and H-5 to C-6, C-7, C-8a, C-9, C-10a. The signals of two methyl groups (δ 1.77, H-4′ and 1.84, H-5′), methylene protons (δ 3.45, H-1′) and an olefinic methine proton (δ 5.30, H-2′) were the signals of a prenyl moiety. In HMBC the correlation of H-1′ to C-1, C-2 and C-3 suggested that the prenyl unit was at C-2. Two *doublet* resonances at δ 8.09 and 5.79 were assigned for two vicinal protons H-4″ and H-3″ of a chromene ring. The chemical shift of H-4″ suggested that the chromene ring was nearby the carbonyl group. Irradiation of an olefinic proton (H-3″, δ 5.79) in the NOE experiment resulted in an enhancement of the signals of methylene protons (H-5″, δ 1.82-1.78) and signal of methyl protons (2″-CH_3, δ 1.46). The evidences indicated that the chromene ring consisted of a methyl group and CH_2-R as shown in below.



The remaining resonances: two *singlet* signals of two methyl groups at δ 1.58 (H-9″) and 1.67 (H-10″), a *triplet* signal of an olefinic proton (H-7″) at δ 5.09 and a *multiplet* signal of methylene protons (H-6″) at δ 2.13 were assigned for a prenyl unit. Irradiation at olefinic proton H-7″ (δ 5.09) in a NOE experiment gave the enhancement of the signal of H-6″ (δ 2.13). Irradiation at the methylene protons H-6″ effected the signals of the methylene protons H-5″ (δ 1.82-1.78). These results confirmed that the R group was a prenyl unit. The arrangement of the aromatic protons and substituent unit was confirmed by HMBC. The ^{13}C NMR and DEPT experiments were shown in **Table 41**. **GD17** was then identified as 1,3,6-trihydroxy-2-(3-methyl-2-butenyl)-2″-methyl-2″-(4-methyl-3-pentenyl)chromeno(5″,6″:8,7)xanthone. The proposed structure, the spectral data and melting point was corresponded to cowagarcinone D (Chairerk, 2001).



Major HMBC correlations of **GD17**

Table 41 The NMR spectral data of **GD17**

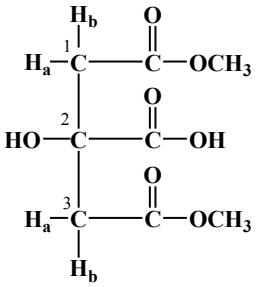
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.46 (C)	-	-
2	108.36 (C)	-	-
3	161.76 (C)	-	-
4	93.39 (CH)	6.31 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	155.31 (C)	-	-

Table 41 (Continued)

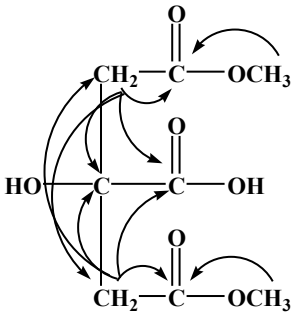
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
5	102.30 (CH)	6.82 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	150.74 (C)	-	-
7	136.79 (C)	-	-
8	119.56 (C)	-	-
8a	108.39 (C)	-	-
9	182.53 (C=O)	-	-
9a	103.78 (C)	-	-
10a	153.00 (C)	-	-
1′	21.43 (CH_2)	3.45 (2H, *d*, 7.0)	C-1, C-2, C-3, C-2′, C-3′
2′	121.37 (CH)	5.30 (1H, *br t*, 6.6)	C-1′, C-4′, C-5′
3′	135.74 (C)	-	-
4′	25.84 (CH_3)	1.77 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.92 (CH_3)	1.84 (3H, *s*)	C-2′, C-3′, C-4′
2″	79.37 (C)	-	-
3″	131.43 (CH)	5.79 (1H, *d*, 9.9)	C-2″, C-4″
4″	121.45 (CH)	8.09 (1H, *d*, 9.9)	C-7, C-2″
5″	40.36 (CH_2)	1.82-1.78 (2H, *m*)	C-2″, C-6″
6″	22.75 (CH_2)	2.13 (2H, *m*)	C-7″, C-8″
7″	123.64 (CH)	5.09 (1H, *t*, 6.6)	C-5″, C-6″, C-9″
8″	132.15 (C)	-	-
9″	17.66 (CH_3)	1.58 (3H, *s*)	C-7″, C-8″, C-10″
10″	25.67 (CH_3)	1.67 (3H, *s*)	C-7″, C-8″, C-9″
1-OH	-	13.70 (1H, *s*)	C-1, C-2, C-9a
3-OH	-	6.26 (1H, *s*)	-
6-OH	-	6.41 (1H, *s*)	C-5, C-6, C-7, C-10a
2″-CH_3	25.64 (CH_3)	1.46 (3H, *s*)	C-2″, C-3″, C-5″

* Carbon type was deduced from DEPT experiments.

GD18 : 2-Hydroxy-1,2,3-propanetricarboxylic acid-1,3-dimethyl ester



GD18 is a white solid, m.p. 110-112 °C. The ^{1}H NMR spectrum (**Table 42**) showed a sharp *singlet* of two methoxy groups 1-COOC$\underline{H}_3$ and 3-COOC$\underline{H}_3$ at δ 3.67 (6H) and two *doublets* of two *gem*-methylene protons H_a-1, H_a-3 and H_b-1, H_b-3 at δ 2.91 (2H, J = 15.5 Hz) and 2.83 (2H, J = 15.5 Hz). The correlations of 1-COOC$\underline{H}_3$ to 1-C=O; 3-COOC$\underline{H}_3$ to 3-C=O; H-1 to 1-C=O, C-2, C-3, 2-C=O and H-3 to C-1, C-2, 2-C=O, 3-C=O confirmed the positions of two methoxy groups and two methylene protons. The ^{13}C NMR spectral data showed the signals of three carbonyl carbons (δ 175.25 and 170.48 x2), a quaternary carbon (δ 72.64), two methylene carbons (δ 42.80 x2) and two methyl carbons (δ 51.84 x2). Accordingly the structure of **GD18** was proposed to be 2-hydroxy-1,2,3-propanetricarboxylic acid-1,3-dimethyl ester. It was known as 1,5-dimethoxy citrate (Pyo, *et al.*, 2000).



Major HMBC correlations of **GD18**

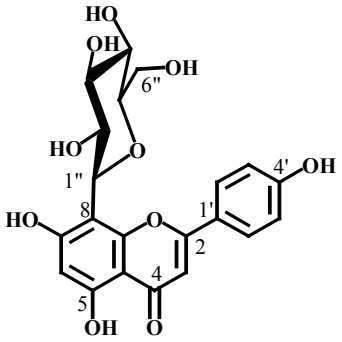
Table 42 The NMR spectral data of **GD18**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1-C=O, 3-C=O	170.48 (C=O)	-	-
1	42.80 (CH_2)	H_a: 2.91 (1H, *d*, 15.5)[a]	C-2, C-3, 1-C=O,
		H_b: 2.83 (1H, *d*, 15.5)[b]	2-C=O
2	72.64 (C)	-	-
3	42.80 (CH_2)	H_a: 2.91 (1H, *d*, 15.5)[a]	C-1, C-2, 2-C=O,
		H_b: 2.83 (1H, *d*, 15.5)[b]	3-C=O
2-C=O	175.25 (C=O)	-	-
1-COO$\underline{CH_3}$, 3-COO$\underline{CH_3}$	51.84 (CH_3)	3.67 (6H, *s*)	1-C=O, 3-C=O

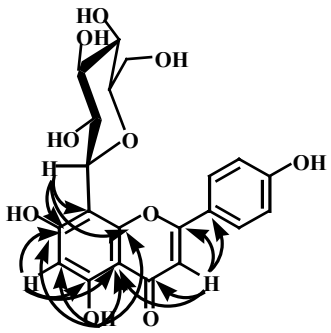
* Carbon type was deduced from DEPT experiments.

[a, b] Assignment maybe interchangeable.

GD19 : 8-β-D-Glucopyranosyl-5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-1-benzopyran-4-one (vitexin or apigenin 8-*C*-glucoside)



GD19 is a yellow solid, m.p. 258-259 °C. The ^{1}H NMR spectrum (**Table 43**) indicated a flavone nucleus by the appearance of an α-methine proton at δ 6.78 (*s*, H-3). This proton was confirmed from the results of ^{3}J cross peak of H-3 to C-4a, C-1′ and ^{2}J of H-3 to C-2, C-4. A *singlet* signal of a chelated hydroxy group was displayed at δ 13.15 (5-OH). A *singlet* signal of aromatic proton H-6 was shown at δ 6.27. Two *doublets* (J = 8.4 Hz) with integrating for two protons each at δ 8.02 (H-2′ and H-6′) and 6.90 (H-3′ and H-5′) suggested the presence of a 1,4-disubstituted benzene nucleus. The resonances of a sugar moiety were observed at δ 4.67-3.25 whereas an anomeric proton resonated at δ 4.67 (*d*, H-1′′). The coupling constant of 9.6 Hz suggested that it was a β-glucose moiety. According to HMBC correlation of H-1′′ (δ 4.67) to C-8 (δ 105.06) indicated the location of the glucose moiety at C-8. Therefore **GD19** was characterized as 8-β-D-glucopyranosyl-5,7-dihydroxy-2-(4-hydroxyphenyl)-4H-1-benzopyran-4-one or known as vitexin or apigenin 8-*C*-glucoside (Evans, *et al.*, 1957; Kartnig, *et al.*, 1991).



Major HMBC correlations of **GD19**

Table 43 The NMR spectral data of **GD19**

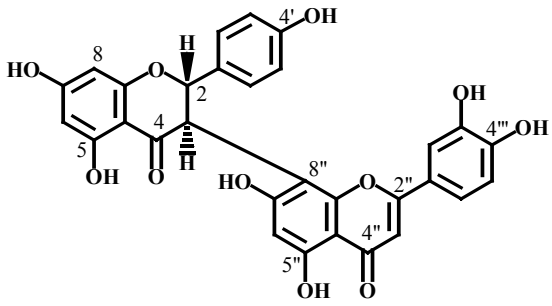
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	163.06 (C)	-	-
3	102.90 (CH)	6.78 (1H, *s*)	C-2, C-4, C-4a, C-1′
4	182.56 (C=O)	-	-
4a	104.50 (C)	-	-
5	161.60 (C)	-	-
6	98.60 (CH)	6.27 (1H, *s*)	C-4a, C-5, C-8
7	156.00 (C)	-	-
8	105.06 (C)	-	-
8a	160.87 (C)	-	-
1′	122.07 (C)	-	-
2′, 6′	129.43 (CH)	8.02 (2H, *d*, 8.4)	C-2, C-2′,6′, C-4′
3′, 5′	116.29 (CH)	6.90 (2H, *d*, 1.8)	C-1′, C-3′,5′, C-4′
4′	164.50 (C)	-	-
Glc-1″	73.83 (CH)	4.67 (1H, *d*, 9.6)	C-7, C-8, C-8a, C-3″
2″	79.11 (CH)	3.52-3.40 (1H, *m*)	C-2″
3″	135.34 (CH)	3.52-3.40 (1H, *m*)	C-4″, C-5″

Table 43 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
4″	82.29 (CH)	3.25 (1H, *m*)	C-4″, C-5″
5″	25.79 (CH)	3.82 (1H, *t*, 8.7)	C-3″
6″	61.75 (CH_2)	3.85-3.84 (2H, *m*)	C-4″, C-5″
5-OH	-	13.15 (1H, *s*)	C-4a, C-5, C-6

* Carbon type was deduced from DEPT experiments.

GD20 : 5,7,4′,5″,7″,3‴,4‴-Heptahydroxy-[3,8″]-flavonylflavanone (morelloflavone)

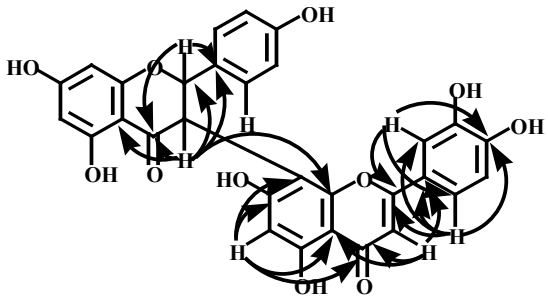


GD20 is yellow crystals, m.p. 305-307 °C. EIMS showed the molecular ion of 556 which corresponded to $C_{30}H_{20}O_{11}$. Duplication of signals (in a ratio of 1: 0.38) in the ^{1}H NMR spectrum at 295 K suggested the existence of two conformers. The major reason led to the existence of such conformers being rotational restrictions about the interflavanyl C-3, C-8″ bond. The minor signals given at 295 K sligthly disappeared at high temperature (340 K and 360 K) and only one set of signals was observed at 380 K. The ^{1}H NMR spectrum at 380 K (**Table 44**) showed two *singlet* signals of two chelated hydroxy protons 5-OH and 5″-OH at δ 12.80 and 12.00, two *doublet* resonances of H-2′, H-6′ and H-3′, H-5′ at δ 7.12 (2H, *d*, *J* = 8.4 Hz) and 6.54 (2H, *d*, *J* = 8.4 Hz), a *broad singlet* of H-6 and H-8 at δ 6.02 (2H), two *doublets* of H-2 and H-3 at δ 5.76 (*J* = 12.0 Hz) and 4.90 (*J* = 12.0 Hz), a *singlet* signal of a vinylic proton H-3″ at δ 6.47 and a *singlet* signal of an isolated aromatic proton H-6″ at δ 6.24. The resonances of aromatic protons H-2‴, H-6‴ and H-5‴ were shown as ABX pattern at δ 7.32 (*d*, *J* = 2.4 Hz), 7.21 (*dd*, *J* = 8.4 and 2.4 Hz) and 6.84 (*d*, *J* = 8.4 Hz), respectively. The stereochemistry at C-2, C-3 positions is *trans* as judged from the *J*-value ($\delta_{H\text{-}2}$ 5.76, *J* = 12.0 Hz and $\delta_{H\text{-}3}$ 4.90, *J* = 12.0 Hz). ^{13}C NMR spectrum at 380 K showed twenty eight signals (**Table 44**). The HMBC correlations at 380 K of H-2 to C-1′, C-4; H-3 to C-2, C-4, C-1′, C-7″, C-8″, C-8a″ and H-6″ to C-4″, C-

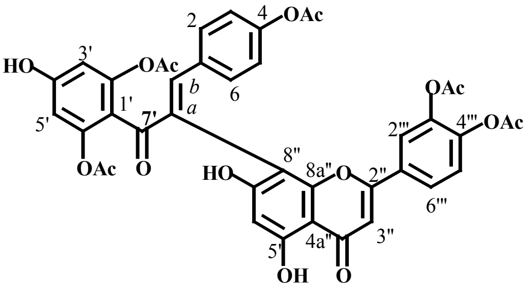
4a″, C-8″ suggested that C-2 was connected to C-1′ and C-3 was connected to C-8″. In addition, the correlation of H-3″ to C-4″, C-4a″, C-1‴ indicated that C-2″ was connected to C-1‴.

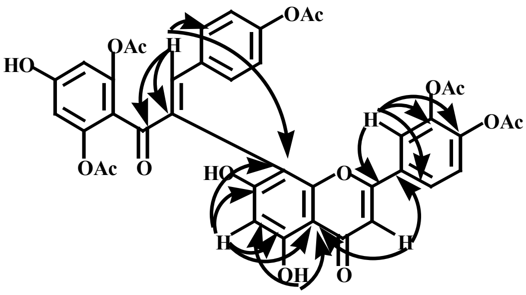
The ^{13}C NMR spectrum at 295 K also showed duplicate double signals of fifty-six carbons. The signals of major conformer (**Table 45**) showed two *singlet* signals of two chelated hydroxy protons 5-OH and 5″-OH at δ 13.10 and 12.30, two *doublet* resonances of H-2′, H-6′ and H-3′, H-5′ at δ 7.17 (2H, J = 8.4 Hz) and 6.41 (2H, J = 8.4 Hz), respectively. The spectrum further showed two *singlets* of H-6 and H-8 at δ 5.99 and 6.06, two *doublets* of H-2 and H-3 at δ 5.73 (J = 12.0 Hz) and 4.92 (J = 12.0 Hz), a *singlet* signal of a vinylic proton H-3″ at δ 6.60 and a *singlet* signal of an isolated aromatic proton H-6″ at δ 6.26. The resonances of aromatic protons H-2‴, H-5‴ and H-6‴ were shown as an ABX pattern at δ 7.45 (*d*, J = 3.4 Hz), 6.92 (*d*, J = 8.4 Hz) and 7.27 (*dd*, J = 8.4 and 3.4 Hz), respectively. The HMBC at 295 K showed the correlations of H-2 to C-1′, C-4 and H-3 to C-2, C-4, C-4a, C-1′, C-8a″. It's therefore confirmed that C-2 was connected to the 4-substituted ring at C-1′ and C-3 was connected to another flavone nucleus at C-8″. In addition, the correlations of H-6″ to C-4″, C-4a″, C-7″, C-8″ and H-3″ to C-4″, C-4a″, C-1‴ supported the assignment. The signals of the minor conformer showed two *singlet* signals of two chelated hydroxy protons 5-OH and 5″-OH at δ 12.95 and 12.15, two *doublet* resonances of H-2′, H-6′ and H-3′, H-5′ at δ 7.12 (*d*, J = 8.4 Hz) and 6.41 (*d*, J = 8.4 Hz), two *broad singlets* of H-6 and H-8 at δ 5.99 and 6.60, two *doublets* of H-2 and H-3 at δ 5.60 (J = 12.0 Hz) and 5.01 (J = 12.0 Hz), a *singlet* signal of a vinylic proton H-3″ at δ 6.60 and a *singlet* signal of an isolated aromatic proton H-6″ at δ 6.26. The resonances of aromatic protons H-2‴, H-5‴ and H-6‴ were shown as an ABX pattern at δ 7.45 (*d*, J = 3.4 Hz), 6.99 (*d*, J = 8.4 Hz) and 7.27 (*dd*, J = 8.4 and 3.4 Hz), respectively. The HMBC of the minor conformer showed the same pattern of correlations as of the major conformer.

Acetylation of **GD20** with pyridine-acetic anhydride gave a pentaacetate **GD20(A)**, m.p. 188-190 °C. The ^{1}H NMR spectrum (**Table 46**) showed a *singlet* signal of a chelated hydroxy proton 5″-OH at δ 12.75, two *doublet* resonances of H-2, H-6 and H-3, H-5 at δ 7.41 (2H, *d*, *J* = 8.5 Hz) and 7.06 (2H, *d*, *J* = 8.5 Hz), respectively. The spectra showed two *doublets* of H-3′ and H-5′ at δ 6.62 (*J* = 2.0 Hz) and 6.60 (*J* = 2.0 Hz), respectively, a *singlet* signal of a vinylic proton H-3″ at δ 6.99 and a *singlet* signal of an isolated aromatic proton H-6″ at δ 6.98. The resonances of aromatic protons H-2‴, H-5‴ and H-6‴ were shown as an ABX pattern at δ 7.39 (*d*, *J* = 1.7 Hz), 7.29 (*d*, *J* = 8.5 Hz) and 7.21 (*dd*, *J* = 8.5 and 1.7 Hz), respectively. The interesting observation was the disappearence of two *doublet* signals at δ 5.76 (*J* = 12.0 Hz) and 4.90 (*J* = 12.0 Hz) due to H-2 and H-3 of **GD20**, respectively and instead a downfield *singlet* was seen at δ 6.63 (H-β). During acetylation, opening of the chromanone ring had occurred transforming the flavanone to the corresponding chalcone. The integration for five acetoxy groups was observed.



Major HMBC correlations of **GD20**





Structure of **GD20(A)** Major HMBC correlations of **GD20(A)**

Table 44 The NMR spectral data of **GD20** at 380 K

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	82.01 (CH)	5.76 (1H, *d*, 12.0)	C-4, C-2′,6′, C-8
3	49.06 (CH)	4.90 (1H, *d*, 12.0)	C-2, C-4, C-1′, C-7′′, C-8′′, C-8a′′
4	196.47 (C=O)	-	-
4a	102.40 (C)	-	-
5	164.41 (C)	-	-
6	95.92 (CH)	6.02 (1H, *s*)	C-4, C-4a, C-5, C-7, C-8
7	167.16 (C)	-	-
8	97.03 (CH)	6.02 (1H, *s*)	C-4, C-7, C-8a
8a	163.51 (C)	-	-
1′	128.87 (C)	-	-
2′, 6′	128.70 (CH)	7.12 (2H, *d*, 8.4)	C-2, C-2′,6′, C-3′,5′, C-4′
3′, 5′	115.32 (CH)	6.54 (2H, *d*, 8.4)	C-2′,6′, C-3′,5′, C-4′
4′	158.01 (C)	-	-
2′′	146.33 (C)	-	-
3′′	103.51 (CH)	6.47 (1H, *s*)	C-4′′, C-4a′′, C-5′′, C-1′′′
4′′	182.15 (C=O)	-	-
4a′′	104.25 (C)	-	-

Table 44 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
5″	164.41 (C)	-	-
6″	99.28 (CH)	6.24 (1H, *s*)	C-4″, C-4a″, C-8″
7″	162.50 (C)	-	-
8″	101.20 (C)	-	-
8a″	155.90 (C)	-	-
1‴	122.49 (C)	-	-
2‴	114.32 (CH)	7.32 (1H, *d*, 2.4)	C-2″, C-3‴, C-4‴, C-6‴
3‴	161.14 (C)	-	-
4‴	150.14 (C)	-	-
5‴	116.91 (CH)	6.84 (1H, *d*, 8.4)	C-1‴, C-4‴
6‴	119.38 (CH)	7.21 (1H, *dd*, 8.4, 2.4)	C-2‴, C-3‴, C-4‴
5-OH	-	12.80 (1H, *s*)	-
5″-OH	-	12.00 (1H, *s*)	-

* Carbon type was deduced from DEPT experiments.

Table 45 The NMR spectral data of **GD20** at 295 K

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	major	minor	major	minor	
2	81.38 (CH)	82.28	5.73 (1H, *d*, 12.0)	5.60	C-4, C-1′
3	49.06 (CH)	48.74	4.92 (1H, *d*, 12.0)	5.01	C-2, C-4, C-4a, C-1′, C-8a″
4	196.68 (C=O)	196.91	-	-	-
4a	102.15 (C)	101.96	-	-	-
5	164.26 (C)	164.34	-	-	-
6	95.78 (CH)	95.78	5.99 (1H, *s*)	6.06	C-4, C-5, C-7, C-8
7	167.01 (C)	167.44	-	-	-

Table 45 (Continued)

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	major	minor	major	minor	
8	96.70 (CH)	96.70	6.06 (1H, *s*)	5.99	C-4, C-7
8a	163.32 (C)	162.97	-	-	-
1′	128.62 (C)	128.10	-	-	-
2′	128.98 (CH)	129.32	7.17 (1H, *d*, 8.4)	7.12	C-2, C-4′, C-5′, C-6′
3′	114.89 (CH)	115.62	6.41 (1H, *d*, 8.4)	6.41	C-2′, C-4′, C-5′
4′	157.79 (C)	158.03	-	-	-
5′	114.89 (CH)	115.09	6.41 (1H, *d*, 8.4)	6.41	C-3′, C-4′, C-6′
6′	128.98 (CH)	128.10	7.17 (1H, *d*, 8.4)	7.12	C-2, C-2′, C-4′, C-5′
2″	146.10 (C)	146.44	-	-	-
3″	102.68 (CH)	103.50	6.60 (1H, *s*)	6.60	C-4″, C-4a″, C-1‴
4″	182.15 (C=O)	182.12	-	-	-
4a″	103.62 (C)	104.12	-	-	-
5″	163.94 (C)	163.94	-	-	-
6″	99.08 (CH)	98.45	6.26 (1H, *s*)	6.26	C-4″, C-4a″, C-7″, C-8″
7″	162.14 (C)	162.14	-	-	-
8″	101.01 (C)	100.52	-	-	-
8a″	155.71 (C)	155.01	-	-	-
1‴	121.50 (C)	121.99		-	-
2‴	113.72 (CH)	114.22	7.45 (1H, *d*, 3.4)	7.45	C-2″, C-4‴, C-6‴
3‴	160.98 (C)	160.71	-	-	-
4‴	150.15 (C)	150.15	-	-	-
5‴	116.61 (CH)	115.62	6.92 (1H, *d*, 8.4)	6.99	C-1‴, C-4‴
6‴	119.78 (CH)	118.49	7.27(1H,*dd*,8.4, 3.4)	7.27	C-2″, C-1‴, C-2‴, C-4‴
5-OH	-	-	13.10 (1H, *s*)	12.95	-
5″-OH	-	-	12.30 (1H, *s*)	12.15	C-4a″, C-5″, C-6″

* Carbon type was deduced from DEPT experiments.

Table 46 The NMR spectral data of **GD20(A)**

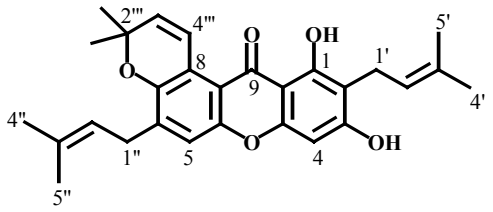
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	135.76 (C)	-	-
2, 6	128.86 (CH)	7.41 (2H, *d*, 8.5)	C-2,6, C-4
3, 5	122.02 (CH)	7.06 (2H, *d*, 8.5)	C-1, C-3,5, C-4
4	151.49 (C)	-	-
α	108.10 (C)	-	-
β	108.90 (CH)	6.63 (1H, *s*)	C-2, C-α, C-7′, C-8″
1′	107.30 (C)	-	-
2′	159.30 (C)	-	-
3′	109.20 (CH)	6.62 (1H, *d*, 2.0)	C-1′, C-4′, C-5′
4′	153.20 (C)	-	-
5′	110.06 (CH)	6.60 (1H, *d*, 2.0)	C-1′, C-3′, C-4′, C-6′
6′	149.62 (C)	-	-
7′	182.62 (C=O)	-	-
2″	162.63 (C)	-	-
3″	77.25 (CH)	6.99 (1H, *s*)	C-4a″, C-1‴
4″	182.62 (C=O)	-	-
4a″	107.78 (C)	-	-
5″	151.35 (C)	-	-
6″	96.05 (CH)	6.98 (1H, *s*)	C-4a″, C-5″, C-7″, C-8″
7″	145.48 (C)	-	-
8″	107.20 (C)	-	-
8a″	159.80 (C)	-	-
1‴	129.49 (C)	-	-
2‴	121.64 (CH)	7.39 (1H, *d*, 1.7)	C-2″, C-3‴, C-4‴, C-6‴
3‴	144.78 (C)	-	-
4‴	145.00 (C)	-	-
5‴	124.42 (CH)	7.29 (1H, *d*, 8.5)	C-1‴, C-3‴, C-4‴

Table 46 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
6′′′	124.75 (CH)	7.21 (1H, *dd*, 8.5, 1.7)	C-2′′, C-2′′′, C-4′′′
5′′-OH	-	12.75 (1H, *s*)	C-4a′′, C-6′′
5xO<u>C</u>OCH$_3$	169.29 (C=O)	-	-
	168.94 (C=O)	-	-
	168.47 (C=O)	-	-
	167.82 (C=O)	-	-
	167.67 (C=O)	-	-
5xOCO<u>CH</u>$_3$	21.13 (CH$_3$)	2.25 (3H, *s*)	C=O
		2.24 (3H, *s*)	C=O
	21.00 (CH$_3$)	2.49 (3H, *s*)	C=O
	20.70 (CH$_3$)	2.34 (3H, *s*)	C=O
	20.63 (CH$_3$)	2.37 (3H, *s*)	C=O

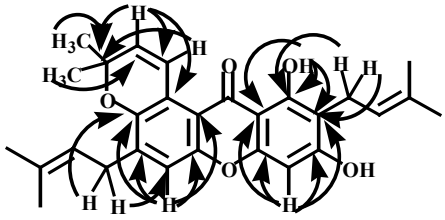
* Carbon type was deduced from DEPT experiments.

GD21 : 1,3-Dihydroxy-2,6-bis(3-methyl-2-butenyl)-2,2-dimethylchromeno (5‴,6‴:8,7)xanthone



GD21 is a yellow solid, m.p. 119-120 °C. The HRMS showed the molecular ion of 446.1628 $[M]^+$ corresponded to $C_{28}H_{30}O_5$. The UV spectrum showed maxima absorptions at 329.8, 300.5, 287.9, 265.0, 246.6 and 207.9 nm. The IR spectrum exhibited the absorption bands of O-H stretching at 3402 cm^{-1} and C=O stretching at 1622 cm^{-1}. The ^1H NMR spectrum (**Table 47**) exhibited the resonances of a chelated hydroxy proton 1-OH (δ 13.70, *s*), H-4 (δ 6.26, *s*) and H-5 (δ 6.82, *s*). The assignment of H-4 was confirmed by the correlation of H-4 to C-2, C-3, C-4a and C-9a whereas the position of H-5 was proved by the correlation of H-5 to C-6, C-7, C-8a, C-9 and C-10a. The signals of two olefinic protons at δ 5.27 (*br t*, H-2′) and 5.30 (*br t*, H-2″), two benzylic methylene protons at δ 3.57 (*d*, H-1′) and 3.46 (*d*, H-1″) and four methyl groups at δ 1.84 (H-4′), 1.50 (H-5′), 1.77 (H-4″) and 1.87 (H-5″) indicated the presence of two prenyl groups. The HMBC correlations of H-1′ to C-1, C-2 and C-3 and H-1″ to C-5, C-6 and C-7 supported that two prenyl groups were at C-2 and C-6. The signals of two methyl groups at δ 1.50 (6H, *s*, 2‴-Me_2) and vicinal olefinic protons at δ 5.77 (*d*, *J* = 10.2 Hz, H-3‴) and 7.99 (*d*, *J* = 10.2 Hz, H-4‴) associated with a chromene ring were present. The HMBC correlations of H-4‴ to C-2‴ and H-3‴ to C-8, C-2‴ and C-4‴ indicated that the chromene ring was fused to the xanthone nucleus at C-7 and C-8. These assignment indicated that **GD21** was 1,3-

dihydroxy-2,6-bis(3-methyl-2-butenyl)-2,2-dimethylchromeno(5‴,6‴:8,7)xanthone. This compound was a new xanthone derivative.



Major HMBC correlations of **GD21**

Table 47 The NMR spectral data of **GD21**

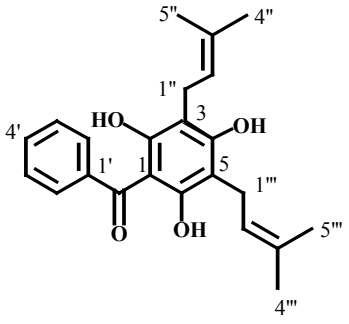
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	157.79 (C)	-	-
2	104.39 (C)	-	-
3	159.97 (C)	-	-
4	94.28 (CH)	6.26 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	156.54 (C)	-	-
5	102.42 (CH)	6.82 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	136.85 (C)	-	-
7	150.93 (C)	-	-
8	119.70 (C)	-	-
8a	108.56 (C)	-	-
9	182.47 (C=O)	-	-
9a	103.89 (C)	-	-
10a	153.07 (C)	-	-
1′	21.45 (CH_2)	3.57 (2H, *d*, 7.2)	C-1, C-2, C-3
2′	121.07 (CH)	5.27 (1H, *br t*, 7.5)	C-2, C-4′, C-5′

Table 47 (Continued)

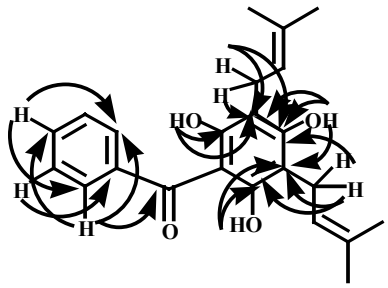
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
3′	131.33 (C)	-	-
4′	25.81 (CH_3)	1.84 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.98 (CH_3)	1.68 (3H, *s*)	C-2′, C-3′, C-4′
1″	22.58 (CH_2)	3.46 (2H, *d*, 7.2)	C-5, C-7, C-2″, C-3″
2″	121.50 (CH)	5.30 (1H, *br t*, 7.5)	C-6, C-4″, C-5″
3″	132.64 (C)	-	-
4″	25.86 (CH_3)	1.77 (3H, *s*)	C-2″, C-3″, C-5″
5″	17.94 (CH_3)	1.87 (3H, *s*)	C-2″, C-3″, C-4″
2‴	77.99 (C)	-	-
3‴	132.34 (CH)	5.77 (1H, *d*, 10.2)	C-8, C-2‴, C-4‴
4‴	120.95 (CH)	7.99 (1H, *d*, 10.2)	C-8a, C-2‴
2‴-$(CH_3)_2$	27.35 (CH_3)	1.50 (6H, *s*)	C-2‴, C-3‴
1-OH	-	13.70 (1H, *s*)	C-1, C-2, C-9a
3-OH	-	6.35 (1H, *s*)	C-2

* Carbon type was deduced from DEPT experiments.

GD22 : 2,4,6-Trihydroxy-3,5-bis(3-methyl-2-butenyl)benzophenone (clusiaphenone B)



GD22 was isolated as yellow needles. The ^{1}H NMR spectrum (**Table 48**) showed the resonances of aromatic protons H-2′, H-6′ (δ 7.66-7.62, 2H, *m*), H-3′, H-5′ (δ 7.55-7.47, 2H, *m*) and H-4′ (δ 7.60-7.54, *m*), corresponded to a fragment at *m/z* 105 in the mass spectrum which refered to a benzophenone with an unsubstituted ring. The substitution pattern of the second aromatic ring could be deduced by the resonances of two equivalent chelated hydroxy groups at δ 8.92 (2H, *s*, 2-OH and 6-OH), a non hydrogen bonded hydroxy group at δ 6.37 (*s*, 4-OH) and two equivalent prenyl side chains: four methyl groups at δ 1.78 (6H, H-5′′ and H-5′′′) and 1.74 (6H, H-4′′ and H-4′′′), two olefinic methine protons at δ 5.22 (2H, *br t*, J = 6.6 Hz, H-2′′ and H-2′′′) and two methylene protons at δ 3.34 (4H, *d*, J = 7.0 Hz, H-1′′ and H-1′′′). The resulting structure was confirmed by ^{13}C NMR spectral data and HMBC correlations (**Table 48**). 2,4,6-Trihydroxy-3,5-bis(3-methyl-2-butenyl)benzophenone was assigned for **GD22**. It was known as clusiaphenone B (Delle Monache, *et al*., 1991).



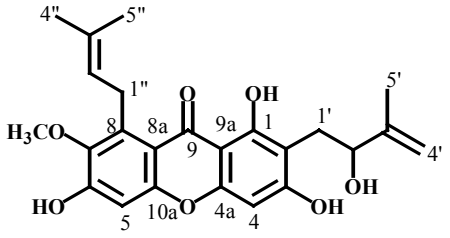
Major HMBC correlations of **GD22**

Table 48 The NMR spectral data of **GD22**

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	GD22	**clusiaphenone B**	**GD22**	**clusiaphenone B**	
1	104.58 (C)	104.56	-	-	-
2, 6	157.65 (C)	157.62	-	-	-
3, 5	106.33 (C)	106.33	-	-	-
4	161.07 (C)	161.03	-	-	-
1′	140.31 (C)	140.28	-	-	-
2′, 6′	129.02 (CH)	128.98	7.66-7.62(2H,*m*)	7.64-7.46	C-3′,5′, C-4′, C=O
3′, 5′	127.95 (CH)	127.93	7.55-7.47(2H,*m*)	(5H, *m*)	C-1′, C-2′,6′
4′	132.04 (CH)	132.00	7.60-7.54(1H,*m*)		C-2′,6′
1″, 1‴	21.84 (CH_2)	21.82	3.34 (4H, *d*,7.0)	3.33 (4H, *d*, 7.0)	C-2,6, C-3,5, C-4, C-2″,2‴, C-3″,3‴
2″, 2‴	121.85 (CH)	121.83	5.22(2H, *brt*,6.6)	5.22 (2H, *br t*)	C-1″,1‴, C-4″,4‴, C-5″,5‴
3″, 3‴	135.06 (C)	134.98	-	-	-
4″, 4‴	25.80 (CH_3)	25.77	1.74 (6H, *s*)	1.73 (6H, *s*)	C-2″,2‴, C-5″,5‴
5″, 5‴	17.87 (CH_3)	17.85	1.78 (6H, *s*)	1.78 (6H, *s*)	C-2″,2‴, C-4″,4‴
C=O	198.05	198.03	-	-	-
2-OH	-	-	8.92 (1H, *s*)	8.92 (1H, *s*)	C-2, C-3
4-OH	-	-	6.37 (1H, *s*)	6.37 (1H, *s*)	C-5, C-6
6-OH	-	-	8.92 (1H, *s*)	8.92 (1H, *s*)	C-3, C-4, C-5

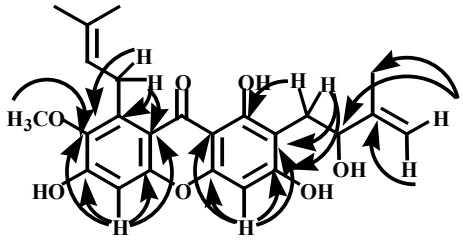
* Carbon type was deduced from DEPT experiments.

GD23 : 1,3,6-Trihydroxy-2-(2-hydroxy-3-methyl-3-butenyl)-7-methoxy-8-(3-methyl-2-butenyl)xanthone (mangostenol)



GD23 was isolated as a yellow solid with m.p. 163-164 °C. The ^{1}H NMR spectrum (**Table 49**) showed four *singlet* signals of a deshielded hydroxy proton 1-OH (δ 13.90), methoxy protons (δ 3.79), H-4 (δ 6.37) and H-5 (δ 6.83). A prenyl side chain and a 2-hydroxy-3-methyl-3-butenyl moiety were detected. The resonances of the prenyl side chain appeared as follow; two *singlets* of two methyl groups at δ 1.88 (H-5″) and 1.70 (H-4″), a *doublet* of methylene protons (H-1″) at δ 4.09 and a *broad triplet* of an olefinic methine proton (H-2″) at δ 5.27. The resonances of 2-hydroxy-3-methyl-3-butenyl were appeared as follow; two *singlets* of methylene protons (H-4′) at δ 5.00 and 4.88, a *doublet of doublet* of a hydroxy methine proton (H-2′) at δ 4.41, two *doublet of doublet* signals of methylene protons (H-1′) at δ 3.18 and 2.88, and a sharp *singlet* of methyl protons (H-5′) at δ 1.83. The HMBC spectrum was used to support the structural assignment. In HMBC, H-1′ showed long-range heteronuclear connectivities with C-1, C-2, C-3, C-2′, C-3′; H-2′ was coupled with C-2, C-1′, C-3′, C-4′, C-5′; H-1″ exhibited interactions with C-7, C-8, C-8a, C-2″, C-3″ and the methoxy signal (OCH_3) showed a cross-peak with C-7. Thus it was indicated that the methoxy, prenyl and 2-hydroxy-3-methyl-3-butenyl moieties were at C-7, C-8 and C-2, respectively. The ^{13}C NMR spectrum and DEPT experiments showed the resonances of twelve quaternary carbons, four methine carbons, three methylene carbons, four methyl carbons and a carbonyl carbon. Therefore **GD23** was assigned as 1,3,5-

trihydroxy-2-(2-hydroxy-3-methyl-3-butenyl)-7-methoxy-8-(3-methyl-2-butenyl) xanthone. It was the first reported xanthone in *G. dulcis*. Its physical and spectral data were in agreement with mangostenol which was previously isolated from *G. mangostana* (Suksamrarn, *et al*., 2002).



Major HMBC correlations of **GD23**

Table 49 The NMR spectral data of **GD23**

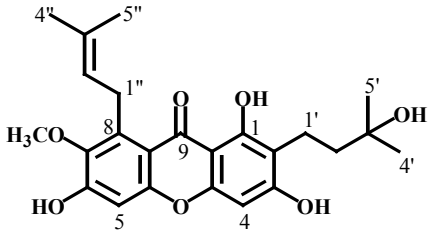
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.74 (C)	-	-
2	107.83 (C)	-	-
3	162.94 (C)	-	-
4	93.78 (CH)	6.37 (1H, *s*)	C-2, C-3, C-4a, C-9, C-9a
4a	155.65 (C)	-	-
5	101.79 (CH)	6.83 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	155.56 (C)	-	-
7	143.08 (C)	-	-
8	137.29 (C)	-	-
8a	111.63 (C)	-	-
9	181.97 (C=O)	-	-
9a	103.12 (C)	-	-

Table 49 (Continued)

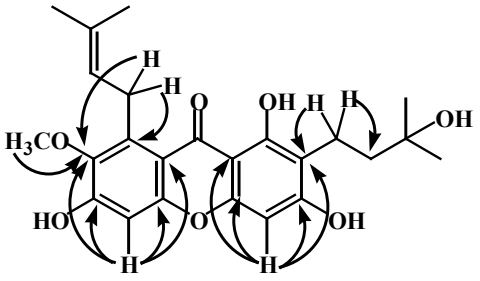
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
10a	155.40 (C)	-	-
1′	28.61 (CH_2)	2.88 (1H, *dd*, 15.0, 8.1)	C-1, C-2, C-3, C-2′, C-3′
		3.18 (1H, *dd*, 15.0, 2.1)	C-1, C-2, C-3, C-2′, C-3′
2′	76.42 (CH)	4.41 (1H, *d*, 7.5)	C-2, C-1′, C-3′, C-4′, C-5′
3′	147.08 (C)	-	-
4′	109.97 (CH_2)	4.88 (1H, *s*)	C-2′, C-3′, C-5′
		5.00 (1H, *s*)	C-2′, C-3′, C-5′
5′	18.29 (CH_3)	1.83 (3H, *s*)	C-2′, C-3′, C-4′
1″	26.32 (CH_2)	4.09 (2H, *d*, 6.3)	C-7, C-8, C-8a, C-2″, C-3″
2″	123.38 (CH)	5.27 (1H, *br t*, 6.3)	C-8, C-4″, C-5″
3″	131.66 (C)	-	-
4″	25.73 (CH_3)	1.70 (3H, *s*)	C-2″, C-3″, C-5″
5″	18.08 (CH_3)	1.88 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.90 (1H, *s*)	C-1, C-2, C-9a
7-OCH_3	61.18 (CH_3)	3.79 (3H, *s*)	C-7

* Carbon type was deduced from DEPT experiments.

GD24 : 1,3,6-Trihydroxy-2-(3-hydroxy-3-methylbutyl)-7-methoxy-8-(3-methyl-2-butenyl)xanthone (cratoxylone)



GD24 was isolated as yellow needles. The ^{1}H NMR spectrum (**Table 50**) exhibited the resonances of a chelated hydroxy proton 1-OH (δ 13.80, *s*), H-4 (δ 6.39, *s*), H-5 (δ 6.85, *s*), 7-OCH_3 (δ 3.80), a prenyl group and a 3-hydroxy-3-methylbutyl side chain. The resonances of the prenyl group were displayed at δ 5.28 (*br t*, H-2″), 4.14 (*d*, H-1″), 1.66 (*s*, H-4″) and 1.84 (*s*, H-5″). The HMBC correlation of H-1″ to C-7 and C-8 indicated that the prenyl group was at C-8. The resonances of 3-hydroxy-3-methylbutyl side chain were shown at δ 1.26 (6H, *s*, H-4′ and H-5′), 2.77 (2H, *m*, H-1′) and 1.71 (2H, *m*, H-2′). The assignment of H-4 was confirmed by the correlation of H-4 to C-2, C-3, C-4a and C-9a whereas the position of H-5 was proved by the correlation of H-5 to C-6, C-7, C-8a and C-10a. These assignment indicated that **GD24** was 1,3,6-trihydroxy-2-(3-hydroxy-3-methylbutyl)-7-methoxy-8-(3-methyl-2-butenyl) xanthone. It was known as cratoxylone (Bennett, *et al*., 1993).



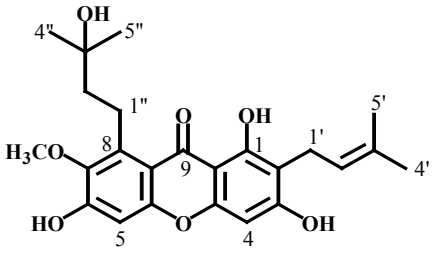
Major HMBC correlations of **GD24**

Table 50 The NMR spectral data of **GD24**

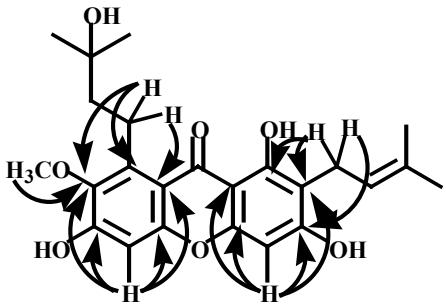
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	163.00 (C)	-	-
2	112.37 (C)	-	-
3	161.70 (C)	-	-
4	93.40 (CH)	6.39 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	155.68 (C)	-	-
5	102.71 (CH)	6.85 (1H, *s*)	C-6, C-7, C-8a, C-10a
6	157.70 (C)	-	-
7	144.20 (C)	-	-
8	138.09 (C)	-	-
8a	111.93 (C)	-	-
9	182.89 (C=O)	-	-
9a	103.53 (C)	-	-
10a	156.23 (C)	-	-
1′	17.89 (CH_2)	2.77 (2H, *m*)	C-2, C-2′
2′	43.23 (CH_2)	1.71 (2H, *m*)	C-2, C-3′, C-4′,5′
3′	70.63 (C)	-	-
4′, 5′	29.58 (CH_3)	1.26 (6H, *s*)	C-2′, C-3′, C-4′,5′
1″	26.87 (CH_2)	4.14 (2H, *d*, 6.0)	C-7, C-8, C-2″, C-3″
2″	124.78 (CH)	5.28 (1H, *br t*, 6.0)	C-8, C-1″, C-4″, C-5″
3″	131.43 (C)	-	-
4″	25.95 (CH_3)	1.66 (3H, *s*)	C-2″, C-3″, C-5″
5″	18.29 (CH_3)	1.84 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.80 (1H, *s*)	-
7-OCH_3	61.28 (CH_3)	3.80 (3H, *s*)	C-7

* Carbon type was deduced from DEPT experiments.

GD25 : 1,3,6-Trihydroxy-8-(3-hydroxy-3-methylbutyl)-7-methoxy-2-(3-methyl-2-butenyl)xanthone (garcinone D)



GD25 is a yellow solid, m.p. 200-203 °C. It was an isomer of **GD24**. The difference was the position of side chains. The location of the prenyl group at C-2 was assigned to be at C-2 by the HMBC correlation of H-1′ to C-1, C-2 and C-3 whereas the 3-hydroxy-3-methylbutyl side chain was located at C-8 by the HMBC correlation of H-1″ to C-7, C-8 and C-8a. **GD25** was then identified as 1,3,6-trihydroxy-8-(3-hydroxy-3-methylbutyl)-7-methoxy-2-(3-methyl-2-butenyl)xanthone. The proposed structure, the spectral data was agreed with the structure of garcinone D (Sen, *et al*., 1986; Bennett, *et al*., 1993).



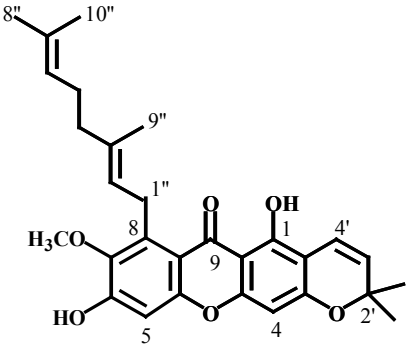
Major HMBC correlations of **GD25**

Table 51 The NMR spectral data of **GD25**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	161.61 (C)	-	-
2	110.97 (C)	-	-
3	163.18 (C)	-	-
4	93.13 (CH)	6.40 (1H, *s*)	C-2, C-3, C-4a, C-9, C-9a
4a	157.60 (C)	-	-
5	102.52 (CH)	6.81 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	155.68 (C)	-	-
7	144.44 (C)	-	-
8	139.94 (C)	-	-
8a	111.83 (C)	-	-
9	182.79 (C=O)	-	-
9a	103.48 (C)	-	-
10a	156.24 (C)	-	-
1′	21.98 (CH_2)	3.33 (2H, *d*, 7.2)	C-1, C-2, C-3, C-2′, C-3′
2′	123.55 (CH)	5.28 (1H, *br t*, 7.0)	C-2, C-4′, C-5′
3′	131.28 (C)	-	-
4′	25.90 (CH_3)	1.65 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.91 (CH_3)	1.79 (3H, *s*)	C-2′, C-3′, C-4′
1″	23.22 (CH_2)	3.46 (2H, *m*)	C-7, C-8, C-8a, C-2″
2″	45.65 (CH_2)	1.77 (2H, *m*)	C-1″, C-3″
3″	70.61 (C)	-	-
4″, 5″	29.40 (CH_3)	1.33 (6H, *s*)	C-2″, C-3″, C-4″,5″
1-OH	-	13.82 (1H, *s*)	C-1, C-2, C-9a
7-OCH_3	61.48 (CH_3)	3.85 (3H, *s*)	C-7

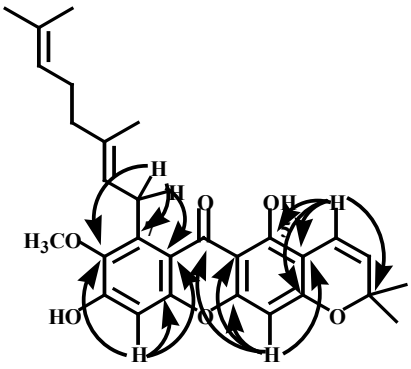
* Carbon type was deduced from DEPT experiments.

RD1 : 1,6-Dihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl)-2′,2′-dimethylchromeno(5′,6′:2,3)xanthone (fuscaxanthone A)



RD1 was isolated as yellow needles. The ^{1}H NMR spectrum (**Table 52**) showed a sharp *singlet* signal of a chelated hydroxyl proton (1-OH) at δ 13.72 and two *singlet* signals of aromatic protons H-4 and H-5 at δ 6.24 and 6.83. H-5 and H-4 were deduced from the HMBC correlations of H-5 to C-7, C-8a, C-9, C-10a and H-4 to C-2, C-4a, C-9, C-9a. A sharp *singlet* signal of methoxy protons was observed at δ 3.80 and the methoxy group was suggested to be at C-7, from the correlation of OCH_3 to C-7. The ^{1}H NMR spectrum also showed a characteristic signal of a dimethylchromene ring, of which the signal of *gem*-dimethyl protons was at δ 1.46 (*s*) and two olefinic protons (H-4′ and H-3′) were at δ 6.73 (*d*) and 5.56 (*d*). The correlation of H-4′ to C-2 and C-1 precisely determined that the dimethylchromene ring was next to C-1. Three *singlets* of three methyl groups at δ 1.82 (H-9″), 1.60 (H-8″) and 1.54 (H-10″), a *doublet* of methylene protons at δ 4.09 (H-1″), two *multiplets* of methylene protons at δ 2.04-2.01 (H-5″) and 2.01-1.98 (H-4″) and two *triplets* of two olefinic methine protons at δ 5.25 (H-2″) and 5.01 (H-6″) implied the presence of a geranyl moiety. The deshielded chemical shift of the methylene protons H-1″ (δ 4.09) suggested that the geranyl side chain was at *peri* position to the carbonyl group. The HMBC correlation of H-1″ to C-7, C-8 and C-8a confirmed the location of the geranyl unit at

C-8. According to the assignment, **RD1** was 1,6-dihydroxy-7-methoxy-8-(3,7-dimethyl-2,6-octadienyl)-2′,2′-dimethylchromeno(5′,6′:2,3)xanthone. This compound was identical with fuscaxanthone A (Ito, *et al*., 2003b) which was first isolated from *Garcinia fusca*.



Major HMBC correlations of **RD1**

Table 52 The NMR spectral data of **RD1**

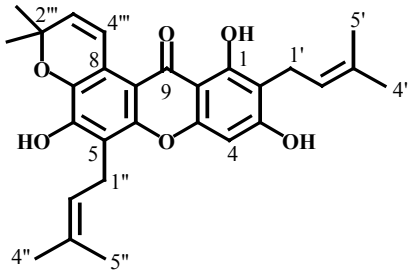
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.82 (C)	-	-
2	104.46 (C)	-	-
3	157.93 (C)	-	-
4	94.12 (CH)	6.24 (1H, *s*)	C-2, C-4a, C-9, C-9a
4a	156.26 (C)	-	-
5	101.66 (CH)	6.83 (1H, *s*)	C-7, C-8a, C-9, C-10a
6	154.65 (C)	-	-
7	142.74 (C)	-	-
8	137.09 (C)	-	-
8a	112.17 (C)	-	-

Table 52 (Continued)

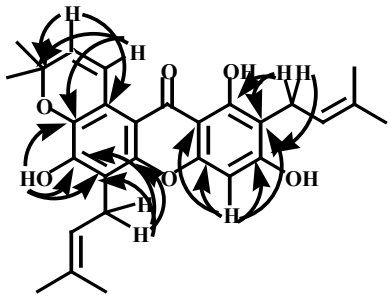
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
9	181.94 (C=O)	-	-
9a	103.72 (C)	-	-
10a	155.71 (C)	-	-
2′	77.90 (C)	-	-
3′	127.12 (CH)	5.56 (1H, *d*, 9.9)	C-2, C-2′, 2′-$(CH_3)_2$
4′	115.71 (CH)	6.73 (1H, *d*, 9.9)	C-1, C-2, C-3, C-2′
1″	26.55 (CH_2)	4.09 (2H, *d*, 6.0)	C-7, C-8, C-8a, C-2″, C-3″, C-4″
2″	123.19 (CH)	5.25 (1H, *br t*, 6.0)	C-8, C-1″, C-4″, C-9″
3″	135.57 (C)	-	-
4″	39.69 (CH_2)	2.01-1.98 (2H, *m*)	C-1″, C-2″, C-3″, C-9″
5″	26.46 (CH_2)	2.04-2.01 (2H, *m*)	C-3″, C-4″, C-6″, C-7″
6″	124.27 (CH)	5.01 (1H, *br t*, 6.0)	C-4″, C-5″, C-10″
7″	131.26 (C)	-	-
8″	25.59 (CH_3)	1.60 (3H, *s*)	C-6″, C-7″, C-10″
9″	16.47 (CH_3)	1.82 (3H, *s*)	C-1″, C-2″, C-3″, C-4″, C-5″
10″	17.64 (CH_3)	1.54 (3H, *s*)	C-6″, C-7″, C-8″
1-OH	-	13.72 (1H, *s*)	-
7-OCH_3	61.97 (CH_3)	3.80 (3H, *s*)	C-7
2′-$(CH_3)_2$	28.29 (CH_3)	1.46 (6H, *s*)	C-2′, C-3′, C-4′

* Carbon type was deduced from DEPT experiments.

RD2 : 1,3,6-Trihydroxy-2,5-bis(3-methyl-2-butenyl)-2‴,2‴-dimethylchromeno (5‴,6‴:8,7)xanthone (tovophyllin A)



RD2 is a yellow solid, m.p. 212-215 °C. The ^{1}H NMR spectral data (**Table 53**) demonstrated the resonances of a chelated hydroxy group 1-OH (δ 13.90, *s*), 6-OH (δ 6.32, *s*) and H-4 (δ 6.37, *s*). A *singlet* signal of two methyl groups 2‴-Me$_2$ (δ 1.52, 6H) and two *doublet* signals of two *geminal* olefinic protons H-3‴ (δ 5.79, J = 9.9 Hz) and H-4‴ (δ 8.02, J = 9.9 Hz) implied the presence of a 2,2-dimethylchromene ring. The deshielded effect on the resonance of H-4‴ suggested the location of the chromene ring nearby the carbonyl group. Two *triplets* at δ 5.32 (H-2′) and 5.29 (H-2″), two *doublets* at δ 3.50 (H-1′) and 3.60 (H-1″) and four *singlets* at δ 1.70 (H-4′), 1.89 (H-5′), 1.80 (H-4″) and 1.87 (H-5″) were the typical resonances of two prenyl groups. HMBC correlations of H-1′ to C-1, C-2, C-3 and H-1″ to C-5, C-6, C-10a indicated that the prenyl side chains were at C-2 and C-5. The assignment of H-4 was confirmed by the correlation of H-4 to C-2, C-3, C-4a and C-9a. The position of 6-OH was proved by the correlation of 6-OH to C-5, C-6 and C-7. The ^{13}C NMR spectral data showed the resonances of a carbonyl carbon, five methyl carbons, two methylene carbons, five methine carbons and fourteen quaternary carbons. **RD2** was then identified as 1,3,6-trihydroxy-2,5-bis(3-methyl-2-butenyl)-2‴,2‴-dimethylchromeno (5‴,6‴:8,7)xanthone. The proposed structure, the spectral data were in good agreement with the structure of tovophyllin A (Bennett, *et al*., 1993).



Major HMBC correlations of **RD2**

Table 53 The NMR spectral data of **RD2**

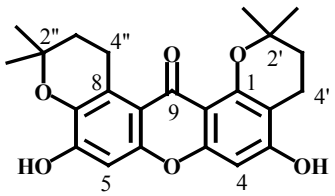
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.80 (C)	-	-
2	106.65 (C)	-	-
3	161.80 (C)	-	-
4	94.26 (CH)	6.37 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	156.00 (C)	-	-
5	115.63 (C)	-	-
6	148.50 (C)	-	-
7	136.82 (C)	-	-
8	117.16 (C)	-	-
8a	119.90 (C)	-	-
9	181.50 (C=O)	-	-
9a	102.40 (C)	-	-
10a	150.90 (C)	-	-
1′	22.56 (CH_2)	3.50 (2H, *d*, 5.4)	C-1, C-2, C-3, C-2′, C-3′
2′	121.00 (CH)	5.32 (1H, *br t*, 6.9)	C-4′, C-5′
3′	132.50 (C)	-	-
4′	27.43 (CH_3)	1.70 (3H, *s*)	C-2′, C-3′, C-5′

Table 53 (Continued)

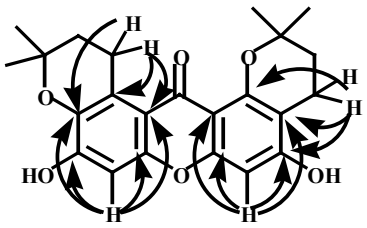
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
5′	17.97 (CH_3)	1.89 (3H, *s*)	C-2′, C-3′, C-4′
1″	22.69 (CH_2)	3.60 (2H, *d*, 7.2)	C-5, C-6, C-10a, C-2″, C-3″
2″	120.50 (CH)	5.29 (1H, *br t*, 6.9)	C-5, C-4″, C-5″
3″	132.32 (C)	-	-
4″	27.33 (CH_3)	1.80 (3H, *s*)	C-2″, C-3″, C-5″
5″	18.17 (CH_3)	1.87 (3H, *s*)	C-2″, C-3″, C-4″
2‴	78.00 (C)	-	-
3‴	131.55 (CH)	5.79 (1H, *d*, 9.9)	C-8, C-2‴
4‴	120.93 (CH)	8.02 (1H, *d*, 9.9)	C-7, C-2‴
1-OH	-	13.90 (1H, *s*)	C-1, C-2, C-9a
6-OH	-	6.32 (1H, *s*)	C-5, C-6, C-7
2‴-$(CH_3)_2$	29.69 (CH_3)	1.52 (6H, *s*)	C-2‴, C-3‴, 2‴-$(CH_3)_2$

* Carbon type was deduced from DEPT experiments.

RD3 : 3,6-Dihydroxy-2′,2′-dimethylchromano(5′,6′:2,1)-2′′,2′′-Dimethylchromano(5′′′,6′′′:8,7)xanthone (isonormangostin)



RD3 is a yellow solid, m.p. 210-212 °C. Its molecular formula of $C_{23}H_{24}O_6$ was established on the basis of mass spectrum ($[M]^+$ *m/z* 396.1571). The UV spectrum showed maximum absorptions bands at 355.3, 307.5, 254.5 and 212.2 nm. In the IR spectrum, absoption bands of O-H stretching and C=O stretching were shown at 3424 and 1609 cm^{-1}, respectively. The ^1H NMR spectrum (**Table 54**) contained two sharp *singlet* signals of isolated aromatic protons H-4 and H-5 at δ 6.27 and 6.65, respectively. The assignments were supported by the cross peaks of H-4 to C-2, C-3, C-4a, C-9, C-9a and H-5 to C-6, C-7, C-8a, C-9, C-10a. The resonances of *gem*-dimethyl protons 2′′-Me_2 at δ 1.36 (6H, *s*), and two methylene protons H-3′′ and H-4′′ at δ 1.84 (2H, *t*, *J* = 6.6 Hz) and 3.55 (2H, *t*, *J* = 6.6 Hz) implied the presence of a 2,2-dimethylchromane ring. This ring was placed to be at C-8 and C-7 by the correlation of H-4′′ to C-6, C-7, C-8 and C-8a in HMBC. The spectrum further showed the signals of *gem*-dimethyl protons at δ 1.45 (*s*, 6H, 2′-Me_2) and two methylene protons at δ 1.82 (*t*, 6.9 Hz, H-3′) and 2.65 (*t*, 6.9 Hz, H-4′) corresponding to the second dimethylchromane ring. According to the HMBC correlation of H-4′ to C-1, C-2 and C-3, this ring was then assigned to be fused at C-1 and C-2. The evidences then suggested that **RD3** was 3,6-dihydroxy-2′,2′-dimethylchromano(5′,6′:2,1)-2′′,2′′-dimethylchromano(5′′,6′′:8,7)xanthone or known as isonormangostin. It was a new naturally occurring but synthetically known compound (Lee, 1981).



Major HMBC correlations of **RD3**

Table 54 The NMR spectral data of **RD3**

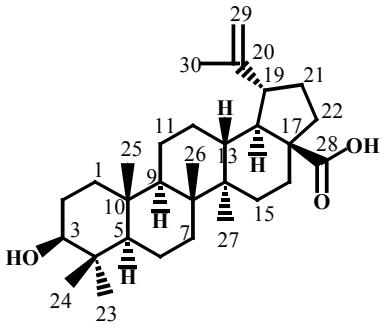
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	155.87 (C)	-	-
2	104.72 (C)	-	-
3	160.11 (C)	-	-
4	93.18 (CH)	6.27 (1H, *s*)	C-2, C-3, C-4a, C-9, C-9a
4a	156.80 (C)	-	-
5	99.80 (CH)	6.65 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	151.86 (C)	-	-
7	138.07 (C)	-	-
8	121.71 (C)	-	-
8a	113.36 (C)	-	-
9	177.89 (C=O)	-	-
9a	106.56 (C)	-	-
10a	150.73 (C)	-	-
2′	75.71 (C)	-	-
3′	31.46 (CH_2)	1.82 (2H, *t*, 6.9)	C-2′, C-4′, 2′-$(CH_3)_2$
4′	16.93 (CH_2)	2.65 (2H, *t*, 6.9)	C-1, C-2, C-3, C-2′, C-3′
2″	74.76 (C)	-	-
3″	32.94 (CH_2)	1.84 (2H, *t*, 6.6)	C-8, C-2″, C-4″, 2″-$(CH_3)_2$

Table 54 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
4′′	22.51 (CH_2)	3.55 (2H, *t*, 6.6)	C-6, C-7, C-8, C-8a, C-2′′, C-3′′
2′-(CH_3)$_2$	26.26 (CH_3)	1.45 (6H, *s*)	C-2′, C-3′, 2′-(CH_3)$_2$
2′′-(CH_3)$_2$	26.34 (CH_3)	1.36 (6H, *s*)	C-2′′, C-3′′, 2′′-(CH_3)$_2$

* Carbon type was deduced from DEPT experiments.

RD4 : 3β-Hydroxylup-20(29)-en-oic acid (betulinic acid)



RD4 was isolated as a white solid, m.p. 282-285 °C. The ^{1}H NMR spectrum (**Table 55**) showed the resonances of an oxymethine proton (δ 3.18, *dd*, *J* = 11.0 and 5.0 Hz, H-3), five methyl groups (δ 0.97, H-27; 0.96, H-23; 0.94, H-26; 0.81, H-25 and 0.75, H-24) and isopropenyl side chain (δ 4.73, *br d*, *J* = 2.5 Hz, H_a-29; 4.77, *br qd*, *J* = 2.5 and 1.5 Hz, H_b-29; 1.69, *s*, H-30). ^{13}C NMR spectral data (**Table 55**) showed the signal of a carbonyl carbon at δ 178.56. ^{1}H NMR and ^{13}C NMR spectral data as well as melting point were in good agreement with those of 3β-hydroxylup-20(29)-en-oic acid or betulinic acid (Macías*, et al*., 1994).

Table 55 The NMR spectral data of **RD4**

Position	**RD4** δ_C (C-Type)*	**betulinic acid** δ_C **	**RD4** δ_H (*multiplicity*, J_{Hz})	**betulinic acid** δ_H (J_{Hz})**
1	38.72 (CH_2)	38.5 (*t*)	H_{ax}: 0.88 (1H, *dd*, 13.0, 4.5)	H_{ax}: 0.90
			H_{eq}: 1.65 (1H, *m*)	H_{eq}: 1.58
2	27.38 (CH_2)	28.2 (*t*)	H_{ax}: 1.59 (1H, *m*)	H_{ax}: 1.82 (8.3)
			H_{eq}: 1.59 (1H, *m*)	H_{eq}: 1.82 (7.5)
3	78.76 (CH)	78.1 (*d*)	3.18 (1H, *dd*, 11.0, 5.0)	3.45 (8.3, 7.5)
4	38.86 (C)	39.4 (*s*)	-	-
5	55.34 (CH)	55.9 (*d*)	0.68 (1H, *d*, 10.0)	0.80
6	18.30 (CH_2)	18.7 (*t*)	H_{ax}: 1.37 (1H, *m*)	H_{ax}: 1.40
			H_{eq}: 1.55 (1H, *m*)	H_{eq}: 1.40
7	34.34 (CH_2)	34.7 (*t*)	1.37 (2H, *m*)	1.36
8	40.73 (C)	41.0 (*s*)	-	-
9	50.53 (CH)	50.9 (*d*)	1.27 (1H, *m*)	1.36
10	37.17 (C)	37.5 (*s*)	-	-
11	20.87 (CH_2)	21.1 (*t*)	H_{ax}: 1.40 (1H, *m*)	H_{ax}: 1.36
			H_{eq}: 1.23 (1H, *m*)	H_{eq}: 1.15
12	25.54 (CH_2)	26.0 (*t*)	H_{ax}: 1.15 (1H, *m*)	H_{ax}: 1.18
			H_{eq}: 1.71 (1H, *m*)	H_{eq}: 1.84
13	38.23 (CH)	39.2 (*d*)	2.28 (1H, *m*)	2.71
14	42.43 (C)	42.8 (*s*)	-	-
15	29.72 (CH_2)	30.2 (*t*)	H_{ax}: 1.52 (1H, *m*)	H_{ax}: 1.73
			H_{eq}: 1.16 (1H, *m*)	H_{eq}: 1.19
16	32.33 (CH_2)	32.8 (*t*)	H_{ax}: 1.50 (1H, *m*)	H_{ax}: 1.53
			H_{eq}: 2.25 (1H, *m*)	H_{eq}: 2.63
17	56.12 (C)	56.6 (*s*)	-	-
18	49.20 (CH)	49.7 (*d*)	1.57 (1H, *m*)	1.70 (8.5)
19	46.90 (CH)	47.7 (*d*)	3.04 (1H, *dt*, 11.0, 5.0)	3.51 (8.5, 4.1)

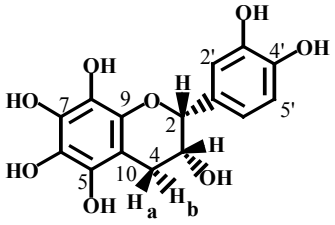
Table 55 (Continued)

Position	**RD4** δ_C (C-Type)*	**betulinic acid** δ_C **	**RD4** δ_H (*multiplicity*, J_{Hz})	**betulinic acid** δ_H (J_{Hz})**
20	150.58 (C)	151.4 (*s*)	-	-
21	30.67 (CH_2)	31.1 (*t*)	H_α: 1.94 (1H, *m*)	H_α: 2.20 (8.5)
			H_β: 1.41 (1H, *m*)	H_β: 1.52 (4.1)
22	37.09 (CH_2)	37.4 (*t*)	H_α: 1.98 (1H, *m*)	H_α: 2.20
			H_β: 1.38 (1H, *m*)	H_β: 1.54
23	28.01 (CH_3)	38.5 (*q*)	0.96 (3H, *s*)	1.20
24	15.44 (CH_3)	16.2 (*q*)	0.75 (3H, *s*)	0.98
25	16.13 (CH_3)	16.3 (*q*)	0.81 (3H, *s*)	0.79
26	16.04 (CH_3)	16.2 (*q*)	0.94 (3H, *s*)	1.03
27	14.67 (CH_3)	14.8 (*q*)	0.97 (3H, *s*)	1.04
28	178.56 (C=O)	179.0 (*s*)	-	-
29	109.36 (CH_2)	110.0 (*t*)	H_a: 4.73 (1H, *br d*, 2.5)	H_a: 4.92 (1.9)
			H_b: 4.77 (1H, *br qd*, 2.5, 1.5)	H_b: 4.74 (1.9)
30	19.38 (CH_3)	19.4 (*q*)	1.69 (3H, *s*)	1.76

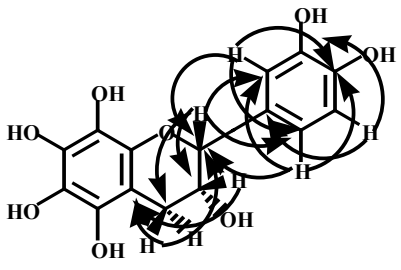
* Carbon type was deduced from DEPT experiments.

** Spectrum in pyridine-d_5.

RD5 : 3,5,6,7,8,3′,4′-Heptahydroxyflavan



RD5 is a light brown crystals, m.p. 240-242 °C. The molecular weight of 290.0771 $[M\text{-}O_2]^+$ corresponded to $C_{15}H_{14}O_8$. The optical rotation was $[\alpha]_D^{29}$: - 72.0 ° (c = 0.012 in CH_3OH). The UV spectrum showed maximum absorptions at 280.6, 228.5 and 212.1 nm. The IR spectrum exhibited strong absorptions of O-H stretching at 3358 cm^{-1} and C=C stretching at 1609 and 1517 cm^{-1}. The ^1H NMR spectrum of **RD5** (**Table 56**) exhibited the signals of aromatic protons H-5′, H-6′ at δ 6.82 (2H) and H-2′ at δ 7.00. The resonances of methine protons H-2, H-3 were shown as *singlets* at δ 4.85 and 4.22 whereas the methylene protons H_a-4 and H_b-4 appeared as *doublet of doublets* at δ 2.87 (J =15.0 and 4.5 Hz) and 2.82 (J =15.0 and 3.0 Hz). The correlations of H-2 to H-3; H-3 to H-2, H-4 and H-4 to H-3 in the COSY experiment confirmed the assignment of protons. The enhancement of the resonances of H-3 and H_a-4 by irradiation of the H-2 signal in the NOE experiment indicated that these three protons were in the *cis*-configuration. The complete HMBC correlations confirmed the assigned structure. **RD5** was then assigned as 3,5,6,7,8,3′,4′-heptahydroxyflavan. This compound is an C-3 epimer of elephantorrhizol (Moyo, *et al*., 1999). **RD5** appears to be novel.



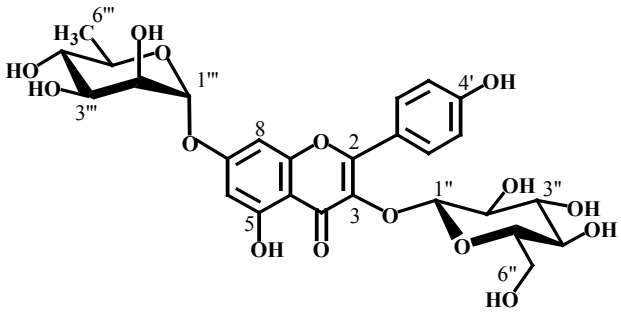
Major HMBC correlations of **RD5**

Table 56 The NMR spectral data of **RD5**

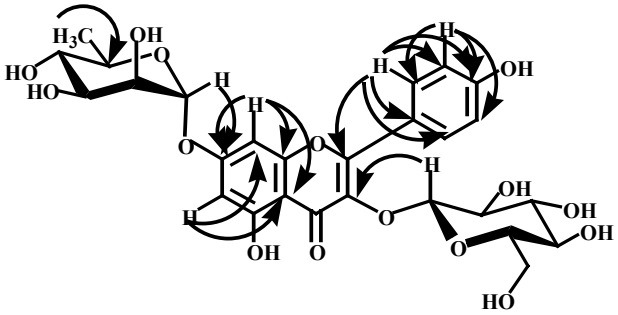
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	COSY	HMBC
2	78.47 (CH)	4.85 (1H, *s*)	H-3	C-3, C-4, C-1′, C-2′, C-6′
3	66.15 (CH)	4.22 (1H, *br s*)	H-2, H-4	C-4a, C-1′
4	27.89 (CH_2)	H_a: 2.87 (1H, *dd*, 15.0, 4.5)	H-3	C-2, C-3, C-4a, C-5
		H_b: 2.82 (1H, *dd*, 15.0, 3.0)	H-3	C-2, C-3, C-4a, C-5
4a	98.76 (C)	-	-	-
5	155.90 (C)	-	-	-
6	130.66 (C)	-	-	-
7	155.78 (C)	-	-	-
8	156.43 (C)	-	-	-
8a	144.52 (C)	-	-	-
1′	130.66 (C)	-	-	-
2′	113.92 (CH)	7.00 (1H, *s*)	H-6′	C-2, C-1′, C-3′, C-4′, C-6′
3′	144.39 (C)	-	-	-
4′	144.52 (C)	-	-	-
5′	114.84 (CH)	6.82 (1H, *br s*)	H-6′	C-1′, C-3′
6′	118.20 (CH)	6.82 (1H, *br s*)	H-5′	C-2, C-1′, C-2′, C-4′

* Carbon type was deduced from DEPT experiments.

RD6 : Kaempferol 3-*O*-β-glucopyranosyl-7-*O*-α-rhamnopyranoside



The glycoside **RD6** was obtained as a yellow solid, m.p. 249-250 °C. The ^{1}H NMR spectrum (**Table 57**) exhibited a *singlet* signal of a chelated hydroxy proton 5-OH at δ 12.25 and the resonances of H-2′, H-6′ and H-3′, H-5′ as an AA′BB′ pattern at δ 7.95 (J = 9.0 Hz, 2H) and 6.85 (J = 9.0 Hz, 2H), respectively. The resonances of *meta* protons H-6 and H-8 were observed at δ 6.37 (*d*, J = 2.1 Hz, 1H) and 6.67 (*d*, J = 2.1 Hz, 1H). It therefore indicated that **RD6** was a derivative of kaemferol. The remaining resonances were the resonances of two sugar moieties which were assigned to be glucose and rhamnose. The resonance of the anomeric proton of glucose (H-1′′) was at δ 5.19 (*d*, J = 7.2 Hz) whereas the resonance of the anomeric proton of rhamnose (H-1′′′) was at δ 5.47 (*br s*). In ^{13}C NMR the signals of the anomeric carbons of glucose and rhamnose were at δ 102.54 and 99.22, respectively. HMBC correlations of H-1′′ to C-3 and H-1′′′ to C-7 indicated the glucose moiety was linked to kaempferol at C-3 and the rhamnose unit was at C-7. The ^{13}C NMR signals (**Table 57**) and DEPT spectra showed resonances of a carbonyl carbon, eight quaternary carbons, fourteen methine carbons, a methylene carbon and a methyl carbon. Thus glycoside **RD6** was kaempferol 3-*O*-β-glucopyranosyl-7-*O*-α-rhamnopyranoside (Mahabusarakam, 1992).



Major HMBC correlations of **RD6**

Table 57 The NMR spectral data of **RD6**

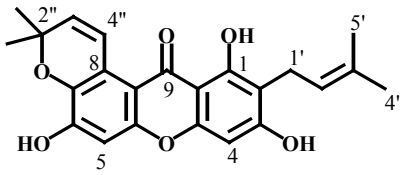
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	158.95 (C)	-	-
3	134.97 (C)	-	-
4	179.00 (C=O)	-	-
4a	107.12 (C)	-	-
5	161.58 (C)	-	-
6	101.04 (CH)	6.37 (1H, *d*, 2.1)	C-4a, C-5, C-8
7	162.83 (C)	-	-
8	96.00 (CH)	6.67 (1H, *d*, 2.1)	C-4a, C-7, C-8a
8a	157.37 (C)	-	-
1′	122.24 (C)	-	-
2′, 6′	132.50 (CH)	7.95 (2H, *d*, 9.0)	C-2, C-2′,6′, C-4′
3′, 5′	116.74 (CH)	6.85 (2H, *d*, 9.0)	C-1′, C-3′,5′, C-4′
4′	160.95 (C)	-	-
Glc-1″	102.54 (CH)	5.19 (1H, *d*, 7.2)	C-3
2″	70.98 (CH)	3.13-3.12 (1H, *m*)	C-3″, C-4″
3″	77.31 (CH)	3.25 (1H, *t*, 5.4)	C-1″, C-4″
4″	78.04 (CH)	3.09 (1H, *t*, 5.4)	C-3″

Table 57 (Continued)

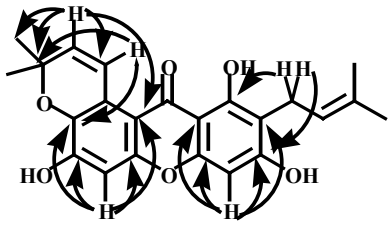
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
5″	71.36 (CH)	3.70-3.69 (1H, *m*)	C-6″
6″	61.98 (CH_2)	3.51 (2H, *m*)	C-4″
Rha-1‴	99.22 (CH)	5.47 (1H, *br s*)	C-7, C-5″
2‴	71.12 (CH)	3.68-3.67 (1H, *m*)	C-3″, C-4″
3‴	75.28 (CH)	3.31 (1H, *m*)	C-4″, C-5″
4‴	73.03 (CH)	3.36-3.35 (1H, *m*)	C-2″, C-4″, C-5″, C-6″
5‴	70.84 (CH)	3.49 (1H, *m*)	C-3″, C-4″
6‴	18.81 (CH_3)	1.06 (3H, *d*, 9.0)	C-4″, C-5″
5-OH	-	12.25 (1H, *s*)	C-4a, C-5, C-6

* Carbon type was deduced from DEPT experiments.

RD7 : 1,3,6-Trihydroxy-2-(3-methyl-2-butenyl)-2″,2″-dimethylchromeno (5″,6″:8,7)xanthone (garcinone B)



RD7 is an orange solid, m.p. 186-187 °C. The ^{1}H NMR spectrum (**Table 58**) demonstrated a *singlet* resonance of a chelated hydroxy group 1-OH (δ 13.69) and two *singlet* signals of H-4 and H-5 (δ 6.31 and 6.8l). Two *singlet* signals of two methyl groups 2″-Me_2 (δ 1.50 and 1.25) and two *doublet* signals of two *geminal* olefinic protons H-3″ and H-4″ (δ 5.82, J = 10.0 Hz and 8.02, J = 10.0 Hz) which were a part of a chromene ring were observed. The deshielded effect on the resonance of H-4 (δ 8.02) suggested that the chromene ring attached to the xanthone nucleus nearby the carbonyl group. The *singlet* of two methyl groups (δ 1.84, H-5′ and 1.77, H-4′), a methylene protons (δ 3.45, H-1′) and an olefinic methine proton (δ 5.29, H-2′) were typical signals of a prenyl moiety. HMBC correlation of H-1′ to C-1 and C-3 indicated that the prenyl side chain was at C-2. The assignment of H-4 was confirmed by the correlation of H-4 to C-2, C-3, C-4a and C-9a whereas the position of H-5 was proved by the correlation of H-5 to C-6, C-7, C-9 and C-10a. The ^{13}C NMR spectral data (**Table 58**) indicated a carbonyl carbon, four methyl carbons, a methylene carbon, five methine carbons and twelve quaternary carbons. **RD7** was then identified as 1,3,6-trihydroxy-2-(3-methyl-2-butenyl)-2″,2″-dimethylchromeno(5″,6″:8,7)xanthone. The proposed structure was identical to garcinone B (Sen, *et al*., 1982).



Major HMBC correlations of **RD7**

Table 58 The NMR spectral data of **RD7**

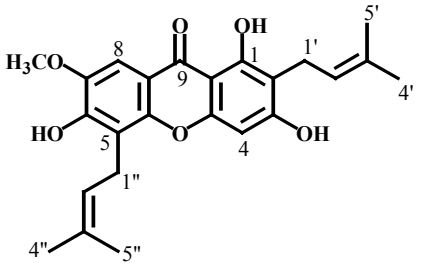
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.41 (C)	-	-
2	102.29 (C)	-	-
3	161.80 (C)	-	-
4	93.36 (CH)	6.31 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	155.80 (C)	-	-
5	102.29 (CH)	6.81 (1H, *s*)	C-6, C-7, C-9, C-10a
6	151.00 (C)	-	-
7	136.50 (C)	-	-
8	125.50 (C)	-	-
8a	119.72 (C)	-	-
9	182.42 (C=O)	-	-
9a	108.50 (C)	-	-
10a	153.80 (C)	-	-
1′	21.41 (CH_2)	3.45 (2H, *d*, 7.0)	C-1, C-3, C-2′, C-3′
2′	121.54 (CH)	5.29 (1H, *br t*, 7.0)	C-1′, C-4′, C-5′
3′	134.00 (C)	-	-
4′	25.83 (CH_3)	1.77 (3H, *s*)	C-2′, C-5′
5′	17.91 (CH_3)	1.84 (3H, *s*)	C-2′, C-4′

Table 58 (Continued)

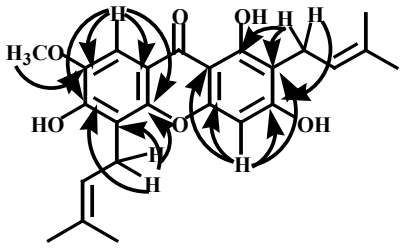
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2′′	77.20 (C)	-	-
3′′	132.24 (CH)	5.82 (1H, *d*, 10.0)	C-8a, C-2′′, C-4′′, C-5′′
4′′	120.99 (CH)	8.02 (1H, *d*, 10.0)	C-7, C-2′′
2′′-$(CH_3)_2$	27.30 (CH_3)	1.50 (3H, *s*)	C-2′′, C-3′′, 2′′-$(CH_3)_2$
	31.92 (CH_3)	1.25 (3H, *s*)	C-2′′, C-3′′, 2′′-$(CH_3)_2$
1-OH	-	13.69 (1H, *s*)	-

* Carbon type was deduced from DEPT experiments.

RD8 : 1,3,6-Trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl)xanthone



RD8 is a bright yellow solid, m.p. 223-224 °C. The ^{1}H NMR spectrum (**Table 59**) exhibited the resonances of hydroxy protons 1-OH at δ 13.22 (*s*), 3-OH at δ 8.99 (*s*) and 6-OH at δ 7.11 (*s*), aromatic protons H-8 at δ 7.44 (*s*) and H-4 at δ 6.37 (*s*) and 7-OCH_3 at δ 3.96 (*s*). The NOE effect of H-8 (δ 7.44) to the methoxy resonance suggested the OCH_3 at C-7. The signals of two prenyl groups were displayed as followed: two *broad triplets* of olefinic methine protons H-2′ (δ 5.26) and H-2′′ (δ 5.25), two *doublets* of benzylic methylene protons H-1′ (δ 3.38) and H-1′′ (δ 3.56) and four *singlets* of methyl groups H-4′ (δ 1.69), H-5′ (δ 1.80), H-4′′ (δ 1.65) and H-5′′ (δ 1.85). The HMBC correlations of H-1′ to C-1, C-2, C-3 and H-1′′ to C-5, C-6, C-10a indicated that the prenyl side chains were at C-2 and C-5. The assignment of H-4 was confirmed by the correlation of H-4 to C-2, C-3, C-4a, C-9 and C-9a whereas the signal of H-8 was proved by the correlation of H-8 to C-6, C-7, C-8a, C-9 and C-10a. These assignment indicated that **RD8** was 1,3,6-trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl)xanthone. The structure of **RD8** and its melting point were identical to the previously isolated compound from *Garcinia cowa* (Na Pattalung, *et al*., 1994).



Major HMBC correlations of **RD8**

Table 59 The NMR spectral data of **RD8**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.00 (C)	-	-
2	109.65 (C)	-	-
3	160.12 (C)	-	-
4	93.55 (CH)	6.37 (1H, *s*)	C-2, C-3, C-4a, C-9, C-9a
4a	155.86 (C)	-	-
5	115.30 (C)	-	-
6	150.05 (C)	-	-
7	144.05 (C)	-	-
8	101.99 (CH)	7.44 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
8a	112.94 (C)	-	-
9	180.21 (C=O)	-	-
9a	101.99 (C)	-	-
10a	149.50 (C)	-	-
1′	21.36 (CH_2)	3.38 (2H, *d*, 6.9)	C-1, C-2, C-3, C-2′, C-3′
2′	121.90 (CH)	5.26 (1H, *br t*, 7.2)	C-1′, C-4′, C-5′
3′	133.60 (C)	-	-
4′	25.70 (CH_3)	1.69 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.83 (CH_3)	1.80 (3H, *s*)	C-2′, C-3′, C-4′

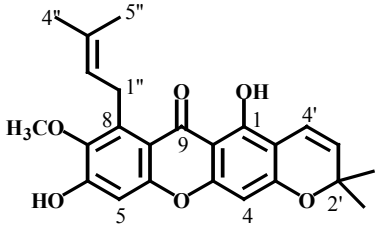
Table 59 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1″	22.34 (CH_2)	3.56 (2H, *d*, 7.2)	C-5, C-6, C-10a, C-2″, C-3″
2″	121.03 (CH)	5.25 (1H, *br t*, 7.2)	C-1″, C-4″, C-5″
3″	132.57 (C)	-	-
4″	25.75 (CH_3)	1.65 (3H, *s*)	C-2″, C-3″, C-5″
5″	17.90 (CH_3)	1.85 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.22 (1H, *s*)	C-1, C-2, C-9a
3-OH	-	8.99 (1H, *s*)[a]	-
6-OH	-	7.11 (1H, *s*)[a]	-
7-OCH_3	56.33 (CH_3)	3.96 (3H, *s*)	C-7

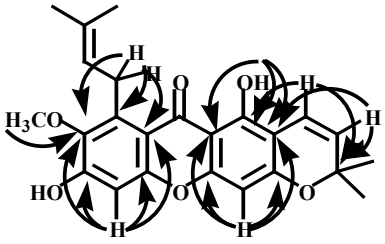
* Carbon type was deduced from DEPT experiments.

[a] Assignment maybe interchangeable.

RD9 : 1,6-Dihydroxy-7-methoxy-8-(3-methyl-2-butenyl)-2′,2′-dimethylchromeno (5′,6′:2,3)xanthone



RD9 was isolated as a yellow solid, m.p. 159-160 °C. The ^{1}H NMR spectrum (**Table 60**) showed four *singlet* signals of 1-OH (δ 13.60), H-5 (δ 6.75), H-4 (δ 6.15) and 7-OCH_3 (δ 3.71). The ^{1}H NMR spectrum showed characteristic signals of a dimethylchromene ring, of which the signal of *gem*-dimethyl protons resonated as a *singlet* at δ 1.37 and two *doublet* signals of two olefinic protons (H-4′ and H-3′) were at δ 6.64 and 5.48. The ^{3}J correlations of H-4′ to C-1 and H-3′ to C-2 indicated that the dimethylchromene ring was fused to C-2 and C-3. In addition, the signals of two methyl groups at δ 1.60 (H-4′′) and 1.74 (H-5′′), methylene protons at δ 3.99 (H-1′′) and an olefinic methine proton at δ 5.17 (H-2′′) which were characteristic signals of a prenyl moiety were present in the spectrum. The chemical shift of the methylene protons H-1′′ (δ 3.99) implied that H-1′′ was deshielded by the carbonyl group, accordingly the prenyl side chain was proposed to be at C-8, a *peri* position to the carbonyl group. The HMBC correlation of H-1′′ to C-7, C-8 and C-8a confirmed the location of the prenyl unit at C-8. According to the assignment and HMBC correlations, 1,6-dihydroxy-7-methoxy-8-(3-methyl-2-butenyl)-2′,2′-dimethylchromeno(5′,6′:2,3)xanthone was the structure of **RD9** (Sen, *et al*., 1980).



Major HMBC correlations of **RD9**

Table 60 The NMR spectral data of **RD9**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.87 (C)	-	-
2	104.50 (C)	-	-
3	157.92 (C)	-	-
4	94.16 (CH)	6.15 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	156.27 (C)	-	-
5	101.69 (CH)	6.75 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	154.61 (C)	-	-
7	142.65 (C)	-	-
8	136.99 (C)	-	-
8a	112.17 (C)	-	-
9	182.00 (C=O)	-	-
9a	103.73 (C)	-	-
10a	155.74 (C)	-	-
2′	77.95 (C)	-	-
3′	127.16 (CH)	5.48 (1H, *d*, 10.2)	C-2, C-2′
4′	115.71 (CH)	6.64 (1H, *d*, 10.2)	C-1, C-2′
1″	26.55 (CH_2)	3.99 (2H, *d*, 6.3)	C-7, C-8, C-8a, C-2″, C-3″
2″	123.11 (CH)	5.17 (1H, *br t*)	C-1″, C-4″, C-5″

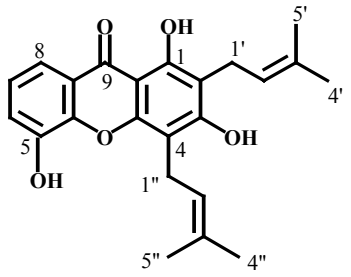
Table 60 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
3′′	132.22 (C)	-	-
4′′	25.84 (CH_3)	1.60 (3H, *s*)	C-2′′, C-3′′, C-5′′
5′′	18.23 (CH_3)	1.74 (3H, *s*)	C-2′′, C-3′′, C-4′′
2′-$(CH_3)_2$	28.30 (CH_3)	1.37 (6H, *s*)	C-2′, C-3′, C-4′, 2′-$(CH_3)_2$
1-OH	-	13.60 (1H, *s*)	C-1, C-2, C-9a
7-OCH_3	62.05 (CH_3)	3.71 (3H, *s*)	C-7

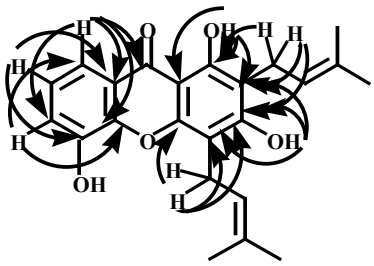
* Carbon type was deduced from DEPT experiments.

RD10 : 1,3,5-Trihydroxy-2,4-bis(3-methyl-2-butenyl)xanthone

(8-desoxygartanin)



RD10 is a yellow solid, m.p. 167-168 °C. The ^{1}H NMR spectral data (**Table 61**) demonstrated the resonances of a chelated hydroxy group 1-OH (δ 13.18, *s*), 3-OH (δ 6.53, *s*) and 5-OH (δ 5.74, *br s*). Two *doublet of doublet* signals at δ 7.76 (J = 7.8 and 1.8 Hz) and 7.27 (J = 7.8 and 1.8 Hz), and a *triplet* signal at δ 7.23 (J = 7.8 Hz) implied the presence of H-8, H-6 and H-7, respectively. The deshielded effect on resonance of H-8 (δ 7.76) suggested the location of H-8 nearby the carbonyl group. Two *broad triplet* signals at δ 5.29 (H-2′) and 5.26 (H-2′′), two *doublet* signals at δ 3.48 (H-1′) and 3.54 (H-1′′) and three *singlet* signals at δ 1.86 (H-5′ and H-5′′), 1.79 (H-4′) and 1.75 (H-4′′) were the resonances of two prenyl side chains. HMBC correlations of H-1′ to C-1, C-2, C-3 and H-1′′ to C-3, C-4, C-4a indicated that the prenyl side chains were at C-2 and C-4. The assignment of 3-OH was confirmed by the correlation of 3-OH to C-2, C-3 and C-4. The ^{13}C NMR spectral data and HMBC correlations corresponded to 1,3,5-trihydroxy-2,4-bis(3-methyl-2-butenyl)xanthone or 8-desoxygartanin (Govindachari, *et al*., 1971).



Major HMBC correlations of **RD10**

Table 61 The NMR spectral data of **RD10**

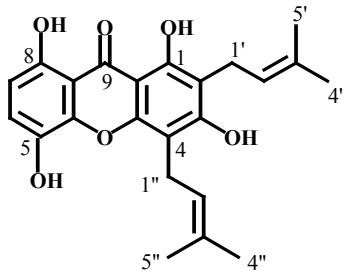
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	158.68 (C)	-	-
2	109.13 (C)	-	-
3	160.91 (C)	-	-
4	105.44 (C)	-	-
4a	152.40 (C)	-	-
5	144.42 (C)	-	-
6	119.77 (CH)	7.27 (1H, *dd*, 7.8, 1.8)	C-8, C-10a
7	123.83 (CH)	7.23 (1H, *t*, 7.8)	C-5, C-8a
8	116.91 (CH)	7.76 (1H, *dd*, 7.8, 1.8)	C-6, C-8a, C-9, C-10a
8a	120.89 (C)	-	-
9	181.11 (C=O)	-	-
9a	103.32 (C)	-	-
10a	144.40 (C)	-	-
1′	22.09 (CH_2)	3.48 (2H, *d*, 7.2)	C-1, C-2, C-3, C-2′, C-3′
2′	121.19 (CH)	5.29 (1H, *br t*, 7.2)	C-1′
3′	136.18 (C)	-	-
4′	25.66 (CH_3)	1.79 (3H, *s*)	C-2′, C-3′, C-5′

Table 61 (Continued)

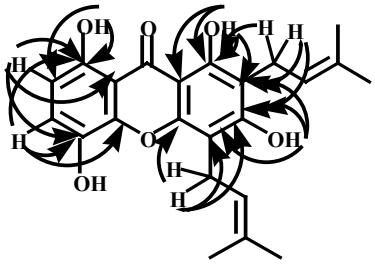
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
5′	17.95 (CH_3)	1.86 (3H, *s*)	C-2′, C-3′, C-4′
1″	21.65 (CH_2)	3.54 (2H, *d*, 6.6)	C-3, C-4, C-4a, C-2″, C-3″
2″	122.23 (CH)	5.26 (1H, *br t*, 7.2)	C-4, C-1″
3″	133.53 (C)	-	-
4″	25.87 (CH_3)	1.75 (3H, *s*)	C-2″, C-3″, C-5″
5″	17.95 (CH_3)	1.86 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.18 (1H, *s*)	C-1, C-2, C-9a
3-OH	-	6.53 (1H, *s*)	C-2, C-3, C-4
5-OH	-	5.74 (1H, *br s*)	-

* Carbon type was deduced from DEPT experiments.

RD11 : 1,3,5,8-Tetrahydroxy-2,4-bis(3-methyl-2-butenyl)xanthone (gartanin)



RD11 is a yellow solid, m.p. 165-167 °C. The ^{1}H NMR spectral data (**Table 62**) demonstrated the resonances of two chelated hydroxy groups 1-OH (δ 12.36, *s*), 8-OH (δ 11.28, *s*) and non chelated hydroxy group 3-OH (δ 6.62, *s*). Two *doublet* signals at δ 7.25 (J = 8.7 Hz) and 6.69 (J = 8.7 Hz) implied the presence of H-6 and H-7, respectively. Two *broad triplet* signals at δ 5.29 (H-2′) and 5.26 (H-2′′), two *doublet* signals at δ 3.49 (H-1′) and 3.55 (H-1′′) and three *singlet* signals at δ 1.88 (H-5′ and H-5′′), 1.81 (H-4′) and 1.78 (H-4′′) were the resonances of two prenyl side chains. HMBC correlations of H-1′ to C-1, C-2, C-3 and H-1′′ to C-3, C-4, C-4a indicated that the prenyl side chains were at C-2 and C-4. The assignment of 3-OH was confirmed by the correlation of 3-OH to C-2, C-3 and C-4. The ^{13}C NMR spectral data and HMBC correlations corresponded to 1,3,5,8-tetrahydroxy-2,4-bis(3-methyl-2-butenyl)xanthone or gartanin (Govindachari, *et al*., 1971).



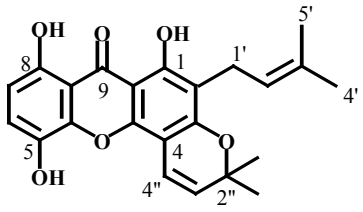
Major HMBC correlations of **RD11**

Table 62 The NMR spectral data of **RD11**

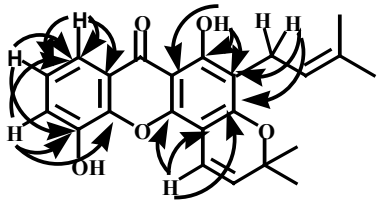
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	158.16 (C)	-	-
2	109.51 (C)	-	-
3	161.65 (C)	-	-
4	105.81 (C)	-	-
4a	152.50 (C)	-	-
5	136.31 (C)	-	-
6	122.86 (CH)	7.25 (1H, *d*, 8.7)	C-5, C-8, C-10a
7	109.78 (CH)	6.69 (1H, *d*, 8.7)	C-5, C-8, C-8a
8	153.85 (C)	-	-
8a	107.17 (C)	-	-
9	184.73 (C=O)	-	-
9a	102.23 (C)	-	-
10a	142.84 (C)	-	-
1′	21.60 (CH_2)	3.49 (2H, *d*, 6.9)	C-1, C-2, C-3, C-2′, C-3′
2′	120.99 (CH)	5.29 (1H, *br t*, 6.9)	C-4′, C-5′
3′	135.72 (C)	-	-
4′	25.89 (CH_3)	1.81 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.98 (CH_3)	1.88 (3H, *s*)	C-2′, C-3′, C-4′
1″	22.01 (CH_2)	3.55 (2H, *d*, 6.9)	C-3, C-4, C-4a, C-2″, C-3″
2″	121.84 (CH)	5.26 (1H, *br t*, 6.9)	C-4″, C-5″
3″	133.95 (C)	-	-
4″	25.70 (CH_3)	1.78 (3H, *s*)	C-2″, C-3″, C-5″
5″	17.98 (CH_3)	1.88 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	12.36 (1H, *s*)	C-1, C-2, C-9a
3-OH	-	6.62 (1H, *s*)	C-2, C-3, C-4
8-OH	-	11.28 (1H, *s*)	C-7, C-8

* Carbon type was deduced from DEPT experiments.

RD12 : 1,5,8-Trihydroxy-2-(3-methyl-2-butenyl)-2,2-dimethylchromeno (5″,6″:4,3)xanthone (morusignin J)



RD12 was isolated as a yellow solid with m.p. 183-185 °C. The ^{1}H NMR spectrum (**Table 63**) consisted of the signals of two chelated hydroxy protons 1-OH at δ 12.38, 8-OH at δ 11.35 and *ortho* protons H-6 and H-7 at δ 7.26 (*d*, *J* = 9.0 Hz) and 6.69 (*d*, *J* = 9.0 Hz). The resonances of prenylated unit were shown at δ 3.35 (2H, *d*, *J* = 7.5 Hz, H-1′), 5.24 (1H, *br t*, *J* = 8.0 Hz, H-2′), 1.70 (3H, *s*, H-4′) and 1.82 (3H, *s*, H-5′). The resonances of methyl groups and methine proton associated to the characteristic signals of a chromene ring appeared at δ 1.50 (6H, *s*, 2″-Me_2), 5.66 (1H, *d*, *J* = 10.0 Hz, H-3″) and 6.77 (1H, *d*, *J* = 10.0 Hz, H-4″). The ^{3}J correlations of H-6 to C-5, C-8, C-10a and H-7 to C-5, C-8, C-8a as well as 8-OH to C-7, C-8, C-8a supported the position of *ortho* H-6 and H-7. The HMBC correlation of H-4″ to C-3, C-4, C-4a confirmed the location of chromene ring. **RD12** is 1,5,8-trihydroxy-2-(3-methyl-2-butenyl)-2,2-dimethylchromeno(5″,6″:4,3)xanthone or known as morusignin J (Hano, *et al.*, 1993).



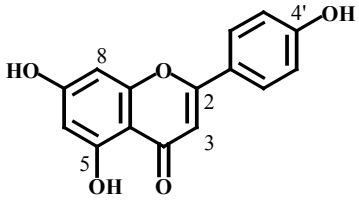
Major HMBC correlations of **RD12**

Table 63 The NMR spectral data of **RD12**

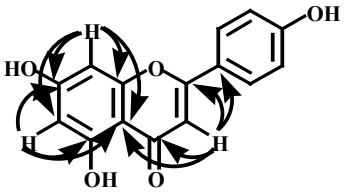
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.29 (C)	-	-
2	112.55 (C)	-	-
3	159.97 (C)	-	-
4	102.06 (C)	-	-
4a	149.36 (C)	-	-
5	135.54 (C)	-	-
6	123.24 (CH)	7.26 (1H, *d*, 9.0)	C-5, C-8, C-10a
7	110.05 (CH)	6.69 (1H, *d*, 9.0)	C-5, C-8, C-8a
8	154.08 (C)	-	-
8a	107.34 (C)	-	-
9	184.43 (C=O)	-	-
9a	100.87 (C)	-	-
10a	142.70 (C)	-	-
1′	21.19 (CH_2)	3.35 (2H, *d*, 7.5)	C-2, C-3, C-2′, C-3′
2′	121.67 (CH)	5.24 (1H, *br t*, 8.0)	C-1′, C-4′, C-5′
3′	131.87 (C)	-	-
4′	25.82 (CH_3)	1.70 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.92 (CH_3)	1.82 (3H, *s*)	C-2′, C-3′, C-4′
2″	78.39 (C)	-	-
3″	127.65 (CH)	5.66 (1H, *d*, 10.0)	C-4, C-2″
4″	114.78 (CH)	6.77 (1H, *d*, 10.0)	C-3, C-4, C-4a, C-2″
1-OH	-	12.38 (1H, *s*)	C-1, C-2, C-9a
8-OH	-	11.35 (1H, *s*)	C-7, C-8, C-8a
2″-$(CH_3)_2$	28.25 (CH_3)	1.50 (6H, *s*)	C-2″, C-3″, 2″-$(CH_3)_2$

* Carbon type was deduced from DEPT experiments.

RD13 : 5,7,4′-Trihydroxyflavone (apigenin)



RD13 was a yellow solid, melting at 168-170 °C. The ^{1}H NMR spectrum (**Table 64**) indicated a flavone nucleus by the appearance of *singlet* signal of an α-methine proton (H-3) at δ 6.41. The signal for a chelated hydroxy group 5-OH (δ 12.75, *s*) and the signals of AA′BB′ system of H-2′, H-6′ (δ 7.66, *d*, *J* = 8.5 Hz) and H-3′, H-5′ (δ 6.87, *d*, *J* = 8.5 Hz) were displayed in the spectrum. The resonances of *meta* coupling of H-6 and H-8 were detected at δ 6.17 (*d*, *J* = 2.1 Hz) and 6.35 (*d*, *J* = 2.1 Hz), respectively. The ^{13}C NMR signals from DEPT spectra showed resonances of a carbonyl carbon, seven quaternary carbons and five methine carbons. The proof of vinylic proton H-3 was obtained from the results of ^{3}J cross peaks of H-3 to C-4a and C-1′ (δ 104.13 and 121.62) and ^{2}J cross peaks of H-3 to C-2 and C-4 (δ 163.91 and 102.93). Therefore **RD13** was characterized as 5,7,4′-trihydroxyflavone which was known as apigenin (Berghöfer and Hölzl, 1987).



Major HMBC correlations of **RD13**

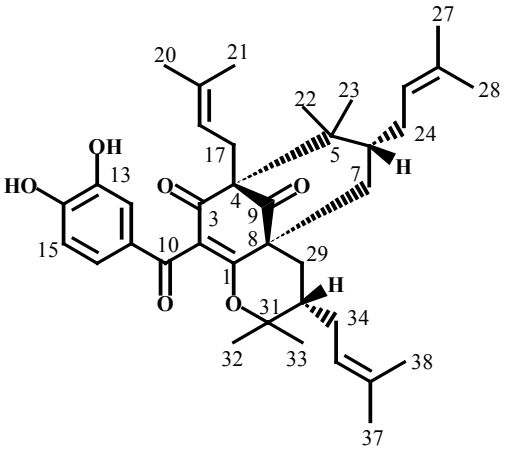
Table 64 The NMR spectral data of **RD13**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	163.91 (C)	-	-
3	102.93 (CH)	6.41 (1H, *s*)	C-2, C-4, C-4a, C-1′
4	181.94 (C=O)	-	-
4a	104.13 (C)	-	-
5	161.64 (C)	-	-
6	99.05 (CH)	6.17 (1H, *d*, 2.1)	C-4a, C-5, C-8
7	157.45 (C)	-	-
8	93.87 (CH)	6.35 (1H, *d*, 2.1)	C-4, C-4a, C-6, C-7, C-8a
8a	163.93 (C)	-	-
1′	121.62 (C)	-	-
2′, 6′	115.88 (CH)	7.66 (2H, *d*, 8.5)	C-2, C-1′, C-3′,5′, C-4′
3′, 5′	127.76 (CH)	6.87 (2H, *d*, 8.5)	C-2′,6′, C-4′
4′	160.86 (C)	-	-
5-OH	-	12.75 (1H, *s*)	-
7-OH	-	10.14 (1H, *s*)[a]	-
4′-OH	-	9.75 (1H, *s*)[a]	-

* Carbon type was deduced from DEPT experiments.

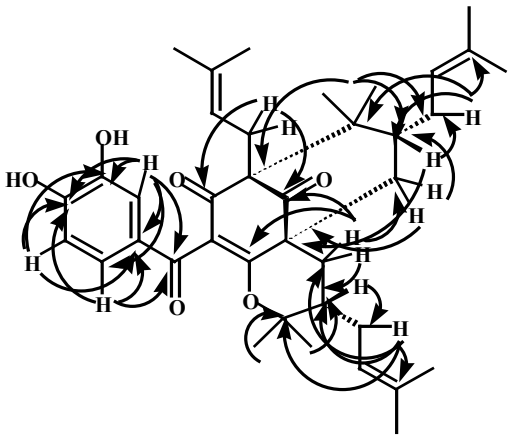
[a] Assignment maybe interchangeable.

RD14 : (4*R*,6*R*,8*S*,30*S*)-2-(3,4-dihydroxybenzoyl)-5,5,31,31-tetramethyl-4,6,30-tris(3-methyl-2-butenyl)oxatricyclo[7.3.1.0]tridec-1-ene-3,9-dione (cambogin)



RD14 is a yellow solid, m.p. 238-240 °C. The optical rotation was $[\alpha]_D^{29}$ – 198.0 ° (c = 0.03 in CH_3OH). The ^1H NMR spectrum (**Table 65**) showed the resonances of aromatic protons H-15 (δ 6.72, *d*, *J* = 7.7 Hz), H-16 (δ 6.93, *dd*, *J* = 7.7, 2.2 Hz) and H-12 (δ 7.13, *d*, *J* = 2.2 Hz) which refered to the presence of 3,4-dihydroxybenzoyl group. The presence of three prenyl groups was observed. The signals of a prenyl group resonated at δ 4.77 (H-18), 2.49 and 2.31 (H-17), 1.51 (H-20), 1.49 (H-21) accordingly HMBC correlation of H-17 to C-3, C-9, was link to quaternary carbon C-4. The signals of two prenyl groups resonated at δ 5.16 (H-25), 2.56 and 1.98 (H-24), 1.72 (H-27), 1.57 (H-28) and δ 4.90 (H-35), 2.49 (H-34), 1.64 (H-37), 1.59 (H-38). These two groups were then connected to methine carbons C-6 and C-30, respectively, indicated by HMBC correlations of H-24 to C-5, C-7 and H-34 to C-29, C-30, C-31. The methine protons H-6 and H-30 resonated at δ 1.33 (*m*) and 1.43 (*m*). Two methyl groups on a saturated carbon C-5 were observed at δ 0.82 (*s*, H-22), 1.18 (*s*, H-23) and two methyl groups on a saturated carbon C-31 at δ 1.04 (*s*, H-32), 0.88 (*s*, H-33). Two *doublet of doublet* signals at δ 2.85 (1H, *J* = 13.3 and 3.8 Hz)

and 0.99 (1H, J = 13.3 and 1.5 Hz) were assigned for methylene protons H-7. The *multiplet* and *doublet* signals at δ 1.98 and 2.13 were suggested for resonated by methylene proton H-29. The fully HMBC data confirmed the assigned structure. **RD14** was then identified as (4*R*,6*R*,8*S*,30*S*)-2-(3,4-dihydroxybenzoyl)-5,5,31,31-tetramethyl-4,6,30-tris(3-methyl-2-butenyl)oxatricyclo[7.3.1.0]tridec-1-ene-3,9-dione which agreed with the structure of cambogin (Rama Rao, *et al*., 1980).



Major HMBC correlations of **RD14**

Table 65 The NMR spectral data of **RD14**

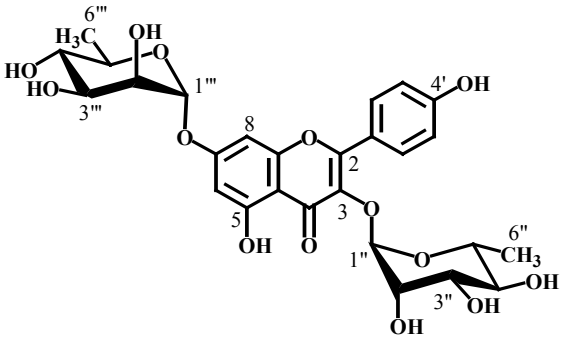
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	170.64 (C)	-	-
2	125.01 (C)	-	-
3	193.51 (C=O)	-	-
4	86.53 (C)	-	-
5	45.78 (C)	-	-
6	42.41 (CH)	1.33 (1H, *m*)	C-23
7	27.73 (CH_2)	2.85 (1H, *dd*, 13.3, 3.8)	C-1, C-4, C-6, C-8, C-9, C-29
		0.99 (1H, *dd*, 13.3, 1.5)	C-4, C-6, C-8, C-9, C-29
8	50.83 (C)	-	-
9	206.68 (C=O)	-	-
10	191.61 (C=O)	-	-
11	129.04 (C)	-	-
12	115.40 (CH)	7.13 (1H, *d*, 2.2)	C-10, C-11, C-13, C-14, C-16
13	145.38 (C)	-	-
14	151.05 (C)	-	-
15	115.17 (CH)	6.72 (1H, *d*, 7.7)	C-11, C-13, C-14
16	122.12 (CH)	6.93 (1H, *dd*, 7.7, 2.2)	C-10, C-12, C-14
17	25.21 (CH_2)	2.49 (1H, *m*)	C-9, C-18, C-19
		2.31 (1H, *dd*, 13.3, 3.8)	C-3, C-18, C-19
18	120.71 (CH)	4.77 (1H, *br t*, 6.6)	C-17, C-20, C-21
19	132.73 (C)	-	-
20	25.92 (CH_3)	1.51 (3H, *s*)	C-18, C-19, C-21
21	18.12 (CH_3)	1.49 (3H, *s*)	C-18, C-19, C-20
22	28.51 (CH_3)	0.82 (3H, *s*)	C-4, C-6, C-23
23	21.17 (CH_3)	1.18 (3H, *s*)	C-4, C-5, C-6, C-22, C-24
24	28.97 (CH_2)	2.56 (1H, *m*)	C-26
		1.98 (1H, *m*)	C-5, C-7

Table 65 (Continued)

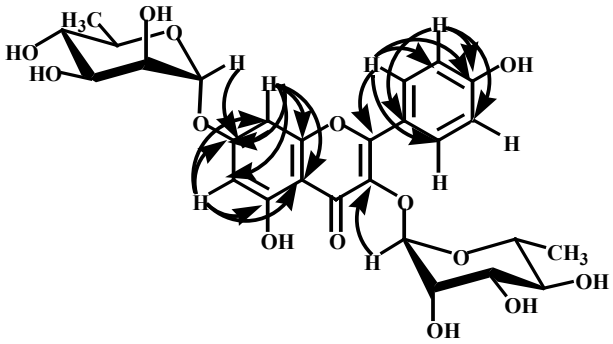
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
25	122.12 (CH)	5.16 (1H, *br t*, 6.6)	C-6, C-24, C-27, C-28
26	132.89 (C)	-	-
27	25.18 (CH_3)	1.72 (3H, *s*)	C-25, C-26, C-28
28	17.98 (CH_3)	1.57 (3H, *s*)	C-25, C-26, C-27
29	38.44 (CH_2)	2.13 (1H, *d*, 13.3)	C-1, C-7, C-8, C-9, C-30
		1.98 (1H, *m*)	C-1, C-7, C-8, C-9, C-30
30	45.38 (CH)	1.43 (1H, *m*)	C-8, C-29, C-31, C-34
31	67.73 (C)	-	-
32	22.22 (CH_3)	1.04 (3H, *s*)	C-30, C-31, C-33
33	26.35 (CH_3)	0.88 (3H, *s*)	C-30, C-31, C-32
34	25.21 (CH_2)	2.49 (2H, *m*)	C-29, C-30, C-31, C-36
35	125.34 (CH)	4.90 (1H, *br t*, 6.6)	C-34, C-37, C-38
36	132.17 (C)	-	-
37	25.89 (CH_3)	1.64 (3H, *s*)	C-35, C-36, C-38
38	18.09 (CH_3)	1.59 (3H, *s*)	C-35, C-36, C-37

* Carbon type was deduced from DEPT experiments.

RD15 : Kaempferol 3,7-di-*O*-α-rhamnopyranoside



RD15 was isolated as a yellow solid, m.p. 232-233 °C. The ^{1}H NMR spectrum (**Table 66**) indicated that **RD15** was a kaemferol glycoside. The aglycone moiety showed the pattern of *para* disubstitution of which H-2′, H-6′ and H-3′, H-5′ resonated as *doublets* at δ 7.77 and 6.95 (J = 8.2 Hz). The *meta* coupling of H-6 and H-8 were suggested from the two *broad singlets* resonances at δ 6.67 and 6.40. A *singlet* signal at δ 12.45 indicated that the hydroxy group (5-OH) was *peri* to a carbonyl group (C-4). Two *broad singlet* signals at δ 5.43 and 5.52 were the resonance of anomeric protons H-1′′ and H-1′′′, respectively. Two *doublets* with three protons each at δ 0.90 and 1.23 were the resonances of two methyl groups H-6′′ and H-6′′′, respectively. The resonances of sugar moieties corresponded to two molecules of rhamnose. The HMBC experiments revealed the correlations between the H-1′′ (δ 5.43) to C-3 (δ 134.93) and H-1′′′ (δ 5.52) to C-7 (δ 162.11), suggested that the C-1′′ and C-1′′′ of rhamnosyl units were linked to the 3-hydroxy and 7-hydroxy of the aglycone. Then it was assigned to be kaempferol 3,7-di-*O*-α-rhamnopyranoside. This compound has been isolated from *Measa ramentacea* (Mahabusarakam, 1992).



Major HMBC correlations of **RD15**

Table 66 The NMR spectral data of **RD15**

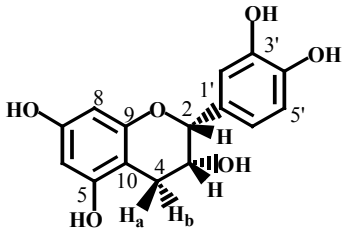
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	COSY	HMBC
2	158.12 (C)	-	-	-
3	134.93 (C)	-	-	-
4	178.36 (C=O)	-	-	-
4a	106.37 (C)	-	-	-
5	156.57 (C)	-	-	-
6	94.52 (CH)	6.67 (1H, *br s*)	H-8	C-4a, C-5, C-7, C-8
7	162.11 (C)	-	-	-
8	99.63 (CH)	6.40 (1H, *br s*)	H-6	C-4a, C-6, C-7, C-8a
8a	161.60 (C)	-	-	-
1′	120.83 (C)	-	-	-
2′, 6′	130.77 (CH)	7.77 (2H, *d*, 8.2)	H-3′,5′	C-2, C-2′,6′, C-3′,5′, C-4′
3′, 5′	115.76 (CH)	6.95 (2H, *d*, 8.2)	H-2′,6′	C-1′, C-3′,5′, C-4′
4′	160.43 (C)	-	-	-
Rha-1″	101.93 (CH)	5.43 (1H, *br s*)	H-2″	C-3
2″	70.20 (CH)	4.14 (1H, *br s*)	H-1″	C-1″, C-3″
3″	70.12 (CH)	3.90-3.20 (1H, *m*)	-	C-1″, C-4″, C-5″

Table 66 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	COSY	HMBC
4″	71.84 (CH)	3.90-3.20 (1H, *m*)	-	C-2″, C-5″
5″	70.77 (CH)	3.90-3.20 (1H, *m*)	-	C-4″, C-6″
6″	17.58 (CH_3)	0.90 (3H, *d*, 6.0)	-	C-5″
Rha-1‴	98.70 (CH)	5.52 (1H, *br s*)	H-2‴	C-7, C-3‴
2‴	70.10 (CH)	3.99 (1H, *br s*)	H-1‴	C-1‴, C-4‴
3‴	70.99 (CH)	3.90-3.20 (1H, *m*)	-	C-2‴, C-4‴
4‴	72.24 (CH)	3.90-3.20 (1H, *m*)	-	C-2‴, C-6‴
5‴	70.39 (CH)	3.90-3.20 (1H, *m*)	-	C-4‴, C-6‴
6‴	18.04 (CH_3)	1.23 (3H, *d*, 5.4)	-	C-5‴
5-OH	-	12.45 (1H, *s*)	-	-

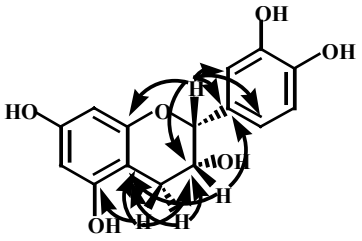
* Carbon type was deduced from DEPT experiments.

RD16 : 3,5,7,3′,4′-Pentahydroxyflavan ((-) epicatechin)

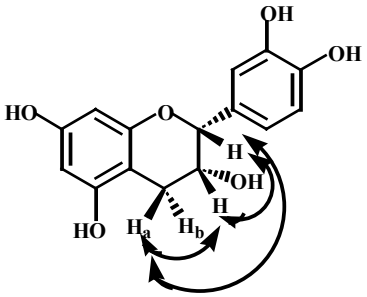


RD16 was isolated as light brown crystals, m.p. 235-236 °C. The optical rotation was $[\alpha]_D^{29}$ – 72.0 ° (c = 0.038 in CH_3OH). The ^1H NMR spectrum (**Table 67**) suggested the presence of five aromatic protons, two methine protons, one methylene proton and five hydroxy groups. Two *doublet* resonances at δ 5.99 and 5.87 with the coupling constant of 1.8 Hz corresponded to the resonances of *meta* protons H-6 and H-8, respectively. A *doublet* at δ 6.99 (J = 1.8 Hz), a *doublet of doublet* at δ 6.74 (J = 7.2 and 1.8 Hz) and a *doublet* at δ 6.77 (J = 7.2 Hz) were assigned for the resonances of H-2′, H-6′ and H-5′, respectively. The spectra further showed the resonances of H-2, H-3, H_a-4 and H_b-4 at δ 4.78 (*s*), 4.13 (*s*), 2.66 (*d*, J = 16.8 and 4.5 Hz) and 2.79 (*d*, J = 16.8 and 2.5 Hz). The chemical shift of H-2 and H-3 indicated that these two protons were next to oxygen-bearing carbons. In addition, the *broad singlet* resonances of H-2 and H-3 suggested that the configuration of H-2 and H-3 are *cis* (Sethi, *et al*., 1984). The evidence from the NOE experiments: irradiation at the resonances of H-2 and H-3 resulted in the enhancement of the resonances of H-3, H_a-4 and H-2, H_a-4, respectively, indicated that H-2, H-3 and H_a-4 are *cis*. The remaining resonances are the resonances of five hydroxy groups (δ 8.99, 8.84, 8.64, 8.50 and 4.26). The ^{13}C NMR spectrum (**Table 67**) showed the signals of fifteen carbons; five aromatic methine carbons, two oxymethine carbons, a methylene carbon and seven quaternary aromatic carbons. In HMBC (**Table 67**) ^3J correlations between H-2 to C-4, C-2′, C-6′, C-9; H-2′ to C-2, C-4′, C-6′ and H-5′ to C-1′, C-3′ suggested that the aromatic ring

was linked to C-2. Consequently, **RD16** was proposed to be (-) epicatechin of which the (-) isomer was indicated from optical rotation ($[\alpha]_D^{29}$ –72.0 °). The assignment was in agreement with the previous data of (-) epicatechin (Sheehan, *et al*., 1983).



Major HMBC correlations of **RD16**



NOE difference experiments of **RD16**

Table 67 The ^{1}H NMR spectral data of **RD16**

Position	**RD16**			**(-) epicatechin**	
	δ_C (C-Type)*	δ_H (*mult.*, J_{Hz})[a]	HMBC	δ_C	δ_H (*mult.*, J_{Hz})[b]
2	78.33 (CH)	4.78 (1H, *s*)	C-3, C-4, C-9, C-1′, C-2′, C-6′	78.1	4.84 (1H, *s*)
3	65.63 (CH)	4.13 (1H, *br s*)	C-10, C-1′	65.6	4.19 (1H, *br s*)
4	28.13 (CH_2)	H_a: 2.66 (1H, *dd*, 16.8, 4.5)	C-2, C-3, C-5, C-10	27.9	2.84 (1H, *dd*, 16.5, 4.5)
		H_b: 2.79 (1H, *dd*, 16.8, 2.5)	C-3, C-5, C-10		2.76 (1H, *dd*, 16.5, 2.5)
5	156.58 (C)	-	-	156.4	-
6	95.71 (CH)	5.99 (1H, *d*, 1.8)	C-5, C-7, C-8, C-10	95.6	6.05 (1H, *d*, 2.0)
7	156.34 (C)	-	-	156.2	-
8	94.69 (CH)	5.87 (1H, *d*, 1.8)	C-6, C-7, C-9, C-10	94.5	5.96 (1H, *d*, 2.0)

Table 67 (Continued)

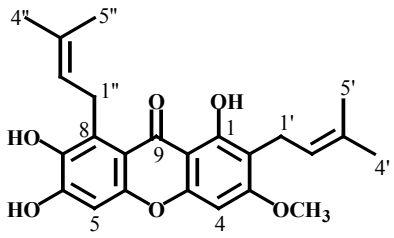
Position	RD16			(-) epicatechin	
	δ_C (C-Type)*	δ_H (*mult.*, J_{Hz})[a]	HMBC	δ_C	δ_H (*mult.*, J_{Hz})[b]
9	155.73 (C)	-	-	155.5	-
10	98.69 (C)	-	-	98.3	-
1′	130.61 (C)	-	-	130.4	-
2′	114.50(CH)	6.99 (1H, *d*, 1.8)	C-2, C-1′, C-3′, C-4′, C-6′	114.8	7.25 (1H, *d*, 2.0)
3′	144.45 (C)	-	-	144.2	-
4′	144.56 (C)	-	-	144.4	-
5′	115.05(CH)	6.77 (1H, *d*, 7.2)	C-1′, C-3′, C-4′	117.8	6.83 (1H, *d*, 8.0)
6′	118.08(CH)	6.74 (1H, *dd*, 7.2, 1.8)	C-2, C-2′, C-4′, C-5′	114.1	6.80 (1H, *d*, 8.0, 2.0)
3-OH	-	4.26 (1H, *br s*)	-	-	4.66 (1H, *br s*)
5-OH	-	8.99 (1H, *br s*)	C-5, C-6, C-10	-	9.14 (1H, *br s*)
7-OH	-	8.84 (1H, *br s*)	C-7, C-8	-	8.94 (1H, *br s*)
3′-OH	-	8.64 (1H, *br s*)	C-2′, C-4′	-	8.82 (1H, *br s*)
4′-OH	-	8.50 (1H, *br s*)	C-3′, C-5′	-	8.74 (1H, *br s*)

* Carbon type was deduced from DEPT experiments.

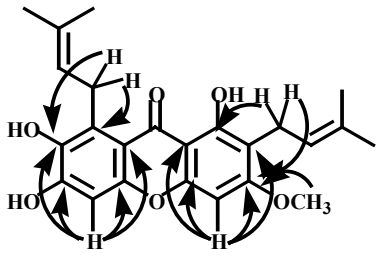
[a] Spectrum in $CDCl_3$ + DMSO-d_6

[b] Spectrum in CD_3COCD_3 + DMSO-d_6

RD17 : 1,6,7-Trihydroxy-3-methoxy-2,8-bis(3-methyl-2-butenyl)xanthone



RD17 is a yellow solid, m.p. 170-172 °C, HREIMS *m/z* 410.1731 $[M]^+$ (calcd for $C_{24}H_{26}O_6$, 410.1729). The UV spectrum showed maxima absorptions at 367.5, 316.6, 260.5, 243.9 and 208.9 nm. The IR spectrum exhibited the absorption band of O-H stretching (3406 cm^{-1}) and C=O stretching (1642 cm^{-1}). The ^1H NMR spectrum (**Table 68**) exhibited the *singlet* resonances of a hydrogen bonded hydroxy proton 1-OH at δ 13.35, H-4 at δ 6.26, H-5 at δ 6.75 and 3-OCH_3 at δ 3.83. The methoxy group was thought to be at C-3 by the NOE effect of the methoxy resonance to H-4. The presence of two prenyl groups were characterized from two *broad triplets* at δ 5.16 (H-2′) and 5.24 (H-2′′), two *doublets* (J = 6.0 Hz) at δ 3.28 (H-1′) and 4.27 (H-1′′) and four *singlets* at δ 1.72 (H-5′, H-4′′), 1.60 (H-4′) and 1.82 (H-5′′). These groups were placed at C-2 and C-8 from the HMBC correlations of H-1′ to C-1, C-3 and H-1′′ to C-7, C-8. The assignment of H-4 was confirmed by the correlation of H-4 to C-2, C-3, C-4a and C-9a whereas the position of H-5 was proved by the correlation of H-5 to C-6, C-7, C-8a and C-10a. The complete HMBC confirmed the structure of **RD17** as 1,6,7-trihydroxy-3-methoxy-2,8-bis(3-methyl-2-butenyl)xanthone. It was a new xanthone derivative.



Major HMBC correlations of **RD17**

Table 68 The NMR spectral data of **RD17**

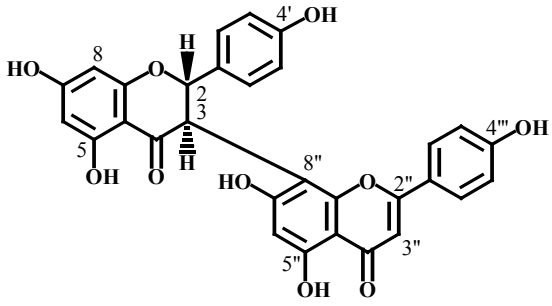
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.69 (C)	-	-
2	111.37 (C)	-	-
3	163.50 (C)	-	-
4	88.75 (CH)	6.26 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	155.29 (C)	-	-
5	101.13 (CH)	6.75 (1H, *s*)	C-6, C-7, C-8a, C-10a
6	150.67 (C)	-	-
7	139.60 (C)	-	-
8	127.41 (C)	-	-
8a	111.67 (C)	-	-
9	182.57 (C=O)	-	-
9a	101.13 (C)	-	-
10a	153.50 (C)	-	-
1′	21.35 (CH_2)	3.28 (2H, *d*, 6.3)	C-1, C-3, C-2′, C-3′
2′	122.35 (CH)	5.16 (1H, *br t*, 6.0)	C-2, C-1′, C-4′, C-5′
3′	132.00 (C)	-	-
4′	25.81 (CH_3)	1.60 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.78 (CH_3)	1.72 (3H, *s*)	C-2′, C-3′, C-4′

Table 68 (Continued)

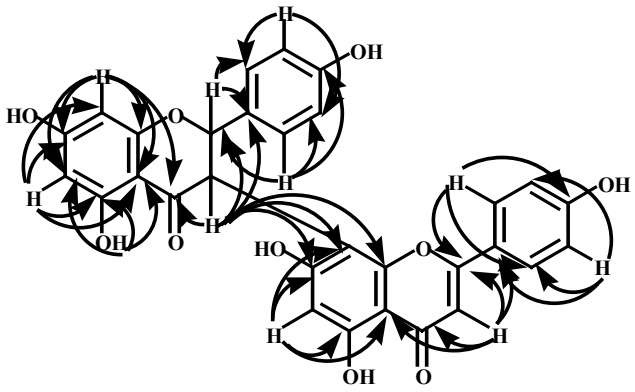
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1″	26.00 (CH_2)	4.27 (2H, *d*, 6.3)	C-7, C-8, C-8a, C-2″, C-3″
2″	121.52 (CH)	5.24 (1H, *br t*, 6.0)	C-8, C-1″, C-4″, C-5″
3″	136.00 (C)	-	-
4″	25.85 (CH_3)	1.72 (3H, *s*)	C-2″, C-3″, C-5″
5″	18.08 (CH_3)	1.82 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.35 (1H, *s*)	C-1, C-2, C-9a
3-OCH_3	55.82 (CH_3)	3.83 (3H, *s*)	C-3

* Carbon type was deduced from DEPT experiments.

FD1 : (2*S*,3*R*)-2,3-dihydro-5,5′′,7,7′′-tetrahydroxy-2,2′′-bis(4-hydroxyphenyl)-[3,8′′-Bi-4H-1-benzopyran]-4,4′′-dione (volkensiflavone)



FD1 was isolated as yellow needles, m.p. 247-250 °C. Duplication of signals (in a ratio of 1: 0.67) in the ^{1}H NMR spectrum of the optically active **FD1** in DMSO-d_6 suggested the existence of two conformers at room temperature. The major reasons leading to the existence of such conformers is the rotational restriction about the interflavanyl C-3, C-8′′ bond. The sharp paired signals given at 295 K became the sharp signals at 390 K. The signals of major conformer (**Table 69**) showed the similar pattern to those of **GD20**. Except the resonances of aromatic protons H-2′′′, H-6′′′ and H-3′′′, H-5′′′ were shown as AA′BB′ pattern at δ 7.70 (2H, *d*, *J* = 8.4 Hz) and 6.84 (2H, *d*, *J* = 8.4 Hz), respectively. The ^{13}C NMR data and HMBC correlations corresponded to the assigned structure. Thus **FD1** was assigned to be (2*S*,3*R*)-2,3-dihydro-5,5′′,7,7′′-tetrahydroxy-2,2′′-bis(4-hydroxyphenyl)-[3,8′′-Bi-4H-1-benzopyran]-4,4′′-dione which was known as volkensiflavone (Herbin, *et al.*, 1970).



Major HMBC correlations of **FD1**

Table 69 The NMR spectral data of **FD1** at 390 K

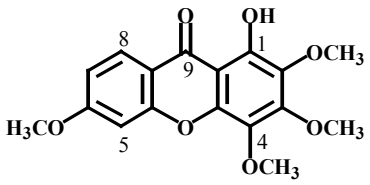
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	82.00 (CH)	5.65 (1H, *d*, 12.0)	C-1′, C-2′,6′
3	48.72 (CH)	4.90 (1H, *d*, 12.0)	C-2, C-4, C-2′,6′, C-7″, C-8″, C-8a″
4	196.64 (C=O)	-	-
4a	102.33 (C)	-	-
5	164.39 (C)	-	-
6	95.84 (CH)	5.90 (1H, *br s*)	C-4, C-4a, C-5, C-7, C-8
7	167.20 (C)	-	-
8	96.87 (CH)	6.00 (1H, *br s*)	C-4, C-4a, C-6, C-7, C-8a
8a	163.45 (C)	-	-
1′	129.81 (C)	-	-
2′, 6′	128.79 (CH)	7.05 (2H, *d*, 8.4)	C-2, C-2′,6′, C-3′,5′
3′, 5′	115.18 (CH)	6.49 (2H, *d*, 8.4)	C-2′,6′, C-3′,5′
4′	162.60 (C)	-	-
2″	164.27 (C)	-	-
3″	103.38 (CH)	6.51 (1H, *s*)	C-2″, C-4″, C-4a″, C-1‴

Table 69 (Continued)

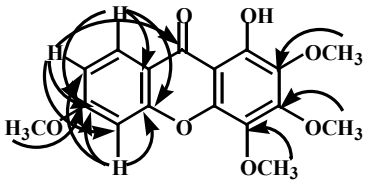
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
4″	182.21 (C=O)	-	-
4a″	104.18 (C)	-	-
5″	161.04 (C)	-	-
6″	99.09 (CH)	6.15 (1H, *s*)	C-4a″, C-5″, C-7″, C-8″
7″	161.60 (C)	-	-
8″	101.16 (C)	-	-
8a″	157.99 (C)	-	-
1‴	121.79 (C)	-	-
2‴, 6‴	128.77 (CH)	7.70 (2H, *d*, 8.4)	C-2″, C-2‴,6‴, C-4‴
3‴, 5‴	116.47 (CH)	6.84 (2H, *d*, 8.4)	C-1‴, C-2‴,6‴, C-3‴, 5‴
4‴	161.03 (C)	-	-
5-OH	-	12.10 (1H, *s*)	C-4a, C-5, C-6
5″-OH	-	12.85 (1H, *s*)	-

* Carbon type was deduced from DEPT experiments.

FD2 : 1-Hydroxy-2,3,4,6-tetramethoxyxanthone



FD2 is a yellow solid, m.p. 125-128 °C, HREIMS *m/z* 332.0892 $[M]^+$ (calcd for $C_{17}H_{16}O_7$, 332.0896). The UV spectrum showed maxima absorptions of xanthone type at 376.9, 309.3, 273.8 and 241.4 nm. The IR spectrum showed the stretchings of hydroxyl group at 3400 cm^{-1} and carbonyl group at 1646 cm^{-1}. The ^1H NMR spectrum (**Table 70**) showed a *singlet* signal of a chelated hydroxy proton (1-OH) at δ 12.60. The signals in aromatic region, δ 7.84 (*dd*), 7.32 (*d*) and 7.26 (*d*) appearing as an ABX type were proposed for the signals of H-7, H-8 and H-5, respectively. These assignment were supported by the correlations of H-7 to C-5, C-6, C-9; H-8 to C-6, C-8a, C-10a and H-5 to C-6, C-7, C-10a on the HMBC experiment. Four *singlet* signals at δ 4.04, 4.16, 3.97 and 4.05 were assigned for four methoxy groups of 2-OCH_3, 3-OCH_3, 4-OCH_3 and 6-OCH_3, respectively and were confirmed by the ^3J coupling of methoxy protons to C-2, C-3, C-4 and C-6, respectively in HMBC. The ^{13}C NMR and DEPT experiments indicated the presence of a carbonyl carbon, nine quaternary carbons, three methine carbons and four methyl carbons. The assignment suggested that **FD2** was 1-hydroxy-2,3,4,6-tetramethoxyxanthone. This compound appears to be novel.



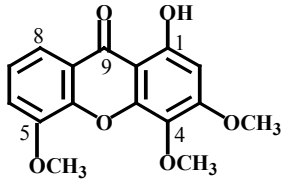
Major HMBC correlations of **FD2**

Table 70 The NMR spectral data of **FD2**

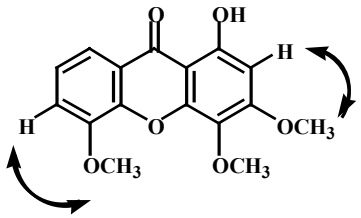
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	150.60 (C)	-	-
2	132.75 (C)	-	-
3	154.19 (C)	-	-
4	135.48 (C)	-	-
4a	145.75 (C)	-	-
5	115.92 (CH)	7.26 (1H, *d*, 1.5)	C-6, C-7, C-10a
6	148.73 (C)	-	-
7	116.56 (CH)	7.84 (1H, *dd*, 7.8, 1.5)	C-5, C-6, C-9
8	123.71 (CH)	7.32 (1H, *d*, 7.8)	C-6, C-8a, C-10a
8a	120.91 (C)	-	-
9	181.71 (C=O)	-	-
9a	104.50 (C)	-	-
10a	146.40 (C)	-	-
1-OH	-	12.60 (1H, *s*)	-
2-OCH_3	61.95 (CH_3)	4.04 (3H, *s*)	C-2
3-OCH_3	61.74 (CH_3)	4.16 (3H, *s*)	C-3
4-OCH_3	61.23 (CH_3)	3.97 (3H, *s*)	C-4
6-OCH_3	56.50 (CH_3)	4.05 (3H, *s*)	C-6

* Carbon type was deduced from DEPT experiments.

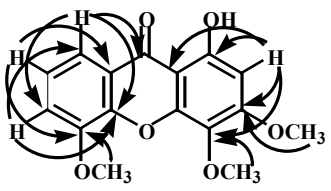
FD3 : 1-Hydroxy-3,4,5-trimethoxyxanthone



FD3 is a yellow solid, m.p. 203-205 °C. EIMS showed the molecular ion of 302 which corresponded to $C_{16}H_{14}O_6$. The ^{1}H NMR spectral data (**Table 71**) exhibited a *singlet* signal of a chelated hydroxy group 1-OH at δ 12.76. A *singlet* signal of an isolated aromatic proton, δ 6.62, was observed and was assigned to be of H-2 according to the correlation to C-1, C-3, C-4 and C-9a on the HMBC experiment. Two *doublet of doublet* signals at δ 7.82 (J = 7.2 and 1.8 Hz) and 7.24 (J = 7.2 and 1.8 Hz), and a *triplet* signal at δ 7.30 (J = 7.2 Hz) implied the presence of H-8, H-6 and H-7, respectively. The deshielded effect on the resonance of H-8 (δ 7.82) suggested the location of H-8 nearby the carbonyl group. Three *singlet* signals of three methoxy groups appeared at δ 4.03 (5-OCH_3), 3.97 (3-OCH_3) and 3.93 (4-OCH_3). The assignment for three methoxy groups were supported by ^3J coupling of 5-OCH_3 to C-5; 3-OCH_3 to C-3 and 4-OCH_3 to C-4 on the HMBC experiment. The ^{13}C NMR spectral data and HMBC correlations corresponded to 1-hydroxy-3,4,5-trimethoxyxanthone (Stout, *et al*., 1973).



NOE difference experiments of **FD3**



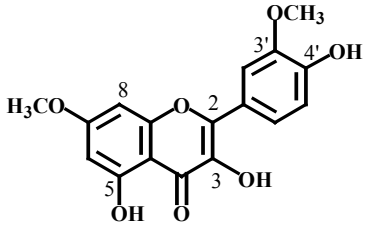
Major HMBC correlations of **FD3**

Table 71 The NMR spectral data of **FD3**

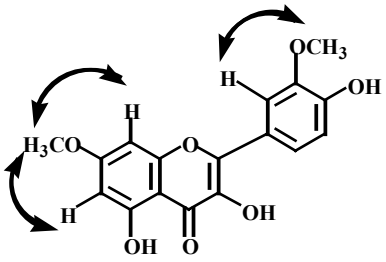
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	154.09 (C)	-	-
2	90.92 (CH)	6.62 (1H, *s*)	C-1, C-3, C-4, C-9a
3	160.01 (C)	-	-
4	131.89 (C)	-	-
4a	153.17 (C)	-	-
5	148.23 (C)	-	-
6	115.47 (CH)	7.24 (1H, *dd*, 7.2, 1.8)	C-8, C-10a
7	123.62 (CH)	7.30 (1H, *t*, 7.2)	C-5, C-8a
8	116.66 (CH)	7.82 (1H, *dd*, 7.2, 1.8)	C-6, C-9, C-10a
8a	121.15 (C)	-	-
9	181.12 (C=O)	-	-
9a	104.28 (C)	-	-
10a	146.24 (C)	-	-
1-OH	-	12.76 (1H, *s*)	-
3-OCH_3	56.41 (CH_3)	3.97 (3H, *s*)	C-3
4-OCH_3	60.90 (CH_3)	3.93 (3H, *s*)	C-4
5-OCH_3	56.43 (CH_3)	4.03 (3H, *s*)	C-5

* Carbon type was deduced from DEPT experiments.

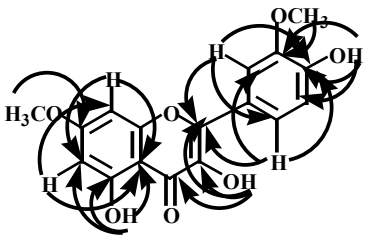
FD4 : 5,4′-Dihydroxy-7,3′-dimethoxyflavonol (rhamnazin)



FD4 was obtained as a yellow solid, m.p. 215-216 °C. EIMS showed the molecular ion of 330 which corresponded to $C_{17}H_{14}O_7$. ^{1}H NMR spectrum (**Table 72**) showed the resonances of a hydrogen-bonded hydroxy proton at δ 12.45 (*s*, 5-OH), two free hydroxy groups at δ 9.50 (*s*, 3-OH) and 9.76 (*s*, 4′-OH). Two *doublet* resonances (J = 2.3 Hz) at δ 6.34 (1H) and 6.76 (1H) were in agreement with the *meta*-coupling of aromatic protons H-6 and H-8. Two *doublet* signals at δ 7.78 (J = 2.3 Hz) and 6.94 (J = 8.7 Hz) and a *doublet of doublet* signal at δ 7.73 (J = 8.7 and 2.3 Hz) implied the presence of H-2, H-5 and H-6, respectively. Two methoxy signals at δ 3.86 and 3.85 were assigned for 7-OCH_3 and 3′-OCH_3. These assignment supported by the differential NOE technique: irradiation of 3′-OCH_3 effected the signal of H-2′ and irradiation of 7-OCH_3 effected the signals of H-6 and H-8. The complete HMBC data confirmed the structure. 5,4′-Dihydroxy-7,3′-dimethoxyflavonol or known as rhamnazin was then assigned for **FD4** (Subhadhirasakul, *et al*., 2003).



NOE difference experiments of **FD4**



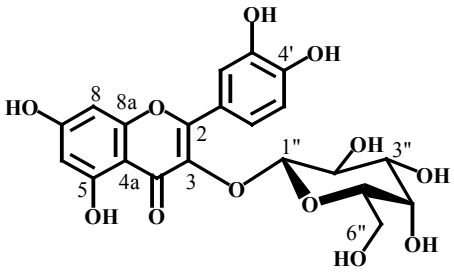
Major HMBC correlations of **FD4**

Table 72 The NMR spectral data of **FD4**

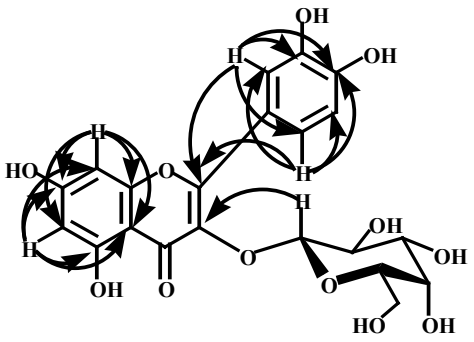
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
2	147.28 (C)	-	-
3	136.32 (C)	-	-
4	176.20 (C=O)	-	-
4a	104.23 (C)	-	-
5	160.54 (C)	-	-
6	97.69 (CH)	6.34 (1H, *d*, 2.3)	C-4a, C-5, C-7, C-8
7	165.15 (C)	-	-
8	92.30 (CH)	6.76 (1H, *d*, 2.3)	C-4, C-4a, C-6, C-7, C-8a
8a	156.30 (C)	-	-
1′	122.00 (C)	-	-
2′	112.02 (CH)	7.78 (1H, *d*, 2.3)	C-2, C-1′, C-3′, C-4′, C-6′
3′	147.63 (C)	-	-
4′	149.18 (C)	-	-
5′	115.76 (CH)	6.94 (1H, *d*, 8.7)	C-3′, C-4′, C-6′
6′	122.10 (CH)	7.73 (1H, *dd*, 8.7, 2.3)	C-2, C-2′, C-4′
3-OH	-	9.50 (1H, *s*)	C-2, C-3, C-4
5-OH	-	12.45 (1H, *s*)	C-4a, C-5, C-6
7-OCH_3	56.25 (CH_3)	3.86 (3H, *s*)	C-7
3′-OCH_3	56.08 (CH_3)	3.85 (3H, *s*)	C-3′
4′-OH	-	9.76 (1H, *s*)	C-3′, C-4′, C-5′

* Carbon type was deduced from DEPT experiments.

FD5 : 2-(3,4-Dihydroxyphenyl)-3-(*β*-D-galactopyranosyloxy)-5,7-dihydroxy-4H-1-benzopyran-4-one (hyperin or quercetin 3-*O*-*β*-galactopyranoside)



The glycoside **FD5** was isolated as a yellow solid, m.p. 235-236 °C. The optical rotation was $[\alpha]_D^{29}$: - 26.0 ° (c = 0.03 in CH_3OH). The ^1H NMR spectrum (**Table 73**) exhibited a *singlet* signal of a chelated hydroxy proton 5-OH at δ 12.60 and the resonances of H-2′, H-5′ and H-6′ as an ABX pattern at δ 7.54 (*d*, *J* = 2.0 Hz), 6.81 (*dd*, *J* = 7.2 Hz) and 7.65 (*d*, *J* = 7.2, 2.0 Hz), respectively. The resonances of *meta* protons H-6 and H-8 were observed at δ 6.19 (*d*, *J* = 1.8 Hz) and 6.39 (*d*, *J* = 1.8 Hz). It therefore indicated that **FD5** was a derivative of quercetin. The remaining resonances were the resonances of a sugar moiety which was assigned to be galactose. The resonances of anomeric proton (H-1′′) was at δ 5.35 (*d*, *J* = 7.2 Hz). In the ^{13}C NMR spectrum the anomeric carbon was at δ 102.12. HMBC correlation of H-1′′ to C-3 indicated that galactose was linked to quercetin at C-3. Thus glycoside **FD5** was 2-(3,4-dihydroxyphenyl)-3-(*β*-D-galactopyranosyloxy)-5,7-dihydroxy-4H-1-benzopyran-4-one or known as quercetin 3-*O*-*β*-galactopyranoside (Kartnig, *et al*., 1985; Yasukawa and Takido, 1987).



Major HMBC correlations of **FD5**

Table 73 The NMR spectral data of **FD5**

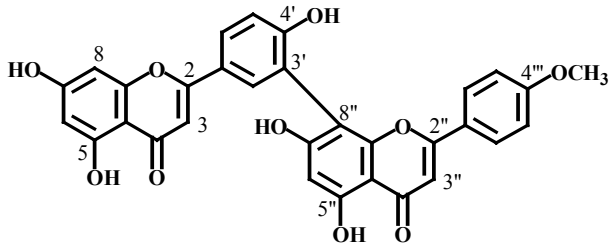
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
2	156.49 (C)	-	-
3	133.74 (C)	-	-
4	177.72 (C=O)	-	-
4a	104.11 (C)	-	-
5	161.46 (C)	-	-
6	98.98 (CH)	6.19 (1H, *d*, 1.8)	C-4a, C-5, C-7, C-8
7	164.57 (C)	-	-
8	93.81 (CH)	6.39 (1H, *d*, 1.8)	C-4, C-4a, C-6, C-7, C-8a
8a	156.58 (C)	-	-
1′	121.34 (C)	-	-
2′	116.23 (CH)	7.54 (1H, *d*, 2.0)	C-2, C-3′, C-4′, C-6′
3′	145.08 (C)	-	-
4′	148.74 (C)	-	-
5′	115.45 (CH)	6.81 (1H, *d*, 7.2)	C-1′, C-3′, C-4′
6′	122.19 (CH)	7.65 (1H, *dd*, 7.2, 2.0)	C-2, C-2′, C-4′, C-5′

Table 73 (Continued)

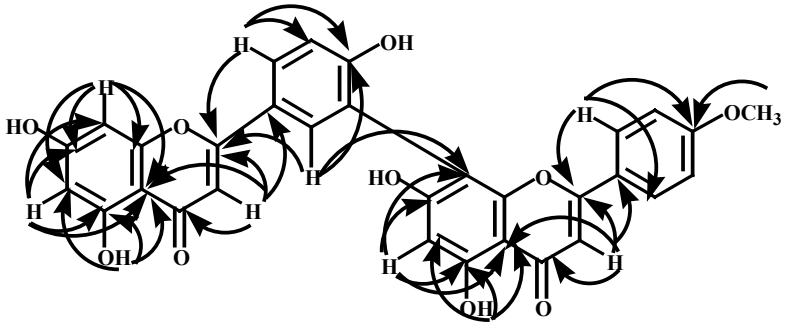
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
Gal-1″	102.12 (CH)	5.35 (1H, *d*, 7.2)	C-3
2″	71.47 (CH)	3.57 (1H, *t*, 7.2)	C-1″, C-5″
3″	76.07 (CH)	3.30 (1H, *m*)	C-4″
4″	68.18 (CH)	3.66 (1H, *d*, 2.7)	C-2″, C-5″
5″	73.45 (CH)	3.37 (1H, *m*)	C-2″
6″	60.39 (CH_2)	3.46 (1H, *dd*, 9.5, 5.0)	C-3″, C-4″
		3.29 (1H, *dd*, 9.5, 2.5)	C-3″, C-4″
5-OH	-	12.60 (1H, *s*)	-

* Carbon type was deduced from DEPT experiments.

FD6 : 5,7,5″,7″-Tetrahydroxy-2-(4-hydroxyphenyl)-2″-(4-methoxyphenyl)-[3′,8″-Bi-4H-1-benzopyran]-4,4″-dione (podocarpusflavone A)



FD6 was isolated as a yellow solid, m.p. 270-271 °C. EIMS showed the molecular ion of 552 which corresponded to $C_{31}H_{20}O_{10}$. The ^{1}H NMR spectrum (**Table 74**) showed the presence of an ABX pattern (δ 7.89, H-2′; 7.20, H-5′ and 7.82, H-6′), an aromatic protons with *meta* coupling (δ 6.27, H-6 and 6.39, H-8), an AA′BB′ system (δ 7.55, H-2‴, H-6‴ and 6.84, H-3‴, H-5‴), an isolated aromatic proton (δ 6.55, *s*, H-6″), two methine olefinic protons (δ 6.55, *s*, H-3 and 6.57, *s*, H-3″) and a methoxy group (δ 3.79, *s*, 4‴-OCH_3). The HMBC correlation of methoxy protons to C-4‴ supported the location of 4‴-OCH_3. The HMBC correlations of H-3 to C2, C-4, C-4a, C-1′ and H-3″ to C-2″, C-4″, C-4a″, C-1‴ confirmed that C-2 was connected to the 4-hydroxysubstituted ring at C-1′ and C-2″ connected to the methoxysubstituted ring at C-1‴. These data indicated a linkage of two flavone units between C-3′ and C-8″. Thus **FD6** was assigned to be 5,7,5″,7″-tetrahydroxy-2-(4-dihydroxyphenyl)-2″-(4-methoxyphenyl)-[3′,8″-Bi-4H-1-benzopyran]-4,4″-dione which was known as podocarpusflavone A (Pelter, *et al*., 1971; Dasgupta, *et al*., 1981; Markham, *et al*., 1987).



Major HMBC correlations of **FD6**

Table 74 The NMR spectral data of **FD6**

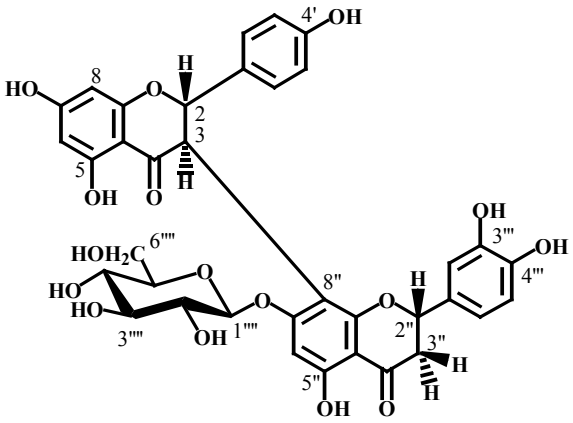
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	163.78 (C)	-	-
3	103.06 (CH)	6.55 (1H, *s*)	C-2, C-4, C-4a, C-1′
4	181.80 (C=O)	-	-
4a	103.32 (C)	-	-
5	161.54 (C)	-	-
6	98.97 (CH)	6.27 (1H, *d*, 2.3)	C-4a, C-5, C-7, C-8
7	163.74 (C)	-	-
8	93.75 (CH)	6.39 (1H, *d*, 2.3)	C-4a, C-6, C-7, C-8a
8a	157.35 (C)	-	-
1′	121.70 (C)	-	-
2′	130.96 (CH)	7.89 (1H, *d*, 2.4)	C-2, C-3, C-4′, C-6′, C-8′′
3′	119.64 (C)	-	-
4′	158.80 (C)	-	-
5′	116.33 (CH)	7.20 (1H, *d*, 8.6)	C-1′, C-3′, C-4′
6′	127.15 (CH)	7.82 (1H, *dd*, 8.6, 2.4)	C-2, C-2′, C-4′
2′′	163.24 (C)	-	-

Table 74 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
3″	103.07 (CH)	6.57 (1H, *s*)	C-2″, C-4″, C-4a″, C-1‴
4″	182.24 (C=O)	-	-
4a″	104.06 (C)	-	-
5″	160.97 (C)	-	-
6″	99.06 (CH)	6.55 (1H, *s*)	C-4a″, C-5″, C-7″, C-8″
7″	163.74 (C)	-	-
8″	104.33 (C)	-	-
8a″	161.35 (C)	-	-
1‴	123.01 (C)	-	-
2‴, 6‴	127.43 (CH)	7.55 (2H, *d*, 9.6)	C-2″, C-2‴, C-4‴, C-6‴
3‴, 5‴	113.97 (CH)	6.84 (2H, *d*, 9.6)	C-1‴, C-3‴, C-4‴
4‴	161.93 (C)	-	-
5-OH	-	12.82 (1H, *s*)	C-4a, C-5, C-6
5″-OH	-	12.96 (1H, *s*)	C-4a″, C-5″, C-6″
4‴-OCH_3	55.00 (CH_3)	3.79 (3H, *s*)	C-4‴

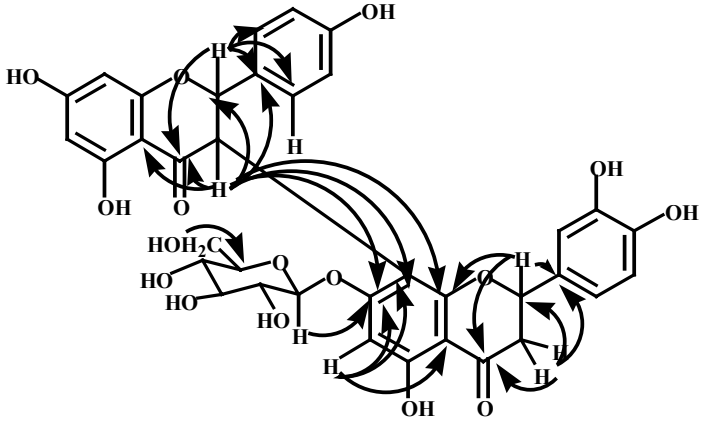
* Carbon type was deduced from DEPT experiments.

FD7 : (2*S*,2″*S*,3*R*)-2″-(3,4-dihydroxyphenyl)-7″-(*β*-D-glucopyranosyloxy)-2,2″,3,3″-tetrahydro-5,5″,7-trihydroxy-2-(4-hydroxyphenyl)-[3,8″-Bi-4H-1-benzopyran]-4,4″-dione (xanthochymusside)



FD7 was isolated as a yellow solid, m.p. 222-224 °C. EIMS showed the molecular ion of 720 which corresponded to $C_{36}H_{32}O_{16}$. Duplication of signals (in a ratio of 1 : 0.6) in the ^{1}H NMR spectrum of the optically active **FD7** in CD_3OD suggested the existence of two conformers at room temperature, the major reasons leading to the existence of such conformers was rotational restrictions about the interflavanone C-3,C-8″ bond. The ^{1}H and ^{13}C NMR spectra at 300 K also showed the signals forming their respective pairs. The ^{1}H signals of major conformer (**Table 75**) showed the resonances of an AA′BB′ pattern (δ 7.23, H-2′, H-6′ and 6.64, H-3′, H-5′), an aromatic protons with *meta* coupling (δ 5.90, H-6 and 5.88, H-8), an ABX pattern (δ 6.81, H-2‴; 6.73, H-5‴ and 6.70, H-6‴), an isolated aromatic proton (δ 6.38, H-6″), a methine proton (δ 5.08, H-2″) and a methylene protons (δ 2.95 and 2.56, H-3″). The HMBC correlations of H-2″ to C-4″, C-8a″, C-1‴ and H-3″ to C-2″, C-4″, C-1‴ supported the assignment. The HMBC correlations of H-2 to C-1′, C-2′, C-6′ and H-3 to C-7″, C-8″, C-8a″ confirmed that C-2 was connected to 4-substituted ring at C-1′ and C-3 was connected to another flavanone nucleus at C-8″.

The resonances of β-glucose were observed of which an anomeric proton H-1′′′′ resonated at δ 4.99 (1H, *d*, *J* = 6.0 Hz), a methylene protons H-6′′′′ were at δ 3.92 (1H, *d*, *J* = 12.0 Hz) and 3.75 (1H, *m*) and the other protons were at δ 3.30-3.49. According to HMBC correlation of H-1′′′′ to C-7′′ indicated the location of glucose moiety was at C-7′′. On the basis of above considerations **FD7** was assigned to be (2*S*,2′′*S*,3*R*)-2′′-(3,4-dihydroxyphenyl)-7′′-(β-D-glucopyranosyloxy)-2,2′′,3,3′′-tetrahydro-5,5′′,7-trihydroxy-2-(4-hydroxyphenyl)-[3,8′′-Bi-4H-1-benzopyran]-4,4′′-dione which was known as xanthochymusside (Konoshima, *et al*., 1970b).



Major HMBC correlations of **FD7**

Table 75 The NMR spectral data (major conformer) of **FD7** at 300 K

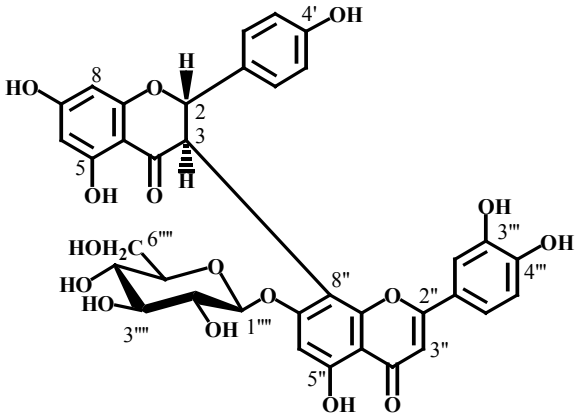
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	83.75 (CH)	5.70 (1H, *d*, 12.0)	C-3, C-4, C-1′, C-2′,6′
3	49.94 (CH)	5.03 (1H, *d*, 12.0)	C-2, C-4, C-4a, C-1′, C-7″, C-8″, C-8a″
4	198.41 (C=O)	-	-
4a	103.05 (C)	-	-
5	165.42 (C)	-	-
6	97.55 (CH)	5.90 (1H, *br s*)	C-4a, C-5, C-7, C-8
7	167.90 (C)	-	-
8	97.15 (CH)	5.88 (1H, *br s*)	C-4a, C-6, C-7
8a	163.93 (C)	-	-
1′	131.46 (C)	-	-
2′, 6′	129.23 (CH)	7.23 (2H, *d*, 7.9)	C-2, C-2′,6′, C-4′
3′, 5′	114.76 (CH)	6.64 (2H, *br d*, 7.9)	C-1′, C-3′,5′, C-4′
4′	158.77 (C)	-	-
2″	80.88 (CH)	5.08 (1H, *br t*)	C-4″, C-8a″, C-1‴
3″	44.81 (CH_2)	2.95 (1H, *br dd*)	C-2″, C-4″, C-1‴
		2.56 (1H, *br dd*)	C-2″, C-4″, C-1‴
4″	198.41 (C=O)	-	-
4a″	104.78 (C)	-	-
5″	165.42 (C)	-	-
6″	96.14 (CH)	6.38 (1H, *s*)	C-4a″, C-5″, C-7″, C-8″
7″	164.71 (C)	-	-
8″	104.29 (C)	-	-
8a″	161.93 (C)	-	-
1‴	131.46 (C)	-	-
2‴	130.70 (CH)	6.81 (1H, *br d*, 2.0)	C-2″, C-1‴, C-3‴, C-4‴, C-6‴
3‴	146.34 (C)	-	-
4‴	146.65 (C)	-	-

Table 75 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
5‴	116.42 (CH)	6.73 (1H, *br d*, 8.0)	C-1‴, C-3‴
6‴	119.10 (CH)	6.70 (1H, *br dd*, 8.0, 2.0)	C-2″, C-1‴, C-2‴, C-4‴, C-5‴
Glc-1⁗	101.54 (CH)	4.99 (1H, *d*, 6.0)	C-7″, C-3⁗, C-5⁗
2⁗	75.01 (CH)	3.32-3.30 (1H, *m*)	C-3⁗, C-5⁗
3⁗	78.25 (CH)	3.49-3.47 (1H, *m*)	C-2⁗, C-3⁗, C-4⁗, C-5⁗
4⁗	70.95 (CH)	3.38 (1H, *br t*)	C-3⁗, C-5⁗, C-6⁗
5⁗	78.11 (CH)	3.46-3.44 (1H, *m*)	C-3⁗, C-5⁗, C-6⁗
6⁗	62.36 (CH_2)	3.92 (1H, *d*, 12.0)	C-1⁗, C-4⁗
		3.75 (1H, *m*)	C-1⁗, C-4⁗

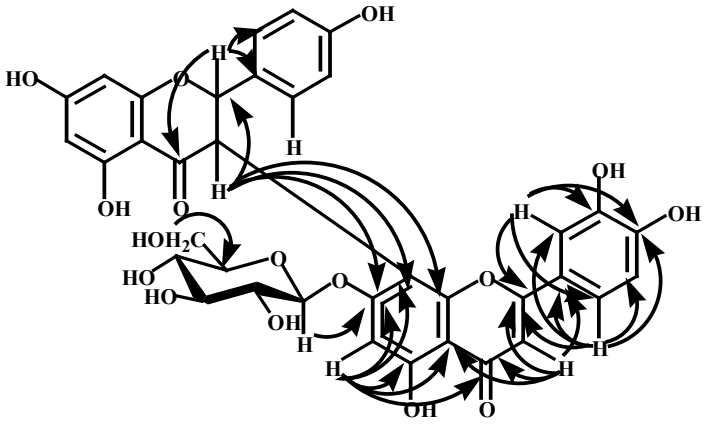
* Carbon type was deduced from DEPT experiments.

FD8 : (2*S*,3*R*)-2″-(3,4-Dihydroxyphenyl)-7″-(*β*-D-glucopyranosyloxy)-2,3-dihydro-5,7,5″-trihydroxy-2-(4-hydroxyphenyl)-[3,8″-Bi-4H-1-benzopyran]-4,4″-dione (fukugeside)



FD8 was isolated as a yellow solid, m.p. 245-247 °C. EIMS showed the molecular ion of 718 which corresponded to $C_{36}H_{30}O_{16}$. Duplication of signals (in a ratio of 1 : 0.27) in the ^{1}H NMR spectrum in CD_3OD suggested the existence of two conformers at room temperature, the major reason leading to the existence of such conformers is rotational restriction about the interflavanyl C-3,C-8″ bond. The ^{1}H NMR spectrum at 300 K also showed the signals forming their respective pairs. The ^{13}C NMR spectrum at 300 K showed fifty five signals with thirty two pairs. The ^{1}H major conformer (**Table 76**) showed the AA′BB′ resonances of H-2′, H-6′ at δ 7.09 (2H, *d*, J = 8.3 Hz) and H-3′, H-5′ at δ 6.34 (2H, *d*, J = 8.3 Hz), *broad singlets* of H-6 at δ 5.90 and H-8 at δ 5.97, *doublets* of H-2 at δ 5.70 (J = 11.9 Hz) and H-3 at δ 4.86 (J = 11.9 Hz), *singlet* of H-3″ at δ 6.35 and *singlet* of H-6″ at δ 6.58. The HMBC correlations of H-6″ to C-4″, C-4a″, C-5″, C-7″, C-8″ and H-3″ to C-2″, C-4″, C-4a″, C-1‴ supported the assignment. The resonances of H-2‴ (δ 7.29, *br s*), H-6‴ (δ 7.24, *br d*, J = 8.9 Hz) and H-5‴ (δ 6.84, *br d*, J = 8.9 Hz) were shown as an ABX pattern. The HMBC correlation of H-2 to C-4, C-1′ and C-2′ confirmed that C-2 was

connected to the 4-substituted ring at C-1′. The correlation of H-3 to C-2, C-7″, C-8″ and C-8a″ suggested that C-3 was connected to another flavone nucleus at C-8″. The resonances of sugar moiety were observed at δ 5.14-3.30 of which anomeric proton H-1‴′ resonating at δ 5.14 (1H, *d*). The coupling constant of 7.6 Hz suggested a β-glucose moiety. According to HMBC correlation of H-1‴′ to C-7″ indicated the location of glucose moiety at C-7″. On the basis of above considerations **FD8** was assigned to be (2*S*,3*R*)-2″-(3,4-dihydroxyphenyl)-7″-(β-D-glucopyranosyloxy)-2,3-dihydro-5,7,5″-trihydroxy-2-(4-hydroxyphenyl)-[3,8″-Bi-4H-1-benzopyran]-4,4″-dione which was known as fukugeside (Kanoshima, *et al*., 1970a; 1970b).



Major HMBC correlations of **FD8**

Table 76 The NMR spectral data (major conformer) of **FD8** at 300 K

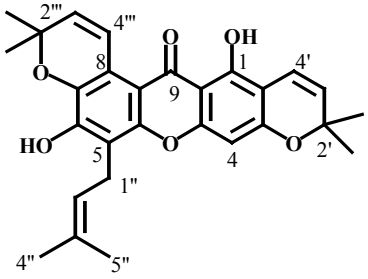
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	82.82 (CH)	5.70 (1H, *d*, 11.9)	C-4, C-1′, C-2′
3	50.96 (CH)	4.86 (1H, *d*, 11.9)	C-2, C-4, C-7″, C-8″, C-8a″
4	197.76 (C=O)	-	-
4a	103.44 (C)	-	-
5	166.52 (C)	-	-
6	97.74 (CH)	5.90 (1H, *br s*)	C-4a, C-5, C-7, C-8
7	168.23 (C)	-	-
8	96.50 (CH)	5.97 (1H, *br s*)	C-4a, C-6, C-7, C-8a
8a	164.76 (C)	-	-
1′	130.36 (C)	-	-
2′, 6′	129.35 (CH)	7.09 (2H, *d*, 8.3)	C-2, C-1′, C-2′,6′, C-3′,5′, C-4′
3′, 5′	115.40 (CH)	6.34 (2H, *d*, 8.3)	C-1′, C-2′,6′, C-3′,5′, C-4′
4′	158.37 (C)	-	-
2″	165.65 (C)	-	-
3″	104.02 (CH)	6.35 (1H, *s*)	C-2″, C-4″, C-4a″, C-1‴
4″	183.79 (C=O)	-	-
4a″	106.39 (C)	-	-
5″	162.62 (C)	-	-
6″	99.43 (CH)	6.58 (1H, *s*)	C-4″, C-4a″, C-5″, C-7″, C-8″
7″	161.52 (C)	-	-
8″	104.46 (C)	-	-
8a″	156.57 (C)	-	-
1‴	130.25 (C)	-	-
2‴	114.40 (CH)	7.29 (1H, *br s*)	C-2″, C-3‴, C-4‴, C-6‴
3‴	146.52 (C)	-	-
4‴	151.02 (C)	-	-
5‴	116.79 (CH)	6.84 (1H, *br d*, 8.9)	C-3‴, C-4‴

Table 76 (Continued)

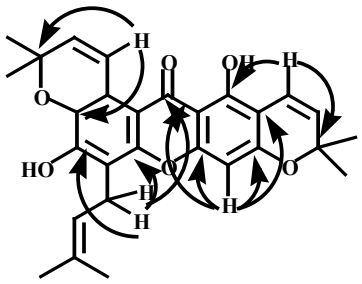
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
6‴	120.88 (CH)	7.24 (1H, *br d*, 8.9)	C-2″, C-2‴, C-4‴, C-5‴
Glc-1⁗	101.40 (CH)	5.14 (1H, *d*, 7.6)	C-7″
2⁗	75.14 (CH)	3.51 (1H, *m*)	C-1⁗, C-3⁗, C-4⁗
3⁗	78.43 (CH)	3.49 (1H, *m*)	C-1⁗, C-2⁗, C-4⁗
4⁗	71.01 (CH)	3.30 (1H, *m*)	C-3⁗, C-5⁗, C-6⁗
5⁗	78.26 (CH)	3.34 (1H, *m*)	C-4⁗, C-6⁗
6⁗	62.40 (CH_2)	3.92 (1H, *d*, 10.9)	C-4⁗, C-5⁗
		3.73 (1H, *dd*, 5.6)	C-4⁗, C-5⁗

* Carbon type was deduced from DEPT experiments.

FD9 : 1,6-Dihydroxy-5-(3-methyl-2-butenyl)-2′,2′-dimethylchromeno(5′,6′:2,3)-2‴,2‴-dimethylchromeno(5‴,6‴:8,7)xanthone



FD9 was isolated as an orange solid, m.p. 218-220 °C. HRFABMS *m/z* 460.1929 $[M]^+$ (calcd for $C_{28}H_{28}O_6$, 460.1886). The UV spectrum exhibited maximum absorption bands at 335.4, 301.0, 289.1, 221.0 and 205.6 nm. The absorption bands of O-H stretching and C=O stretching were shown in the IR spectrum at 3424 and 1615 cm^{-1}, respectively. The ^{1}H NMR spectrum (**Table 77**) showed the signals of two phenolic hydroxy groups at δ 13.70 (1-OH) and 6.34 (6-OH), an isolated aromatic proton at δ 6.30 (H-4). Characteristic signals of a prenyl group was present at δ 3.57 (H-1″), 5.28 (H-2″), 1.69 (H-4″) and 1.88 (H-5″) and the group was located at C-5 according to HMBC correlation of H-1″ to C-6 and C-10a. The signals of four methyl groups at δ 1.49 (2‴-Me_2), 1.47 (2′-Me_2) and the vicinal olefinic protons at δ 5.77 (*d*, H-3‴), 7.98 (*d*, H-4‴), 5.57 (*d*, H-3′) and 6.73 (*d*, H-4′) associated with two chromene rings were present. The ^3J correlations of H-4‴ to C-7 and H-4′ to C-1 suggested that the chromene ring were connected to the parent structure at C-7, C-8 and C-2, C-3. The complete HMBC data confirmed the structure; 1,6-dihydroxy-5-(3-methyl-2-butenyl)-2′,2′-dimethylchromeno(5′,6′:2,3)-2‴,2‴-dimethylchromeno (5‴,6‴:8,7)xanthone was assinged for **FD9**. This compound appears to be novel.



Major HMBC correlations of **FD9**

Table 77 The NMR spectral data of **FD9**

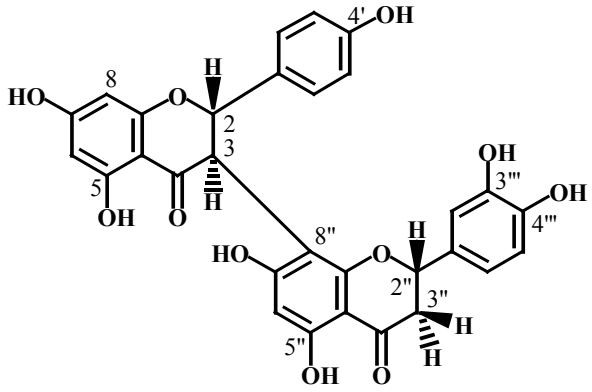
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.81 (C)	-	-
2	103.83 (C)	-	-
3	157.78 (C)	-	-
4	94.20 (CH)	6.30 (1H, *s*)	C-3, C-4′, C-2, C-9, C-4a
4a	150.96 (C)	-	-
5	108.36 (C)	-	-
6	148.63 (C)	-	-
7	136.58 (C)	-	-
8	117.14 (C)	-	-
8a	115.33 (C)	-	-
9	182.83 (C=O)	-	-
9a	104.29 (C)	-	-
10a	156.51 (C)	-	-
2′	77.95 (C)	-	-
3′	127.09 (CH)	5.57 (1H, *d*, 10.2)	C-2′, C-2
4′	115.71 (CH)	6.73 (1H, *d*, 10.2)	C-2′, C-1
1′′	22.59 (CH_2)	3.57 (2H, *d*, 7.5)	C-6, C-10a, C-8a

Table 77 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2″	120.96 (CH)	5.28 (1H, *br t*, 5.7)	C-5, C-4″, C-5″
3″	132.67 (C)	-	-
4″	25.81 (CH_3)	1.69 (3H, *s*)	C-2″, C-3″, C-5″
5″	18.00 (CH_3)	1.88 (3H, *s*)	C-2″, C-3″, C-4″
2‴	76.87 (C)	-	-
3‴	131.39 (CH)	5.77 (1H, *d*, 10.2)	C-2‴, C-8
4‴	120.99 (CH)	7.98 (1H, *d*, 10.2)	C-2‴, C-7
1-OH	-	13.70 (1H, *s*)	C-2, C-1, C-9a
6-OH	-	6.34 (1H, *s*)	-
2′-$(CH_3)_2$	28.37 (CH_3)	1.47 (6H, *s*)	C-2′, C-3′, 2′-$(CH_3)_2$
2‴-$(CH_3)_2$	27.43 (CH_3)	1.49 (6H, *s*)	C-2‴, C-3‴, 2‴-$(CH_3)_2$

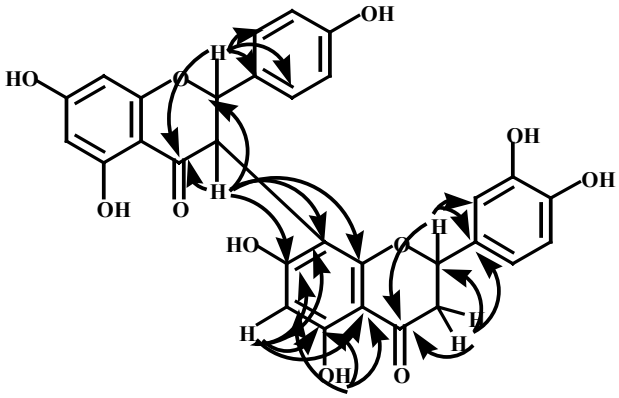
* Carbon type was deduced from DEPT experiments.

FD10 : (2*S*,2″*S*,3*R*)-2″-(3,4-dihydroxyphenyl)-2,3,2″,3″-tetrahydro-5,7,5″,7″-tetrahydroxy-2-(4-hydroxyphenyl)-[3,8″-Bi-4H-1-benzopyran]-4,4″-dione (GB-2a)



FD10 was isolated as a pale yellow solid, m.p. 215-216 °C. Duplication of signals (in a ratio of 1 : 0.4) in the ^{1}H NMR spectrum of the optically active **FD10** in DMSO-d_6 suggested the existence of two conformers at room temperature, the major reasons leading to the existence of such conformers being rotational restrictions about the interflavanone C-3, C-8″ bond. The major conformer (**Table 78**) showed the resonances of aromatic protons H-2′, H-6′ and H-3′, H-5′ as an AA′BB′ system at δ 7.13 and 6.79 (2H each, J = 8.5 Hz) and the resonances of H-2‴, H-5‴ and H-6‴ as an ABX pattern at δ 7.10 (*d*, J = 2.0 Hz), 6.64 (*d*, J = 8.5 Hz) and 6.73 (*dd*, J = 8.5 and 2.0 Hz). It further showed the resonances of *meta* protons H-6 and H-8 at δ 5.90 and 5.79 (*br s* each) and an isolated aromatic proton H-6″ at δ 5.86 (*s*). The resonances of *trans*-coupled protons H-2 and H-3 were observed at δ 5.73 and 4.56 (*d*, J = 12.3 Hz) whereas H-2″ and H-3″ resonated at δ 5.43 (*br t*) and 2.90 (*m*), 2.60 (*m*), respectively. The HMBC correlation of H-2 to C-1′, C-2′ and C-6′ confirmed that the 4-substituted ring was connected to at C-2 and the correlation of H-2″ to C-1‴ and C-2‴ confirmed that the 3,4-disubstituted ring was connected to C-2″. The 3,8″-link of two flavanone was suggested from HMBC correlation of H-3 to C-7″, C-8″ and C-8a″.

The complete HMBC confirmed the structure of **FD10** as (2*S*,3*R*,2′′*S*)-2′′-(3,4-dihydroxyphenyl)-2,3,2′′,3′′-tetrahydro-5,7,5′′,7′′-tetrahydroxy-2-(4-hydroxyphenyl)-[3,8′′-Bi-4H-1-benzopyran]-4,4′′-dione or known as GB-2a (Jackson, *et al*. 1971; Gunatilaka, *et al*., 1984).



Major HMBC correlations of **FD10**

Table 78 The NMR spectral data (major conformer) of **FD10** at 300 K

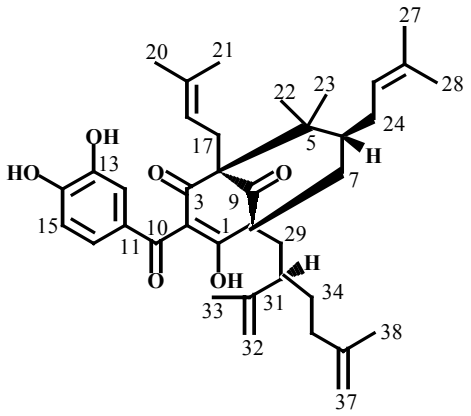
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	82.20 (CH)	5.73 (1H, *d*, 12.3)	C-4, C-1′, C-2′,6′
3	47.76 (CH)	4.56 (1H, *d*, 12.3)	C-2, C-4, C-7′′, C-8′′, C-8a′′
4	197.14 (C=O)	-	-
4a	101.81 (C)	-	-
5	165.34 (C)	-	-
6	96.51 (CH)	5.90 (1H, *br s*)	C-4, C-4a, C-5, C-7, C-8
7	166.86 (C)	-	-
8	95.93 (CH)	5.79 (1H, *br s*)	C-4, C-4a, C-7, C-8a
8a	163.27 (C)	-	-

Table 78 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1′	130.23 (C)	-	-
2′, 6′	129.45 (CH)	7.13 (2H, *d*, 8.5)	C-2, C-1′, C-2′,6′, C-4′
3′, 5′	114.38 (CH)	6.79 (2H, *d*, 8.5)	C-2′,6′, C-3′,5′, C-4′
4′	158.13 (C)	-	-
2″	79.02 (CH)	5.43 (1H, *br t*)	C-4″, C-1‴, C-2‴
3″	43.14 (CH_2)	2.90 (1H, *m*)	C-2″, C-4″, C-1‴
		2.60 (1H, *m*)	C-2″, C-4″, C-1‴
4″	196.62 (C=O)	-	-
4a″	102.12 (C)	-	-
5″	164.09 (C)	-	-
6″	95.50 (CH)	5.86 (1H, *s*)	C-4, C-4a″, C-5″, C-7″, C-8″
7″	161.19 (C)	-	-
8″	101.76 (C)	-	-
8a″	162.48 (C)	-	-
1‴	128.37 (C)	-	-
2‴	129.04 (CH)	7.10 (1H, *d*, 2.0)	C-2″, C-3‴, C-4‴, C-6‴
3‴	145.68 (C)	-	-
4‴	146.17 (C)	-	-
5‴	115.32 (CH)	6.64 (1H, *d*, 8.5)	C-1‴, C-3‴, C-4‴
6‴	118.25 (CH)	6.73 (1H, *dd*, 8.5, 2.0)	C-2″, C-1‴, C-2‴, C-4‴
5-OH	-	12.19 (1H, *s*)	C-4a, C-5, C-6
4′-OH	-	9.61 (1H, *s*)	C-4′, C-3′,5′
5″-OH	-	12.15 (1H, *s*)	C-4a″, C-5″, C-6″
3‴-OH	-	9.20 (1H, *s*)	C-3″, C-4″
4‴-OH	-	9.08 (1H, *s*)	C-3″, C-4″, C-5″

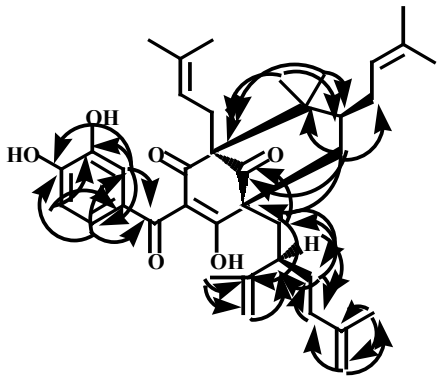
* Carbon type was deduced from DEPT experiments.

FD11 : (4*R*,6*R*,8*S*)-2-(13,14-dihydroxybenzoyl)-1-hydroxy-8-[(2*S*)-2-isopropenyl-5-methyl-5-hexenyl]-5,5-dimethyl-4,6-bis(3-methyl-2-butenyl)bicyclo [3.3.1]non-1-ene-3,9-dione (xanthochymol)



FD11 is a yellow solid, m.p. 139-140 °C. The optical rotation was $[\alpha]_D^{29}$ + 135.5 ° (c = 0.03 in CH_3OH). The resonances appearing as an ABX system at δ 6.66 (*d*, *J* = 8.5 Hz, H-15), 6.99 (*dd*, *J* = 8.5, 1.5 Hz, H-16) and 7.04 (*d*, *J* = 1.5 Hz, H-12) and the resonance of carbonyl carbon at δ 198.08 refered the presence of 3,4-dihydroxybenzoyl group. The resonances of protons of a prenyl group were observed at δ 5.10 (H-18), 2.77 (H-17) and 1.72 (H-20, H-21) and was found to be linked to quaternary carbon C-4 according to HMBC correlation of H-17 to C-3 and C-5. The resonances at δ 4.93 (H-25), 1.70 (H-27), 1.56 (H-28) and 1.28 (H-24) suggested the presence of the second prenyl group and it was indicated to be C-6 by ^3J correlation of H-24 to C-5 and C-7. The methylene protons H-7 (δ 2.37), H-29 (δ 2.22), H-34 (δ 1.35) and H-35 (δ 2.04) were assigned from the HMBC experiments as followed: H-29 to C-9, C-34; H-30 to C-35; H-34 to C-29, C-30 and C-35. The resonances of H-32 (δ 4.43, 2H), H-33 (δ 1.83, 3H), H-37 (δ 4.65, 2H) and H-38 (δ 1.76, 3H) of isopropenyl groups were assigned to be linked to C-30 and C-35 by ^3J correlations of H-32 to C-30; H-33 to C-31, C-32; H-37 to C-35, C-38 and H-38 to C-36, C-37. Methyl groups

on a saturated carbon resonated at δ 1.04 (H-22) and 1.19 (H-23) whereas methine protons H-6 and H-30 resonated at δ 1.90 and 2.62. The ^{13}C NMR spectrum showed a non-enolisable carbonyl carbon at δ 209.41 and three enolisable carbonyl carbons at δ 198.08, 194.22 and 193.98. The HMBC correlations corresponded to the assigned structure. **FD11** was then identified as (4*R*,6*R*,8*S*)-2-(3,4-dihydroxybenzoyl)-1-hydroxy-8-[(2*S*)-2-isopropenyl-5-methyl-5-hexenyl]-5,5-dimethyl-4,6-bis(3-methyl-2-butenyl)bicyclo[3.3.1]non-1-ene-3,9-dione which agreed with the structure of xanthochymol (Blount and Williams, 1976; Rama Rao, *et al*., 1980).



Major HMBC correlations of **FD11**

Table 79 The NMR spectral data of **FD11**

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	FD11	**xanthochymol**	**FD11**	**xanthochymol**	
1	193.98(C=O)	194.0 (C=O)	-	-	-
2	115.83 (C)	115.2 (C)	-	-	-
3	194.22(C=O)	194.9 (C=O)	-	-	-
4	69.68 (C)	70.0 (C)	-	-	-
5	49.55 (C)	49.8 (C)	-	-	-
6	46.74 (CH)	46.7 (CH)	1.90 (1H, *m*)	1.00-2.30 (*m*)	C-5, C-8, C-25
7	42.52 (CH_2)	42.9 (CH_2)	2.37 (2H, *m*)	1.00-2.30 (*m*)	C-5, C-8, C-9, C-24
8	57.78 (C)	58.1 (C)	-	-	-
9	209.41(C=O)	209.2 (C=O)	-	-	-
10	198.08(C=O)	198.6 (C=O)	-	-	-
11	127.89 (C)	127.9 (C)	-	-	-
12	116.45 (CH)	116.6 (CH)	7.04 (1H, *d*, 1.5)	7.00 (*d*, 2.0)	C-10, C-13, C-14, C-16
13	143.72 (C)	143.8 (C)	-	-	-
14	147.35 (C)	147.5 (C)	-	-	-
15	114.33 (CH)	114.2 (CH)	6.66 (1H, *d*, 8.5)	6.60 (*d*, 9.0)	C-11, C-13, C-14
16	120.04 (CH)	120.13 (CH)	6.99(1H,*dd*,8.5,1.5)	6.95 (*d*,9.0,2.0)	C-10, C-12, C-14, C-15
17	27.16[a](CH_2)	27.2[aa] (CH_2)	2.77 (2H, *m*)	1.00-2.30 (*m*)	C-3, C-5
18	123.85 (CH)	123.9 (CH)	5.10[e] (1H, *m*)	5.00[ee] (*m*)	C-17, C-20, C-21
19	132.87 (C)	133.1 (C)	-	-	-
20	26.01[b](CH_3)	26.3[bb] (CH_3)	1.72[f] (3H, *s*)	1.71[ff] (3H, *s*)	C-18, C-19, C-21
21	18.10[c](CH_3)	18.2[cc] (CH_3)	1.72[f] (3H, *s*)	1.56[ff] (3H, *s*)	C-18, C-19, C-20
22	26.91 (CH_3)	26.6 (CH_3)	1.04 (3H, *s*)	1.02 (3H, *s*)	C-4, C-5, C-6, C-23
23	17.14 (CH_3)	17.4 (CH_3)	1.19 (3H, *s*)	1.18 (3H, *s*)	C-4, C-5, C-6, C-22
24	29.26[a](CH_2)	29.2[aa] (CH_2)	1.28 (2H, *br s*)	1.00-2.30	C-5, C-7, C-25, C-26
25	124.11(CH)	124.2 (CH)	4.93[e] (1H, *m*)	4.90[ee] (1H, *m*)	C-24, C-27, C-28
26	135.21 (C)	135.4 (C)	-	-	-
27	25.78[b](CH_3)	26.1[bb] (CH_3)	1.70[f] (3H, *s*)	1.71[ff] (3H, *s*)	C-25, C-26, C-28
28	17.84[c](CH_3)	18.5[cc] (CH_3)	1.56[f] (3H, *s*)	1.56[ff] (3H, *s*)	C-25, C-26, C-27

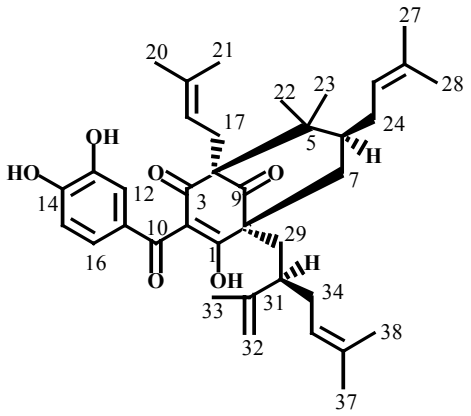
Table 79 (Continued)

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	FD11	**xanthochymol**	**FD11**	**xanthochymol**	
29	36.46 (CH_2)	36.8 (CH_2)	2.22 (2H, *m*)	1.00-2.30 (*m*)	C-9, C-34
30	43.27 (CH)	43.6 (CH)	2.62 (1H, *m*)	1.00-2.30 (*m*)	C-8, C-35
31	149.79 (C)	149.9 (C)	-	-	-
32	113.21(CH_2)	113.5 (CH_2)	4.43 (2H, *br d*, 4.0)	4.43 (2H, *s*)	C-30, C-33
33	22.53[d](CH_3)	22.8[dd] (CH_3)	1.83 (3H, *s*)	1.81 (3H, *s*)	C-31, C-32
34	31.58 (CH_2)	32.1 (CH_2)	1.35 (2H, *m*)	1.00-2.30 (*m*)	C-29, C-30, C-35
35	35.42 (CH_2)	35.7 (CH_2)	2.04 (2H, *m*)	1.00-2.30 (*m*)	C-34, C-37, C-38
36	145.94 (C)	146.1 (C)	-	-	-
37	109.58(CH_2)	109.8 (CH_2)	4.65 (2H, *br d*,12.5)	4.65 (2H, *s*)	C-35, C-38
38	22.64[d](CH_3)	23.0[dd] (CH_3)	1.76 (3H, *s*)	1.75 (3H, *s*)	C-36, C-37

* Carbon type was deduced from DEPT experiments.

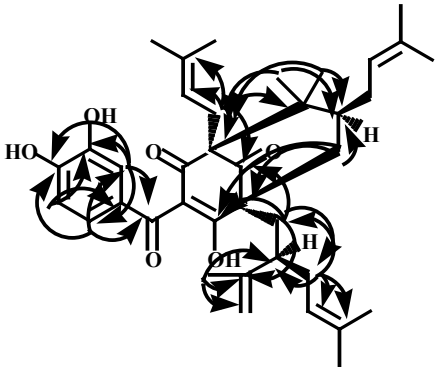
[a-f, aa-ff] Assignment maybe interchangeable.

FD12 : (4*S*,6*R*,8*S*)-2-(3,4-dihydroxybenzoyl)-1-hydroxy-8-[(2*S*)-2-isopropenyl-5-methyl-4-hexenyl]-5,5-dimethyl-4,6-bis(3-methyl-2-butenylbicyclo[3.3.1] non-1-ene-3,9-dione (guttiferone E)



FD12 is a yellow solid, m.p. 128-130 °C. The optical rotation was $[\alpha]_D^{29}$ + 96.0 ° (c = 0.03 in CH_3OH). The ^1H NMR spectrum (**Table 80**) showed the ABX resonances of H-15 at δ 6.65 (*d*, *J* = 8.1 Hz), H-16 at δ 6.95 (*dd*, *J* = 8.1, 2.0 Hz) and H-12 at δ 7.01 (*d*, *J* = 2.0 Hz). The presence of three prenyl groups were observed. The signals at δ 5.09 (H-18), 2.75 and 2.60 (H-17), 1.81 (H-20), 1.71 (H-21) associated to a prenyl group at C-4. Whereas those at δ 5.05 (H-25), 1.74 (H-28), 1.71 (H-27), 1.32 (H-24) and δ 4.94 (H-35), 2.20 (H-34), 1.68 (H-37), 1.61 (H-38) belonged to the prenyl groups attached to CH-carbons. HMBC correlations of H-17 to C-4, C-5; H-24 to C-7 and H-34 to C-29, C-30, C-35, C-36 indicated that the prenyl groups were at C-4, C-6 and C-30, respectively. The signals of isopropenyl group at δ 4.44, 4.39 (H-32) and 1.55 (H-33) of which this group was located at C-30 according to the HMBC correlations of H-32 and H-33 to C-30. Two methyl groups on a saturated carbon were resonated at δ 1.17 (H-22) and 1.02 (H-23) and were located at C-5 from the correlations of H-22 to C-4, C-5, C-6 and H-23 to C-4, C-6 in HMBC. Two groups of methylene protons were assigned from the resonances at δ 2.12, 2.05 (H-7) and 2.15,

1.91 (H-29) whereas two methine protons were indicated from the resonances at δ1.45 (H-6) and 2.36 (H-30). Four signals of carbonyl carbons were shown in the ^{13}C NMR spectrum which corresponded to a non-enolisable carbonyl carbon (δ209.25) and three enolisable carbonyl carbons (δ198.59, 194.56 and 193.90). **FD12** is virtually identical to **GD1** (camboginol or garcinol). However, the optical rotation of **FD12** was opposite in sign compared to that of **GD1,** $[\alpha]_D^{29}$ –128.5°. Thus, **FD12** was then identified as (4*S*,6*R*,8*S*)-2-(3,4-dihydroxybenzoyl)-1-hydroxy-8-[(2*S*)-2-isopropenyl-5-methyl-4-hexenyl]-5,5-dimethyl-4,6-bis(3-methyl-2-butenyl)bicyclo[3.3.1]non-1-ene-3,9-dione or known as guttiferone E (Gustafson, *et al*., 1992).



Major HMBC correlations of **FD12**

Table 80 The NMR spectral data of **FD12**

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	FD12	**guttiferoneE**	**FD12**	**guttiferone E**	
1	194.56 (C)	194.8	-	-	-
2	115.88 (C)	118.6	-	-	-
3	193.90(C=O)	194.0	-	-	-
4	69.74 (C)	69.4	-	-	-
5	49.59 (C)	49.9	-	-	-
6	46.83 (CH)	48.0	1.45 (1H, *m*)	1.47 (*m*)	C-4, C-8, C-22, C-23, C-25
7	42.63 (CH_2)	43.3	2.05 (1H, *m*)	2.06 (*dd*,14.1,7.2)	C-1, C-6, C-8
			2.12 (1H, *m*)	2.21 (*dd*,14.0,1.0)	C-1, C-6, C-8
8	57.88 (C)	59.8	-	-	-
9	209.25(C=O)	208.9	-	-	-
10	198.59(C=O)	195.8	-	-	-
11	127.86 (C)	129.7	-	-	-
12	116.51(CH)	117.2	7.01 (1H, *d*, 2.0)	7.22 (*d*, 2.2)	C-10, C-13, C-14, C-16
13	143.73 (C)	146.2	-	-	-
14	148.03 (C)	152.5	-	-	-
15	114.34 (CH)	115.0	6.65 (1H, *d*, 8.1)	6.69 (*d*, 8.3)	C-11, C-13, C-14
16	124.10 (CH)	125.2	6.95(1H,*dd*,8.1,2.0)	7.00 (*dd*, 8.3, 2.2)	C-10, C-12, C-14
17	26.38 (CH_2)	27.0	2.60 (1H, *br d*)	2.48 (*dd*,13.3,4.6)	C-4, C-5, C-18, C-19
			2.75 (1H, *br d*)	2.67 (*dd*,13.3,9.4)	C-4, C-5, C-18, C-19
18	120.13(CH)	121.5	5.09 (1H, *br t*)	4.98 (*m*)	C-20, C-21
19	135.21 (C)	135.3	-	-	-
20	26.05 (CH_3)	26.4	1.81 (3H, *s*)	1.71 (*d*, 1.0)	C-18, C-19, C-21
21	17.94 (CH_3)	18.5[a]	1.71 (3H, *s*)	1.65 (*s*)	C-18, C-19, C-20
22	22.71 (CH_3)	23.2	1.17 (3H, *s*)	1.12 (*s*)	C-4, C-5, C-6, C-23
23	27.02 (CH_3)	27.3	1.02 (3H, *s*)	0.95 (*s*)	C-4, C-6, C-22
24	29.68 (CH_2)	30.5	1.32 (2H, *br s*)	2.06 (2H, *m*)	C-7, C-26
25	122.65(CH)	125.6	5.05 (1H, *br t*)	4.88 (*m*)	C-6, C-27, C-28
26	132.90 (C)	133.5	-	-	-

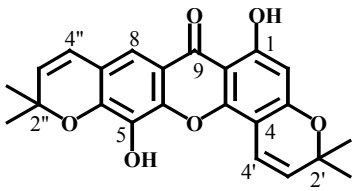
Table 80 (Continued)

Position	δ_C (C-Type)*		δ_H (*multiplicity*, J_{Hz})		HMBC
	FD12	**guttiferoneE**	**FD12**	**guttiferone E**	
27	25.82 (CH_3)	25.9[b]	1.71 (3H, *s*)	1.65 (*s*)	C-25, C-26, C-28
28	18.16 (CH_3)	18.3[a]	1.74 (3H, *s*)	1.52 (*s*)	C-25, C-26, C-27
29	39.19 (CH_2)	36.6	1.91 (1H, *m*)	1.71 (*dd*,13.8,3.7)	C-9, C-31, C-34
			2.15 (1H, *m*)	2.23(*dd*,13.8,10.6)	C-1, C-30
30	43.60 (CH)	45.9	2.36 (1H, *m*)	2.34 (*m*)	C-8, C-33, C-34
31	149.81 (C)	150.0	-	-	-
32	112.68(CH_2)	112.5	4.39 (1H, *br s*)	4.35 (*d*, 2.4)	C-30, C-33
			4.44 (1H, *br s*)	4.54 (*dd*, 2.4, 1.2)	C-30, C-33
33	17.64 (CH_3)	18.2	1.55 (3H, *s*)	1.73 (*s*)	C-30, C-31, C-32
34	28.93 (CH_2)	33.9	2.20 (2H, *m*)	2.01 (*m*)	C-29, C-30, C-35, C-36
35	123.90(CH)	123.9	4.94 (1H, *br t*)	4.98 (*m*)	C-37, C-38
36	131.95 (C)	132.8	-	-	-
37	25.73 (CH_3)	26.0[b]	1.68 (3H, *s*)	1.63 (*d*, 1.2)	C-35, C-36, C-38
38	17.89 (CH_3)	18.1	1.61 (3H, *s*)	1.57 (*d*, 1.0)	C-35, C-36, C-37

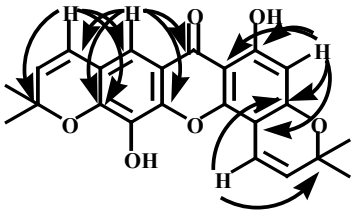
* Carbon type was deduced from DEPT experiments.

[a, b] Assignment maybe interchangeable.

FD13 : 1,5-Dihydroxy-2′,2′-dimethylchromeno(5′,6′:4,3)-2′′,2′′-dimethylchromeno(5′′,6′′:7,6)xanthone (rheediaxanthone A)



FD13 was obtained as a yellow solid with m.p. 256-257 °C. The ^{1}H NMR spectrum (**Table 81**) consisted of the characteristic signal of a chelated hydroxy proton (1-OH) at δ 13.18, a sharp *singlet* signal of isolated aromatic proton H-8 at δ 7.54 and a *doublet* signal of aromatic proton H-2 at δ 6.31 (J = 0.6 Hz). Aromatic protons H-8 and H-2 were deduced from the HMBC correlations of H-8 to C-6, C-9, C-10a, C-4′′ and H-2 to C-1, C-3, C-4, C-9a. The ^{1}H NMR spectrum further showed the characteristic signals of two dimethylchromene rings. *Gem*-dimethyl protons resonated as a *singlet* at δ 1.59 (6H) and two olefinic protons (H-3′′ and H-4′′) appeared as two *doublet* signals at δ 5.79 and 6.51 (1H each, J = 10.5 Hz). Irradiation of the lowest-field aromatic H-8 caused a NOE enhancement of the olefinic proton H-4′′, suggesting the fusion of the dimethylchromene ring to C-6 and C-7 with an ether linkage at C-6. In addition, HMBC correlations of H-4′′ to C-6 and C-8 were shown. The *gem*-dimethyl protons and two olefinic protons (H-3′ and H-4′) of another dimethylchromene ring resonated at δ 1.54 (*s*, 6H), 5.67 (*d*, J = 9.6 Hz, H-3′) and 6.95 (*dd*, J = 9.6, 0.6 Hz, H-4′), respectively. The HMBC correlations of H-4′ to C-3 and H-3′ to C-4 precisely determined that it was at C-3 and C-4. The ^{13}C NMR and DEPT experiments indicated the existence of a carbonyl carbon, four methyl carbons, six methine carbons and twelve quaternary carbons. **FD13** then was assigned for 1,5-dihydroxy-2,2-dimethylchromeno(5′,6′:4,3)-2,2-dimethylchromeno(5′′,6′′:7,6) xanthone which corresponded to rheediaxanthone A (Delle Monache, *et al.*, 1981).



Major HMBC correlations of **FD13**

Table 81 The NMR spectral data of **FD13**

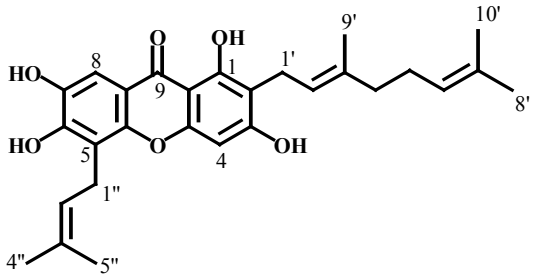
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	163.09 (C)	-	-
2	99.38 (CH)	6.31 (1H, *d*, 0.6)	C-1, C-3, C-4, C-9a
3	160.53 (C)	-	-
4	101.36 (C)	-	-
4a	151.57 (C)	-	-
5	132.37 (C)	-	-
6	145.01 (C)	-	-
7	114.73 (C)	-	-
8	113.48 (CH)	7.54 (1H, *s*)	C-6, C-9, C-10a, C-4″
8a	117.79 (C)	-	-
9	180.31 (C=O)	-	-
9a	102.35 (C)	-	-
10a	144.72 (C)	-	-
2′	78.19 (C)	-	-
3′	127.14 (CH)	5.67 (1H, *d*, 9.6)	C-4, C-2′
4′	115.16 (CH)	6.95 (1H, *dd*, 9.6, 0.6)	C-3, C-2′
2″	78.98 (C)	-	-
3″	131.01 (CH)	5.79 (1H, *d*, 10.5)	C-2″, C-4″

Table 81 (Continued)

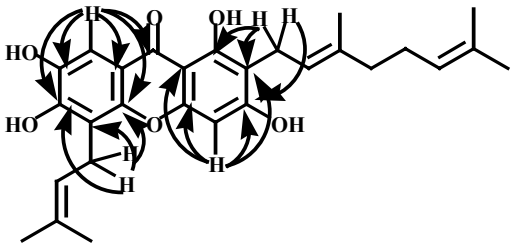
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
4″	121.43 (CH)	6.51 (1H, *d*, 10.5)	C-6, C-8, C-2″
1-OH	-	13.18 (1H, *s*)	-
2′-$(CH_3)_2$	28.27 (CH_3)	1.54 (6H, *s*)	C-2′, C-3′, 2′-$(CH_3)_2$
2″-$(CH_3)_2$	28.45 (CH_3)	1.59 (6H, *s*)	C-2″, C-3″, 2″-$(CH_3)_2$

* Carbon type was deduced from DEPT experiments.

FD14 : 1,3,6,7-Tetrahydroxy-2-(3,7-dimethyl-2,6-octadienyl)-5-(3-methyl-2-butenyl)xanthone



FD14 is a yellow solid, m.p. 185-187 °C. Its molecular formula of $C_{28}H_{32}O_6$ was established on the basis of mass spectrum ($[M]^+$ *m/z* 464.2199). The UV spectrum showed the maxima absorption bands at 369.1, 322.7, 258.4, 242.9 and 207.4 nm. The IR spectrum showed the absorption bands of hydroxy group at 3450 cm^{-1} and conjugated carbonyl group at 1711 cm^{-1}. The ^1H NMR spectrum (**Table 82**) exhibited the resonances of a chelated hydroxy proton 1-OH at δ 13.19, aromatic protons H-4 at δ 6.42 and H-8 at δ 7.33. The characteristic signals of a prenyl unit were displayed at δ 3.60 (*d*, H-1″), 5.29 (*br t*, H-2″), 1.69 (*s*, H-4″), 1.88 (*s*, H-5″). The prenyl unit was located at C-5 by HMBC correlation of H-1″ to C-5, C-6 and C-10a. It also exhibited the typical signal of a geranyl group: three *singlets* of three methyl groups at δ 1.57 (H-8′), 1.80 (H-9′) and 1.52 (H-10′), a *doublet* of methylene protons at δ 3.37 (H-1′), two *multiplets* of methylene protons at δ 1.99 (H-4′) and 2.03 (H-5′) and two *broad triplets* of two olefinic methine protons at δ 5.29 (H-2′) and 5.02 (H-6′). The correlation of H-1′ to C-1, C-2 and C-3 in the HMBC indicated that the geranyl side chain was at C-2. The ^{13}C NMR spectral data (**Table 89**) showed 28 signals for 28 carbon atoms. These evidences indicated that **FD14** was 1,3,6,7-tetrahydroxy-2-(3,7-dimethyl-2,6-octadienyl)-5-(3-methyl-2-butenyl)xanthone. This compound was a new xanthone derivative.



Major HMBC correlations of **FD14**

Table 82 The NMR spectral data of **FD14**

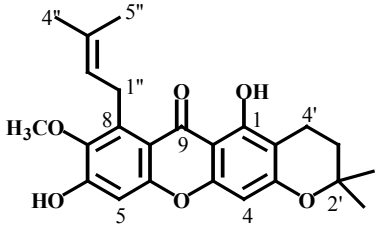
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.82 (C)	-	-
2	110.43 (C)	-	-
3	162.59 (C)	-	-
4	93.44 (CH)	6.42 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	156.12 (C)	-	-
5	112.77 (C)	-	-
6	150.79 (C)	-	-
7	141.91 (C)	-	-
8	105.14 (CH)	7.33 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
8a	115.57 (C)	-	-
9	180.64 (C=O)	-	-
9a	102.57 (C)	-	-
10a	150.26 (C)	-	-
1′	21.46 (CH_2)	3.37 (2H, *d*, 6.0)	C-1, C-2, C-3, C-2′, C-3′
2′	122.45 (CH)	5.29 (1H, *br t*)	C-1′, C-4′
3′	132.24 (C)	-	-
4′	39.84 (CH_2)	1.99 (2H, *m*)	C-3′, C-5′, C-6′
5′	21.71 (CH_2)	2.03 (2H, *m*)	C-3′, C-4′, C-6′

Table 82 (Continued)

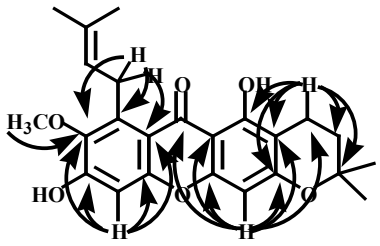
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
6′	124.27 (CH)	5.02 (1H, *br t*)	C-5′, C-8′, C-10′
7′	131.54 (C)	-	-
8′	25.58 (CH_3)	1.57 (3H, *s*)	C-6′, C-7′, C-10′
9′	17.85 (CH_3)	1.80 (3H, *s*)	C-2′, C-3′, C-4′, C-5′
10′	17.62 (CH_3)	1.52 (3H, *s*)	C-6′, C-7′, C-8′
1″	22.45 (CH_2)	3.60 (2H, *d*, 6.0)	C-5, C-6, C-10a, C-2″, C-3″
2″	121.38 (CH)	5.29 (1H, *br t*)	C-1″, C-4″, C-5″
3″	135.90 (C)	-	-
4″	25.81 (CH_3)	1.69 (3H, *s*)	C-2″, C-3″, C-5″
5″	16.20 (CH_3)	1.88 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.19 (1H, *s*)	-

* Carbon type was deduced from DEPT experiments.

FD15 : 1,6-Dihydroxy-7-methoxy-8-(3-methyl-2-butenyl)-2′,2′-dimethylchromano (5′,6′:2,3)xanthone (3-isomangostin)



FD15 was isolated as a yellow solid, m.p. 154-156 °C. The ^{1}H NMR spectrum (**Table 83**) showed four *singlet* signals of 1-OH at δ 13.72, H-5 at δ 6.83, H-4 at δ 6.23 and 7-OCH_3 at δ 3.80. The signals of *gem*-dimethyl protons and two groups of methylene protons (H-4′ and H-3′) associated with a chroman ring resonated at δ 1.37 (*s*), 2.71 (*t*) and 1.83 (*t*), respectively. The correlation of H-4′ to C-1, C-2 and C-3 precisely determined that the dimethylchroman ring was next to C-1 and C-4. In addition, the signals of two methyl groups, methylene protons and an olefinic methine proton which were the characteristic signals of a prenyl moiety were present at δ 1.69 (H-4′′), 1.83 (H-5′′), 4.09 (H-1′′) and 5.27 (H-2′′), respectively. The chemical shift of the methylene protons H-1′′ (δ 4.09) implied that H-1′′ was deshielded by a carbonyl group, accordingly the prenyl side chain was proposed to be at C-8, a *peri* position to the carbonyl group. The HMBC correlation of H-1′′ to C-7, C-8 and C-8a confirmed the location of the prenyl unit at C-8. According to the assignment and HMBC correlations (**Table 83**), 1,6-dihydroxy-7-methoxy-8-(3-methyl-2-butenyl)-2′,2′-dimethylchromano(5′,6′:2,3)xanthone or 3-isomangostin was proposed for **FD15** (Mahabusarakam, *et al*., 1987).



Major HMBC correlations of **FD15**

Table 83 The NMR spectral data of **FD15**

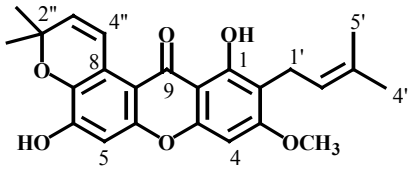
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.57 (C)	-	-
2	103.75 (C)	-	-
3	154.68 (C)	-	-
4	93.99 (CH)	6.23 (1H, *s*)	C-2, C-3, C-4a, C-9, C-9a, C-4′
4a	160.69 (C)	-	-
5	101.61 (CH)	6.83 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	155.83 (C)	-	-
7	142.37 (C)	-	-
8	136.89 (C)	-	-
8a	112.07 (C)	-	-
9	182.00 (C=O)	-	-
9a	102.83 (C)	-	-
10a	154.47 (C)	-	-
2′	76.02 (C)	-	-
3′	31.86 (CH_2)	1.83 (2H, *t*, 5.8)	C-2, C-2′, C-4′, 2′-$(CH_3)_2$
4′	16.08 (CH_2)	2.71 (2H, *t*, 5.8)	C-1, C-2, C-3, C-2′, C-3′
1″	26.51 (CH_2)	4.09 (2H, *d*, 5.6)	C-7, C-8, C-8a, C-2″, C-3″
2″	123.23 (CH)	5.27 (1H, *br t*, 5.6)	C-8, C-4″, C-5″

Table 83 (Continued)

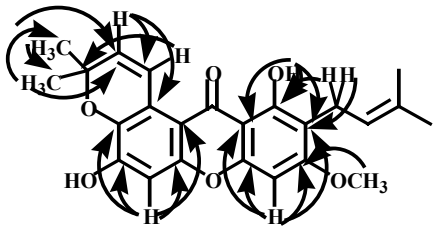
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
3′′	132.06 (C)	-	-
4′′	25.82 (CH_3)	1.69 (3H, *s*)	C-2′′, C-3′′, C-5′′
5′′	18.20 (CH_3)	1.83 (3H, *s*)	C-2′′, C-3′′, C-4′′
1-OH	-	13.72 (1H, *s*)	C-1, C-9a
7-OCH_3	-	3.80 (3H, *s*)	C-7
2′-$(CH_3)_2$	26.72 (CH_3)	1.37 (6H, *s*)	C-2′, C-3′, 2′-$(CH_3)_2$

* Carbon type was deduced from DEPT experiments.

FD16 : 1,6-Dihydroxy-2-(3-methyl-2-butenyl)-3-methoxy-2″,2″-dimethylchromeno(5″,6″:8,7)xanthone



FD16 is a yellow solid, m.p. 213-215 °C. Its molecular formula of $C_{24}H_{24}O_6$ were established on the basis of mass spectrum ($[M]^+$ *m/z* 408.1573). The UV spectrum showed maxima absorptions at 331.2, 322.6, 265.8, 244.8 and 208.8 nm. The IR spectrum exhibited the absorption bands of O-H stretching at 3479 cm^{-1} and C=O stretching at 1587 cm^{-1}. The ^{1}H NMR spectrum of **FD16** (**Table 84**) indicated that it was a methoxy derivative of **RD7**. The ^{1}H NMR spectrum showed the resonances of a chelated hydroxy group 1-OH at δ 13.35 (*br s*), aromatic protons H-4 at δ 6.36 (*s*), H-5 at δ 6.83 (*s*), methoxy protons 3-OCH_3 at δ 3.91 (*s*) and proton resonances corresponded to a prenyl group at δ 1.80 (H-5′, *s*), 1.68 (H-4′, *s*), 3.36 (H-1′, *d*) and 5.23 (H-2′, *br t*). The charecteristic signals of two methyl groups (2″-Me_2) and vicinal olefinic protons (H-3″, H-4″) associated with a chromene ring were shown at δ 1.50, 5.83 and 8.04, respectively. The deshielded effect on resonance of H-4″ suggested that the chromene ring was attached to the xanthone nucleus nearby the carbonyl group. The enhancement of the resonance of H-4 by irradiation of methoxy protons in the NOE experiment suggested that the methoxy group was at C-3. HMBC correlation of H-1′ to C-1, C-2 and C-3 indicated that the prenyl unit was at C-2. The assigned structure was further confirmed by HMBC correlations. Thus, **FD16** was proposed to be 1,6-dihydroxy-2-(3-methyl-2-butenyl)-3-methoxy-2″,2″-dimethylchromeno (5″,6″:8,7)xanthone. This compound appears to be novel.



Major HMBC correlations of **FD16**

Table 84 The NMR spectral data of **FD16**

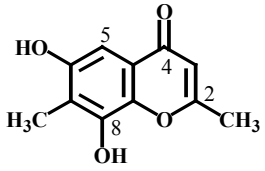
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.60 (C)	-	-
2	111.46 (C)	-	-
3	163.61 (C)	-	-
4	88.93 (CH)	6.36 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	155.52 (C)	-	-
5	102.20 (CH)	6.83 (1H, *s*)	C-6, C-7, C-8a, C-10a
6	150.75 (C)	-	-
7	136.77 (C)	-	-
8	119.73 (C)	-	-
8a	108.78 (C)	-	-
9	182.41 (C=O)	-	-
9a	102.20 (C)	-	-
10a	153.01 (C)	-	-
1′	21.33 (CH_2)	3.36 (2H, *d*, 6.7)	C-1, C-2, C-3, C-2′, C-3′
2′	122.27 (CH)	5.23 (1H, *br t*, 7.0)	C-1′, C-4′, C-5′
3′	131.74 (C)	-	-
4′	25.81 (CH_3)	1.68 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.78 (CH_3)	1.80 (3H, *s*)	C-2′, C-3′, C-4′

Table 84 (Continued)

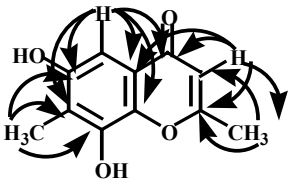
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2′′	71.00 (C)	-	-
3′′	132.21 (CH)	5.83 (1H, *d*, 9.7)	C-8, C-4′′
4′′	121.02 (CH)	8.04 (1H, *d*, 9.7)	C-2′′
2′′-$(CH_3)_2$	27.34 (CH_3)	1.50 (3H, *s*)	C-3′′, 2′′-$(CH_3)_2$
	29.69 (CH_3)	1.50 (3H, *s*)	C-3′′, 2′′-$(CH_3)_2$
1-OH	-	13.35 (1H, *br s*)	C-1, C-2, C-9a
3-OCH_3	55.84 (CH_3)	3.91 (3H, *s*)	C-3

* Carbon type was deduced from DEPT experiments.

FD17 : 6,8-Dihydroxy-2,7-dimethyl-4H-chromen-4-one



FD17 was isolated as a yellow solid, m.p. 227-229 °C. Its molecular formula of $C_{11}H_{10}O_4$ were established on the basis of mass spectrum ($[M]^+$ *m/z* 206.0570). The UV spectrum showed maximum absorption bands at 327.2, 300.5, 258.6, 252.7, 226.6, 219.6 and 207.9 nm. The IR spectra showed absorption bands of O-H stretching (3343 cm^{-1}) and C=O stretching (1657 cm^{-1}). The ^{13}C NMR spectrum showed a carbonyl carbon at δ 181.58. The ^{1}H NMR spectrum showed a *singlet* signal of olefinic proton H-3 at δ 5.99, a *singlet* signal of aromatic proton H-5 at δ 6.33 and two *singlet* signals of methyl protons 2-CH_3 at δ 2.39 and 7-CH_3 at δ 2.13. These assignment were supported by the HMBC correlations of H-3 to C-2, C-4, C-4a, 2-CH_3; H-5 to C-4, C-4a, C-6, C-7, C-8a; 2-CH_3 to C-2, C-3 and 7-CH_3 to C-6, C-7, C-8. **FD17** then was assigned for 6,8-dihydroxy-2,7-dimethyl-4H-chromen-4-one which was a new natural occurring compound.



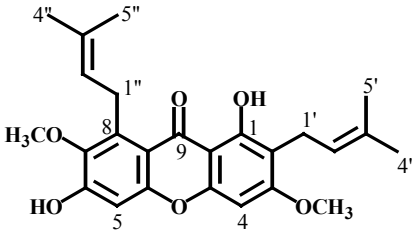
Major HMBC correlations of **FD17**

Table 85 The NMR spectral data of **FD17**

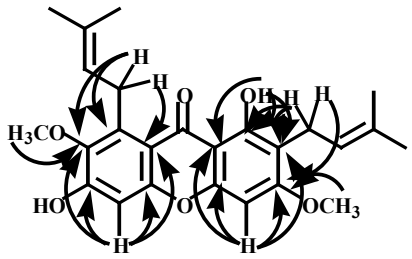
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	165.63 (C)	-	-
3	106.88 (CH)	5.99 (1H, *s*)	C-2, C-4, C-4a, 2-CH_3
4	181.58 (C=O)	-	-
4a	102.99 (C)	-	-
5	97.57 (CH)	6.33 (1H, *s*)	C-4, C-4a, C-6, C-7, C-8a
6	160.98 (C)	-	-
7	101.22 (C)	-	-
8	154.60 (C)	-	-
8a	158.20 (C)	-	-
2-CH_3	19.38 (CH_3)	2.39 (3H, *s*)	C-2, C-3
7-CH_3	6.43 (CH_3)	2.13 (3H, *s*)	C-6, C-7, C-8

* Carbon type was deduced from DEPT experiments.

FD18 : 1,6-Dihydroxy-3,7-dimethoxy-2,8-bis(3-methyl-2-butenyl)xanthone (*β*-mangostin)



FD18 is a yellow solid, m.p. 179-180 °C. The ^{1}H NMR spectrum (**Table 86**) indicated the presence of a chelated hydroxy group (1-OH) at δ 13.44, a non chelated hydroxy group (6-OH) at δ 6.40, two isolated aromatic protons (H-4 and H-5) at δ 6.35 and 6.85, two methoxy groups (3-OCH_3 and 7-OCH_3) at δ 3.91 and 3.82, and two prenylated units. The resonances of two prenylated units were shown as followed: four methyl groups at δ 1.69 (*s*, H-4′), 1.80 (*s*, H-5′), 1.70 (*s*, H-4′′) and 1.83 (*s*, H-5′′), two olefinic methine protons at δ 5.24 (*br t*, H-2′) and 5.27 (*br t*, H-2′′) and two benzylic methylene protons at δ 3.36 (*d*, H-1′) and 4.10 (*d*, H-1′′). The HMBC correlations confirmed that **FD18** is 1,6-dihydroxy-3,7-dimethoxy-2,8-bis(3-methyl-2-butenyl)xanthone or known as *β*-mangostin (Yates and Bhat, 1968).



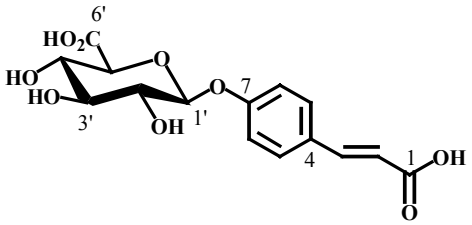
Major HMBC correlations of **FD18**

Table 86 The NMR spectral data of **FD18**

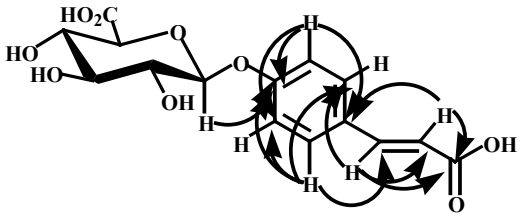
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.76 (C)	-	-
2	111.51 (C)	-	-
3	163.52 (C)	-	-
4	88.81 (CH)	6.35 (1H, *s*)	C-2, C-3, C-4a, C-9, C-9a
4a	155.71 (C)	-	-
5	101.48 (CH)	6.85 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	154.44 (C)	-	-
7	142.57 (C)	-	-
8	137.03 (C)	-	-
8a	112.38 (C)	-	-
9	181.98 (C=O)	-	-
9a	101.13 (C)	-	-
10a	155.24 (C)	-	-
1′	21.35 (CH_2)	3.36 (2H, *d*, 7.0)	C-1, C-2, C-3, C-2′, C-3′
2′	122.31 (CH)	5.24 (1H, *br t*, 7.0)	C-1′, C-4′, C-5′
3′	131.72 (C)	-	-
4′	25.83 (CH_3)	1.69 (3H, *s*)	C-2′, C-3′, C-5′
5′	17.79 (CH_3)	1.80 (3H, *s*)	C-2′, C-3′, C-4′
1″	26.55 (CH_2)	4.10 (2H, *d*, 6.5)	C-7, C-8, C-8a, C-2″, C-3″
2″	123.20 (CH)	5.27 (1H, *br t*, 6.5)	C-1″, C-4″, C-5″
3″	132.10 (C)	-	-
4″	25.84 (CH_3)	1.70 (3H, *s*)	C-2″, C-3″, C-5″
5″	18.23 (CH_3)	1.83 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.44 (1H, *s*)	C-1, C-2, C-9a
6-OH	-	6.40 (1H, *s*)	-
3-OCH_3	55.84 (CH_3)	3.91 (3H, *s*)	C-3
7-OCH_3	56.05 (CH_3)	3.82 (3H, *s*)	C-7

* Carbon type was deduced from DEPT experiments.

FD19 : 6-{4-[(*E*)-2-Carboxyethenyl]phenoxy}-3,4,5-trihydroxytetrahydro-2H-pyran-2-carboxylic acid



FD19 was isolated as a white solid, m.p. 281-283 °C. It had molecular formula $C_{15}H_{16}O_9$ ($[M+K]^+$ *m/z* 379.0428). The IR spectrum exibited absorption bands for O-H stretching stretching (3439 cm^{-1}) and C=O stretching (1642 cm^{-1}). An AA′BB′ pattern at δ 7.61 (*d*, H-5, H-9) and 7.06 (*d*, H-6, H-8) in the ^{1}H NMR spectrum (**Table 87**) indicated the *para*-substituted nucleus of which the substitutents were β-glucouronic acid and vinylic carbonyl groups. The resonance of anomeric proton of sugar moiety was observed as a *doublet* at δ 4.92 (H-1′) with coupling constant of 7.1 Hz whereas the anomeric carbon resonated at δ 100.43 and the carboxyl carbon (C-6′) was at δ 172.28. The signals of *trans* vinylic protons were present at δ 7.50 (*d*, H-3) and 6.39 (*d*, H-2) with the coupling constant of 15.9 Hz. The vinylic carboxyl group was suggested from the carbonyl resonance at δ 168.57 and HMBC correlation of H-3 to C-1, C-2, C-5 and C-9. **FD19** was then assigned to be 6-{4-[(*E*)-2-carboxyethenyl] phenoxy}-3,4,5-trihydroxytetrahydro-2H-pyran-2-carboxylic acid.



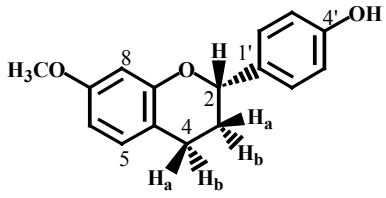
Major HMBC correlations of **FD19**

Table 87 The NMR spectral data of **FD19**

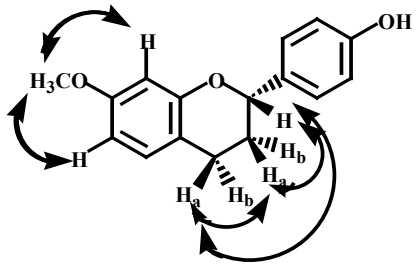
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	168.57 (C=O)	-	-
2	118.38 (CH)	6.39 (1H, *d*, 15.9)	C-1, C-4
3	143.37 (CH)	7.50 (1H, *d*, 15.9)	C-1, C-2, C-5,9
4	128.53 (C)	-	-
5, 9	130.01 (CH)	7.61 (2H, *d*, 8.6)	C-3, C-5,9, C-6,8, C-7
6, 8	117.02 (CH)	7.06 (2H, *d*, 8.6)	C-4, C-6,8, C-7
7	159.33 (C)	-	-
1′	100.43 (CH)	4.92 (1H, *d*, 7.1)	C-7
2′	73.51 (CH)	3.50-3.10 (1H, *m*)	-
3′	72.39 (CH)	3.50-3.10 (1H, *m*)	-
4′	74.41 (CH)	3.50-3.10 (1H, *m*)	-
5′	76.90 (CH)	3.50-3.10 (1H, *m*)	-
6′	172.28 (C=O)	-	-

* Carbon type was deduced from DEPT experiments.

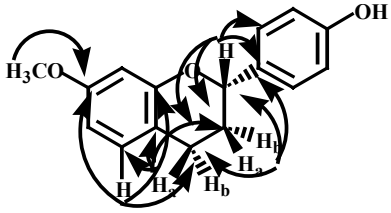
SD1 : (2*S*)-4′-Hydroxy-7-methoxyflavan



SD1 was isolated as a colourless solid, m.p. 140-142 °C. The optical rotation was $[\alpha]_D^{29}$ – 10.6 ° (c = 0.018 in CH_3OH). The ^{1}H NMR spectrum of **SD1** indicated that it was a methoxy derivative of **SD11**. The resonance of a methoxy group was displayed at δ 3.73. The group was suggested to be at C-7 by the ^3J coupling of the methoxy protons to C-7. The resonances of AA′BB′ system for H-2′, H-6′ (δ 7.28, 2H, J = 9.2 Hz) and H-3′, H-5′ (δ 6.87, 2H, J = 9.2 Hz) and the resonances of an ABX system for H-5 (δ 6.96, *d*, J = 8.5 Hz), H-6 (δ 6.44, *dd*, J = 8.5, 2.6 Hz) and H-8 (δ 6.38, *d*, J = 2.6 Hz) were observed. The spectra further showed a *doublet of doublet* resonance of H-2 at δ 4.96 (1H, J = 13.1, 2.9 Hz), a *quartet of doublet* of H_a-3 at δ 2.12 (J = 12.0, 2.4 Hz) and a *multiplet* resonance of H_b-3 at δ 1.98, a *doublet of doublet of doublet of doublet* of H_a-4 at δ 2.88 (1H, J = 5.0, 1.0 Hz) and a *doublet of doublet of doublet* resonance of H_b-4 at δ 2.68 (J = 12.0, 5.0 and 3.0 Hz). The negative $[\alpha]_D$ value indicated that C-2 possesses an *S* configuration (Achenbach, *et al*., 1988). The enhancement of the signal of H-2 and H_a-4 upon irradiation at the resonance of H_a-3 indicated that proton H-2, H_a-3 and H_a-4 are *cis*. In HMBC (**Table 88**) ^3J correlations of H-2 to C-4, C-2′,6′ and H-2′,6′ to C-2, C-6′,2′, C-4′ suggested that the aromatic ring was linked to C-2. Thus **SD1** was proposed to be (2*S*)-4′-hydroxy-7-methoxyflavan (Achenbach, *et al*., 1988).



NOE difference experiments of **SD1**



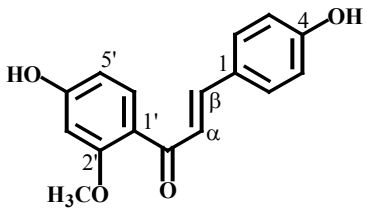
Major HMBC correlations of **SD1**

Table 88 The NMR spectral data of **SD1**

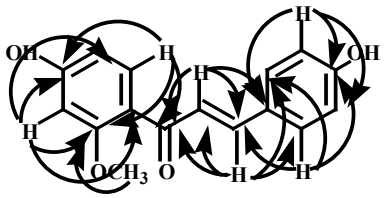
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	78.28 (CH)	4.96 (1H, *dd*, 13.1, 2.9)	C-3, C-4, C-1′, C-2′,6′
3	30.64 (CH_2)	H_a: 2.12 (1H, *qd*, 12.0, 2.4)	C-2, C-4, C-4a, C-1′
		H_b: 1.98 (1H, *m*)	C-2, C-4, C-4a, C-1′
4	25.01 (CH_2)	H_a: 2.88 (1H, *dddd*, 5.0, 1.0)	C-2, C-3, C-4a, C-5, C-8a
		H_b: 2.68 (1H, *ddd*, 12.0, 5.0, 3.0)	C-2, C-3, C-4a, C-5, C-8a
4a	115.56 (C)	-	-
5	130.71 (CH)	6.96 (1H, *d*, 8.5)	C-4, C-6, C-7, C-8a
6	107.68 (CH)	6.44 (1H, *dd*, 8.5, 2.6)	C-4a, C-7, C-8
7	159.98 (C)	-	-
8	102.16 (CH)	6.38 (1H, *d*, 2.6)	C-4a, C-6, C-7, C-8a
8a	156.89 (C)	-	-
1′	133.72 (C)	-	-
2′, 6′	128.23 (CH)	7.28 (2H, *d*, 9.2)	C-2, C-2′,6′, C-3′,5′, C-4′
3′, 5′	115.84 (CH)	6.87 (2H, *d*, 9.2)	C-1′, C-2′,6′, C-3′,5′, C-4′
4′	157.80 (C)	-	-
7-OCH_3	55.37 (CH_3)	3.73 (3H, *s*)	C-7
4′-OH		8.40 (1H, *br s*)	-

* Carbon type was deduced from DEPT experiments.

SD2 : 4,4′-Dihydroxy-2′-methoxychalcone (isoliquiritigenin 2′-methyl ether)



SD2 was isolated as a yellow solid, m.p. 218-220 °C. The ^{1}H NMR spectrum (**Table 89**) showed an AA′BB′ pattern, of which two *doublet* signals at δ 7.54 (J = 9.2 Hz) and 6.81 (J = 9.2 Hz) belonged to H-2, H-6 and H-3, H-5, respectively. It was thus indicated that **SD2** contained a *para*-substituted nucleus. A *doublet* at δ 6.50 (J = 2.3 Hz), a *doublet of doublet* at δ 6.44 (J = 8.1, 2.3 Hz) and a *doublet* at δ 7.50 (J = 8.1 Hz) were assigned for the resonances of H-3′, H-5′ and H-6′, respectively. Two *doublet* signals at δ 7.35 and 7.45 with a coupling constant of 16.1 Hz corresponded to *trans* vinylic protons, H-α and H-β. A methoxy group resonated at δ 3.83 and was located at C-2′ by the ^{3}J coupling of methoxy protons to C-2′. The correlations of H-α to C=O, C-β, C-1 and H-β to C=O, C-α , C-2, C-6 in HMBC suggested the positions of H-α and H-β. The ^{13}C NMR spectrum showed: a carbonyl carbon, five quaternary carbons, seven methine carbons and a methyl carbons corresponded with the assigned structure. **SD2** was therefore assigned to be 4,4′-dihydroxy-2′-methoxychalcone (Achenbach, *et al*., 1988).



Major HMBC correlations of **SD2**

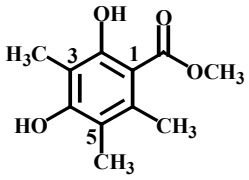
Table 89 The NMR spectral data of **SD2**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	126.20 (C)	-	-
2, 6	130.40 (CH)	7.54 (2H, *d*, 9.2)	C-2,6, C-4, C-β
3, 5	116.05 (CH)	6.81 (2H, *d*, 9.2)	C-1, C-3,5, C-4
4	159.79 (C)	-	-
1′	120.45 (C)	-	-
2′	162.72 (C)	-	-
3′	99.46 (CH)	6.50 (1H, *d*, 2.3)	C-1′, C-2′, C-4′, C-5′
4′	160.57 (C)	-	-
5′	108.04 (CH)	6.44 (1H, *dd*, 8.1, 2.3)	C-1′, C-3′
6′	132.37 (CH)	7.50 (1H, *d*, 8.1)	C-2′, C-4′, C=O
α	124.13 (CH)	7.35 (1H, *d*, 16.1)	C-1, C-β, C=O
β	141.56 (CH)	7.45 (1H, *d*, 16.1)	C-2,6, C-α, C=O
2′-OCH_3	55.83 (CH_3)	3.83 (3H, *s*)	C-2′
C=O	189.12 (C=O)	-	-

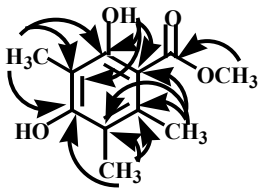
* Carbon type was deduced from DEPT experiments.

SD3 : 2,4-dihydroxy-3,5,6-trimethylbenzoic acid methyl ester

(methyl 2,4-dihydroxy-3,5,6-trimethylbenzoate)



SD3 was isolated as a yellow solid, m.p. 78-80 °C. The ^{1}H NMR spectrum (**Table 90**) showed six *singlet* signals. They were assigned for a chelated hydroxy proton 2-OH (δ 11.48), a non chelated hydroxy proton 4-OH (δ 5.25), methoxy protons (δ 3.95) and methyl protons 3-CH_3, 5-CH_3 (δ 2.15, 6H, *s*) and 6-CH_3 (δ 2.45, 3H, *s*). The presence of a carbonyl group was suggested from carbon resonance at δ 172.74. HMBC correlation of methoxy protons to C=O suggested that the methoxy group was linked to carbonyl carbon. Six quaternary carbons were indicated from the ^{13}C NMR spectrum. **SD3** then was assigned for 2,4-dihydroxy-3,5,6-trimethylbenzoic acid methyl ester which was known as methyl 2,4-dihydroxy-3,5,6-trimethylbenzoate (Soman, *et al*., 1999). These assignment were supported by HMBC correlations.



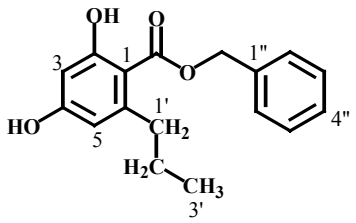
Major HMBC correlations of **SD3**

Table 90 The NMR spectral data of **SD3**

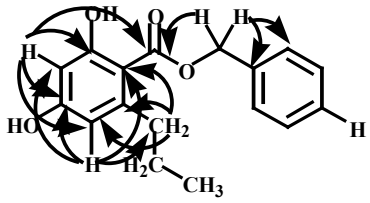
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	106.15 (C)	-	-
2	159.57 (C)	-	-
3	107.32 (C)	-	-
4	156.74 (C)	-	-
5	114.86 (C)	-	-
6	137.53 (C)	-	-
7	101.22 (C)	-	-
2-OH	-	11.48 (1H, *s*)	C-1, C-2, C-3
3-CH_3	8.04 (CH_3)	2.15 (3H, *s*)	C-2, C-3, C-4
4-OH	-	5.25 (1H, *s*)	-
5-CH_3	11.88 (CH_3)	2.15 (3H, *s*)	C-4, C-5, C-6
6-CH_3	18.82 (CH_3)	2.45 (3H, *s*)	C-1, C-5, C-6
C=O	172.74 (C=O)	-	-
OCH_3	51.88 (CH_3)	3.95 (3H, *s*)	C=O

* Carbon type was deduced from DEPT experiments.

SD4 : 2,4-Dihydroxy-6-propyl benzoic acid phenylmethyl ester



SD4 was isolated as a colourless solid, m.p. 89-90 °C. The ^{1}H NMR spectrum (**Table 91**) showed a *singlet* signal of a chelated hydroxy proton 2-OH at δ 12.00 and two *doublet* signals of *meta* protons H-3 (δ 6.31, J = 2.7 Hz) and H-5 (δ 6.21, J = 2.7 Hz). The resonances of a propyl side chain was displayed at δ 2.69 (2H, *br t*, H-1′), 1.40 (2H, *sextet*, H-2′) and 0.66 (3H, *t*, H-3′). The propyl group was suggested to be at C-6 by the correlation of H-1′ to C-1, C-5, C-6. The ^{1}H NMR showed the signals of oxybenzyl group of which the resonances of an oxymethylene protons were at δ 5.31 and the phenyl protons were at δ 7.35 (2H, *m*, H-2′′and H-6′′), 7.39 (2H, *m*, H-3′′and H-5′′) and 7.37 (1H, *m*, H-4′′). Irradiation at oxymethylene protons (δ 5.31) in NOE experiment gave the enhancement of the signal of H-2′′and H-6′′ (δ 7.35). The compound was then proposed to be ester derivative. These assignment were supported by HMBC correlations as shown in **Table 91**. **SD4** was then assigned for 2,4-dihydroxy-6-propyl benzoic acid phenylmethyl ester which was known as benzyl 2,4- dihydroxy-6-propyl benzoate (Elix, *et al*., 1998).



Major HMBC correlations of **SD4**

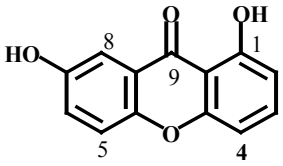
Table 91 The NMR spectral data of **SD4**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	104.69 (C)	-	-
2	165.17 (C)	-	-
3	101.43 (CH)	6.31 (1H, *d*, 2.7)	C-2, C-4, C-5, C=O
4	160.83 (C)	-	-
5	111.22 (CH)	6.21 (1H, *d*, 2.7)	C-1, C-3, C-4, C=O, C-1′
6	148.85 (C)	-	-
1′	38.87 (CH_2)	2.69 (2H, *br t*)	C-1, C-5, C-6, C-2′, C-3′
2′	25.02 (CH_2)	1.40 (2H, *sextet*)	C-6, C-1′, C-3′
3′	13.90 (CH_3)	0.66 (3H, *t*, 7.2)	C-1′, C-2′
1″	134.95 (C)	-	-
2″, 6″	128.68 (CH)[a]	7.35 (2H, *m*)[b]	C-1″, C-2″,6″, C-3″,5″, C-4″
3″, 5″	129.00 (CH)[a]	7.39 (2H, *m*)[b]	C-1″, C-2″,6″, C-3″,5″, C-4″
4″	128.69 (CH)[a]	7.37 (1H, *m*)	C-2″,6″, C-3″,5″
2-OH	-	12.00 (1H, *s*)	-
C=O	171.44 (C=O)	-	-
OCH_2	67.52 (CH_2)	5.31 (2H, *s*)	C-1″, C-2″, C=O

* Carbon type was deduced from DEPT experiments.

[a, b] Assignment maybe interchangeable.

SD5 : 1,7-Dihydroxyxanthone (euxanthone)

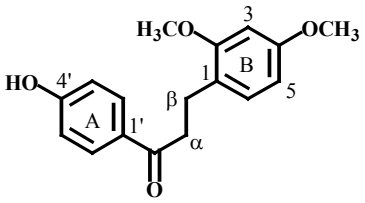


SD5 was isolated as a yellow solid, m.p. 228-230 °C. The ^{1}H NMR (**Table 92**) revealed the presence of a sharp *singlet* signal of a chelated hydroxy proton (1-OH) at δ 12.62. Two *doublet of doublet* signals at δ 6.79 (J = 8.0, 0.5 Hz), 6.93 (J = 8.0, 0.5 Hz) and a *triplet* signal at δ 7.59 (J = 8.0 Hz) were assigned as an ABM pattern of H-2, H-4 and H-3, respectively. A *doublet* signal at δ 7.42 (J = 9.0 Hz), a *doublet* signal at δ 7.62 (J = 3.0 Hz) and a *doublet of doublet* signal at δ 7.32 (J = 9.0 and 3.0 Hz) revealed the presence of an ABX pattern which was assigned for H-5, H-8 and H-6. **SD5** was then identified to be 1,7-dihydroxyxanthone. Its ^{1}H NMR spectral data and melting point were in agreement with euxanthone (Fujita, *et al.*, 1992).

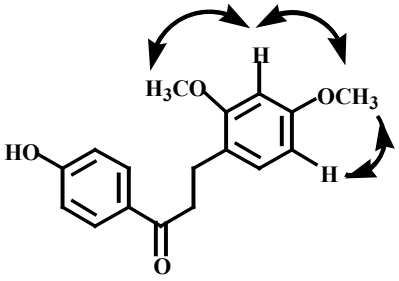
Table 92 The ^{1}H NMR spectral data of **SD5**

Position	δ_H (*multiplicity*, J_{Hz})	
	SD5	**euxanthone**
2	6.79 (1H, *dd*, 8.0, 0.5)	6.77 (1H, *dd*, 8.4, 0.5)
3	7.59 (1H, *t*, 8.0)	7.59 (1H, *t*, 8.8)
4	6.93 (1H, *dd*, 8.0, 0.5)	6.95 (1H, *dd*, 8.4, 0.5)
5	7.42 (1H, *d*, 9.0)	7.41 (1H, *d*, 9.3)
6	7.32 (1H, *dd*, 9.0, 3.0)	7.33 (1H, *dd*, 9.3, 2.9)
8	7.62 (1H, *d*, 3.0)	7.63 (1H, *d*, 2.9)
1-OH	12.62 (1H, *s*)	12.62 (1H, *s*)
7-OH	-	5.01 (1H, *s*)

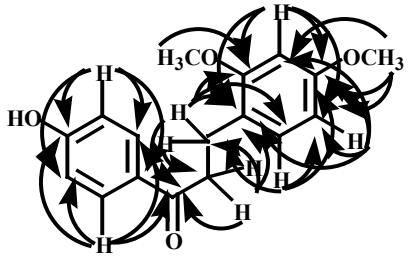
SD6 : 4′-Hydroxy-2,4-dimethoxydihydrochalcone (loureirin A)



SD6 was isolated as a colourless solid, m.p. 128-130 °C. The ^{1}H NMR spectrum (**Table 93**) demonstrated the resonances of an ABX pattern of H-3 (δ 6.44, *d*, *J* = 2.4 Hz), H-5 (δ 6.41, *dd*, *J* = 7.8 and 2.4 Hz) and H-6 (δ 7.07, *d*, *J* = 7.8 Hz), and an AA′BB′ pattern of H-2′, H-6′ (δ 7.92, 2H, *d*, *J* = 8.4 Hz) and H-3′, H-5′ (δ 6.90, 2H, *d*, *J* = 8.4 Hz). The presence of two methoxy groups were shown by the resonance at δ 3.79 (6H) and it was indicated at C-2 and C-4 by the ^{3}J coupling of methoxy groups to C-2 and C-4. The enhancement of H-3 by irradiation at the resonance of the methoxy protons suggested that H-3 was nearby the methoxy groups. The spectrum further showed resonances of H-α at δ 3.18 (2H, *t*, *J* = 7.2 Hz) and H-β at δ 2.87 (2H, *t*, *J* = 7.2 Hz). The HMBC correlations of H-α to C=O, H-β, C-1 and H-β to C=O, H-α, C-1, C-2, C-6 suggested an aromatic ring B was attached to C-β. The ^{13}C NMR spectrum and HMBC were in agreement with assigned structure. Therefore, **SD6** was characterized as 4′-hydroxy-2,4-dimethoxydihydrochalcone or known as loureirin A (Meksuriyen and Cordell, 1988).



Major NOE difference experiments of **SD6**



Major HMBC correlations of **SD6**

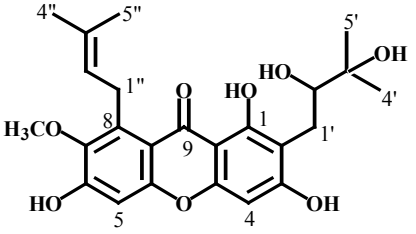
Table 93 The NMR spectral data of **SD6**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	121.64 (C)	-	-
2	158.25 (C)	-	-
3	98.49 (CH)	6.44 (1H, *d*, 2.4)	C-1, C-2, C-4, C-5
4	159.36 (C)	-	-
5	103.89 (CH)	6.41 (1H, *dd*, 7.8, 2.4)	C-1, C-3, C-4
6	130.21 (CH)	7.07 (1H, *d*, 7.8)	C-2, C-4, C-5, C-β
1′	129.19 (C)	-	-
2′, 6′	130.93 (CH)	7.92 (2H, *d*, 8.4)	C-2′,6′, C-3′,5′, C-4′, C=O
3′, 5′	115.47 (CH)	6.90 (2H, *d*, 8.4)	C-1′, C-2′,6′, C-3′,5′, C-4′
4′	161.21 (C)	-	-
α	38.88 (CH_2)	3.18 (2H, *t*, 7.2)	C-1, C-β, C=O
β	25.62 (CH_2)	2.87 (2H, *t*, 7.2)	C-1, C-2, C-6, C-α, C=O
2-OCH_3	55.33 (CH_3)[a]	3.79 (3H, *s*)	C-2
4-OCH_3	55.15 (CH_3)[a]	3.79 (3H, *s*)	C-4
C=O	200.72 (C=O)	-	-

* Carbon type was deduced from DEPT experiments.

[a] Assignment maybe interchangeable.

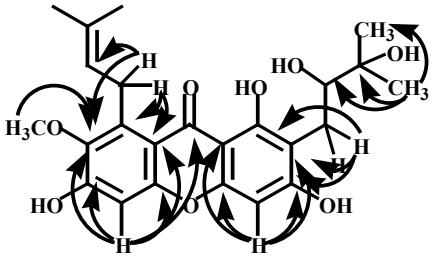
SD7 : 1,3,6-Trihydroxy-2-(2,3-dihydroxy-3-methylbutyl)-7-methoxy-8-(3-methyl-2-butenyl)xanthone



SD7 was isolated as a yellow solid with m.p. 188-190 °C. A xanthone nucleus was elucidated from the UV spectra (λ_{max} 318.4, 244.9 and 213.2 nm). The IR spectra showed absorption bands of hydroxy (3397 cm^{-1}) and conjugated carbonyl (1612 cm^{-1}) functionalities. It had molecular formula $C_{24}H_{28}O_8$ ($[M]^+$ *m/z* 444.1788).

The ^{1}H NMR spectrum (**Table 94**) showed a *singlet* signal of a deshielded hydroxy proton 1-OH (δ 13.82), a *singlet* resonance of methoxy protons 7-OCH_3 (δ 3.79), two *singlet* signals of two isolated aromatic protons H-4 and H-5 (δ 6.26 and 6.74). The typical resonances of a prenyl side chain appeared as follow: two *singlets* of two methyl groups at δ 1.84 (H-5″) and 1.69 (H-4″), a *doublet* at δ 4.00 (H-1″) and a *broad triplet* at δ 5.26 (H-2″). This side chain was assigned at C-8 according to the low field chemical shift of H-1″ (δ 4.00) and confirmed by HMBC correlation of H-1″ to C-7, C-8, C-8a, C-2″ and C-3″. A *doublet of doublet* of methylene protons at δ 3.14 (2H, *J* = 12.3 and 9.3 Hz, H-1′), a *triplet* of hydroxy methine proton at δ 4.77 (1H, *J* = 8.4 Hz, H-2′) and two sharp *singlets* of two methyl groups at δ 1.83 (H-5′) and 1.32 (H-4′) corresponded to the resonances of a 2,3-dihydroxy-3-methylbutyl side chain. It was assigned at C-2 according to the HMBC correlation of H-1′ to C-1, C-2, C-3, C-2′ and C-3′. The resonance of methoxy protons (OCH_3) showed a cross-peak with a quaternary aromatic carbon C-7 signal, this indicated the position of OCH_3 at C-7. The ^{13}C NMR spectrum and DEPT experiments corresponded to the assigned

structure. Therefore, **SD7** was assigned as 1,3,6-trihydroxy-2-(2,3-dihydroxy-3-methylbutyl)-7-methoxy-8-(3-methyl-2-butenyl)xanthone. It was a new naturally occurring xanthone.



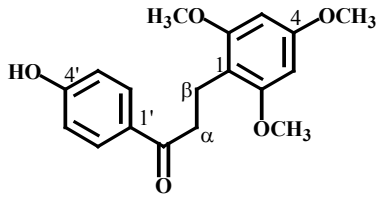
Major HMBC correlations of **SD7**

Table 94 The NMR spectral data of **SD7**

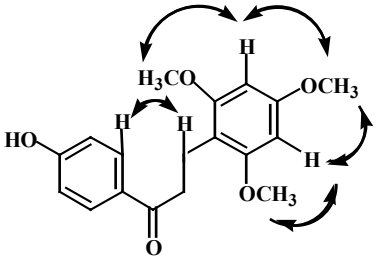
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	157.19 (C)	-	-
2	107.51 (C)	-	-
3	166.33 (C)	-	-
4	88.30 (CH)	6.26 (1H, *s*)	C-2, C-3, C-4a, C-9a
4a	157.19 (C)	-	-
5	101.97 (CH)	6.74 (1H, *s*)	C-6, C-7, C-8a, C-9, C-10a
6	155.67 (C)	-	-
7	143.40 (C)	-	-
8	137.36 (C)	-	-
8a	111.51 (C)	-	-
9	182.24 (C=O)	-	-
9a	104.08 (C)	-	-
10a	156.01 (C)	-	-
1′	26.86 (CH_2)	3.14 (2H, *dd*, 12.3, 9.3)	C-1, C-2, C-3, C-2′, C-3′
2′	91.77 (CH)	4.77 (1H, *t*, 8.4)	C-1′
3′	71.88 (C)	-	-
4′	25.37 (CH_3)	1.32 (3H, *s*)	C-2′, C-3′, C-5′
5′	24.07 (CH_3)	1.83 (3H, *s*)	C-2′, C-3′, C-4′
1″	26.41 (CH_2)	4.00 (2H, *d*, 6.0)	C-7, C-8, C-8a, C-2″, C-3″
2″	123.45 (CH)	5.26 (1H, *br t*, 5.1)	C-1″, C-4″, C-5″
3″	131.91 (C)	-	-
4″	25.87 (CH_3)	1.69 (3H, *s*)	C-2″, C-3″, C-5″
5″	18.20 (CH_3)	1.84 (3H, *s*)	C-2″, C-3″, C-4″
1-OH	-	13.82 (1H, *s*)	C-1, C-2, C-9a
7-OCH_3	61.25 (CH_3)	3.79 (3H, *s*)	C-7

* Carbon type was deduced from DEPT experiments.

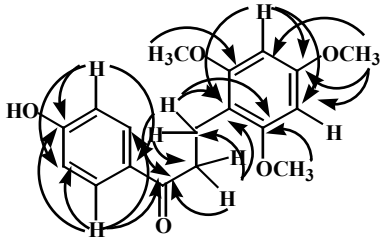
SD8 : 4′-Hydroxy-2,4,6-trimethoxydihydrochalcone (loureirin B)



SD8 was isolated as a colourless solid, m.p. 132-133 °C. The ^{1}H NMR spectrum (**Table 95**) showed the resonances of an AA′BB′ system of H-2′, H-6′ (δ 7.93) and H-3′, H-5′ (δ 6.93) and the resonances of H-α (δ 2.95, 2H) and H-β (δ 2.87, 2H) as in **SD6**. The *singlet* resonance of three methoxy groups (δ 3.80) and two *doublet* resonances of *meta*-protons (δ 6.24) implied the presence of a tetrasubstituted ring B. This assignment was confirmed by irradiation at the resonances of methoxy groups, it gave positive enhancement of the signals of H-3 and H-5. The ^{13}C NMR spectrum (**Table 95**) showed 14 signals for eighteen carbons. Thus **SD8** was elucidated as 4′-hydroxy-2,4,6-trimethoxydihydrochalcone. It was known as loureirin B (Meksuriyen and Cordell, 1988).



Major NOE difference experiments of **SD8**



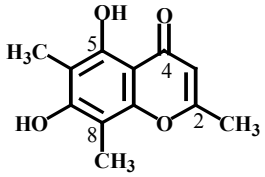
Major HMBC correlations of **SD8**

Table 95 The NMR spectral data of **SD8**

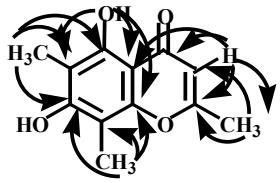
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	110.08 (C)	-	-
2, 6	159.61 (C)	-	-
3, 5	91.38 (CH)	6.24 (2H, *s*)	C-1, C-4, C-3,5
4	160.76 (C)	-	-
1′	130.25 (C)	-	-
2′, 6′	131.30 (CH)	7.93 (2H, *d*, 7.8)	C-2′,6′, C-3′,5′, C-4′, C=O
3′, 5′	115.87 (CH)	6.93 (2H, *d*, 7.8)	C-1′, C-2′,6′, C-3′,5′, C-4′
4′	162.38 (C)	-	-
α	38.89 (CH_2)	2.95 (2H, *dt*, 9.6, 4.0)	C-1, C-β, C=O
β	19.28 (CH_2)	2.87 (2H, *dt*, 9.6, 4.0)	C-1, C-2, C-6, C-α, C=O
2-OCH_3	55.93 (CH_3)	3.80 (3H, *s*)	C-2, C-3
4-OCH_3	55.51 (CH_3)	3.80 (3H, *s*)	C-3, C-4, C-5
6-OCH_3	55.93 (CH_3)	3.80 (3H, *s*)	C-5, C-6
C=O	198.71 (C=O)	-	-

* Carbon type was deduced from DEPT experiments.

SD9 : 5,7-Dihydroxy-2,6,8-trimethylchromone



SD9 was isolated as a light brown solid, m.p. 276-277 °C. The ^{1}H NMR spectrum (**Table 96**) showed the signals of a chelated hydroxy proton 5-OH at δ 13.05 (*s*), an olefinic proton H-3 at δ 6.20 (*s*) and methyl protons 2-CH_3 (δ 2.43, *s*), 6-CH_3 (δ 2.08, *s*) and 8-CH_3 (δ 2.19, *s*). The ^{13}C NMR spectrum and DEPT experiments showed the resonances of a carbonyl carbon, seven quaternary carbons, a methine carbon and three methyl carbons which agreed with the assigned structure. The enhancement of H-3 by irradiation at the resonance of the methyl protons 2-CH_3 confirmed the positions of H-3. HMBC correlations also confirmed the assignment. **SD9** then was assigned for 5,7-dihydroxy-2,6,8-trimethylchromone which was known as 8-methyleugenitol (Ito and Lai, 1978).



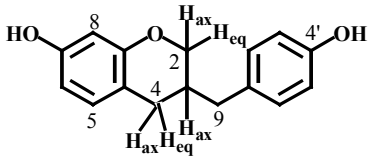
Major HMBC correlations of **SD9**

Table 96 The NMR spectral data of **SD9**

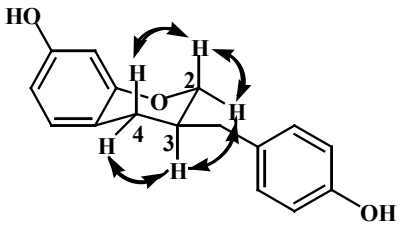
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	167.32 (C)	-	-
3	107.39 (CH)	6.20 (1H, *s*)	C-2, C-4, C-4a, 2-CH_3
4	182.08 (C=O)	-	-
4a	103.11 (C)	-	-
5	155.92 (C)	-	-
6	106.75 (C)	-	-
7	159.66 (C)	-	-
8	101.53 (C)	-	-
8a	152.89 (C)	-	-
2-CH_3	19.85 (CH_3)	2.43 (3H, *s*)	C-2, C-3
5-OH	-	13.05 (1H, *s*)	C-4a, C-5, C-6
6-CH_3	7.99 (CH_3)	2.08 (3H, *s*)	C-5, C-6, C-7
8-CH_3	7.87 (CH_3)	2.19 (3H, *s*)	C-7, C-8, C-8a

* Carbon type was deduced from DEPT experiments.

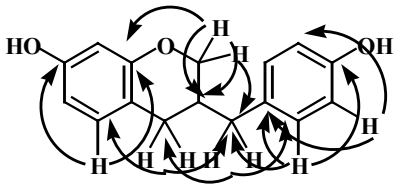
SD10 : 7-Hydroxy-3-(4-hydroxybenzyl)chroman



SD10 was isolated as a pink solid, m.p. 150-152 °C. The optical rotation was $[\alpha]_D^{26}$ + 63.0 ° (c = 0.018 in CH_3OH). The ^1H NMR spectrum (**Table 97**) exhibited the resonances of seven aromatic protons, one methine proton, three methylene protons and two hydroxy groups. The AA′BB′ resonances at δ 7.07 (2H, *J* = 7.2 Hz) and 6.79 (2H, *J* = 7.2 Hz) corresponded to protons H-2′, H-6′ and H-3′, H-5′, respectively. The ABX resonances at δ 6.24 (*d*, *J* = 2.4 Hz), 6.33 (*dd*, *J* = 8.4 and 2.4 Hz) and 6.80 (*d*, *J* = 8.4 Hz) belonged to H-8, H-6 and H-5, respectively. A *doublet of doublet of doublet* resonance of H_{eq}-2 (δ 4.10, 1H, *J* = 9.6, 2.4 and 1.3 Hz), a *doublet of doublet* resonance of H_{ax}-2 (δ 3.72, 1H, *J* = 10.8 and 8.4 Hz), a *multiplet* resonance of H_{ax}-3 (δ 2.16), two *doublet of doublet* signals of H_{eq}-4 and H_{ax}-4 (δ 2.65, 1H, *J* = 15.4 and 5.5 Hz and δ 2.39, 1H, *J* = 15.4 and 8.8 Hz) and two *doublet of doublet* signals of H-9 (δ 2.59 and 2.59, 1H each, *J* = 13.2 and 7.7 Hz) were observed. The remaining signals are the resonances of two hydroxy groups (δ 8.16 and 8.12). The NOE experiment: irradiation at the resonances of H_{ax}-2 (δ 3.72) and H_{ax}-3 (δ 2.16) resulted in the enhancement of the resonance of H_{eq}-2 (δ 4.10). The ^{13}C NMR spectrum (**Table 97**) showed the signals of five quaternary carbons, six methine carbons and three methylene carbons. Consequently, **SD10** was proposed to be 7-hydroxy-3-(4-hydroxybenzyl)chroman. The assignment was in agreement with the previous data of 7-hydroxy-3-(4-hydroxybenzyl)chroman (Masaoud, *et al.*, 1995; Meksuriyen, *et al.*, 1987).



Major NOE difference experiments of **SD10**



Major HMBC correlations of **SD10**

Table 97 The NMR spectral data of **SD10**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	^{1}H-^{1}H COSY	HMBC
2	70.41 (CH_2)	H_{ax}: 3.72 (1H, *dd*, 10.8, 8.4)	H_{eq}-2, H-3	C-3, C-4, C-8a, C-9
		H_{eq}: 4.10 (1H, *ddd*, 9.6, 2.4, 1.3)	H_{ax}-2, H-3	C-3, C-4, C-8a, C-9
3	35.35 (CH)	H_{ax}: 2.16 (1H, *m*)	H-2, H-4, H-9	C-2, C-4, C-9
4	30.95 (CH_2)	H_{ax}: 2.39 (1H, *dd*, 15.4, 8.8)	H-3, H_{eq}-4	C-2, C-3, C-4a, C-5, C-8a, C-9
		H_{eq}: 2.65 (1H, *dd*, 15.4, 5.5)	H-3, H_{ax}-4	C-2, C-3, C-4a, C-5, C-8a, C-9
4a	113.27 (C)	-	-	-
5	131.14 (CH)	6.80 (1H, *d*, 8.4)	H-6	C-4, C-7, C-8a
6	108.76 (CH)	6.33 (1H, *dd*, 8.4, 2.4)	H-5, H-8	C-4a, C-7, C-8
7	156.18 (C)	-	-	-
8	103.54 (CH)	6.24 (1H, *d*, 2.4)	H-6	C-4a, C-6, C-7, C-8a
8a	157.40 (C)	-	-	-

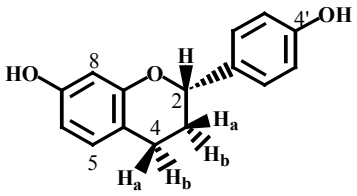
Table 97 (Continued)

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	^{1}H-^{1}H COSY	HMBC
9	37.62 (CH_2)	2.59 (1H, *dd*, 13.2, 7.7)	H-3, H-9	C-2, C-3, C-4, C-1′, C-2′,6′
		2.52 (1H, *dd*, 13.2, 7.7)	H-3, H-9	C-2, C-3, C-4, C-1′, C-2′,6′
1′	130.72 (C)	-	-	-
2′, 6′	131.08 (CH)	7.07 (2H, *d*, 7.2)	H-3′, H-5′	C-9, C-1′, C-3′,5′, C-4′
3′, 5′	115.95 (CH)	6.79 (2H, *d*, 7.2)	H-2′, H-6′	C-1′, C-3′,5′, C-4′
4′	156.58 (C)	-	-	-
7-OH	-	8.16 (1H, *br s*)[a]	-	-
4′-OH	-	8.12 (1H, *br s*)[a]	-	-

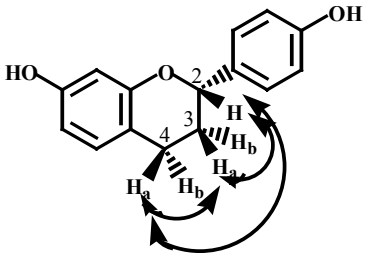
* Carbon type was deduced from DEPT experiments.

[a] Assignment maybe interchangeable.

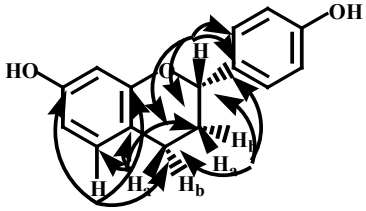
SD11 : (2*S*)-7,4′-Dihydroxyflavan



SD11 was isolated as brown needles. The optical rotation was $[\alpha]_D^{29}$ -129.0 ° (c = 0.023 in CH_3OH). The ^1H NMR spectrum (**Table 98**) showed the resonances of an AA′BB′ system for protons H-2′, H-6′ and H-3′, H-5′ at δ 7.27 (2H, *J* = 8.0 Hz) and 6.86 (2H, *J* = 8.0 Hz) and the resonances of an ABX system for protons H-5, H-6 and H-8 at δ 6.88 (*d*, *J* = 8.0 Hz), 6.38 (*dd*, *J* = 8.0 and 2.4 Hz) and 6.32 (*d*, *J* = 2.4 Hz). The spectra further showed a *doublet of doublet* resonance of H-2 at δ 4.93 (1H, *J* = 10.5 and 1.8 Hz), a *quartet of doublet* of H_a-3 at δ 2.09 (*J* = 12.6 and 2.4 Hz) and a *multiplet* resonance of H_b-3 at δ 1.96, a *multiplet* of H_a-4 at δ 2.85 and a *doublet of doublet of doublet* resonance of H_b-4 at δ 2.64 (*J* = 15.6, 4.8 and 3.6 Hz). The negative $[\alpha]_D$ value indicated that C-2 possesses an *S* configuration (Achenbach, *et al*., 1988). The enhancement of the signals of H-2 and H_a-4 upon irradiation at the resonance of H_a-3 indicated that protons H-2, H_a-3 and H_a-4 are *cis*. In HMBC (**Table 98**), ^3J correlations of H-2 to C-4, C-2′,6′ and H-2′,6′ to C-2, C-6′,2′, C-4′ suggested that the aromatic ring was linked to C-2. The ^{13}C NMR spectrum (**Table 98**) showed 13 signals for fifteen carbons. Consequently, **SD11** was proposed to be (2*S*)-7,4′-dihydroxyflavan (Achenbach, *et al*., 1988).



NOE difference experiments of **SD11**



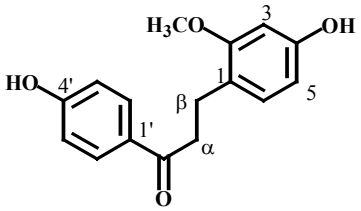
Major HMBC correlations of **SD11**

Table 98 The NMR spectral data of **SD11**

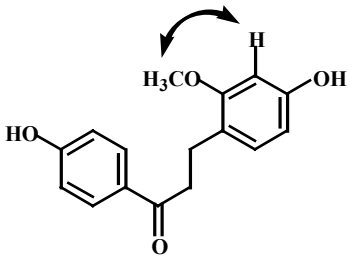
Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
2	78.12 (CH)	4.93 (1H, *dd*, 10.5, 1.8)	C-3, C-4, C-1′, C-2′,6′
3	30.70 (CH_2)	H_a: 2.09 (1H, *qd*, 12.6, 2.4)	C-4, C-4a, C-1′
		H_b: 1.96 (1H, *m*)	C-4, C-4a, C-1′
4	24.98 (CH_2)	H_a: 2.85 (1H, *m*)	C-2, C-3, C-4a, C-5, C-8a
		H_b: 2.64 (1H, *ddd*, 15.6, 4.8, 3.6)	C-2, C-3, C-4a, C-5, C-8a
4a	113.63 (C)	-	-
5	130.70 (CH)	6.88 (1H, *d*, 8.0)	C-4, C-7, C-8a
6	108.69 (CH)	6.38 (1H, *dd*, 8.0, 2.4)	C-4a, C-7, C-8
7	157.67 (C)	-	-
8	103.80 (CH)	6.32 (1H, *d*, 2.4)	C-4a, C-6, C-7, C-8a
8a	156.78 (C)	-	-
1′	133.77 (C)	-	-
2′, 6′	128.18 (CH)	7.27 (2H, *d*, 8.0)	C-2, C-2′,6′, C-3′,5′, C-4′
3′, 5′	115.80 (CH)	6.86 (2H, *d*, 8.0)	C-1′, C-3′,5′, C-4′
4′	157.29 (C)	-	-

* Carbon type was deduced from DEPT experiments.

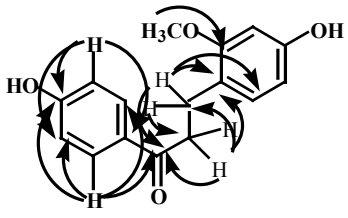
SD12 : 4,4′-Dihydroxy-2-methoxydihydrochalcone (loureirin C)



SD12 was isolated as a pink solid, m.p. 178-179 °C. The ^{1}H NMR spectrum (**Table 99**) showed the resonances of an ABX pattern of H-3 (δ 6.46, *d*), H-5 (δ 6.35, *dd*) and H-6 (δ 6.99, *d*), an AA′BB′ pattern of H-2′, H-6′ (δ 7.92, 2H, *d*) and H-3′, H-5′ (δ 6.92, 2H, *d*) and the resonances of H-α (δ 3.11, 2H) and H-β (δ 2.85, 2H) as in **SD8**. Only one methoxy group was shown by the resonance at δ 3.80 and it was located at C-2 by the ^{3}J correlation of methoxy group to C-2. The enhancement of H-3 by irradiation at the resonance of the methoxy protons confirmed the position of OCH_3 at C-2. ^{13}C NMR spectrum (**Table 99**) and HMBC confirmed the assigned structure. Therefore, **SD12** was characterized as 4,4′-dihydroxy-2-methoxydihydrochalcone which was known as loureirin C (Meksuriyen and Cordell, 1988).



Major NOE difference experiments of **SD12**



Major HMBC correlations of **SD12**

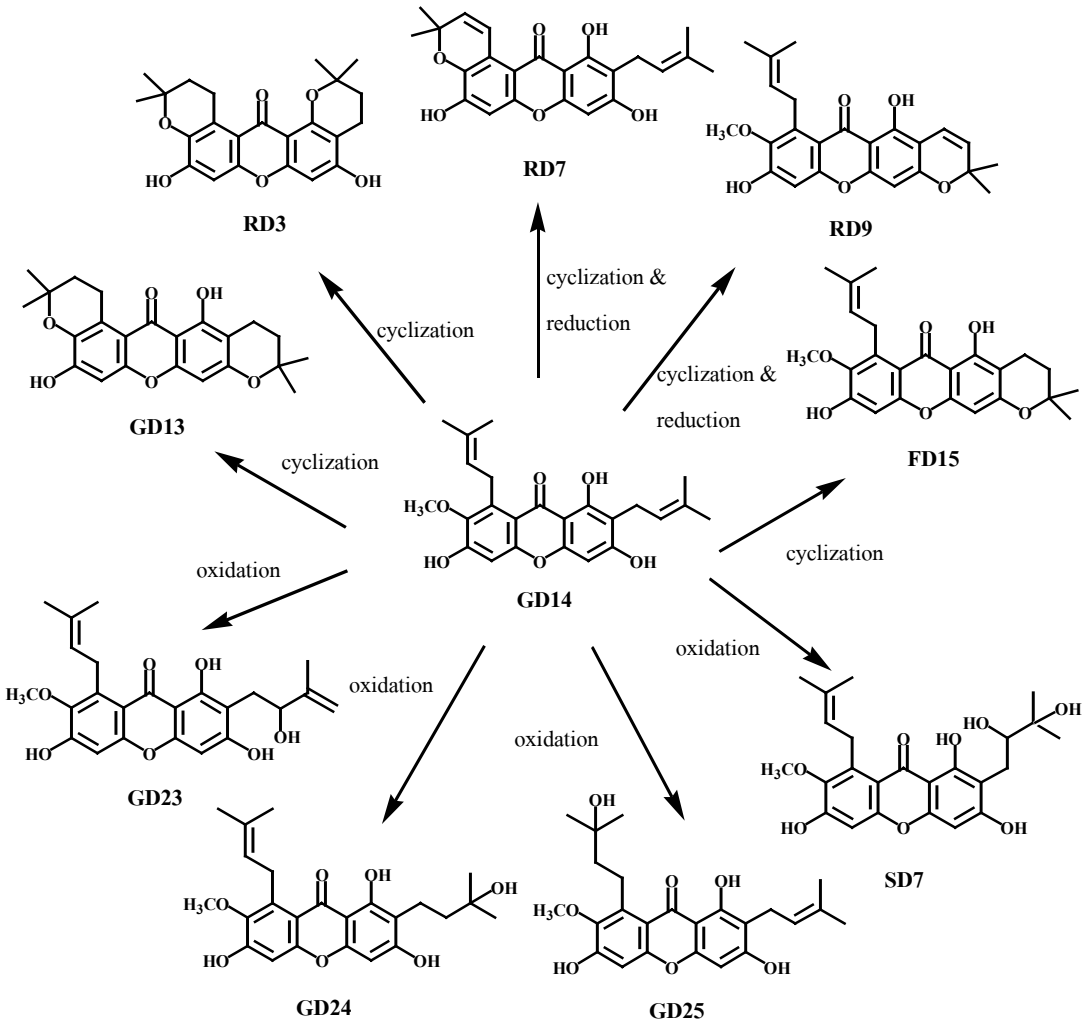
Table 99 The NMR spectral data of **SD12**

Position	δ_C (C-Type)*	δ_H (*multiplicity*, J_{Hz})	HMBC
1	121.07 (C)	-	-
2	159.28 (C)	-	-
3	99.60 (CH)	6.46 (1H, *d*, 3.0)	C-1, C-2, C-4, C-5
4	158.00 (C)	-	-
5	107.35 (CH)	6.35 (1H, *dd*, 8.0, 3.0)	C-1, C-3, C-4
6	130.98 (CH)	6.99 (1H, *d*, 8.0)	C-2, C-4, C-β
1′	130.10 (C)	-	-
2′, 6′	131.24 (CH)	7.92 (2H, *d*, 9.6)	C-2′,6′, C-3′,5′, C-4′, C=O
3′, 5′	115.90 (CH)	6.92 (2H, *d*, 9.6)	C-1′, C-3′,5′, C-4′
4′	162.44 (C)	-	-
α	39.31 (CH_2)	3.11 (2H, *t*, 9.0)	C-1, C-β, C=O
β	25.80 (CH_2)	2.85 (2H, *t*, 9.0)	C-1, C-2, C-6, C-α, C=O
2-OCH_3	55.46 (CH_3)	3.80 (3H, *s*)	C-2
C=O	198.71 (C=O)	-	-

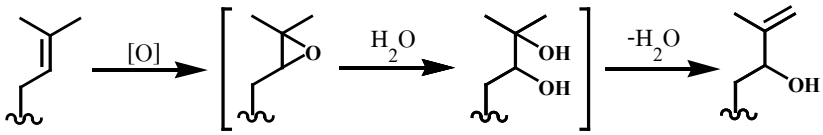
* Carbon type was deduced from DEPT experiments.

3.2 Relationship of compounds from G. dulcis

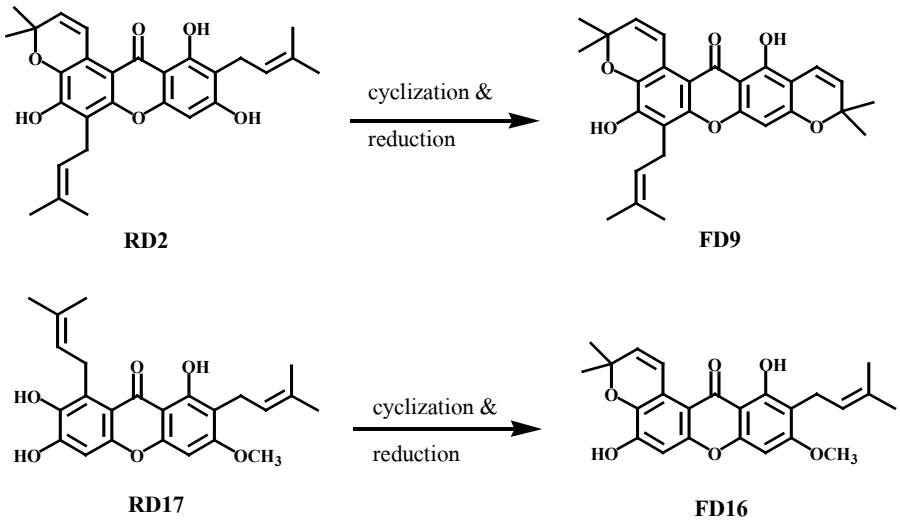
Investigation of *G. dulcis* has revealed that polyisoprenyl benzophenones, biflavonoids and xanthones are three main components in this plant. The flavans, isoflavans, flavones, isoflavones, flavonols, chromones, chalcones, glycerol, triterpene and dimethoxy citrate were also present. The presence of both xanthones and benzophenones *in G. dulcis* is in agreement with the biosynthesis path way that xanthones were formed on an arylpolyketide pathway involving a benzophenone key intermediate (Bennett and Lee, 1989). The relationships among xanthone derivatives can be discussed.

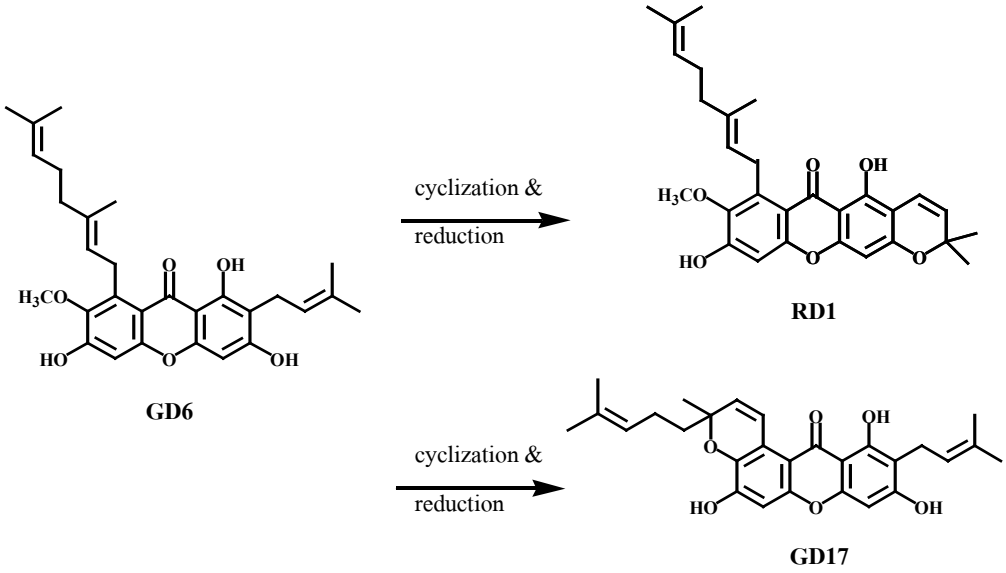


GD14 is a precursor of **GD13**, **GD23**, **GD24**, **GD25**, **RD3**, **RD7**, **RD9**, **FD15** and **SD7**. **GD13**, **RD3** and **FD15** were obtained from cyclization of prenyl side chains. **RD7** and **RD9** were resulted from cyclization and reduction of the prenyl unit. **GD23**, **GD24**, **GD25** and **SD7** were obtained from oxidation of the prenyl side chain. The oxidation of the prenyl side chain to a 2-hydroxy-3-methyl-3-butenyl side chain was reported by Tahara and co-workers (1989).



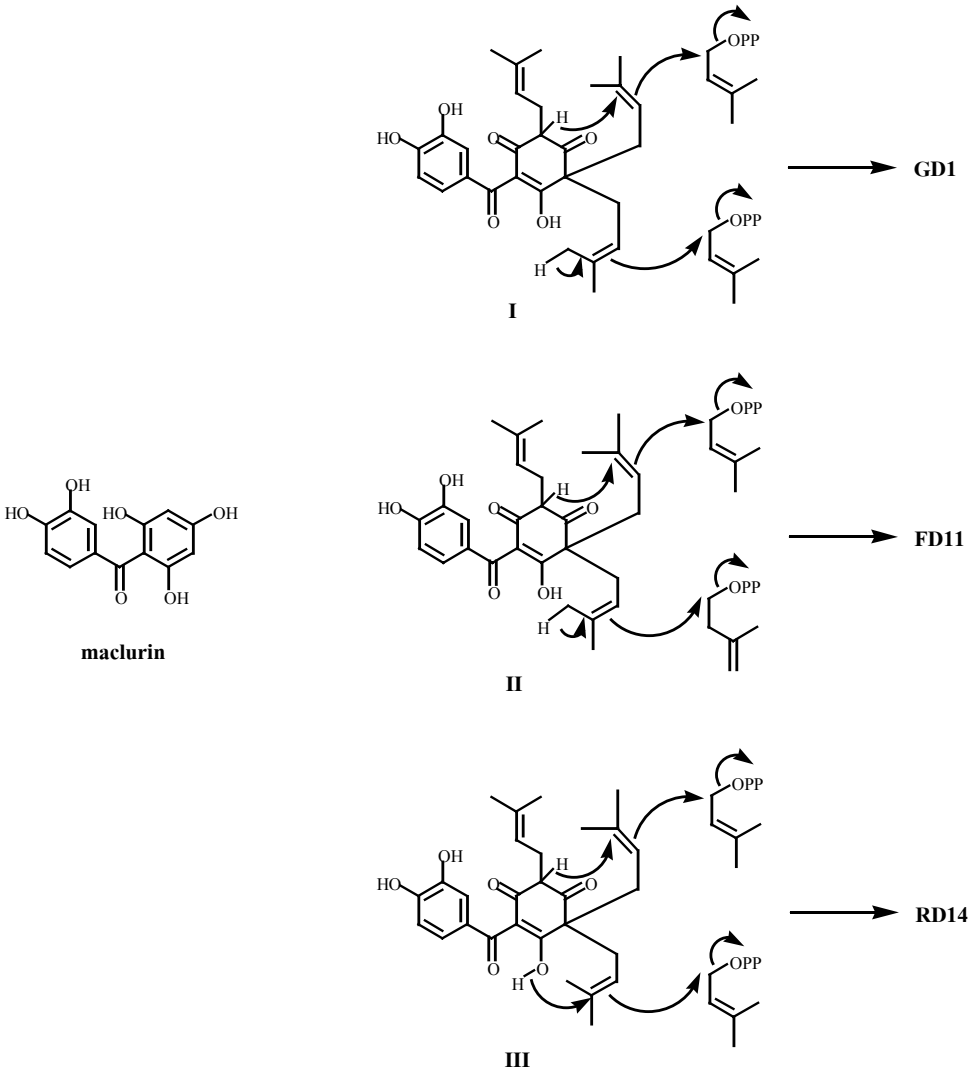
FD9, **FD16** and **RD1** were obtained from cyclization and reduction of the prenyl side chain of **RD2**, **RD17** and **GD6**, respectively. **GD17** was the product from cyclization and reduction of the geranyl side chain of **GD6**.





GD6 **RD1** **GD17**

Benzophenones which were found in *G. dulcis* were **GD1**, **GD22**, **RD14**, **FD11** and **FD12**. Camboginol (**GD1**) is a major component in the green fruits but not in the ripe fruits. Whereas cambogin (**RD14**) which was a cyclization product of **GD1** was isolated from the ripe fruits. It could be assumed that **GD1** was produced in the green fruits then become **RD14** in the ripe fruits. **GD1**, **RD14**, **FD11** and **FD12** might be derived biogenetically from maclurin by the attachment of three or more isoprenyl side chains and successive cyclodehydrogenation and/or cyclization. **GD1** and **RD14** were obtained from reaction of intermediate **I** and **II**, respectively (Ramo Rao, *et al*., 1980; Karanjgoakar, *et al*., 1973; Locksley, *et al*., 1967). Reaction of three dimethylally pyrophosphate (DMAPP) units on the phloroglucinol ring of maclurin can give rise to an intermadiate **I** which can further react with two additional DMAPP to give camboginol (**GD1**) (Rama Rao, *et al*., 1980). Alternatively, reaction of intermediate **II** with one DMAPP and a isopentenylpyrophosphate can lead to xanthochymol (**FD11**) (Rama Rao, *et al*., 1980).



GD20, **FD1**, **FD6**, **FD7**, **FD8** and **FD10** are biflavonoids. **FD6** is C-3′,C-8″ interflavonoid linkage whereas the others are C-3,C-8″ interflavonoid linkage. **GD20**, **FD1** and **FD8** are two related flavanone-flavone dimers. **FD7** and **FD10** contained two flavanone units whereas **FD6** contained two flavone units. **FD7** and **FD8** are biflavonoid glycosides of **FD10** and **GD20**, respectively. Apigenin (**RD13**) was a precursor of these biflavonoids and flavanonols, **RD6** and **RD15**.

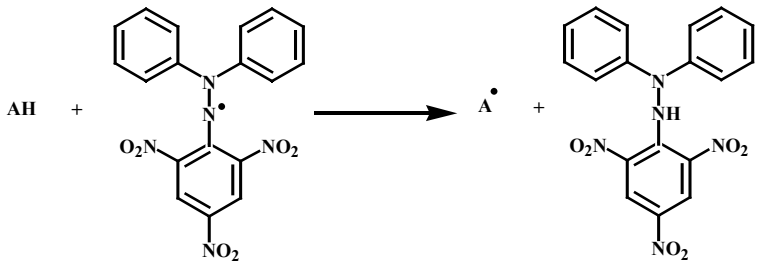
Among seventy-four isolated compounds, only five of them were previously reported to be isolated from this plant. Morelloflavone (**GD20**), volkensiflavone (**FD1**)

and GB-2a (**FD10**) were previously isolated from the leaves whereas podocarpusflavone A (**FD6)** and euxanthone (**SD5)** were obtained from the branches and the stem bark, respectively.

3.3 Evaluation of antioxidation activity

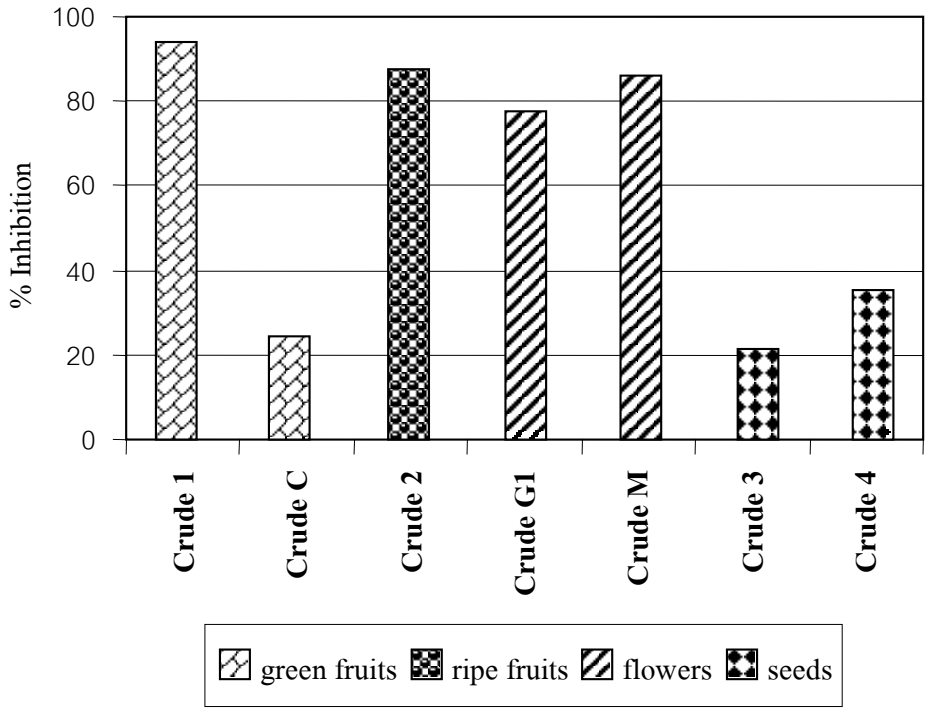
Phenolic compounds were known to be the antioxidant with an excellent hydrogen or electron donors (Shahidi, *et al.*, 1992). The isolated compounds from *G. dulcis* were therefore considerable interest in the studies of antioxidative activity.

Estimation of antioxidative effects has been carried out by various methods. The DPPH assay is one of the methods used for antioxidant testing (Tamura, *et al.*, 1990). DPPH is a stable free radical which shows a purple colour and a strong absorption at 517 nm. When DPPH radical accepts an electron or hydrogen radical, a more stable compound will be formed and consequently its characteristic absorption at 517 nm vanishes. The capacity of the substances to donate electrons can be estimated from the degree of loss of color (Blois, 1958). Coexistence of an antioxidant compound (AH) and free radical ($DPPH^{\bullet}$) leads to the disappearance of DPPH free radical and the appearance of the free radical ($A^{\bullet}$).



3.3.1 Free radical scavenging activity of the crude extracts

To determine the scavenging activity, the crude extracts of *G. dulcis* were tested at the final concentration of 100 μg/mL. The activity was monitored by following the decrease of the absorbance of the solution at 517 nm for 30 min. The results were expressed as % inhibition (**Figure 26**). The activity was exhibited by the acetone extracts from the fruits (**Crude 1** and **Crude 2**) and flowers (**Crude G1**) as well as by the methanolic extract from the flowers (**Crude M**).



Crude 1, **2**, **G1** = acetone extract

Crude C, **M**, **4** = methanolic extract

Crude 3 = dichloromethane extract

Figure 26 Radical scavenging activity of the crude extracts

3.3.2 Free radical scavenging activity of the pure compounds

To determine the active constituents in the extracts and the pure consituents were examined. The samples were tested at the final concentration of 10 μM. The absorption of the solution were measured at 517 nm at 30 min. Ascorbic acid and BHT were used as reference compounds. The activity was expressed in the % inhibition (**Table 22**). The results showed that **GD1**, **GD20**, **RD5**, **RD14**, **RD16**, **FD5**, **FD8**, **FD11** and **FD12** exhibited higher activity than that of BHT (**Table 100** and **Figure 27**). The other compounds showed moderate to weak activity.

Table 100 % inhibition of tested compounds and standard antioxidant (10 μM)

Sample	% Inhibition ± S.D. (10 μM, 30 min)
Control	-
RD5	86.89 ± 0.03
RD16	81.97 ± 0.06
Ascorbic acid	77.05 ± 0.01
GD1	73.77 ± 0.03
RD14	68.85 ± 0.04
FD11	60.66 ± 0.05
FD12	59.02 ± 0.04
FD5	57.38 ± 0.05
FD8	55.74 ± 0.03
GD20	50.81 ± 0.03
BHT	42.62 ± 0.02
FD7	36.07 ± 0.04
FD10	32.79 ± 0.01

Sample	% Inhibition ± S.D. (10 μM, 30 min)
GD10	24.59 ± 0.02
GD9	22.13 ± 0.01
GD11	19.67 ± 0.02
GD12	19.67 ± 0.01
GD3	18.03 ± 0.03
GD4	18.03 ± 0.01
GD14	18.03 ± 0.01
RD8	18.03 ± 0.02
RD13	18.03 ± 0.02
RD17	18.03 ± 0.02
GD19	17.21 ± 0.02
GD7	16.39 ± 0.01
FD9	16.39 ± 0.01
GD15	15.57 ± 0.03

Table 100 (Continued)

Sample	% Inhibition ± S.D. (10 μM, 30 min)
GD5	14.75 ± 0.01
GD6	14.75 ± 0.02
GD8	14.75 ± 0.03
GD13	14.75 ± 0.01
GD16	14.75 ± 0.02
RD6	14.75 ± 0.05
RD7	14.75 ± 0.04
FD14	14.75 ± 0.03
GD17	13.11 ± 0.03
GD22	11.48 ± 0.04
RD12	11.48 ± 0.01
RD15	11.48 ± 0.02
RD3	9.84 ± 0.01
SD10	9.83 ± 0.03
GD23	8.20 ± 0.03
RD10	8.20 ± 0.03
FD4	8.20 ± 0.02
FD13	8.20 ± 0.01
SD1	8.20 ± 0.03
SD5	6.56 ± 0.01
SD7	6.56 ± 0.02

Sample	% Inhibition ± S.D. (10 μM, 30 min)
FD1	4.92 ± 0.01
FD6	4.92 ± 0.05
SD11	4.92 ± 0.01
GD25	3.28 ± 0.05
FD15	3.28 ± 0.01
FD17	3.28± 0.01
SD2	3.28 ± 0.01
SD12	3.28 ± 0.01
GD21	1.64 ± 0.02
RD1	1.64 ± 0.02
RD9	1.64 ± 0.02
RD11	1.64 ± 0.02
FD3	1.64 ± 0.01
FD16	1.64 ± 0.01
FD18	1.64 ± 0.01
FD19	1.64 ± 0.01
SD3	1.64 ± 0.01
SD4	1.64 ± 0.01
SD6	1.64 ± 0.01
SD8	1.64 ± 0.01
SD9	1.64 ± 0.01

control = 0.05 mM DPPH

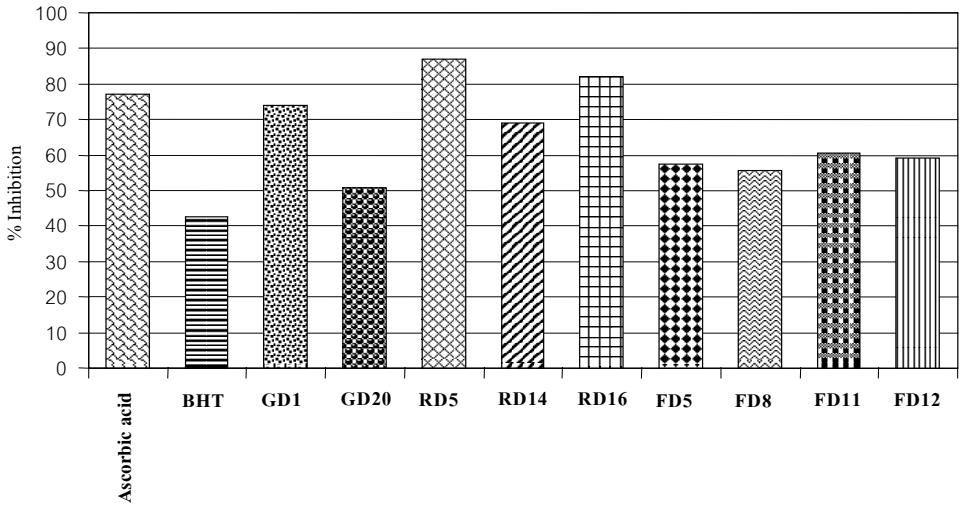


Figure 27 Radical scavenging activity of pure compounds

3.3.3 Evaluation of 50 % inhibitory concentration (IC_{50})

The assessment of the activity was extended for **GD1**, **GD20**, **RD5**, **RD14**, **RD16**, **FD5**, **FD8**, **FD11** and **FD12**. The oxidation effect was evaluated as the concentration required to scavenge 50% DPPH free radical (IC_{50}). Their IC_{50} were exhibited at 6.90, 13.00, 5.90, 7.20, 6.10, 10.50, 11.40, 8.50 and 10.00 μM, respectively whereas IC_{50} of ascorbic acid and BHT were shown at 6.50 and 19.00 μM (**Table 101** and **Figure 28**). Moreover the results indicated that **RD5** and **RD16** acted as a radical scavenger more effective than ascorbic acid.

Table 101 IC_{50} values of tested compounds and standard antioxidant

Sample	IC_{50} ± S.D. (μM, 30 min)
RD5	5.90 ± 0.02
RD16	6.10 ± 0.01
Ascorbic acid	6.50 ± 0.01
GD1	6.90 ± 0.02
RD14	7.20 ± 0.01
FD11	8.50 ± 0.01
FD12	10.00 ± 0.02
FD5	10.50 ± 0.01
FD8	11.40 ± 0.01
GD20	13.00 ± 0.02
BHT	19.00 ± 0.01

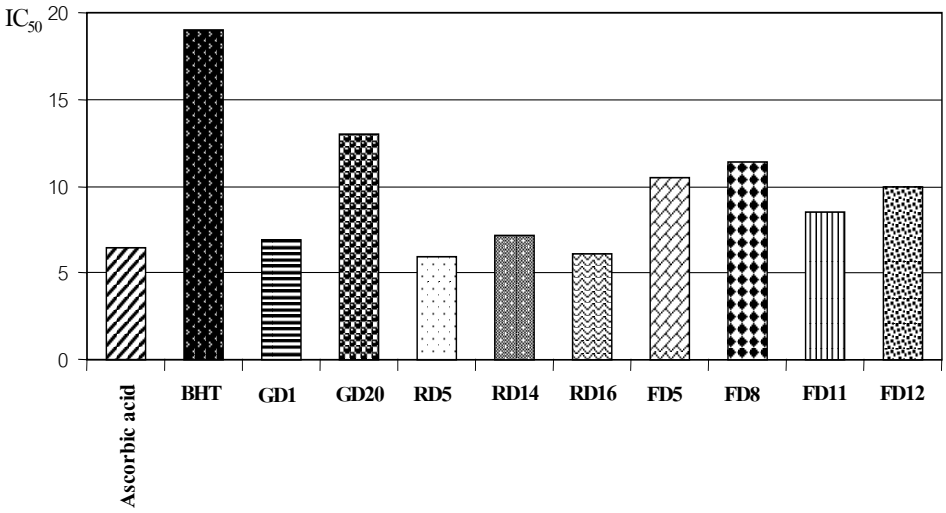
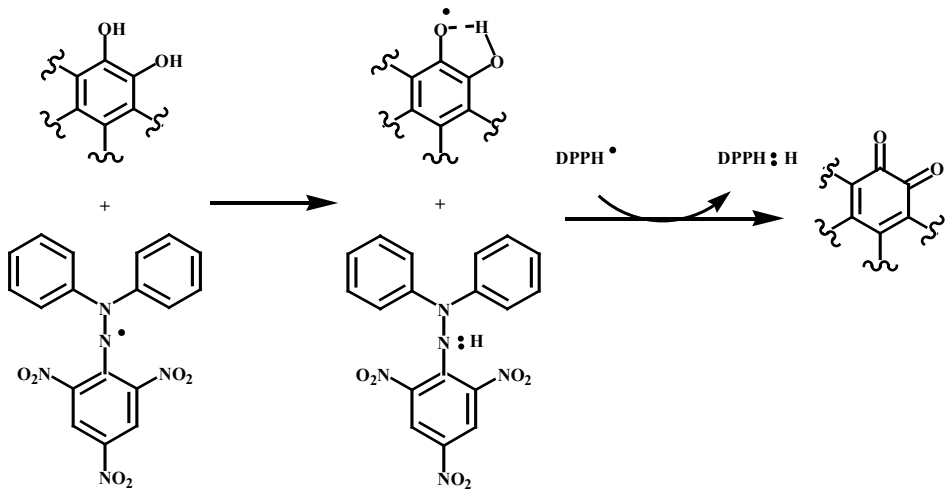


Figure 28 IC_{50} of pure compounds

The mechanism of trapping radical by **GD1**, **GD20**, **RD5**, **RD14**, **RD16**, **FD5**, **FD8**, **FD12** and **FD13** exhibited by a phenolic characteristic which was proposed to donate hydrogen radical to DPPH. The phenoxy radical which formed was stabilized through an intramolecular hydrogen bonding. A subsequent interaction with a second DPPH radical afforded the dehydro form of these compounds as a final product (Shahidi, *et al*., 1992; Keawpradub, *et al*., 2001).



The structure-activity study by Lin and co-worker in 1997 indicated that hydroxyl groups and at least on flavone unit in the biflavonoids are required for activity and C-3, C-8″ linkages is necessary for biflavanones to exhibit activity. Early work by Clemetson and Andersen showed that many flavonoids and other plant phenolics protected againt ascorbic acid destruction. They note that flavonoids with either 3′,4′ B-ring substitution, were active inhibitors (Larson, 1988). **RD5**, **RD16** and **FD8**, are flavonoids with 3′,4′ B-ring substitution. The effect on trapping of the radical of those compounds could be noticed.

Polyhydroxy chalcones are biosynthetic intermediates between cinnamic acids and flavonoids, also show considerable antioxidant activity for tard. Chalcones with two adjacent hydroxy groups were almost fully effective, introduction of

additional hydroxyl groups leading to only slight increases in inhibitory activity whereas hydrogenation of the chalcone double bond increased their antioxidant activity to some extent (Larson, 1988). The unsaturated chalcone **SD2** and saturated chalcones **SD6**, **SD8** and **SD12** have no adjacent hydroxy groups.

3.4 Biological activities of known compounds

This research have led to the isolation of seventy-five compounds from *G. dulcis*. Furthermore we have reviewed the research which involving some of known compounds isolated from *G. dulcis* and found that some of known compounds have been evaluated for some of the biological activities by many research groups. Cowanin (**GD6**), mangostin (**GD14**), 1,3,6-trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl) xanthone (**RD8**) and cowaxanthone (**GD7**) were reported to showed antibacterial activity againts *S. aureus* ATCC 25923 and *S. aureus* penicillin-resistant (Sundaram, *et al*., 1983; Mahabusarakam, *et al*., 1986; Na Pattalung, *et al*., 1994). Cowanin (**GD6**), cowaxanthone (**GD7**), *β*-mangostin (**FD18**) and 1,7-dihydroxyxanthone (**SD5**) exhibited moderate activity againt *Plasmodium falciparum* comparable to that of pyrimethamine (Likhitwitayawuid, *et al*., 1998a; 1998b). *β*-Mangostin (**FD18**), garcinone B (**RD7**), garcinone D (**GD25**), *α*-mangostin (**GD14**), mangostenol (**GD23**) and 1,7-dihydroxy-3-methoxy-2-(3-methyl-2-butenyl)xanthone (**GD8**) have been tested for antituberculosis potential, *α*-mangostin (**GD14**), *β*-mangostin (**FD18**) and garcinone B (**RD7**) exhibited strong inhibitory effect against *Mycobacterium tuberculosis* (Suksamrarn, *et al*., 2003). *α*-Mangostin (**GD14**) and *β*-mangostin (**FD18**) showed significant inhibitory cancer chemopreventive activity. The inhibition activity of cowanin (**GD6**) and cowaxanthone (**GD7**) were weaker than that of *α*- (**GD14**) and *β*-mangostin (**FD18**) (Ito, *et al*., 2003). Camboginol (**GD1**) and xanthochymol (**FD11**)

have shown to prossess antibacterial (Iinuma, *et al*., 1996) and anti-topoisomerase I and II activities (Tosa, *et al*., 1997). Anti-HIV activity has been described for guttiferone E (**FD12**) (Gustafson, *et al*., 1992). Camboginol (**GD1**) has been reported to possess antioxidative, antibiotic and anti-HIV activities and suppressed colonic aberrant crypt foci (ACF) formation (Ito, *et al*., 2003) and antimicrobial properties (Bakana, *et al*., 1987). Camboginol (**GD1**) and cambogin (**RD14**) has been reported to antioxidative activity (Ito, *et al*., 2003). Camboginol (**GD1**) is known to be an antioxidant, and its radical scavenging ability against DPPH is greater than that of DL-α-tocophenol. Free radical scavenging effects of camboginol and cambogin were stronger than that of vitamin E. Camboginol (**GD1**) and cambogin (**RD14**) caused rapid decolorization of the DPPH solution, indicating marked radical scavenging potencies (Ito, *et al*., 2003). Morelloflavone (**GD20**) and apigenin (**RD13**) showed the moderate activity in the HIV-1 RT enzyme assay, were test with human PBM cells infected with HIV-1 (strain LAV-1) whereas volkensiflavone (**FD1**) showed weakly active (Lin, *et al*., 1997).