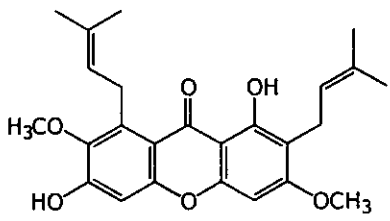
3 RESULTS AND DISCUSSION

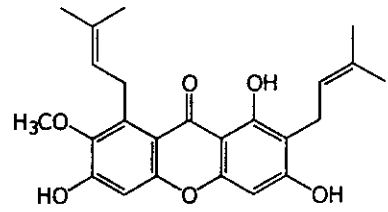
3.1 Structural Determination

The roots of *Cratoxylum cochinchinense* were dried, chopped and extracted with dichloromethane and methanol, successively. The dichloromethane extract was separated by means of chromatography over silica gel to give seven new xanthones (**CC3, CC7, CC8, CC10, CC12, CC13** and **CC14**) and seven known xanthones (**CC1, CC2, CC4, CC5, CC6, CC9** and **CC11**). Their structures were determined by spectroscopic data (1D and 2D NMR spectral data).

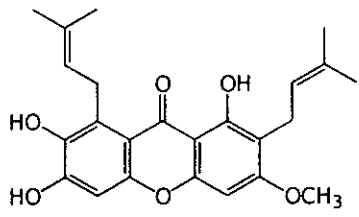
The structure of compounds isolated from the roots of *C. cochinchinense*



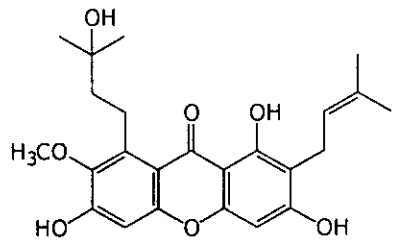
CC1 : β-Mangostin



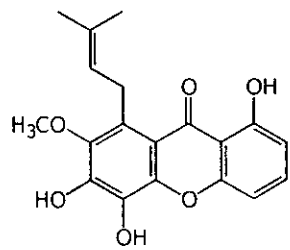
CC2: Mangostin



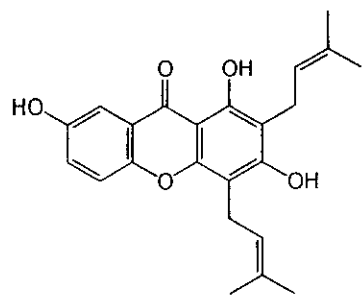
CC3: 1,6,7-Trihydroxy-3-methoxy-2,8-*bis*(3-methyl-2-butenyl)xanthone



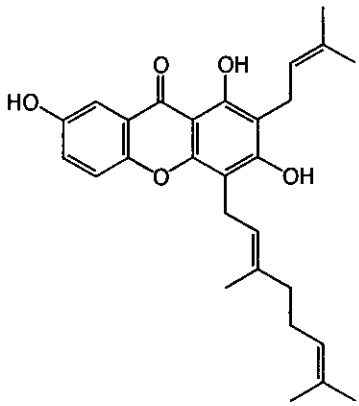
CC4: Garcinone D



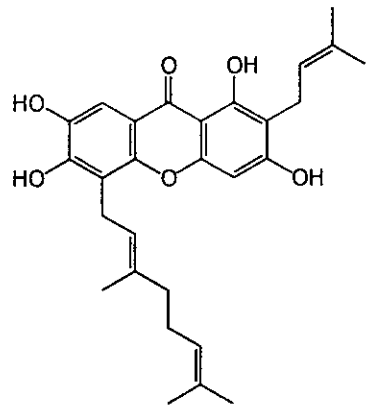
CC5: Celebixanthone



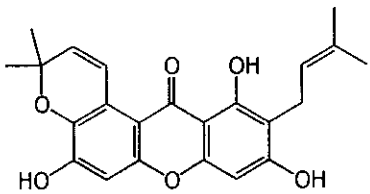
CC6: 1,3,7-Trihydroxy-2,4-*bis*(3-methyl-2-butenyl)xanthone



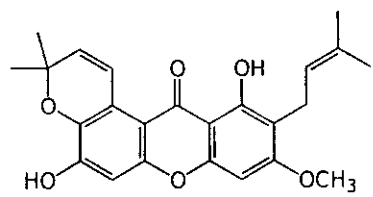
CC7: 1,3,7-Trihydroxy-2-(3-methyl-2-butenyl)-4-(3,7-dimethyl-2,6-octadienyl)xanthone



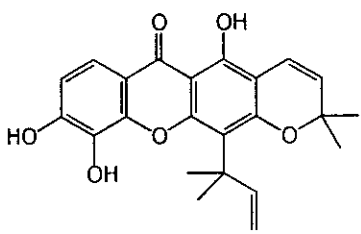
CC8: 1,3,6,7-Tetrahydroxy-2-(3-methyl-2-butenyl)-5-(3-methyl-2-butenyl)-4-(3,7-dimethyl-2,6-octadienyl)xanthone



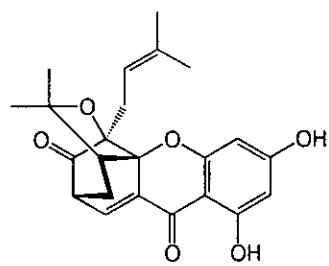
CC9: Garcinone B



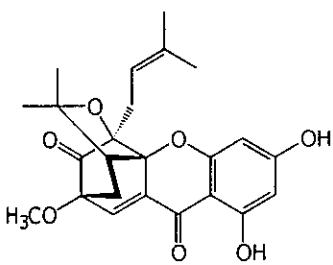
CC10: 3-*O*-Methylgarcinone B



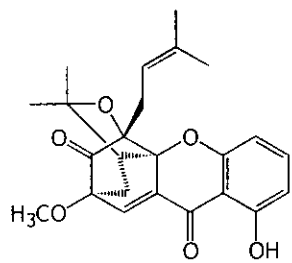
CC11: Macluraxanthone



CC12: Cratoxycochinchinone A

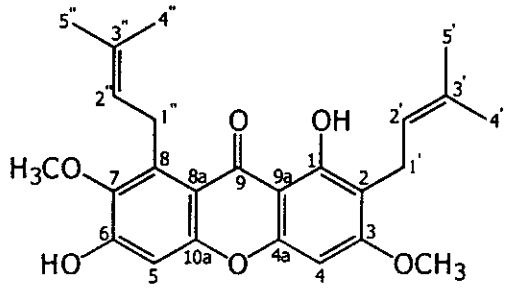


CC13: Cratoxycochinchinone B



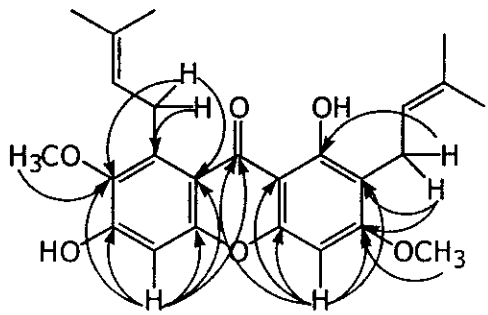
CC14: Cratoxycochinchinone C

3.1.1 CC1: 1,6-dihydroxy-3,7-dimethoxy-2,8-*bis*(3-methyl-2-butenyl)xanthone (*β*-Mangostin)



CC1 is a yellow solid, m.p. 176-180 ^{o}C. The UV spectrum showed maximum absorption bands at 271, 314 and 351 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1642 cm^{-1} and hydroxyl group at 3380 cm^{-1}. The ^{1}H NMR spectrum showed a sharp singlet signal of 1-OH at δ 13.54 and broad singlet signal of free hydroxy proton 6-OH at δ 6.45. Two methoxy signals at δ 3.79 and 3.88 were assigned for 7-OCH_3 and 3-OCH_3, respectively. The appearance of two singlet signals of two isolated aromatic protons at δ 6.77 and 6.28 were assigned for H-4 and H-5. The assignment of H-4 was confirmed by the correlations of H-4 to C-2, C-3, C-4a, C-9 and C-9a whereas H-5 was proved by the correlations of H-5 to C-6, C-7, C-8a, C-9 and C-10a. The signals of two olefinic protons at δ5.23 (*brt*, J = 7.2 Hz, H-2$'$) and δ5.26 (*brt*, J = 6.0 Hz, H-2$''$), two benzylic methylene protons at δ3.33 (*d*, J = 7.2 Hz, H-1$'$) and δ4.07 (*d*, J = 6.0 Hz, H-1$''$) and four methyl groups at δ 1.68 (*s*, 6H), 1.79 (*s*, 3H) and 1.83 (*s*, 3H) belonged to two prenyl side chains. The HMBC correlations of H-1$'$ to C-1, C-2, C-3 and H-1$''$ to C-7, C-8, C-8a indicated that the prenyl side chains were located at C-2 and C-8, respectively. The ^{13}C NMR spectrum and DEPT experiments indicated the presence of a carbonyl carbon (δ 181.86), four methyl carbons (δ 25.80x2, 18.20 and 17.76), two methylene carbons (δ 26.52 and 21.34), four methine carbons (δ 123.26, 122.37, 103.74 and 88.79), two methoxy

carbon (δ 61.98 and 55.77) and twelve quaternary carbons (δ 163.47, 159.67, 155.62, 155.16, 154.42, 142.59, 136.99, 131.98, 131.62, 112.31, 111.45 and 103.74). The assignment suggested that **CC1** was 1,6-dihydroxy-3,7-dimethoxy-2,8-*bis*(3-methyl-2-butenyl)xanthone. It was known as β-mangostin (Likhitwitayawuid, *et al.*,1998).



Major HMBC of **CC1**

Table 7 The NMR spectral data of **CC1**

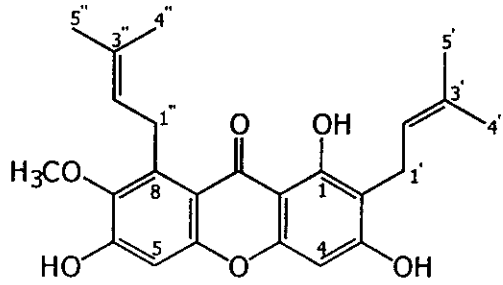
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
1	159.67 (C)	-	-
1-OH	-	13.54 (*s*, OH)	C-1, C-2, C-9a
2	111.45 (C)	-	-
3	163.47 (C)	-	-
3-OCH_3	55.77 (CH_3)	3.88 (*s*, 3H)	C-3
4	88.79 (CH)	6.28 (*s*, 1H)	C-2, C-3, C-4a, C-9, C-9a
4a	155.16 (C)	-	-
5	101.50 (CH)	6.77 (*s*, 1H)	C-6, C-7, C-8a, C-9, C-10a
6	154.42 (C)	-	-
6-OH	-	6.45 (*brs*, OH)	-
7	142.59 (C)	-	-

Table 7 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
7-OCH_3	61.98 (CH_3)	3.79 (*s*, 3H)	C-7
8	136.99 (C)	-	-
8a	112.31 (C)	-	-
9	181.86 (C=O)	-	-
9a	103.74 (C)	-	-
10a	155.62 (C)	-	-
1′	21.34 (CH_2)	3.33 (*d*, 2H, J = 7.2 Hz)	C-1, C-2, C-3, C-2′, C-3′
2′	122.37 (CH)	5.23 (*brt*, 1H, J = 7.2 Hz)	C-4′, C-5′
3′	131.62 (C)	-	-
4′	17.76 (CH_3)	1.79 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.80 (CH_3)	1.68 (*s*, 3H)	C-2′, C-3′, C-4′
1″	26.52 (CH_2)	4.07 (*d*, 2H, J = 6.0 Hz)	C-7, C-8, C-8a, C-2″, C-3″
2″	123.26 (CH)	5.26 (*brt*, 1H, J = 6.0 Hz)	C-8, C-4″, C-5″
3″	131.98 (C)	-	-
4″	18.20 (CH_3)	1.83 (*s*, 3H)	C-2″, C-3″, C-5″
5″	25.80 (CH_3)	1.68 (*s*, 3H)	C-2″, C-3″, C-4″

* Carbon type was deduced from DEPT experiments

3.1.2 CC2: 1,3,6-trihydroxy-7-methoxy-2,8-*bis*(3-methyl-2-butenyl)xanthone (Mangostin)

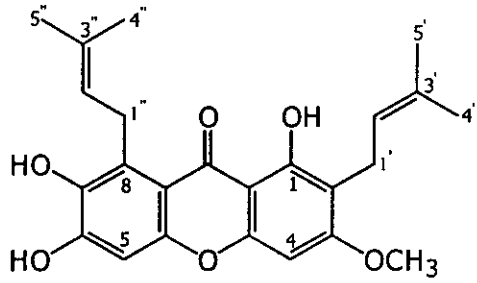


CC2 is a yellow solid, m.p. 180-182 °C. The UV spectrum showed maximum absorption bands at 274, 316 and 353 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1644 cm^{-1} and hydroxyl group at 3419 cm^{-1}. The ^{1}H NMR spectrum exhibited a sharp singlet signal of a hydrogen bonded hydroxy proton at δ 13.80 (1-OH). In addition, two broad singlet signals of two more hydroxy protons were observed at δ 6.41 (6-OH) and 6.28 (3-OH). A sharp singlet signal with three protons at δ 3.81 was the signal of methoxyl group at C-7. Two singlet signals in aromatic region, δ 6.83 and 6.29, were observed and assigned for the signals of H-5 and H-4, respectively. The typical signals of two prenyl units were observed. The signals of two singlet signals of *gem*-dimethyl protons H-4′ (δ 1.84) and H-5′ (δ 1.77), a broad triplet of olefinic protons H-2′ (δ 5.29) and a doublet of benzylic methylene protons H-1′ (δ 3.45) were assigned for the prenyl unit at C-2. Two singlet signals of *gem*-dimethyl protons H-4″ (δ 1.84) and H-5″ (δ 1.69), a broad triplet of olefinic proton H-2″ (δ 5.26) and a doublet of benzylic methylene protons H-1″ (δ 4.09) were assigned for the prenyl unit at C-8. **CC2** then was assigned to be 1,3,6-trihydroxy-7-methoxy-2,8-*bis*(3-methyl-2-butenyl)xanthone which was known as mangostin (Mahabusarakam, *et al.*, 1987). The proposed structure, the spectral data and melting point agreed with the authentic sample.

Table 8 The ^{1}H NMR spectral data of **CC2**

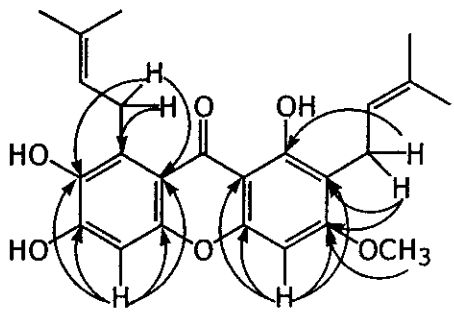
Position	**CC2** δ_H (multiplicity, J_{Hz}) 300 MHz, $CDCl_3$	Mangostin δ_H (multiplicity, J_{Hz}) 400 MHz, $CDCl_3$
1-OH	13.80 (*s*, OH)	13.80 (*s*, OH)
3-OH	6.28 (*brs*, OH)	6.16 (*s*, OH)
4	6.29 (*s*, 1H)	6.28 (*s*, 1H)
5	6.83 (*s*, 1H)	6.82 (*s*, 1H)
6-OH	6.41 (*brs*, OH)	6.31 (*s*, OH)
7-OCH_3	3.81 (*s*, 3H)	3.81 (*s*, 3H)
1′	3.45 (*d*, 2H, J = 7.2 Hz)	3.45 (*d*, 2H, J = 7.0 Hz)
2′	5.29 (*brt*, 1H, J = 7.2 Hz)	5.28 (*t*, 1H, J = 7.0 Hz)
4′	1.84 (*s*, 3H)	1.85 (*s*, 3H)
5′	1.77 (*s*, 3H)	1.78 (*s*, 3H)
1″	4.09 (*d*, 2H, J = 6.3 Hz)	4.11 (*d*, 2H, J = 7.0 Hz)
2″	5.26 (*brt*, 1H, J = 6.3 Hz)	5.28 (*brt*, 1H, J = 7.0 Hz)
4″	1.84 (*s*, 3H)	1.82 (*s*, 3H)
5″	1.69 (*s*, 3H)	1.70 (*s*, 3H)

3.1.3 CC3: 1,6,7-trihydroxy-3-methoxy-2,8-*bis*(3-methyl-2-butenyl)xanthone



CC3 is a yellow solid, m.p. 180-181 °C. The molecular formula was determined as $C_{24}H_{26}O_6$ by HR-MS ($[M]^+$ *m/z* 410.1711). The UV spectrum showed maximum absorption bands at 245, 261, 318 and 370 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1648 cm^{-1} and hydroxyl group at 3360 cm^{-1}. The ^1H NMR spectrum exhibited a resonance of a chelated hydroxyl group 1-OH at δ13.65. Two singlets in aromatic region, δ6.77 and 6.25 belonged to H-5 and H-4, respectively. The correlations of H-4 to C-2, C-3, C-4a, C-9a and H-5 to C-6, C-7, C-8a, C-10a on the HMBC experiment confirmed the position of H-4 and H-5. The presence of a methoxyl group (3-OCH_3) was shown at δ 3.85 (*s*). The ^1H NMR spectrum further revealed a characteristic signal of two prenyl units, of which *gem*-dimethyl protons resonated at δ1.85 (H-4″, *s*), 1.78 (H-4′, *s*), 1.69 (H-5″, *s*) and 1.65 (H-5′, *s*), benzylic methylene protons resonated at δ3.31 (H-1′, *d*) and 4.13 (H-1″, *d*) and olefinic methine protons resonated at δ5.21 (H-2′, *brt*) and 5.30 (H-2″, *brt*). The HMBC correlations of H-1′ to C-1, C-2, C-3, C-2′, C-3′ and H-1″ to C-7, C-8, C-8a, C-2″, C-3″ indicated the location of prenyl side chains at C-2 and C-8, respectively. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 24 signals for 24 carbon atoms: a carbonyl carbon (δ 182.24), four methyl carbons (δ 25.74x2, 18.11 and 17.70), two methylene carbons (δ25.91 and 21.22), four methine carbons (δ123.22, 122.52, 100.54 and 88.50), a methoxy carbon (δ55.69) and twelve

quaternary carbons (δ162.99, 159.48, 155.10, 152.74, 151.08, 140.33, 131.50, 131.21, 127.72, 111.28, 110.66 and 103.64). **CC3** thus was proposed for 1,6,7-trihydroxy-3-methoxy-2,8-*bis*(3-methyl-2-butenyl)xanthone. It is a new xanthone derivative.



Major HMBC of **CC3**

Table 9 The NMR spectral data of **CC3**

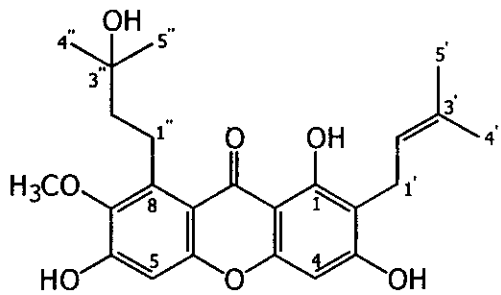
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
1	159.48 (C)	-	-
1-OH	-	13.65 (*s*, OH)	C-1, C-2, C-9, C-9a
2	110.66 (C)	-	-
3	162.99 (C)	-	-
3-OCH_3	55.69 (CH_3)	3.85 (*s*, 3H)	C-3
4	88.50 (CH)	6.25 (*s*, 1H)	C-2, C-3, C-4a, C-9a
4a	155.10 (C)	-	-
5	100.54 (CH)	6.77 (*s*, 1H)	C-6, C-7, C-8a, C-10a
6	151.08 (C)	-	-
7	140.33 (C)	-	-
8	127.72 (C)	-	-
8a	111.28 (C)	-	-
9	182.24 (C=O)	-	-
9a	103.64 (C)	-	-

Table 9 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
10a	152.74 (C)	-	-
1′	21.22 (CH_2)	3.31 (*d*, 2H, J = 7.2 Hz)	C-1, C-2, C-3, C-2′, C-3′
2′	122.52 (CH)	5.21 (*brt*, 1H, J = 7.2 Hz)	C-2, C-1′, C-4′, C-5′
3′	131.21 (C)	-	-
4′	17.70 (CH_3)	1.78 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.74 (CH_3)	1.65 (*s*, 3H)	C-2′, C-3′, C-4′
1″	25.91 (CH_2)	4.13 (*d*, 2H, J = 6.3 Hz)	C-7, C-8, C-8a, C-2″, C-3″
2″	123.22 (CH)	5.30 (*brt*, 1H, J = 6.3 Hz)	C-8, C-4″, C-5″
3″	131.50 (C)	-	-
4″	18.11 (CH_3)	1.85 (*s*, 3H)	C-2″, C-3″, C-5″
5″	25.74 (CH_3)	1.69 (*s*, 3H)	C-2″, C-3″, C-4″

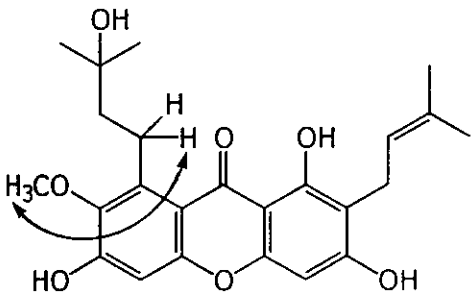
* Carbon type was deduced from DEPT experiments

3.1.4 CC4: 1,3,6-Trihydroxy-7-methoxy-2-(3-methyl-2-butenyl)-8-(3-hydroxy-3-methylbutyl)xanthone (Garcinone D)

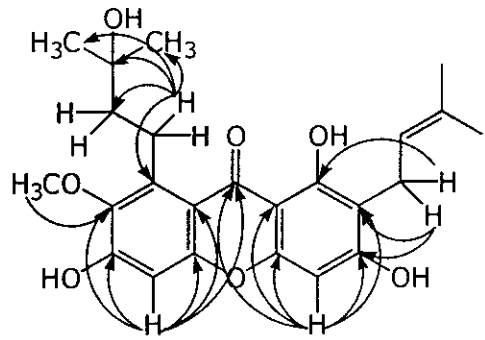


CC4 is a yellow solid, m.p. 205-206 ^{o}C. The UV spectrum showed maximum absorption bands at 244, 258, 318 and 354 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1646 cm^{-1} and hydroxyl group at 3400 cm^{-1}. The ^{1}H NMR spectrum showed a sharp singlet signal of hydroxy proton 1-OH at δ 13.60. The resonances of the methoxy protons and two aromatic protons were exhibited at δ 3.76 (7-OCH$_3$, *s*), 6.67 (H-5, *s*) and 6.26 (H-4, *s*), respectively. The assignment of two aromatic protons H-5 and H-4 were obtained from HMBC correlations of H-5 to C-6, C-7, C-8a, C-9, C-10a and H-4 to C-2, C-3, C-4a, C-9, C-9a. The presence of a 3-hydroxy-3-methylbutyl substituent was shown in the spectrum, of which a singlet signals of *gem*-dimethyl protons (H-4$''$ and H-5$''$) were at δ 1.29 (2x3H), two multiplet signals of methylene protons (H-1$''$ and H-2$''$) were at δ 3.42 and 1.71. This side chain was assigned to be at C-8 due to an anisotropic effect of the carbonyl group to H-1$''$. The differential NOE technique by irradiation of the signal of methoxy protons effected the signal of H-1$''$, accordingly the methoxy group was assigned at C-7. Two singlets of methyl protons (H-4$'$) at δ 1.79 and (H-5$'$) at δ 1.66, a doublet of benzylic methylene protons (H-1$'$) at δ 3.35, a broad triplet of an olefinic methine proton (H-2$'$) at δ 5.19 corresponded to the prenyl unit. It was assigned to be at C-2 according to the correlations of H-1$'$ to C-1, C-2 and C-3. The ^{13}C NMR

spectral data deduced from DEPT and HMQC spectra showed 24 signals for 24 carbon atoms: a carbonyl carbon (δ 162.22), four methyl carbons (δ 29.19x2, 25.77 and 17.81), three methylene carbons (δ 44.49, 21.95 and 21.36), three methine carbons (δ 122.57, 101.96 and 92.67), a methoxy carbon (δ 61.29) and twelve quaternary carbons (δ 162.22, 160.52, 156.18, 155.54, 154.80, 143.16, 138.51, 131.53, 111.13, 110.17, 102.98 and 70.50). **CC4** was proposed to be 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-2-butenyl)-8-(3-hydroxy-3-methyl-butyl)xanthone which was corresponded to garcinone D (Bennett, *et al.*, 1993).



NOE of **CC4**



Major HMBC of **CC4**

Table 10 The NMR spectral data of **CC4**

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
1	162.22 (C)	-	-
1-OH	-	13.60 (*s*, OH)	C-1, C-2, C-9a
2	110.17 (C)	-	-
3	160.52 (C)	-	-
3-OH**	-	9.49 (*s*, OH)	-
4	92.67 (CH)	6.26 (*s*, 1H)	C-2, C-3, C-4a, C-9, C-9a
4a	154.80 (C)	-	-

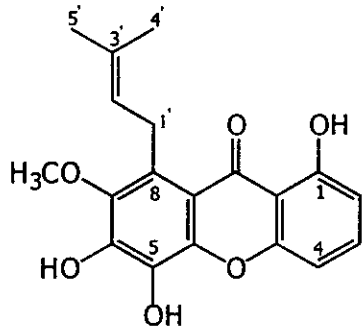
Table 10 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
5	101.96 (CH)	6.67 (*s*, 1H)	C-6, C-7, C-8a, C-9, C-10a
6	155.54 (C)	-	-
6-OH**	-	9.52 (*s*, OH)	-
7	143.16 (C)	-	-
7-OCH_3	61.29 (CH_3)	3.76 (*s*, 3H)	C-7
8	138.51 (C)	-	-
8a	111.13 (C)	-	-
9	181.87 (C=O)	-	-
9a	102.98 (C)	-	-
10a	156.18 (C)	-	-
1′	21.36 (CH_2)	3.35 (*d*, 2H, J = 6.0 Hz)	C-1, C-2, C-3, C-2′, C-3′
2′	122.57 (CH)	5.19 (*brt*, 1H, J = 6.0 Hz)	C-1′, C-4′, C-5′
3′	131.53 (C)	-	-
4′	17.81 (CH_3)	1.79 (*s*, 3H)	C-2, C-2′, C-3′, C-5′
5′	25.77 (CH_3)	1.66 (*s*, 3H)	C-2, C-2′, C-3′, C-4′
1″	44.49 (CH_2)	3.42 (*m*, 2H)	C-8, C-2″, C-3″, C-4″, C-5″
2″	21.95 (CH_2)	1.71 (*m*, 2H)	C-7, C-8, C-8a, C-1″
3″	70.50 (C)	-	-
4″	29.19 (CH_3)	1.29 (*s*, 3H)	C-1″, C-2″, C-3″
5″	29.19 (CH_3)	1.29 (*s*, 3H)	C-1″, C-2″, C-3″

* Carbon type was deduced from DEPT experiments

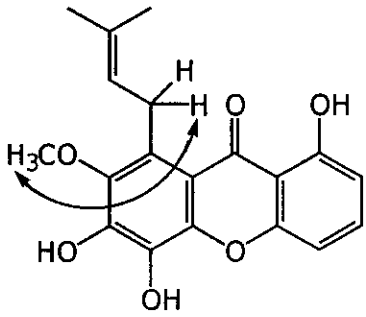
** Interchangeable between the same letters

3.1.5 CC5: 1,5,6-trihydroxy-7-methoxy-8-(3-methyl-2-butenyl)xanthone (Celebixanthone)

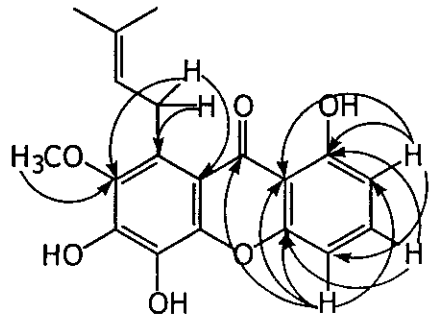


CC5 is a yellow solid, m.p. 219-220 ^{o}C. The UV spectrum showed maximum absorption bands at 241, 249, 333 and 362 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1639 cm^{-1} and hydroxyl group at 3521 cm^{-1}. The ^{1}H NMR spectrum showed a sharp singlet signal of a hydroxy proton (1-OH) at δ13.19 and a sharp singlet due to the signal of 7-OCH$_3$ at δ3.84. The ABM pattern in aromatic region, δ 7.51 (*t*), 6.91 (*dd*) and 6.75 (*dd*) was proposed for the characteristic signals of H-3, H-2 and H-4, respectively. Protons H-2, H-3 and H-4 were confirmed by the cross peaks of H-2 to C-1, C-4, C-9a, H-3 to C-1, C-4a and H-4 to C-2, C-4a, C-9, C-9a. A doublet at δ4.04, a broad triplet at δ5.24 and two singlets at δ1.84 and 1.69 were assigned for benzylic methylene protons H-1′, olefinic methine proton H-2′ and two methyl protons H-4′ and H-5′, respectively of a prenyl moiety. The deshielded chemical shift of H-1′ (δ 4.04) and the enhancement of H-1′ upon irradiation at 7-OCH$_3$ suggested that the prenyl unit was next to a carbonyl group and 7-OCH$_3$, the prenyl group was then assigned to be at C-8. The ^{13}C NMR spectrum and DEPT experiments indicated the presence of a carbonyl carbon (δ183.40), two methyl carbons (δ 25.80 and 18.09), a methylene carbon (δ 25.53), four methine carbons (δ 135.46, 123.89, 109.92 and 106.20), a methoxy carbon (δ 60.97) and ten quaternary carbons (δ 161.84, 155.16, 144.89, 144.60, 143.39, 131.36, 131.04, 127.58, 110.92 and

108.82). Therefore the proposed structure of **CC5** was 1,5,6-trihydroxy-7-methoxy-8-(3-methyl-2-butenyl)xanthone. The structure, the spectral data and melting point was corresponded to celebixanthone (Stout, *et al.*, 1962).



NOE of **CC5**



Major HMBC of **CC5**

Table 11 The NMR spectral data of **CC5**

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
1	161.84 (C)	-	-
1-OH	-	13.19 (*s*, OH)	C-1, C-2, C-3, C-9, C-9a
2	106.20 (CH)	6.91 (*dd*, 1H, J = 8.4, 1.5 Hz)	C-1, C-4, C-9a
3	135.46 (CH)	7.51 (*t*, 1H, J = 8.4 Hz)	C-1, C-4a
4	109.92 (CH)	6.75 (*dd*, 1H, J = 8.4, 1.5 Hz)	C-2, C-4a, C-9, C-9a
4a	155.16 (C)	-	-
5[i]	131.04 (C)	-	-
6[j]	144.89 (C)	-	-
7	143.39 (C)	-	-
7-OCH_3	60.97 (CH_3)	3.84 (*s*, 3H)	C-7
8	127.58 (C)	-	-
8a	110.92 (C)	-	-
9	183.40 (C=O)	-	-

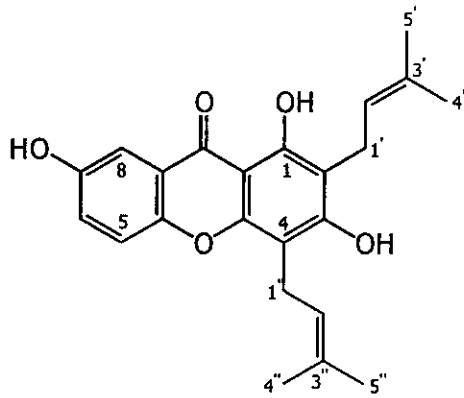
Table 11 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
9a	108.82 (C)	-	-
10a[j]	144.60 (C)	-	-
1′	25.53 (CH_2)	4.04 (*d*, 2H, J = 6.3 Hz)	C-7, C-8, C-8a, C-2′, C-3′
2′	123.89 (CH)	5.24 (*brt*, 1H, J = 6.3 Hz)	C-4′, C-5′
3′[i]	131.36 (C)	-	-
4′	18.09 (CH_3)	1.84 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.80 (CH_3)	1.69 (*s*, 3H)	C-2′, C-3′, C-4′

i and j = Interchangeable between the same letters

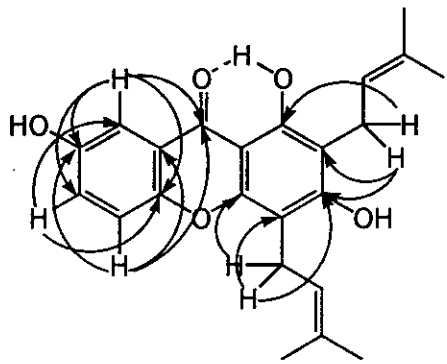
* Carbon type was deduced from DEPT experiments

3.1.6 CC6: 1,3,7-trihydroxy-2,4-*bis*(3-methyl-2-butenyl)xanthone



CC6 is a yellow solid, m.p. 172-173 ^{o}C. The ^{1}H NMR spectrum showed the singlet signal of a deshielded proton (1-OH) at δ 13.26. The ABX pattern in aromatic region, δ 7.63 (*d*), 7.33 (*d*) and 7.26 (*dd*) were proposed for the characteristic signals of H-8, H-5 and H-6, respectively. The most deshielded aromatic proton signal was assigned for H-8 according to anisotropic effect of the carbonyl group. The assignment of H-8, H-5 and H-6 were supported by HMBC correlation of H-8 to C-6, C-7, C-9, C-10; H-6 to C-8, C10a and H-5 to C-7, C-8a, C-9. The remaining signals were assigned for two prenyl units. Those signals were two multiplet signals of two olefinic protons (δ 5.28, H-2$'$ and 5.27, H-2$''$), two doublet signals of benzylic methylene protons (δ 3.47, H-1$'$ and 3.55, H-1$''$) and four singlet signals of four methyl groups at (δ 1.73, H-5$''$, 1.77, H-5$'$, 1.85, H-4$'$ and 1.91, H-4$''$). The HMBC correlations of H-1$'$ to C-1, C-2 and C-3 and H-1$''$ to C-3, C-4 and C-4a indicated that the prenyl side chains were at C-2 and C-4. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 23 signals for 23 carbon atoms : a carbonyl carbon (δ 181.06), four methyl carbons (δ 25.81x2 and 17.92x2), two methylene carbons (δ 21.84 and 21.57), five methine carbons (δ 124.16, 121.97, 121.80, 118.50 and 108.97) and eleven quaternary carbons (δ 160.55, 158.24, 153.92, 153.00, 149.90, 134.34, 133.12, 120.74, 108.97, 105.27 and 103.16. 1,3,7-Trihydroxy-2,4-*bis*(3-methyl-2-butenyl)xanthone then was

assigned for **CC6**. The proposed structure, the spectral data and the melting point were found to be corresponded to the previously isolated compound (Iinuma, *et al.*, 1996).



Major HMBC of **CC6**

Table 12 The NMR spectral data of **CC6**

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
1	158.24 (C)	-	-
1-OH	-	13.26 (*s*, OH)	C-1, C-2, C-9a
2	108.97 (C)	-	-
3	160.55 (C)	-	-
3-OH**	-	7.03 (*s*, OH)	-
4	105.27 (C)	-	-
4a	153.00 (C)	-	-
5	118.50 (CH)	7.33 (*d*, 1H, J = 9.0 Hz)	C-7, C-8a, C-9
6	124.16 (CH)	7.26 (*dd*, 1H, J = 9.0, 3.0 Hz)	C-8, C-10a
7	153.52 (C)	-	-
7-OH**	-	9.08 (*s*, OH)	-
8	108.97 (CH)	7.63 (*d*, 1H, J = 3.0 Hz)	C-6, C-7, C-9, C-10a
8a	120.74 (C)	-	-
9	181.06 (C=O)	-	-
9a	103.16 (C)	-	-

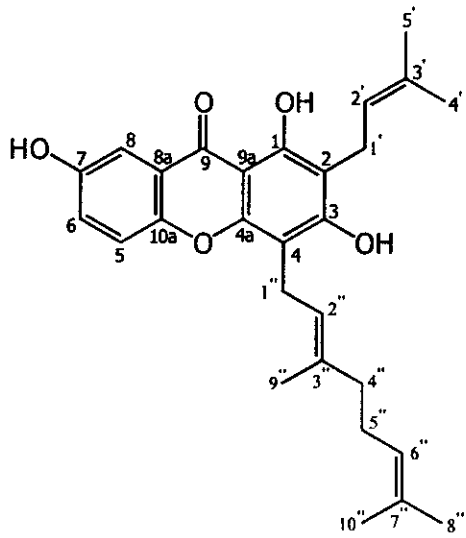
Table 12 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
10a	149.90 (C)	-	-
$1'$	21.57 (CH_2)	3.47 (*d*, 2H, J = 6.9 Hz)	C-1, C-2, C-3, C-$2'$
$2'$	121.80 (CH)	5.28 (*m*, 1H)	C-2, C-$1'$, C-$4'$, C-$5'$
$3'$	134.34 (C)	-	-
$4'$	17.92 (CH_3)	1.85 (*s*, 3H)	C-$2'$, C-$3'$, C-$5'$
$5'$	25.81 (CH_3)	1.77 (*s*, 3H)	C-$2'$, C-$3'$, C-$4'$
$1''$	21.84 (CH_2)	3.55 (*d*, 2H, J = 6.9 Hz)	C-3, C-4, C-4a, C-$2''$, C-$3''$
$2''$	121.97 (CH)	5.27 (*m*, 1H)	C-4, C-$1''$, C-$4''$, C-$5''$
$3''$	133.12 (C)	-	-
$4''$	17.92 (CH_3)	1.91 (*s*, 3H)	C-$2''$, C-$3''$, C-$5''$
$5''$	25.81 (CH_3)	1.73 (*s*, 3H)	C-$2''$, C-$3''$, C-$4''$

* Carbon type was deduced from DEPT experiments

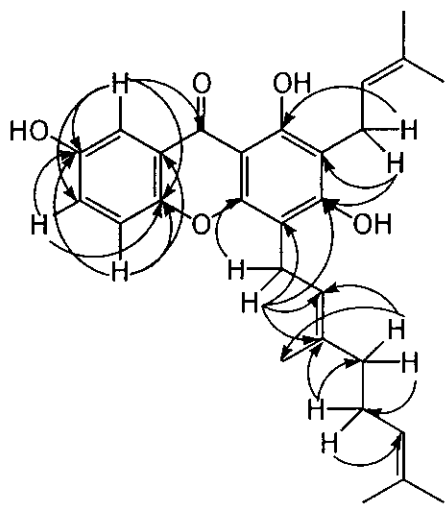
** Interchangeable between the same letters

3.1.7 CC7: 1,3,7-trihydroxy-2-(3-methyl-2-butenyl)-4-(3,7-dimethyl-2,6-octadienyl)xanthone



CC7 is a yellow solid, m.p. 119-120 ^{o}C. Its molecular formular of $C_{28}H_{32}O_5$ was established on the basis of mass spectrum, FABHR-MS ($[M]^+$ *m/z* 448.2299). The UV spectrum showed maximum absorption bands at 232, 268, 316 and 384 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1641 cm^{-1} and hydroxyl group at 3413 cm^{-1}. The ^{1}H NMR spectrum exhibited the singlet signal of a chelated hydroxyl group (1-OH) at δ 12.95. The ABX system in aromatic region, δ 7.59 (*d*, *J* = 3.0 Hz), 7.36 (*d*, *J* = 9.0 Hz) and 7.24 (*dd*, *J* = 9.0, 3.0 Hz) were assigned for H-8, H-5 and H-6, respectively. The placement of protons H-5, H6 and H-8 were supported by the cross peaks of H-5 to C-7, C-8a, C-10a, H-6 to C-7, C-10a and H-8 to C-6, C-7, C-9, C-10a. The characteristic signals of prenyl unit was shown as two singlet signals of *gem*-dimethyl protons (H-4′ and H-5′) at δ 1.84 and 1.76, a doublet signal of benzylic methylene protons (H-1′) at δ 3.47 and a broad triplet signal of olefinic methine proton (H-2′) at δ5.29. This unit was assigned to be at C-2 according to the correlations of H-1′ (δ 3.47) to C-1, C-2 and C-3. A geranyl side chain was suggested and was located at C-4. The proton resonance in geranyl side chain were assigned as follow; signals at δ 1.88 (*s*), 1.64 (*s*) and 1.57 (*s*) were of three vinylic

methyl groups, a doublet signal at δ 3.57 was assigned for benzylic methylene protons H-1″, multiplet signals at δ 2.08-2.11 (*m*) and 2.03-2.06 (*m*) were the signals of methylene protons H-5″ and H-4″ and broad triplet signals at δ 5.27 and 5.05 were the signals of two olefinic methine protons H-2″ and H-6″. HMBC correlations of H-1″ to C-3, C-4, C-4a, C-2″, C-3″ indicated that the geranyl side chain were at C-4. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 28 signals for 28 carbon atoms: a carbonyl carbon (δ 180.90), five methyl carbons (δ 25.86, 25.66, 17.94, 17.69 and 16.27), four methylene carbons (δ 39.72, 26.43, 21.59 and 21.58), six methine carbons (δ 124.12, 123.85, 121.58x2, 118.87 and 108.89), and twelve quaternary carbons (δ 161.13, 158.27, 152.97, 152.43, 150.34, 137.94, 134.92, 131.50, 120.45, 108.90, 105.00 and 102.96). **CC7** was then identified as 1,3,7-trihydroxy-2-(3-methyl-2-butenyl)-4-(3,7-dimethyl-2,6-octadienyl)xanthone. This compound is a new xanthone derivative.



Major HMBC of **CC7**

Table 13 The NMR spectral data of **CC7**

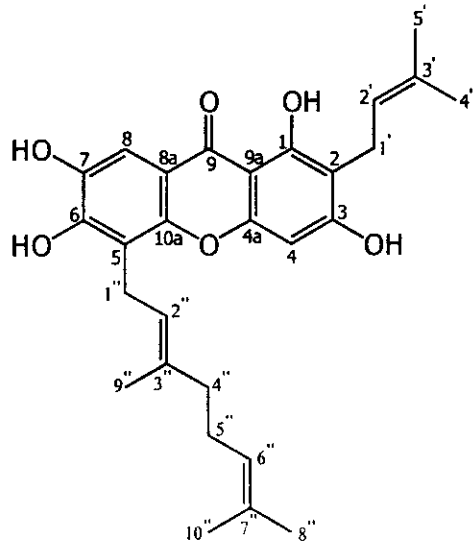
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
1	158.27 (C)	-	-
1-OH	-	12.95 (*s*, OH)	C-1, C-2, C-9a
2	108.90 (C)	-	-
3	161.13 (C)	-	-
4	105.00 (C)	-	-
4a	152.97 (C)	-	-
5	118.87 (CH)	7.36 (*d*, 1H, J = 9.0 Hz)	C-7, C-8a, C-10a
6	124.12 (CH)	7.24 (*dd*, 1H, J = 9.0, 3.0 Hz)	C-7, C-10a
7	152.43 (C)	-	-
8	108.89 (CH)	7.59 (*d*, 1H, J = 3.0 Hz)	C-6, C-7, C-9, C-10a
8a	120.45 (C)	-	-
9	180.90 (C=O)	-	-
9a	102.96 (C)	-	-
10a	150.34 (C)	-	-
1′	21.58 (CH_2)	3.47 (*d*, 2H, J = 7.0 Hz)	C-1, C-2, C-3, C-2′, C-3′
2′	121.58 (CH)	5.29 (*brt*, 1H, J = 7.0 Hz)	C-4′, C-5′
3′	134.92 (C)	-	-
4′	17.94 (CH_3)	1.84 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.86 (CH_3)	1.76 (*s*, 3H)	C-2′, C-3′, C-4′
1″	21.59 (CH_2)	3.57 (*d*, 2H, J = 7.0 Hz)	C-3, C-4, C-4a, C-2″, C-3″
2″	121.58 (CH)	5.27 (*brt*, 1H, J = 7.0 Hz)	C-4, C-4″
3″	137.94 (C)	-	-
4″	39.72 (CH_2)	2.06-2.03 (*m*, 2H)	C-2″, C-5″, C-6″
5″	26.43 (CH_2)	2.11-2.08 (*m*, 2H)	C-3″, C-4″, C-6″
6″	123.85 (CH)	5.05 (*brt*, 1H, J = 7.0 Hz)	C-5″, C-10″
7″	131.50 (C)	-	-

Table 13 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
8″	17.69 (CH_3)	1.57 (*s*, 3H)	C-6″, C-7″, C-10″
9″	16.27 (CH_3)	1.88 (*s*, 3H)	C-2″, C-3″, C-4″
10″	25.66 (CH_3)	1.64 (*s*, 3H)	C-6″, C-7″, C-8″

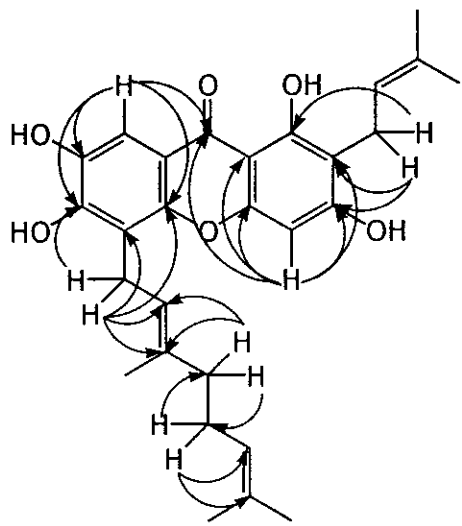
* Carbon type was deduced from DEPT experiments

3.1.8 CC8: 1,3,6,7-tetrahydroxy-2-(3-methyl-2-butenyl)-5-(3,7-dimethyl-2,6-octadienyl)xanthone



CC8 is a yellow solid, m.p. 221-222 °C. The molecular formula was determined as $C_{28}H_{32}O_6$ by HR-MS ($[M]^+$ *m/z* 464.2189). The UV spectrum showed maximum absorption bands at 243, 259, 323 and 372 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1640 cm^{-1} and hydroxyl group at 3350 cm^{-1}. The ^1H NMR spectrum showed a sharp singlet signal of a chelated hydroxyl group 1-OH at δ 13.33. The spectrum also showed two sharp singlet signals at δ 6.40 and 7.48, they were proposed to be H-4 and H-8, respectively. The most deshielded aromatic proton signal was assigned for H-8 according to an anisotropic effect of the carbonyl group. The assignment of these two protons were supported by ^3J and ^4J coupling of H-4 to C-2, C-3, C-4a, C-9, C-9a and H-8 to C-6, C-7, C-9, C-10a on HMBC experiment. The signals of a prenyl group were displayed as broad triplet signal at δ 5.26 (1H, H-2′), a doublet signal at δ 3.35 (2H, H-1′) and two singlet signals at δ 1.78 (3H, H-4′) and 1.66 (3H, H-5′). This group was assigned at C-2 according to the correlations of H-1′ to C-1, C-2 and C-3. The characteristic signals of a geranyl group were observed at δ 3.56 (*d*, H-1″), δ 5.26 (*brt*, H-2″), δ 5.00 (*brt*, H-6″), δ 2.03-1.99 (*m*, H-5″), 1.94-1.91 (*m*, H-4″), δ 1.84 (*s*, H-9″), δ 1.56 (*s*, H-8″)

and δ 1.50 (*s*, H-10″). HMBC correlations of H-1″ to C-5, C-6, C-10a, C-2″ and C-3″ indicated that the geranyl side chain was at C-5. The ^{13}C NMR spectrum and DEPT experiments indicated the presence of a carbonyl carbon (δ 180.11), five methyl carbons (δ 25.72, 25.52, 17.79, 17.57 and 16.23), four methylene carbons (δ 39.37, 26.56, 22.32 and 21.28), five methine carbons (δ 124.12, 122.63, 121.43, 105.95 and 93.34), thirteen quaternary carbons (δ 162.28, 160.00, 155.73, 150.23, 149.46, 141.60, 135.41, 131.40, 131.19, 115.32, 112.85, 110.02 and 102.33). **CC8** was then identified as 1,3,6,7-tetrahydroxy-2-(3-methyl-2-butenyl)-5-(3,7-dimethyl-2,6-octadienyl) xanthone. This compound was a new xanthone derivative.



Major HMBC of **CC8**

Table 14 The NMR spectral data of **CC8**

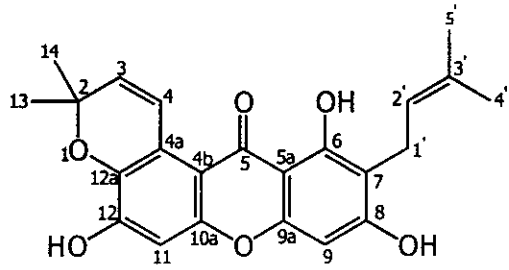
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
1	160.00 (C)	-	-
1-OH	-	13.33 (*s*, OH)	C-1, C-2, C-9a
2	110.02 (C)	-	-
3	162.28 (C)	-	-
4	93.34 (CH)	6.40 (*s*, 1H)	C-2, C-3, C-4a, C-9, C-9a
4a	155.73 (C)	-	-
5	115.32 (C)	-	-
6	150.23 (C)	-	-
7	141.60 (C)	-	-
8	105.95 (CH)	7.48 (*s*, 1H)	C-6, C-7, C-9, C-10a
8a	112.85 (C)	-	-
9	180.11 (C=O)	-	-
9a	102.33 (C)	-	-
10a	149.76 (C)	-	-
1′	21.28 (CH_2)	3.35 (*d*, 2H, J = 7.0 Hz)	C-1, C-2, C-3, C-2′, C-3′
2′	122.63 (CH)	5.26 (*brt*, 1H, J = 7.0 Hz)	C-1′, C-4′, C-5′
3′	131.40 (C)	-	-
4′	17.79 (CH_3)	1.78 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.72 (CH_3)	1.66 (*s*, 3H)	C-2′, C-3′, C-4′
1″	22.32 (CH_2)	3.56 (*d*, 2H, J = 7.0 Hz)	C-5, C-6, C-10a, C-2″, C-3″
2″	121.43 (CH)	5.26 (*brt*, 1H, J = 7.0 Hz)	C-1″, C-4″
3″	135.41 (C)	-	-
4″	39.66 (CH_2)	1.94-1.91 (*m*, 2H)	C-2″, C-3″, C-6″
5″	26.56 (CH_2)	2.03-1.99 (*m*, 2H)	C-4″, C-6″, C-7″
6″	124.12 (CH)	5.00 (*brt*, 1H, J = 7.0 Hz)	C-8″, C-10″
7″	131.19 (C)	-	-

Table 14 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
8″	17.57 (CH_3)	1.50 (*s*, 3H)	C-6″, C-7″, C-10″
9″	16.23 (CH_3)	1.84 (*s*, 3H)	C-2″, C-3″, C-4″
10″	25.52 (CH_3)	1.56 (*s*, 3H)	C-6″, C-7″, C-8″

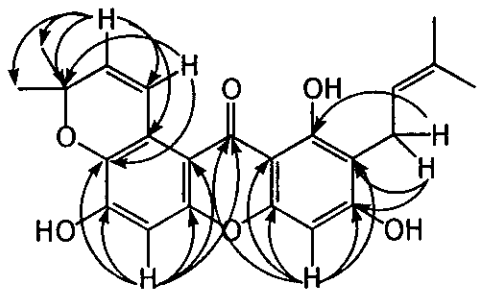
* Carbon type was deduced from DEPT experiments

3.1.9 CC9: 6,8,12-trihydroxy-7-(3-methyl-2-butenyl)-2,2-dimethylpyrano(2′,3′: 7,8)xanthone (Garcinone B)



CC9 is a yellow solid, m.p. 190-192 °C. The ^{1}H NMR spectrum exhibited a singlet signal of a chelated hydroxyl group 6-OH at δ 13.74. In the aromatic region, two singlet resonances at δ 6.82 and 6.31 were assigned for the resonances of H-11 and H-9, respectively. The placement of H-9 and H-11 were supported by the cross peaks of H-9 to C-5, C-5a, C-7, C-8, C-9a and H-11 to C-4b, C-5, C-10a, C-12, C-12a. The appearance of the signals of two methyl groups at δ 1.77 (H-5′) and 1.84 (H-4′), methylene protons (H-1′) at δ 3.46 and an olefinic methine proton (H-2′) at δ 5.30 were suggestive to the signal of a prenyl moiety. The correlations of H-1′ to C-6, C-7 and C-8 supported the position of prenyl side chain at C-7. Two singlet signals of methyl protons H-13 and H-14 (δ 1.50) and two vicinal protons H-4 and H-3 appearing as two doublets (δ 8.03 and 5.83) implied the presence of a chromene ring. The correlations of H-3 to C-2, C-4, C-4a, C-13 and C-14 and H-4 to C-2 and C-12a suggested that chromene ring was fused to xanthone nucleus at C-4a and C-12a. The deshielded effect on resonance of H-4 suggested that the chromene ring was attached to the xanthone nucleus nearby carbonyl group. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 23 signals for 23 carbon atoms : a carbonyl carbon (δ 182.28), four methyl carbons (δ 27.16x2, 25.77 and 17.83), a methylene carbon (δ 21.37), five methine carbons (δ 132.02, 122.54, 121.14, 102.48 and 92.86) and twelve quaternary carbons (δ 162.27, 160.45, 155.04, 152.92, 151.42, 138.01,

131.31, 119.92, 110.11, 106.40, 102.68 and 76.24). **CC9** was assigned to be 6,8,12-trihydroxy-7-(3-methyl-2-butenyl)-2,2-dimethylpyrano(2′,3′:7,8)xanthone. The proposed structure, the spectral data and melting point was corresponded to garcinone B (Sen, *et al.*, 1982).



Major HMBC of **CC9**

Table 15 The NMR spectral data of **CC9**

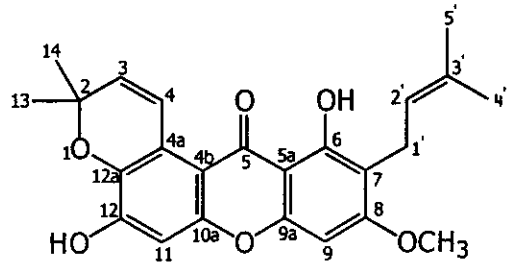
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
2	76.27 (C)	-	-
3	132.02 (CH)	5.83 (*d*, 1H, *J* = 10.5 Hz)	C-2, C-4, C-4a, C-13, C-14
4	121.14 (CH)	8.03 (*d*, 1H, *J* = 10.5 Hz)	C-2, C-12a
4a	119.92 (C)	-	-
4b	106.40 (C)	-	-
5	182.28 (C=O)	-	-
5a	102.68 (C)	-	-
6	160.45 (C)	-	-
6-OH	-	13.69 (*s*, OH)	C-5a, C-6, C-7
7	110.11 (C)	-	-
8	162.27 (C)	-	-
9	92.86 (CH)	6.31 (*s*, 1H)	C-5, C-5a, C-7, C-8, C-9a
9a	155.04 (C)	-	-
10a	152.92 (C)	-	-
11	102.48 (CH)	6.82 (*s*, 1H)	C-4b, C-5, C-10a, C-12, C-12a

Table 15 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
12	151.42 (C)	-	-
12a	138.00 (C)	-	-
13	27.16 (CH_3)	1.50 (*s*, 3H)	C-2, C-3
14	27.16 (CH_3)	1.50 (*s*, 3H)	C-2, C-3
1′	21.37 (CH_2)	3.46 (*d*, 2H, J = 7.2 Hz)	C-6, C-7, C-8, C-2′
2′	122.54 (CH)	5.30 (*brt*, 1H, J = 7.2 Hz)	C-1′, C-4′, C-5′
3′	131.31 (C)	-	-
4′	17.83 (CH_3)	1.84 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.77 (CH_3)	1.78 (*s*, 3H)	C-2′, C-3′, C-4′

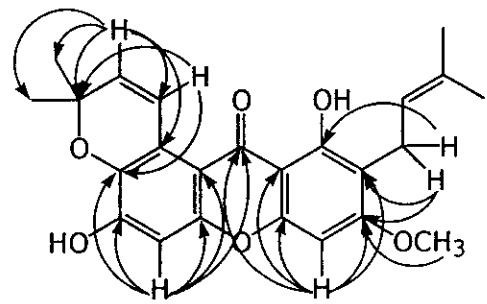
* Carbon type was deduced from DEPT experiments

3.1.10 CC10: 6,12-Dihydroxy-8-methoxy-7-(3-methyl-2-butenyl)-2,2-dimethylpyrano(2′,3′:7,8)xanthone (3-*O*-Methylgarcinone B)



CC10 is a yellow solid, m.p. 246-247 °C. Its molecular formular of $C_{24}H_{24}O_6$ was established on the basis of mass spectrum, HR-MS ($[M]^+$ *m/z* 408.1555). The UV spectrum showed maximum absorption bands at 245, 267, 321, 332 and 382 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1631 cm^{-1} and hydroxyl group at 3483 cm^{-1}. The ^1H NMR spectrum exhibited a signal of hydrogen bonded hydroxy function at δ 13.48 (*s*, 1-OH) and free hydroxy proton at δ 9.19 (*brs*, 12-OH). A sharp singlet resonance with integration of three protons at δ 3.90 belonged to the methoxyl group. A correlation of methoxy protons (OCH_3) to C-8 indicated that the methoxyl group was at C-8. Two singlets in aromatic region, δ 6.81 and 6.35 were assigned for the signals of isolated proton H-9, in addition it was confirmed by correlations of H-9 to C-4b, C-5, C-10a, C-12 and C-12a. The presence of a prenyl side chain was shown in the spectrum, of which the two singlet signals of *gem*-dimethyl protons (H-4′ and H-5′) were at δ 1.78 and δ 1.67, a doublet signal of benzylic methylene protons (H-1′) was at δ 3.32 and a broad triplet signal of olefinic methine proton (H-2′) was at δ 5.20. The prenyl unit was assigned at C-7 according to the correlations of H-1′ to C-6, C-7 and C-8. The ^1H NMR spectrum revealed a characteristic signal of a dimethylchromene ring , of which the signal of *gem*-dimethyl protons resonated as a singlet at δ 1.50 and two doublet signals of two *cis*-olefinic protons (H-4 and H-3) were at δ8.00 and 5.81. The correlations of H-3 to C-2, C-4, C-

4a, C-13 and C-14 and H-4 to C-2 and C-12a precisely determined that dimethylchromene ring was next to C-4b. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 24 signals for 24 carbon atoms : a carbonyl carbon (δ 182.20), five methyl carbons (δ 55.73, 26.98x2, 25.68 and 17.66), a methylene carbon (δ 21.16), five methine carbons (δ 132.08, 122.27, 120.94, 102.63 and 88.80) and twelve quaternary carbons (δ 163.29, 159.35, 155.30, 152.87, 152.45, 138.01, 131.31, 119.94, 110.98, 107.89, 103.71 and 75.70. **CC10** was then identified as 6,12-dihydroxy-8-methoxy-7-(3-methyl-2-butenyl)-2,2-dimethylpyrano(2′,3′:7,8)xanthone, it was a methyl ether derivative of **CC9** (Na Pattalung, *et al.*, 1984).



Major HMBC of **CC10**

Table 16 The NMR spectral data of **CC10**

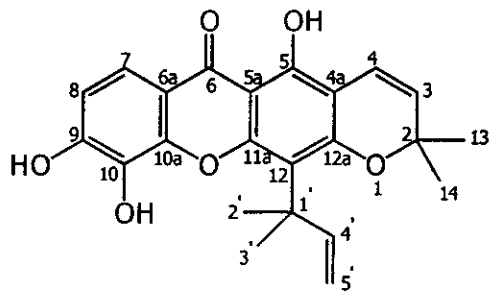
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
2	75.70 (C)	-	-
3	132.08 (CH)	5.81 (*d*, 1H, *J* = 10.2 Hz)	C-2, C-4. C-4a, C-13, C-14
4	120.94 (CH)	8.00 (*d*, 1H, *J* = 10.2 Hz)	C-2, C-12a
4a	119.94 (C)	-	-
4b	107.89 (C)	-	-
5	182.20 (C=O)	-	-
5a	103.71 (C)	-	-
6	159.35 (C)	-	-

Table 16 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	HMBC
6-OH	-	13.48 (*s*, OH)	C-5a, C-6, C-7
7	110.98 (C)	-	-
8	163.29 (C)	-	-
8-OCH_3	55.73 (CH_3)	3.90 (*s*, 3H)	C-8
9	88.80 (CH)	6.35 (*s*, 1H)	C-5, C-5a, C-7, C-8, C-9a
9a	155.30 (C)	-	-
10a	152.87 (C)	-	-
11	102.63 (CH)	6.81 (*s*, 1H)	C-4b, C-5, C-10a, C-12, C-12a
12	152.45 (C)	-	-
12-OH	-	9.19 (*brs*, OH)	-
12a	138.01 (C)	-	-
13	26.98 (CH_3)	1.50 (*s*, 3H)	C-2, C-3
14	26.98 (CH_3)	1.50 (*s*, 3H)	C-2, C-3
1′	21.16 (CH_2)	3.32 (*d*, 2H, J = 7.2 Hz)	C-6, C-7, C-8, C-2′, C-3′
2′	122.27 (CH)	5.20 (*brt*, 1H, J = 7.2 Hz)	C-1′, C-4′, C-5′
3′	131.31 (C)	-	-
4′	17.66 (CH_3)	1.78 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.68 (CH_3)	1.67 (*s*, 3H)	C-2′, C-3′, C-4′

* Carbon type was deduced from DEPT experiments

3.1.11 CC11: 5,9,10-Trihydroxy-12-(1,1-dimethyl-2-propenyl)-*2H*,*6H*-pyrano[3,2-*b*]xanthen-6-one (Macluraxanthone)

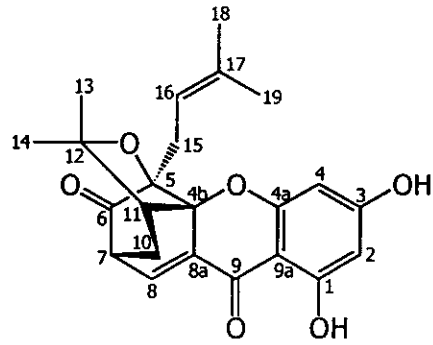


CC11 is a yellow solid, m.p. 170-172 ^{o}C. The ^{1}H NMR spectrum exhibited a signal of hydrogen bonded hydroxy function (5-OH) at δ13.56. Two doublet signals at δ7.71 and 6.97 were observed and assigned to be the signals of aromatic proton H-7 and H-8. The ^{1}H NMR spectrum revealed a characteristic signal of a dimethylchromene ring, of which the signal of *gem*-dimethyl protons resonated as a singlet at δ 1.53 and two doublet signals of two *cis*-olefinic protons (H-4 and H-3) were at δ 6.80 and 5.64. The signals of *gem*-dimethyl protons (H-2′ and H-3′) at δ 1.67, a *cis*-olefinic proton at δ6.76 (H-4′) and terminal olefinic methylene protons at δ 5.24 (H-5′*Z*) and 5.07 (H-5′*E*) corresponded to 1,1-dimethyl-2-propenyl substituent. The ^{13}C NMR spectrum and DEPT experiments indicated the presence of a carbonyl carbon (δ 180.79), four methyl carbons (δ 28.20x2 and 27.94x2), a methylene carbon (δ 103.29), five methine carbons (δ 156.90, 127.16, 117.53, 116.14 and 112.76) and twelve quaternary carbons (δ 158.94, 156.79, 154.11, 149.01, 144.55, 131.05, 113.74, 113.07, 105.59, 103.08, 78.26 and 41.46). The proposed structure, the spectral data and melting point agreed with 5,9,10-trihydroxy-12-(1,1-dimethyl-2-propenyl)-*2H*,*6H*-pyrano[3,2-*b*]xanthen-6-one or macluraxanthone (Iinuma, *et al.*, 1994).

Table 17 The ^{1}H NMR spectral data of **CC11**

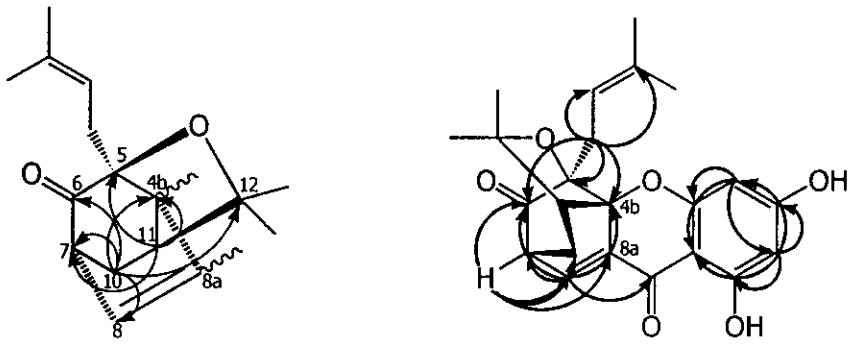
Position	**CC11** δ_H (multiplicity, J_{Hz}) 300 MHz, $CDCl_3$	Macluraxanthone δ_H (multiplicity, J_{Hz}) 270 MHz, acetone-d_6
3	5.64 (*d*, 1H, *J* = 10.2 Hz)	5.70 (*d*, 1H, *J* = 10.0 Hz)
4	6.80 (*d*, 1H, *J* = 10.2 Hz)	6.69 (*d*, 1H, *J* = 10.0 Hz)
5-OH	13.56 (*s*, OH)	13.91 (*s*, OH)
7	7.71 (*d*, 1H, *J* = 9.0 Hz)	7.60 (*d*, 1H, *J* = 9.0 Hz)
8	6.97 (*d*, 1H, *J* = 9.0 Hz)	7.00 (*d*, 1H, *J* = 9.0 Hz)
13	1.53 (*s*, 3H)	1.49 (*s*, 3H)
14	1.53 (*s*, 3H)	1.49 (*s*, 3H)
$2'$	1.67 (*s*, 3H)	1.74 (*s*, 3H)
$3'$	1.67 (*s*, 3H)	1.74 (*s*, 3H)
$4'$	6.76 (*dd*, 1H, *J* = 17.7, 10.8 Hz)	6.52 (*dd*, 1H, *J* = 17.0, 11.0 Hz)
$5'Z$	5.24 (*dd*, 1H, *J* = 17.7, 1.2 Hz)	5.05 (*dd*, 1H, *J* = 17.0, 1.0 Hz)
$5'E$	5.07 (*dd*, 1H, *J* = 10.8, 1.2 Hz)	4.89 (*dd*, 1H, *J* = 11.0, 1.0 Hz)

3.1.12 CC12: Cratoxycochinchinone A (compound 7, Thoison, *et al.*, 2000)



CC12 is a yellow solid, m.p. 208-209 ^{o}C, $[\alpha]_{D}^{29}$ -63^{o} (c 1.19x10^{-3} g/cm^{3} in $CHCl_3$) and the molecular formula was determined as $C_{23}H_{24}O_6$ by HR-MS ($[M]^+$ *m/z* 396.1563). The UV spectrum showed maximum absorption bands at 213, 326 and 350 nm. IR spectrum showed the absorption bands of carbonyl groups at 1738 and 1635 cm^{-1} and hydroxyl group at 3558 cm^{-1}. The ^{1}H NMR spectrum exhibited a signal of hydrogen bonded hydroxy function 1-OH at δ 12.48 (*s*) and 3-OH at δ 7.07 (*brs*). The appearance of two doublet signals with coupling constant of 2.0 Hz at δ 6.12 and 6.06 were assigned for *meta* protons H-4 and H-2, respectively. The signals of a prenyl side chain were shown at δ 1.41 (*s*, H-18), δ 1.12 (*s*, H-19), δ 2.64 (*d*, *J* = 7.5 Hz, H-15) and δ 4.44 (*brt*, *J* = 7.5 Hz, H-16). The prenyl unit was assigned at C-5 according to the correlations of H-15 to C-4b, C-5 and C-6. The ^{1}H NMR spectrum revealed a characteristic signals of a non-aromatic part in the caged-xanthonoid. The *gem*-dimethyl protons (H-13 and H-14) resonated as a singlet at δ 1.71 and 1.32. A deshielded signal at δ 7.44 (*d*, 1H, *J* = 7.0 Hz) due to an anisotropic effect of the carbonyl group was assigned for olefinic proton H-8. A doublet of doublet (H_a-10) and a multiplet signal (H_b-10) of nonequivalent methylene protons were at δ 2.36 and 1.33, respectively. Two methine protons (H-7 and H-11) resonated as a doublet of doublet at δ 3.53 and a doublet at δ 2.48, respectively. The HMBC correlations of H_a-10 to C-4b, C-7, C-8, C-12, H_b-10 to C-6, C-8, H-7 to C-6, C-8, C-8a, C-11 and H-11 to C-4b, C-5,

C-7 indicated that C-10 was between C-7 and C-11. In COSY spectrum correlation of H-8 to H-7, H-7 to H_a-10, H_a-10 to H_b-10 and H_b-10 to H-11 confirmed the assignment of H-8, H-7, H-10 and H-11. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 23 signals for 23 carbon atoms: two carbonyl carbons (δ 202.96 and 179.22), four methyl carbons (δ 28.98, 28.97, 25.52 and 16.90), two methylene carbons (δ28.97 and 25.16), six methine carbons (δ133.83, 118.11, 96.87, 95.23, 48.77 and 46.80) and nine quaternary carbons (δ 165.15x2, 161.15, 135.31, 133.70, 101.08, 90.14, 84.49 and 83.71). **CC12** was then assigned and named as cratoxycochinchinone A. It is a new naturally occurring cage-xanthone but known synthetically compound (Thoison, *et al.*, 2000).



Major HMBC of **CC12**

Table 18 The NMR spectral data of **CC12**

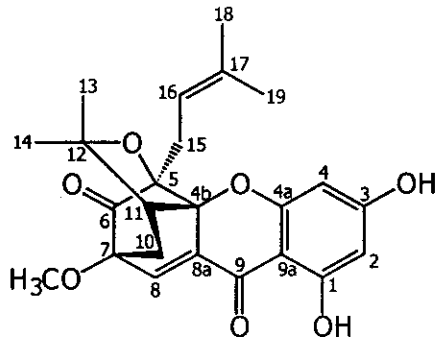
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	COSY ^1H-^1H	HMBC
1	165.15 (C)	-	-	-
1-OH	-	12.48 (*s*, OH)	-	C-1, C-2, C-9a
2	96.87 (CH)	6.06 (*d*, 1H, *J* = 2.0 Hz)	2-4	C-1, C-3, C-4, C-9a
3	165.15 (C)	-	-	-
3-OH	-	7.07 (*brs*, OH)	-	-
4	95.23 (CH)	6.12 (*d*, 1H, *J* = 2.0 Hz)	4-2	C-2, C-4a, C-9a

Table 18 (Continued)

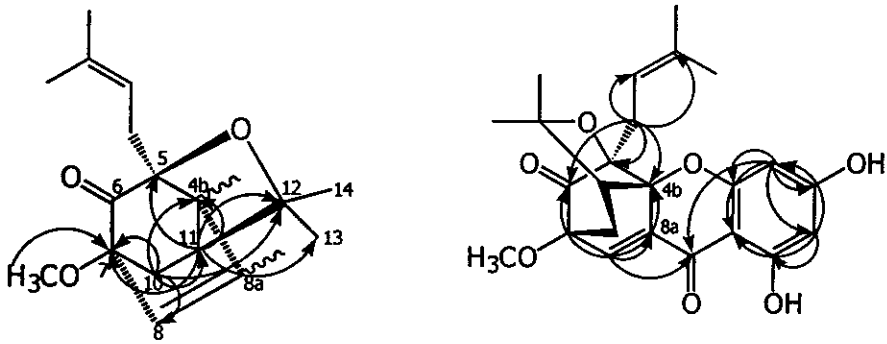
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	COSY ^1H-^1H	HMBC
4a	161.15 (C)	-	-	-
4b	90.14 (C)	-	-	-
5	84.49 (C)	-	-	-
6	202.96 (C=O)	-	-	-
7	46.80 (CH)	3.53 (*dd*, 1H, J = 7.0, 4.0 Hz)	7-8, 7-10_a	C-6, C-8, C-8a, C-11
8	133.83 (CH)	7.44 (*d*, 1H, J = 7.0 Hz)	8-7	C-4b, C-6, C-7, C-9
8a	133.70 (C)	-	-	-
9	179.22 (C=O)	-	-	-
9a	101.08 (C)	-	-	-
10	25.16 (CH_2)	2.36 (*dd*, 1H, J = 13.5, 4.0 Hz, H_a-10)	10_a-7, 10_a-10_b	C-4b, C-6, C-7, C-8, C-12
		1.33 (*m*, 1H, H_b-10)	10_b-10_a, 10_b-11	C-6, C-8
11	48.77 (CH)	2.48 (*d*, 1H, J = 9.6 Hz)	11-10_b	C-4b, C-5, C-7
12	83.71 (C)	-	-	-
13	30.29 (CH_3)	1.71 (*s*, 3H)	-	C-11, C-12
14	28.98 (CH_3)	1.32 (*s*, 3H)	-	C-11, C-12
15	28.97 (CH_2)	2.64 (*d*, 2H, J = 7.5 Hz)	15-16	C-4b, C-5, C-6, C-16, C-17
16	118.11 (CH)	4.44 (*brt*, 1H, J = 7.5 Hz)	16-15	C-18, C-19
17	135.31 (C)	-	-	-
18	25.52 (CH_3)	1.41 (*s*, 3H)	-	C-16, C-17, C19
19	16.90 (CH_3)	1.12 (*s*, 3H)	-	C-16, C-17, C-18

* Carbon type was deduced from DEPT experiments

3.1.13 CC13: Cratoxycochinchinone B



CC13 is a yellow solid, m.p. 218-219 °C and $[\alpha]_D^{29}$ -58° (c 6.90x10^{-4} g/cm^3 in $CHCl_3$). The UV spectrum showed maximum absorption bands at 212, 275, 332 and 357 nm. IR spectrum showed the absorption bands of carbonyl groups at 1738 and 1646 cm^{-1} and hydroxyl group at 3392 cm^{-1}. The ^{1}H NMR spectrum indicated that **CC13** contained a prenyl side chain [δ 4.43 (*brt*, J = 7.5 Hz, H-16), δ 2.63 (*d*, J = 7.5 Hz, H-15), δ 1.40 (*s*, H-18) and δ 1.13 (*s*, H-19)], *gem*-dimethyl protons (δ 1.66 and δ 1.31, *s* each) and tetrasubstituted aromatic ring [δ6.05 (*d*, J = 2.1 Hz, H-4) and 6.03 (*d*, J = 2.1 Hz, H-2)] as in **CC12**. The singlet resonance of olefinic proton H-8 (δ 7.44) and a doublet of doublet signal (δ1.59) of H_b-10 revealed the quaternary carbon at C-7. The methoxyl group (δ 3.62, *s*, 3H) then was assigned at C-7, in addition it was confirmed by the HMBC correlations of 7-OCH_3 to C-7. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 24 signals for 24 carbon atoms: two carbonyl carbons (δ 201.00 and 178.00), four methyl carbons (δ 30.26, 28.94, 25.46 and 16.88), two methylene carbons (δ 29.87 and 28.98), five methine carbons (δ 133.25, 117.86, 96.95, 95.49 and 49.27), a methoxy carbon (δ 53.84) and ten quaternary carbons (δ 167.88, 164.50, 160.50, 135.50, 132.25, 100.50, 88.50, 84.50, 83.78 and 83.76). **CC13** was then assigned and was named as cratoxycochinchinone B. It is a new cage-xanthone derivative.



Major HMBC of **CC13**

Table 19 The NMR spectral data of **CC13**

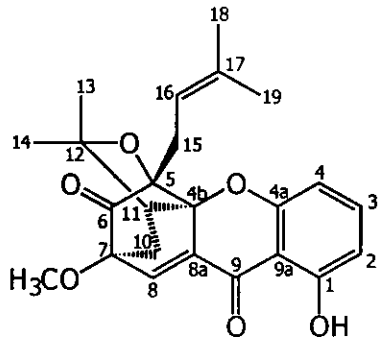
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	COSY ^1H-^1H	HMBC
1	160.50 (C)	-	-	-
1-OH	-	12.39 (*s*, OH)	-	C-1, C-2, C-9a
2	95.49 (CH)	6.03 (*d*, 1H, J = 2.1 Hz)	2-4	C-1, C-4, C-9a
3	167.88 (C)	-	-	-
3-OH	-	8.05 (*brs*, OH)	-	-
4	96.95 (CH)	6.05 (*d*, 1H, J = 2.1 Hz)	4-2	C-2, C-3, C-4a, C-9, C-9a
4a	164.50 (C)	-	-	-
4b	88.50 (C)	-	-	-
5	83.78 (C)	-	-	-
6	201.00 (C=O)	-	-	-
7	84.50 (C)	-	-	-
7-OCH_3	53.84 (CH_3)	3.62 (*s*, 3H)	-	C-7
8	133.25 (CH)	7.44 (*s*, 1H)	-	C-4b, C-6, C-8a, C-9
8a	132.25 (C)	-	-	-

Table 19 (Continued)

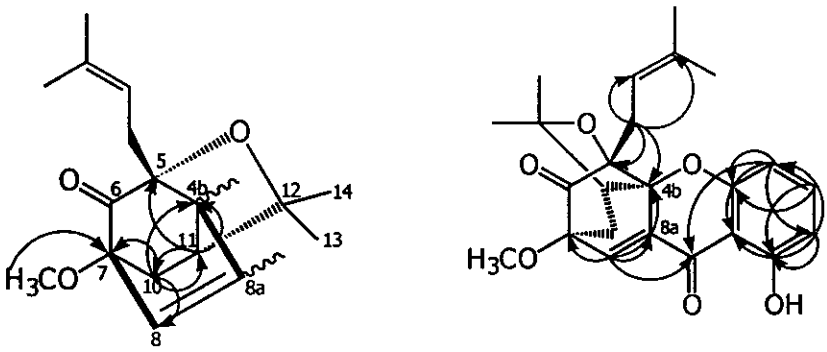
Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	COSY ^1H-^1H	HMBC
9	178.00 (C=O)	-	-	-
9a	100.50 (C)	-	-	-
10	29.87 (CH_2)	2.35 (*d*, 1H, J = 13.2 Hz, H_a-10)	10_a-10_b	C-4b, C-7, C-8, C-12
		1.59 (*dd*, 1H, J = 13.2, 9.6 Hz, H_b-10)	10_b-10_a, 10_b-11	C-6, C-7, C-8, C-11
11	49.27 (CH)	2.50 (*d*, 1H, J = 9.6 Hz)	11-10_b	C-4b, C-7, C-12, C-13
12	83.76 (C)	-	-	-
13	30.26 (CH_3)	1.66 (*s*, 3H)	-	C-11, C-12, C-14
14	28.94 (CH_3)	1.31 (*s*, 3H)	-	C-11, C-12, C-13
15	28.98 (CH_2)	2.63 (*d*, 2H, J = 7.5 Hz)	15-16	C-4b, C-5, C-6, C-16, C-17
16	117.86 (CH)	4.43 (*brt*, 1H, J = 7.5 Hz)	16-15	C-15, C-18, C-19
17	135.50 (C)	-	-	-
18	25.46 (CH_3)	1.40 (*s*, 3H)	-	C-16, C-17, C-19
19	16.88 (CH_3)	1.13 (*s*, 3H)	-	C-16, C-17, C-18

* Carbon type was deduced from DEPT experiments

3.1.14 CC14: Cratoxycochinchinone C



CC14 is a yellow solid, m.p. 147-148 °C and $[\alpha]_D^{29}$ +50° (c 8.90x10^{-4} g/cm^3 in $CHCl_3$). The opposite sign suggested opposite stereochemistry to **CC12**. The UV spectrum showed maximum absorption bands at 206, 222, 307 and 346 nm. IR spectrum showed the absorption bands of hydroxyl group at 3467 cm^{-1} and carbonyl groups at 1642 and 1749 cm^{-1}. The ^{1}H NMR spectrum indicated that **CC14** contained a prenyl side chain [δ4.39 (*brt*, J = 8.1 Hz, H-16), δ2.64 (*d*, J = 8.1 Hz, H-15), δ1.37 (*s*, H-18) and δ1.01 (*s*, H-19)], 7-OCH_3 (δ3.65, *s*), olefinic H-8 (δ7.51, *s*), H_b-10 (δ 1.59, 1H, *dd*) and *gem*-dimethyl protons (δ1.69 and 1.33, *s* each) as in **CC12**. The aromatic protons signals at δ7.41 (*t*, J = 8.4 Hz, H-3), δ6.55 (*dd*, J = 8.4, 0.9 Hz, H-2) and 6.52 (*dd*, J = 8.4, 0.9 Hz, H-4) appearing as ABM pattern implied the trisubstituted aromatic ring. The ^{13}C NMR spectral data deduced from DEPT and HMQC spectra showed 24 signals for 24 carbon atoms: two carbonyl carbons (δ201.16 and 180.73), four methyl carbons (δ30.37, 29.04, 25.51 and 16.69), two methylene carbons (δ29.73 and 29.21), six methine carbons (δ138.97, 135.25, 118.48, 109.57, 107.41 and 49.42), a methoxy carbon (δ54.09) and nine quaternary carbons (δ162.90, 159.44, 135.73, 132.14, 106.15, 88.74, 84.86, 84.18 and 83.96). **CC14** was then assigned and named as cratoxycochinchinone C. It is a new cage-xanthone derivative.



Major HMBC of **CC14**

Table 20 The NMR spectral data of **CC14**

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	COSY ^1H-^1H	HMBC
1	162.90 (C)	-	-	-
1-OH	-	12.00 (*s*, OH)	-	C-1, C-2, C-9a
2	109.57 (CH)	6.55 (*dd*, 1H, *J* = 8.4, 0.9 Hz)	2-3, 2-4	C-1, C-4
3	138.97 (CH)	7.41 (*t*, 1H, *J* = 8.4 Hz)	3-2, 3-4	C-1, C-4a
4	107.41 (CH)	6.52 (*dd*, 1H, *J* = 8.4, 0.9 Hz)	4-2, 4-3	C-2, C-4a, C-9, C-9a
4a	159.44 (C)	-	-	-
4b	88.76 (C)	-	-	-
5	84.18 (C)	-	-	-
6	201.16 (C=O)	-	-	-
7	84.86 (C)	-	-	-
7-OCH_3	54.09 (CH_3)	3.65 (*s*, 3H)	-	C-7
8	135.25 (CH)	7.51 (*s*, 1H)	-	C-4b, C-7, C-8a, C-9

Table 20 (Continued)

Position	δ_C (C-Type)*	δ_H (multiplicity, J_{Hz})	COSY ^1H-^1H	HMBC
8a	132.14 (C)	-	-	-
9	180.73 (C=O)	-	-	-
9a	106.15 (C)	-	-	-
10_a	29.73 (CH_2)	2.39 (*d*, 1H, J = 12.9 Hz, H_a-10)	10_a-10_b	C-4b, C-8, C-11
		1.59 (*dd*, 1H, J = 12.9, 9.9 Hz, H_b-10)	10_b-10_a, 10_b-11	C-7, C-8, C-11
11	49.43 (CH)	2.54 (*d*, 1H, J = 9.9 Hz)	11-10_b	C-4b, C-5, C-10
12	83.96 (C)	-	-	-
13	30.37 (CH_3)	1.69 (*s*, 3H)	-	C-11, C-12, C-14
14	29.04 (CH_3)	1.33 (*s*, 3H)	-	C-11, C-12, C-13
15	29.21 (CH_2)	2.64 (*d*, 2H, J = 8.1 Hz)	15-16	C-4b, C-5, C-16, C-17
16	118.48 (CH)	4.39 (*brt*, 1H, J = 8.1 Hz)	16-15	C-15, C-18, C-19
17	135.73 (C)	-	-	-
18	25.51 (CH_3)	1.37 (*s*, 3H)	-	C-16, C-17, C-19
19	16.69 (CH_3)	1.01 (*s*, 3H)	-	C-16, C-17, C-18

* Carbon type was deduced from DEPT experiments

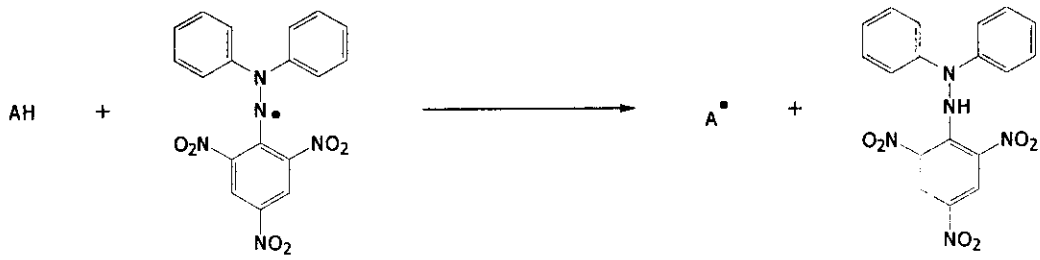
3.2 Evaluation of Antioxidative Activity (Ko, *et al.*, 1995)

Free radicals are potentially dangerous for the cell (Hochstein, *et al.*, 1988 and Chiu, *et al.*, 1989). The reactions of free radicals e.g., hydroxyl and peroxyl radicals on biomolecules are important in physiology and biology (Halliwell, *et al.*, 1989). Free radicals can be generated within cells as intermediates of normal biochemical processes such as those involving redox enzymes and bioenergetic electron transfer. They may also appear under less controlled circumstances and cause reversible or irreversible damage to macromolecules. This damage is a major contributor to aging and to degenerative diseases of aging such as cardiovascular diseases, brain dysfunction, cancers, immune system decline and cataracts. As a result of the relative instability of free radicals and their potential to damage cells and tissues, there are both enzymes and small molecular-weight molecules with antioxidant capabilities that can protect against the adverse effects of free radical reactions. Furthermore, based on the growing interest in free radical biology and the lack of effective therapies for many of the chronic diseases, the usefulness of antioxidants in protecting against the adverse effects of oxidative injury is warranted (Ames, *et al.*, 1993 and Edgington, 1994).

The chemical constituents isolated from *C. cochinchinense* were xanthone derivative that contained free phenolic hydroxy group. It was thus of considerable interest for the studies of antioxidant activity.

The DPPH (2,2-diphenyl-1-picrylhydrazyl) assay is one of the methods used for evaluation of antioxidation activity. DPPH is a stable free radical which shows a purple color and a strong absorption at 517 nm. It has been used as a convenient tool for the antioxidant assay of biological materials. When DPPH radical accepts 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 leads to the disappearance of DPPH free radical and to the appearance the free radical $A^{\bullet}$



Purple

In this research, we evaluated the antioxidative activity of crude extracts and pure compounds.

3.2.1 Free radical scavenging activity of the crude extracts

To determine the scavenging activity, crude extracts of *C. cochinchinense* were tested at the final concentration of 40 μg/mL. The activity was monitored by following the decrease of the absorbance of the solution at 517 nm.

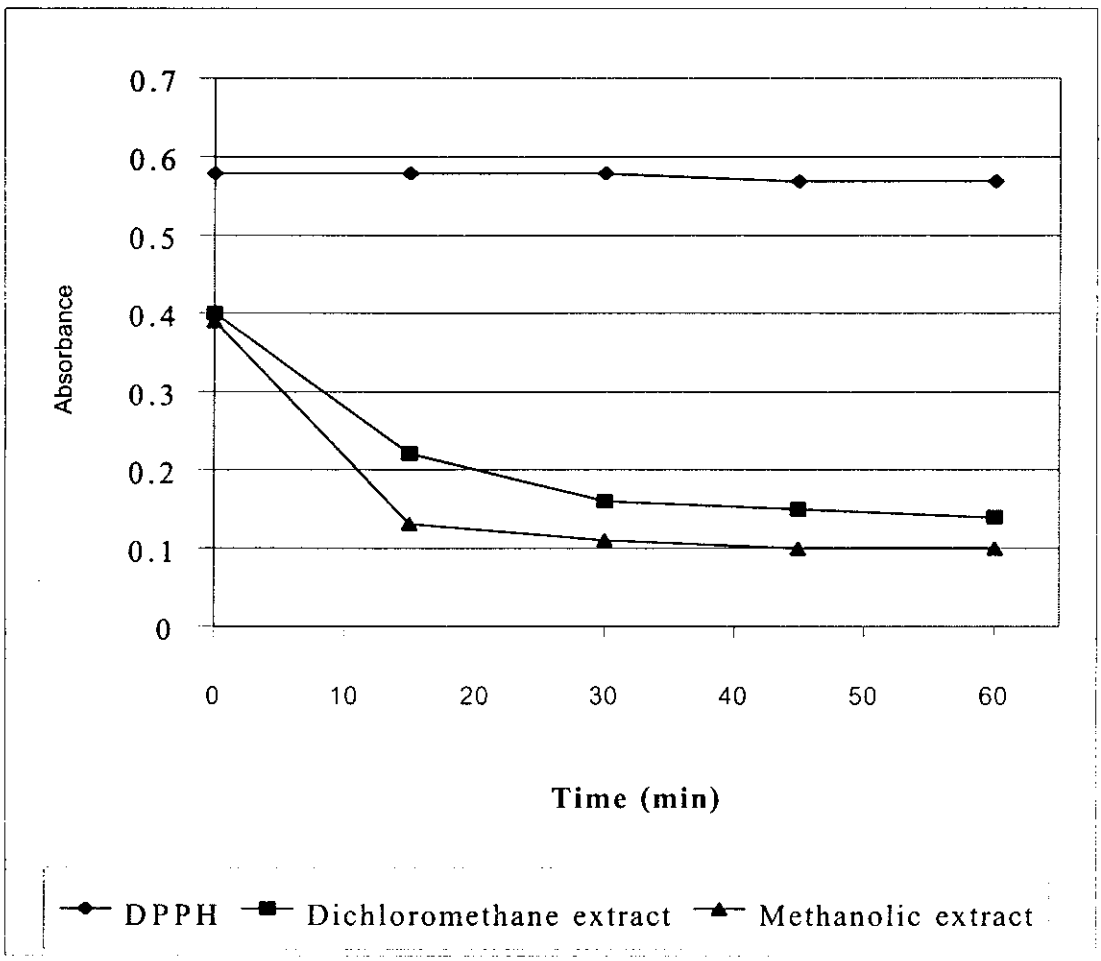


Figure 2 Antioxidative activity of the crude extracts against DPPH radical

The result (Figure 2) indicated that the crude extracts were able to scavenge the DPPH radical significantly. It were found that at a concentration of 40 μg/mL, the methanolic extract is able to scavenge the DPPH radical more than dichloromethane extract.

The assessment of the antioxidation activity of crude extracts were extended. In comparable to the standard antioxidant, BHT and crude extracts were evaluated for IC_{50}. Since the decolorization occurred properly within 30 min, the IC_{50} then was examined at 30 min.

Table 21 Inhibitory concentration (IC_{50}) of the crude extracts and BHT

Sample	IC_{50} (μg/mL, 30 min)
Dichloromethane extract	25.1
Methanolic extract	21.6
BHT	5.8

The results showed that the dichloromethane extract and methanolic extract exhibited IC_{50} at 25.1 and 21.6 μg/mL, respectively whereas BHT exhibited IC_{50} at 5.8 μg/mL.

3.2.2 Free radical scavenging activity of the pure compounds

To determine the active constituent from dichloromethane extract of the roots of *C. cochinchinense*, the pure constituents were examined for the activity. The final concentration of the tested samples were conducted at final concentration of 50 and 100 μM. The absorption of the solution of the tested samples and DPPH were measured at 517 nm. The activity was expressed in the percentage scavenging.

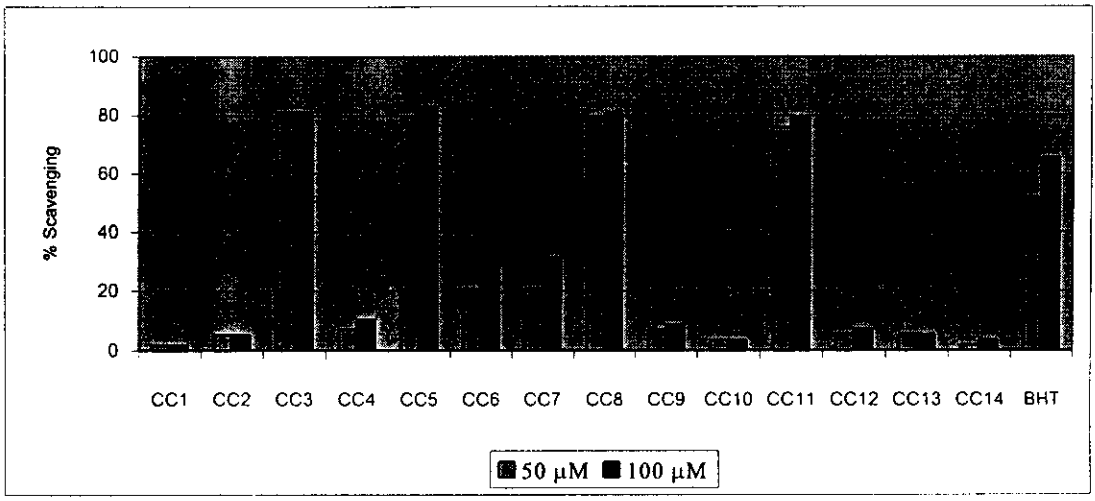


Figure 3 Radical scavenging activity of tested samples at 50 and 100 μM

Radical scavenging activities of pure compounds from the roots of *C. cochinchinense* were evaluated against the DPPH radical. The results indicated that at 50 and 100 μM **CC3**, **CC5**, **CC8** and **CC11** were able to act as radical scavenger more effective than BHT. The activity of **CC3**, **CC5**, **CC8** and **CC11** may be caused by the presence of *ortho* dihydroxyl groups which were known to donate hydrogen radical and form stabilized phenoxy radical through an intramolecular hydrogen bonding. A subsequent interaction with a second DPPH radical afforded the dehydro form of them as a final product (Shahidi, *et al.*, 1992; Keawpradub, *et al.*, 2001).

3.2.3 Evaluation of IC_{50} value of pure compounds

CC3, **CC5**, **CC8** and **CC11** were further examined for IC_{50} value. The absorption of the solution of the tested samples and DPPH were measured at 517 nm for 30 min. The results were shown in Table 22.

Table 22 Inhibitory concentration (IC_{50}) of the pure compounds

Compound	IC_{50} (μM, 30 min)
CC3	17.9
CC5	12.3
CC8	9.4
CC11	19.0
BHT	28.9

The results indicated that the most active compound, **CC8**, was comparable to **CC3**, **CC5**, **CC11** and **BHT**. The IC_{50} of **CC3**, **CC5**, **CC8**, **CC11** and **BHT** were 17.9, 12.3, 9.4, 19.0 and 28.9 μM, respectively.