

A Novel Depsidone and Some New Xanthenes from *Garcinia* Species¹⁾

Chihiro ITO,^{*,a} Yoshiaki MIYAMOTO,^a Minako NAKAYAMA,^a Yuko KAWAI,^a
K. Sundar RAO,^b and Hiroshi FURUKAWA^a

Faculty of Pharmacy, Meijo University,^a Tempaku, Nagoya 468, Japan and National Research Centre for Environmental Toxicology,^b The University of Queensland, 39 Kessels Road, Coopers Plains, QLD 4108, Australia.

Received March 14, 1997; accepted May 30, 1997

Constituents of three EtOH extracts of the stem bark of *Garcinia assigu* LANTB., *Garcinia dulcis* (ROXB.) KURZ., and *Garcinia latissima* MIQ., belonging to the Guttiferae, collected in Central Province of Papua New Guinea, were studied. A novel depsidone named garcinisidone-A (**1**), six new xanthenes named assiguxanthone-A (**3**) and -B (**9**) and dulxanthone-A (**4**), -B (**6**), -C (**7**), and -D (**11**), and four new pyranoxanthenes named latisxanthone-A (**13**), -B (**14**), -C (**15**), and -D (**16**) were isolated, as well as some known xanthone, benzophenone, chromone, and biflavanone derivatives, and their structures were elucidated by spectroscopic methods. Among these components, garcinisidone-A (**1**) is the first example of a depsidone derivative having a five-carbon unit (prenyl) as a substituent to be found in nature. Latisxanthone-B (**14**) was found to contain a hydroperoxy moiety in the molecule. This is the second example of a xanthone hydroperoxide to be found in nature.

Key words *Garcinia*; depsidone; xanthone; hydroperoxide; pyranoxanthone; Guttiferae

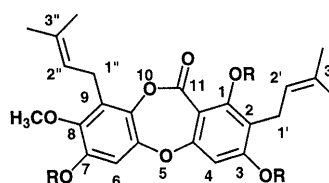
In our previous paper²⁾ on biologically active natural products from Papua New Guinea medicinal plants, the isolation and structural elucidation of a novel dibenzofuran named calophyuran, and two new xanthenes named pancixanthone-A and -B from *Calophyllum paniculatum* A. C. SMITH were described. In our further studies on this project, three ethanolic extracts of the stem bark of *Garcinia assigu* LANTB., *Garcinia dulcis* (ROXB.) KURZ., and *Garcinia latissima* MIQ., belonging to the Guttiferae, were found to exhibit antibacterial activity.^{3,4)} This paper describes the isolation and structural elucidation of a novel depsidone (11H-dibenzo[*b,e*][1,4]dioxepin-11-one derivative) named garcinisidone-A (**1**) and two new xanthenes named assiguxanthone-A (**3**) and -B (**9**) from *G. assigu*, four new xanthenes named dulxanthone-A (**4**), -B (**6**), -C (**7**), and -D (**11**) from *G. dulcis*, and four new pyranoxanthenes named latisxanthone-A (**13**), -B (**14**), -C (**15**) and -D (**16**) from *G. latissima*.

Results and Discussion

The dried stem barks of *G. assigu*, *G. dulcis*, and *G. latissima* were each extracted with EtOH under reflux. The hexane-, CH₂Cl₂-, and EtOAc-soluble portions of each EtOH extract were fractionated by a combination of silica gel column chromatography and preparative TLC to give a novel depsidone, six new xanthenes, and four new pyranoxanthenes along with some known xanthone, benzophenone, chromone, and biflavanone derivatives.

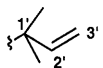
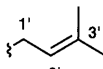
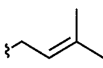
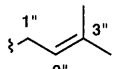
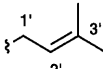
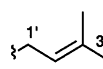
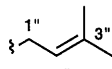
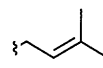
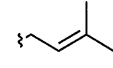
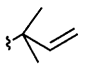
Structure of Garcinisidone-A (1**)** Garcinisidone-A (**1**) was obtained as a pale yellow oil, and the molecular formula was determined as C₂₄H₂₆O₇ by high-resolution mass spectrometry (HR-MS). The IR spectrum showed absorption bands due to hydroxyl groups and a lactone carbonyl group at ν_{\max} 3527, 3300 (br) and 1668, 1267 cm⁻¹, respectively. The ¹H- and ¹³C-NMR spectra (Table 1) coupled with the results of ¹H-detected heteronuclear multiple quantum coherence (HMQC) showed signals assignable to an *O*-methyl group [δ_{H} 3.66 (3H, s); δ_{C} 60.05 (q)], a lactone carbonyl group [δ_{C} 167.17 (s)], two 1H-singlets [δ_{H} 6.26, 6.65], and a hydroxyl group [δ_{H}

9.80 (br)]. Observations of two sets of signals [δ_{H} 3.14 (2H, d, *J* = 7.0 Hz); δ_{C} 21.43 (t), δ_{H} 5.10 (1H, m); δ_{C} 122.31 (d), δ_{C} 130.48 (s), δ_{H} 1.67 (3H, s); δ_{C} 17.66 (q), δ_{H} 1.58 (3H, s); δ_{C} 25.42 (q) and δ_{H} 3.33 (2H, d, *J* = 7.0 Hz); δ_{C} 23.48 (t), δ_{H} 5.08 (1H, m); δ_{C} 121.83 (d), δ_{C} 131.64 (s), δ_{H} 1.74 (3H, s); δ_{C} 17.76 (q), δ_{H} 1.62 (3H, s); δ_{C} 25.46 (q)] indicated the presence of two prenyl side chains in the molecule. Mass fragment ions at *m/z* 370 [$\text{M}^+ - \cdot\text{CH} = \text{C}(\text{CH}_3)_2 - \cdot\text{H}$] and 315 [$\text{M}^+ - \cdot\text{CH} = \text{C}(\text{CH}_3)_2 - \cdot\text{CH} = \text{C}(\text{CH}_3)_2 - \cdot\text{H}$] in the electron impact (EI)-MS also suggested the presence of two prenyl side chains. *O*-Methylation with methyl iodide in acetone in the presence of anhydrous potassium carbonate gave a trimethylated derivative (**2**), suggesting the presence of three phenolic hydroxyl groups in the original molecule. The partial structures *a* and *b* of **1** (Chart 1) were confirmed by ¹H-detected heteronuclear multiple bond connectivity (HMBC) spectroscopy, as shown by arrows in Fig. 1. The linked arrangement of the two moieties (*a* and *b*) was elucidated from the following spectral data. a) An IR absorption due to a lactone carbonyl group at ν_{\max} 1668 cm⁻¹ on **1** was observed at ν_{\max} 1730 cm⁻¹ on **2**, suggesting the presence of an intramolecular hydrogen-bond in the original molecule. b) The carbon signals at δ_{C} 159.09, 145.57, 134.38, and 92.98 in the ¹³C-NMR spectrum were assigned to C-4a, C-5a, and C-9a bonded to an oxygen atom, and C-11a bonded to carbonyl carbon, respectively, based on the HMBC spectrum. c) In the nuclear Overhauser effect (NOE) experiments on **1**, an NOE enhancement between the H-6 (δ 6.65) and H-4 (δ 6.26) signals was observed. These results suggested the structure of garcinisidone-A to be **1**. The results of the NOE experiments on **2** (see Experimental) also support



- 1** R = H
2 R = CH₃

* To whom correspondence should be addressed.

	R_1	R_2	R_3	R_4	R_5	R_6
3	H	OH		H	OH	H
4	H	OCH ₃		H	OH	H
5	H	OCH ₃		CH ₃	OCH ₃	H
6		OCH ₃		H	OH	H
7	H	OCH ₃		H	OCH ₃	
8	H	OH		H	OH	H
17		OH	H	H	OH	H
18	H	OH		H	H	H
19	H	OH	H	H	H	H
20	H	H	H	H	H	H

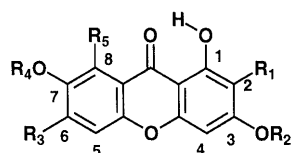
the location of the substituents of **1**. This is the first example of a depsidone derivative having a five-carbon unit (prenyl) to be found in nature.

Structures of Assiguxanthone-A (3), Dulxanthone-A (4), -B (6), and -C (7) Assiguxanthone-A (**3**), dulxanthone-A (**4**), -B (**6**), and -C (**7**) showed analogous UV absorptions having sharp high-intensity, weak, and broad low-intensity bands at λ_{\max} 252–257, 282–285, and 327–329 nm, respectively. These features were similar to those of ugaxanthone (**8**),⁵⁾ indicating the presence of a 1,3,5,6-tetraoxygenated xanthone chromophore. We will discuss the structure and location of the substituent in each xanthone below.

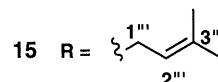
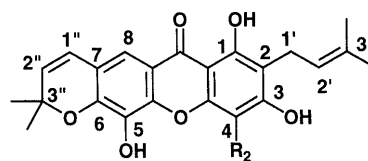
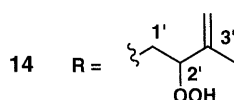
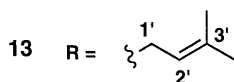
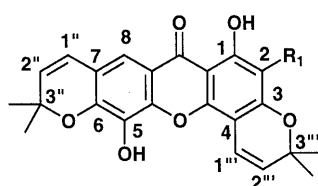
Assiguxanthone-A (**3**) was obtained as a pale yellow powder having the molecular formula C₁₈H₁₆O₆. The IR spectrum exhibited bands at ν_{\max} 3545, 3423, 3200 (br), and 1647 cm⁻¹ due to hydroxyl and carbonyl groups, respectively. In the ¹H-NMR spectrum, a lone 1H singlet at δ 6.29 and AB-type protons at δ 7.56 and 6.97 (each 1H, d, $J=8.4$ Hz) appeared in addition to a chelated hydroxyl signal at δ 13.44. The presence of a 1,1-

dimethylallyl group at C-4 was indicated by ¹H-NMR signals at δ 6.55 (1H, dd, $J=10.6, 17.2$ Hz), 5.05 (1H, br d, $J=17.6$ Hz), 4.89 (1H, br d, $J=10.6$ Hz), and 1.73 (6H, s), and the cross peaks of C-2 (δ_C 99.69) to 1-OH (δ_H 13.44) and C-4 (δ_C 112.69) to H-2 (δ_H 6.29) and to 1'-CH₃ (δ_H 1.73) in the HMBC spectrum. From the aforementioned results and further HMBC results shown by arrows in Fig. 2, the structure of assiguxanthone-A was concluded to be **3**.

Dulxanthone-A (**4**) was isolated as a yellow powder, and the molecular formula was determined as C₁₉H₁₈O₆. The IR spectrum exhibited bands at ν_{\max} 3545 and 1645 cm⁻¹ due to hydroxyl and carbonyl groups, respectively. The presence of a prenyl moiety in the molecule was indicated by ¹H-NMR signals at δ 3.55 (2H, d, $J=7.0$ Hz), 5.27 (1H, m), 1.82 (3H, s), and 1.61 (3H, s) and by a fragment ion peak at m/z 286 [$M^+ - \cdot CH = C(CH_3)_2 - \cdot H$] in the EI-MS. Further, the ¹H-NMR spectrum revealed an intramolecularly hydrogen-bonded hydroxyl group at δ 13.32, a 1H singlet at δ 6.41, and two broad 1H signals at δ 7.61 and 6.97, and a methoxyl signal



	R ₁	R ₂	R ₃	R ₄	R ₅
9		H	OH	H	H
10		CH ₃	OCH ₃	CH ₃	H
11	H	H	OH	CH ₃	
12	H	H	OH	H	
21	H	H	H	H	H
22		H	H	H	H



[δ 3.96 (3H, s)]. In differential NOE experiments, irradiation of the methoxy group at δ 3.96 enhanced the signals at δ 6.41. Treatment of this xanthone with diazomethane in Et₂O–MeOH gave a dimethyl ether (**5**), suggesting the presence of two phenolic hydroxyl groups in the original molecule, in addition to an intramolecularly hydrogen-bonded hydroxyl group at δ 13.05. In differential NOE experiments on **5**, irradiation of the newly formed methoxy group at δ 4.01 (6-OCH₃) enhanced the signals at δ 6.98 (H-7). On irradiation of another newly formed methoxy group at δ 4.00 (5-OCH₃), there was no NOE enhancement at any proton signal. Irradiation of the original methoxy group at δ 3.92 (3-OCH₃) enhanced the signal at δ 6.38 (H-2). In the HMBC spectrum of **5**, the presence of a significant C–H three-bond correlation between a hydrogen-bonded proton at δ_{H} 13.05 and a carbon at δ_{C} 94.25 bearing a proton at δ_{H} 6.38 (H-2) suggested the location of the prenyl moiety at C-4 (not at C-2). Other long-range correlations observed are shown by arrows in Fig. 3. On the basis of these results, the structure of dulxanthone-A is proposed to be **4**.

Dulxanthone-B (**6**) was obtained as a yellow oil, C₂₄H₂₆O₆. The ¹H-NMR spectrum also showed a similar signal pattern to that of **4**, except for the appearance of signals [δ 1.65 (3H, s), 1.78 (3H, s), 3.37 (2H, d, J = 6.6 Hz), and 5.33 (1H, m)] assignable to an additional prenyl side chain [–CH₂CH=C(CH₃)₂], in place of a higher-field sharp 1H singlet at δ 6.41 (H-2) in the spectrum of **4**. Mass fragment ions at m/z 355 [$\text{M}^+ - \cdot\text{CH}=\text{C}(\text{CH}_3)_2$] and 299 [$\text{M}^+ - \cdot\text{CH}=\text{C}(\text{CH}_3)_2 - \cdot\text{CH}=\text{C}(\text{CH}_3)_2 - \cdot\text{H}$] in the EI-MS also suggested the presence of two prenyl side chains in the molecule. In the HMBC spectrum, one of the methylene proton signals of the prenyl moieties at δ_{H} 3.37 showed long-range correlations with the carbon signals at δ_{C} 159.85 (C-1), 117.44 (C-2), and 164.19 (C-3). Another signal at δ_{H} 3.61 was correlated with carbon signals at δ_{C} 153.87 (C-4a), 114.44 (C-4), and 164.19 (C-3). These results suggested the location of the two prenyl moieties at C-2 and C-4, respectively. From these spectral data, we proposed the structure **6** for dulxanthone-B.

Dulxanthone-C (**7**) was isolated as a pale yellow powder, C₂₅H₂₈O₆. The IR spectrum showed absorption bands

Table 1. ^1H - and ^{13}C -NMR Spectra of a Novel Depsidone

	1		2	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}
1		161.06 (s)		159.96 (s)
1-OH	9.80 (br)			
1-OCH ₃			3.66 (3H)	62.07 (q)
2		112.22 (s)		120.15 (s)
3		164.13 (s)		161.91 (s)
3-OCH ₃			3.88 (3H)	56.44 (q)
4	6.26	99.60 (d)	6.83	98.71 (d)
4a		159.09 (s)		161.43 (s)
5a		145.57 (s)		146.95 (s)
6	6.65	105.68 (d)	7.02	103.45 (d)
7		148.14 (s)		149.88 (s)
7-OCH ₃			3.80 (3H)	56.14 (q)
8		142.94 (s)		143.85 (s)
8-OCH ₃	3.66 (3H)	60.05 (q)	3.69 (3H)	60.55 (q)
9		127.46 (s)		127.13 (s)
9a		134.38 (s)		135.11 (s)
11		167.17 (s)		160.88 (s)
11a		92.98 (s)		105.90 (s)
1'	3.14 (2H, d, 7.0)	21.43 (t)	3.19 (2H, d, 7.0)	22.07 (t)
2'	5.10 (m)	122.31 (d)	5.01 (m)	121.90 (d)
3'		130.48 (s)		131.24 (s)
3'-CH ₃	1.67 (3H)	17.66 (q)	1.68 (3H)	17.58 (q)
	1.58 (3H)	25.42 (q)	1.56 (3H)	25.27 (q)
1''	3.33 (2H, d, 7.0)	23.48 (t)	3.34 (2H, d, 7.0)	23.24 (t)
2''	5.08 (m)	121.83 (d)	5.01 (m)	121.47 (d)
3''		131.64 (s)		132.11 (s)
3''-CH ₃	1.74 (3H)	17.76 (q)	1.74 (3H)	17.66 (q)
	1.62 (3H)	25.46 (q)	1.59 (3H)	25.37 (q)

Values in (δ_{H} , δ_{C}) ppm. ^1H - and ^{13}C -NMR spectra were recorded at 600 MHz and 150 MHz, respectively, in $\text{DMSO}-d_6$. All signals correspond to 1H, and were observed as a singlet, unless otherwise stated. Figures in parentheses are coupling constants (J) in hertz (Hz).

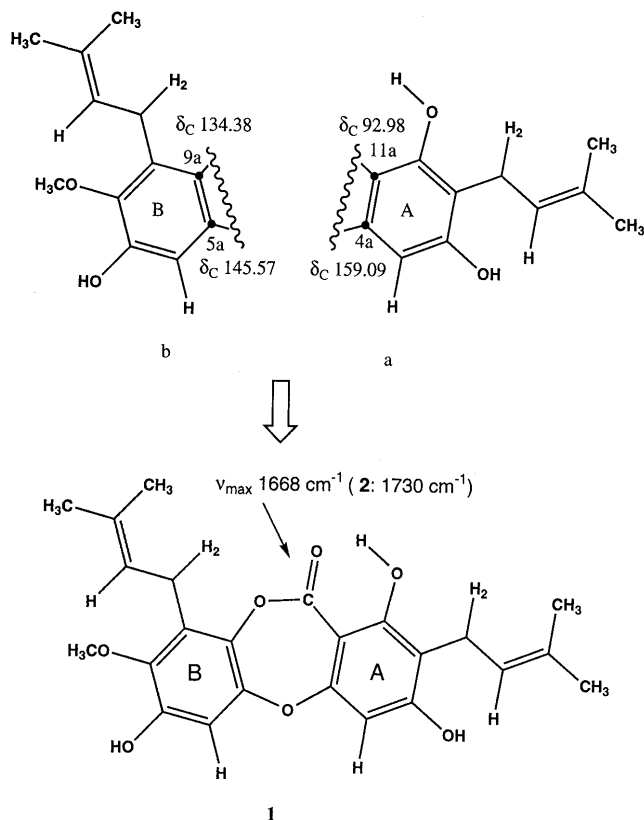


Chart 1. Partial Structures in the Garcinisidone-A (1) Molecule
Chemical shift values in the ^{13}C -NMR spectrum.

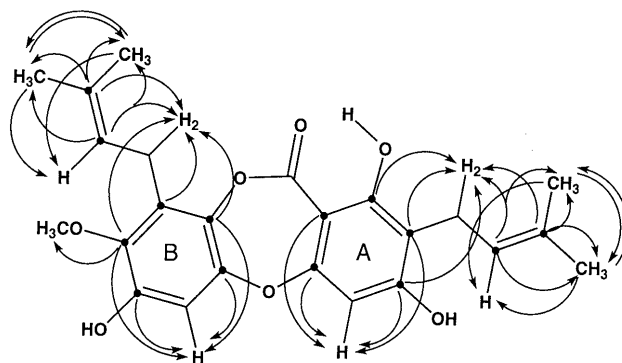


Fig. 1. C-H Long-Range Correlations in the HMBC Spectrum of Garcinisidone-A (1) in $\text{DMSO}-d_6$

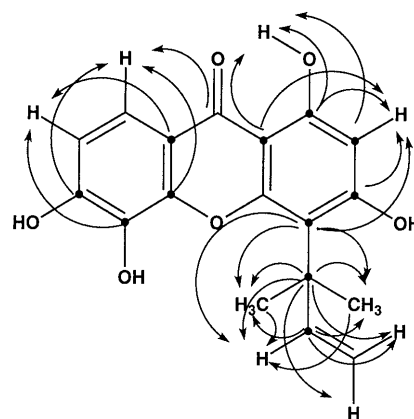


Fig. 2. C-H Long-Range Correlations in the HMBC Spectrum of Assiguxanthone-A (3) in $\text{Acetone}-d_6$

due to hydroxyl and carbonyl groups at ν_{max} 3544 (br) and 1645 cm^{-1} , respectively. In the ^1H -NMR spectrum (CDCl_3), two 1H singlets [δ 6.33, 6.72], an 1H broad signal which disappeared with D_2O [δ 5.49], and two methoxy signals [δ 3.88, 3.98] appeared in addition to a chelated hydroxyl signal at δ 13.42. The presence of two prenyl moieties in the molecule, as in the case of 6, was indicated by ^1H -NMR signals at δ 3.50 (2H, d, $J=7.0$ Hz, H-1'), 5.25 (1H, m, H-2'), 1.83 (3H, s, 3'-CH₃), 1.74 (3H, s, 3''-CH₃) and δ 4.00 (2H, d, $J=7.0$ Hz, H-1''), 5.34 (1H, m, H-2''), 1.74 (3H, s, 3''-CH₃), 1.68 (3H, s, 3''-CH₃), and by fragment ion peaks at m/z 369 [$\text{M}^+ - \cdot\text{CH}=\text{C}(\text{CH}_3)_2$] and 313 [$\text{M}^+ - \cdot\text{CH}=\text{C}(\text{CH}_3)_2 - \cdot\text{CH}=\text{C}(\text{CH}_3)_2 - \text{H}$] in the EI-MS. The observation of the H-1'' proton signal at δ 4.00, which was deshielded by the 9-carbonyl group, indicated the location of one of the prenyls at C-8 on the xanthone nucleus. The location of another prenyl moiety at C-4 was suggested by the presence of a significant C-H three-bond correlation between a hydrogen-bonded proton at δ_{H} 13.42 and a carbon at δ_{C} 94.13 bearing a proton at δ_{H} 6.33 (H-2) in the HMBC spectrum. In differential NOE experiments, irradiation of the methoxy signal at δ 3.88 (3-OCH₃) caused an NOE enhancement of the singlet at δ 6.33 (H-2), and irradiation of another methoxy signal at δ 3.98 (6-OCH₃) produced an NOE enhancement of the singlet at δ 6.72 (H-7). Irradiation of the methylene proton signal at δ 3.50 (H-1') caused NOE enhancements of the signals at δ 5.25 (H-2') and 1.83 (3'-CH₃), respectively. Further, irradiation of another methylene proton signal at δ 4.00 (H-1'') resulted in NOE

Table 2. ^1H -NMR Data for the New Xanthenes in Acetone- d_6

3		4		4 ^{a)}	5 ^{b)}
1-OH	13.44 (s)	13.32 (s)	13.28 (br s)	13.05 (s)	
H-2	6.29 (s)	6.41 (s)	6.47 (s)	6.38 (s)	
3-OCH ₃		3.96 (3H, s)	3.89 (3H, s)	3.92 (3H, s)	
5-OCH ₃				4.00 (3H, s)	
5-OH					
6-OCH ₃				4.01 (3H, s)	
H-7	6.97 (d, $J=8.4$)	6.97 (br)	6.90 (d, $J=8.8$)	6.98 (d, $J=8.8$)	
H-8	7.56 (d, $J=8.4$)	7.61 (br)	7.49 (d, $J=8.8$)	7.98 (d, $J=8.8$)	
Others	6.55 (dd, $J=10.6, 17.2$, H-2')	5.27 (m, H-2')	5.21 (m, H-2')	5.26 (m, H-2')	
	5.05 (br d, $J=17.2$, H-3')	3.55 (2H, d, $J=7.0$, H-1')	3.47 (2H, d, $J=7.3$, H-1')	3.55 (2H, d, $J=7.0$, H-1')	
	4.89 (br d, $J=10.6$, H-3')	1.82 (3H, s, 3'-CH ₃)	1.78 (3H, s, 3'-CH ₃)	1.85 (3H, s, 3'-CH ₃)	
	1.73 (6H, s, 1'-CH ₃)	1.61 (3H, s, 3'-CH ₃)	1.60 (3H, s, 3'-CH ₃)	1.67 (3H, s, 3'-CH ₃)	

6		6 ^{a)}	7 ^{b)}
1-OH	13.53 (s)	13.33 (s)	13.42 (s)
H-2			6.33 (s)
3-OCH ₃	3.82 (3H, s)	3.76 (3H, s)	3.88 (3H, s)
5-OCH ₃			
5-OH			5.49 (br)
6-OCH ₃			3.98 (3H, s)
H-7	6.95 (br)	6.95 (d, 8.8)	6.72 (s)
H-8	7.61 (br)	7.54 (d, 8.8)	
Others	5.33 (m, H-2'')	5.25 (m, H-2'')	5.34 (m, H-2'')
	5.26 (m, H-2')	5.18 (m, H-2')	5.25 (m, H-2')
	3.61 (2H, m, H-1')	3.53 (2H, d, $J=7.0$, H-1')	4.00 (2H, d, $J=7.0$, H-1')
	3.37 (2H, d, $J=6.6$, H-1'')	3.32 (2H, overlapped with H ₂ O)	3.50 (2H, d, $J=7.0$, H-1')
	1.81 (3H, s, 3'-CH ₃)	1.79 (3H, s, 3'-CH ₃)	1.83 (3H, s, 3'-CH ₃)
	1.78 (3H, s, 3''-CH ₃)	1.73 (3H, s, 3''-CH ₃)	1.74 (6H, s, 3'-CH ₃ and 3''-CH ₃)
	1.65 (3H, s, 3''-CH ₃)	1.63 (3H, s, 3''-CH ₃)	1.68 (3H, s, 3''-CH ₃)
	1.62 (3H, s, 3'-CH ₃)	1.62 (3H, s, 3'-CH ₃)	

Values in (δ) ppm. The coupling constants (J) in parentheses are in Hz. All signals correspond to 1H, unless otherwise stated. a) Spectra were taken in DMSO- d_6 . b) Spectra were taken in CDCl₃.

Table 3. ^{13}C -NMR Data for the New Xanthenes in Acetone- d_6

	3	4	5 ^{a)}	6	7 ^{a)}	10 ^{a)}
C-1	162.12 (s)	163.05 (s)	162.02 (s)	159.85 (s)	162.25 (s)	159.31 (s)
C-2	99.69 (d)	94.77 (d)	94.25 (d)	117.44 (s)	94.13 (d)	111.78 (s)
C-3	164.50 (s)	164.82 (s)	164.12 (s)	164.19 (s)	163.47 (s)	163.73 (s)
3-OCH ₃		56.58 (q)	56.03 (q)	62.14 (q)	55.97 (q)	55.87 (q)
C-4	112.69 (s)	108.55 (s)	108.17 (s)	114.44 (s)	106.99 (s)	89.42 (d)
C-4a	156.83 (s)	154.76 (s)	153.99 (s)	153.87 (s)	153.22 (s)	156.14 (s)
C-5	133.63 (s)	133.83 (s)	136.44 (s)	133.89 (s)	131.77 (s)	99.35 (d)
C-6	151.77 (s)	153.23 (s)	157.85 (s)	153.40 (s)	150.12 (s)	155.36 (s)
C-7	113.64 (d)	113.57 (d)	108.33 (d)	114.09 (d)	108.79 (d)	146.64 (s)
C-8	116.96 (d)	117.32 (d)	121.50 (d)	117.44 (d)	136.44 (s)	104.64 (s)
C-8a	114.34 (s)	114.37 (s)	115.16 (s)	113.96 (s)	112.42 (s)	113.51 (s)
C-9	181.52 (s)	181.67 (s)	180.82 (s)	182.23 (s)	182.92 (s)	179.79 (s)
C-9a	103.42 (s)	103.23 (s)	102.92 (s)	105.90 (s)	103.57 (s)	103.47 (d)
C-10a	146.78 (s)	147.42 (s)	150.63 (s)	147.56 (s)	145.84 (s)	152.24 (s)
Other	41.86 (s, C-1')	22.06 (t, C-1')	21.67 (t, C-1')	23.13 (t, C-1')	33.43 (t, C-1'')	21.34 (t, C-1')
	152.39 (d, C-2')	123.43 (d, C-2')	122.20 (d, C-2')	23.05 (t, C-1'')	21.67 (t, C-1')	122.14 (d, C-2')
	107.89 (t, C-3')	131.73 (s, C-3')	132.02 (s, C-3')	124.10 (d, C-2' or C-2'')	122.73 (d, C-2')	131.89 (s, C-3')
	29.93 (q \times 2, 1'-CH ₃ , overlapped with acetone)	25.93 (q, 3'-CH ₃)	25.80 (q, 3'-CH ₃)	123.80 (d, C-2'' or C-2')	122.90 (d, C-2'')	25.81 (q, 3'-CH ₃)
		17.94 (q, 3'-CH ₃)	17.77 (q, 3'-CH ₃)	131.78 (s, C-3' or C-3'')	132.94 (s, C-3'')	17.80 (q, 3'-CH ₃)
			61.31 (q, 5-OCH ₃)	131.68 (s, C-3'' or C-3')	131.50 (s, C-3')	56.46 (q, 6-OCH ₃)
			56.43 (q, 6-OCH ₃)	25.87 (q, 3'-CH ₃ or 3''-CH ₃)	25.86 (q, 3''-CH ₃)	56.36 (q, 7-OCH ₃)
				25.80 (q, 3''-CH ₃ or 3'-CH ₃)	25.73 (q, 3'-CH ₃)	
				18.05 (q, 3'-CH ₃ or 3''-CH ₃)	18.07 (q, 3''-CH ₃)	
				17.95 (q, 3''-CH ₃ or 3'-CH ₃)	17.77 (q, 3'-CH ₃)	
					56.30 (q, 7-OCH ₃)	

Values in (δ) ppm. a) Spectrum were taken in CDCl₃.

enhancements of the signals at δ 6.72 (H-7), 5.34 (H-2''), and 1.74 (3''-CH₃). Based on these spectral data, coupled with the results of HMBC experiments, shown by arrows in Fig. 4, the structure of dulxanthone-C was concluded to be 7.

Structure of Assiguxanthone-B (9) and Dulxanthone-D (11) The close similarity of the UV spectra of the two new xanthenes [assiguxanthone-B (9) and dulxanthone-D (11)] and 1,3,6,7-tetrahydroxy-8-(3-methylbut-2-enyl)-xanthone (12),⁶ which was isolated from the same plant, suggested that these xanthone (9) and (11) may have the same basic skeleton, a 1,3,6,7-tetraoxygenated xanthone.

Assiguxanthone-B (9) was isolated as a pale yellow powder, C₁₈H₁₆O₆. The ¹H-NMR spectrum showed three 1H singlets [δ _H 7.52, 6.87, 6.43] in addition to a chelated hydroxyl signal at δ 13.52 (1-OH). One (δ 7.52) of them was assignable to H-8, which was deshielded by the 9-carbonyl group. The presence of a prenyl moiety in the molecule was indicated by ¹H-NMR signals [δ 3.34 (2H, d, J =7.3 Hz), 5.27 (1H, m), 1.77 (3H, s), and 1.63 (3H, s)] and by a base fragment ion peak at m/z 273 [$M^+ - \cdot\text{CH}=\text{C}(\text{CH}_3)_2$] in the EI-MS. Further confirmation of the structure was performed by treatment of 9 with diazomethane in a usual manner to give a trimethylated derivative (10). The ¹H-NMR spectrum of 10 showed a similar signal pattern to that of 9, except for three 3H singlets at δ _H 4.01, 3.99, and 3.92 due to three methoxy

groups. The location of a prenyl moiety at C-2 (not at C-4) was indicated by a significant C-H three- or two-bond correlation between a hydrogen-bonded proton at δ _H 13.05 and a carbon at δ _C 111.78 (C-2), which was also related to the methylene protons (H-1', δ _H 3.38) on the prenyl moiety, in the HMBC spectrum of 10. Other C-H long-range correlations observed are shown by arrows in Fig. 5. Based on these results, we assigned structure 9 to assiguxanthone-B.

Dulxanthone-D (11) was obtained as a yellow powder, C₁₉H₁₈O₆, and IR bands appeared at ν_{max} 3400 (br) and 1647 cm⁻¹ (hydroxyl and carbonyl groups, respectively). In the ¹H-NMR spectrum, a lone 1H singlet at δ 6.85, *meta*-coupled doublets at δ 6.28 (H-2) and 6.22 (H-4) (each 1H, J =2.2 Hz), and a methoxy signal at δ 3.81 appeared, in addition to a chelated hydroxyl signal at δ 13.43 (1-OH). Further, two 3H singlets (δ 1.83, 1.70), a 2H doublet (δ 4.08, J =6.2 Hz), and a 1H multiplet (δ 5.27) in the ¹H-NMR spectrum, and a fragment ion peak at m/z 285 [$M^+ - \cdot\text{CH}=\text{C}(\text{CH}_3)_2 - \cdot\text{H}$] in the EI-MS indicated the presence of a prenyl moiety in the molecule. The appearance of the deshielded methylene signal at δ 4.08

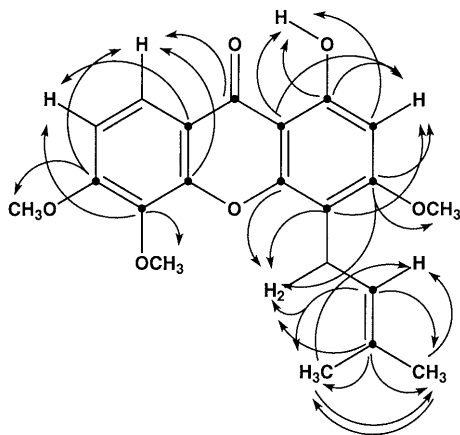


Fig. 3. C-H Long-Range Correlations in the HMBC Spectrum of Dulxanthone-A Dimethyl Ether (5) in CDCl₃

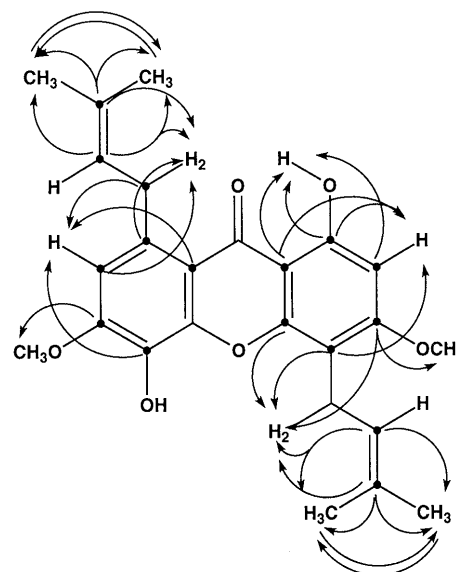


Fig. 4. C-H Long-Range Correlations in the HMBC Spectrum of Dulxanthone-C (7) in CDCl₃

Table 4. ¹H-NMR Data for the New Xanthenes in CDCl₃

	9 ^{a)}	10	11
1-OH	13.52 (s)	13.05 (s)	13.43 (s)
H-2			6.28 (d, J =2.2)
3-OCH ₃		3.92 (3H, s)	
H-4	6.43 (s)	6.41 (s)	6.22 (d, J =2.2)
H-5	6.87 (s)	6.86 (s)	6.85 (s)
6-OCH ₃		4.01 (3H, s)	
7-OCH ₃		3.99 (3H, s)	
H-8	7.52 (s)	7.58 (s)	
Others	5.27 (m, H-2')	5.24 (m, H-2')	5.27 (m, H-2')
	3.34 (2H, d, J =7.3, H-1')	3.38 (2H, d, J =7.0, H-1')	4.08 (2H, d, J =6.2, H-1')
	1.77 (3H, s, 3'-CH ₃)	1.81 (3H, s, 3'-CH ₃)	3.81 (3H, s, 7-OCH ₃)
	1.63 (3H, s, 3'-CH ₃)	1.69 (3H, s, 3'-CH ₃)	1.83 (3H, s, 3'-CH ₃)
			1.70 (3H, s, 3'-CH ₃)

Values in (δ) ppm. The coupling constants (J) in parentheses are in Hz. All signals correspond to 1H, unless otherwise stated. a) Spectrum was taken in acetone-*d*₆.

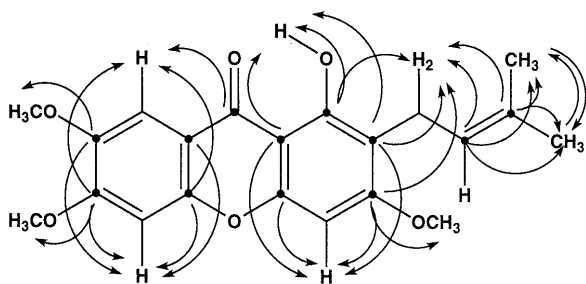


Fig. 5. C-H Long-Range Correlations in the HMBC Spectrum of Assiguxanthone-B Methyl Ether (**10**) in CDCl_3

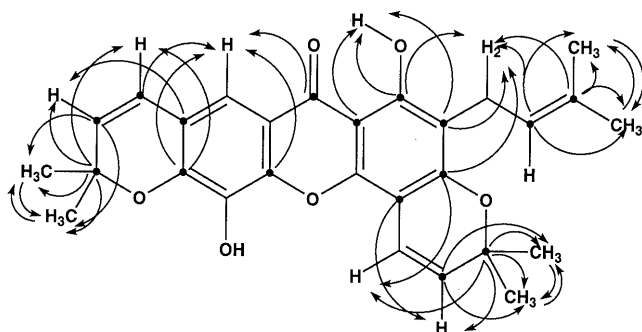


Fig. 6. C-H Long-Range Correlations in the HMBC Spectrum of Latisxanthone-A (**13**) in CDCl_3

(H-1') indicated the presence of the prenyl moiety at C-8 on the xanthone nucleus. In differential NOE experiments, irradiation of the methoxy signal at δ 3.81 (7-OCH₃) caused a 3% NOE enhancement of the signal at δ 4.08 (H-1'). From the above results, the structure of dulxanthone-D was concluded to be **11**, corresponding to the methylated derivative of a known compound (**12**).⁵⁾

Structure of Latisxanthone-A (13**)** Latisxanthone-A (**13**) was obtained as a yellow powder. The molecular formula was determined to be $\text{C}_{28}\text{H}_{28}\text{O}_6$ by HR-MS. The UV (see Experimental) and IR bands at ν_{max} 3539 (br, OH) and 1635 (C=O) cm^{-1} suggested the presence of a 1,3,5,6-tetraoxygenated xanthone chromophore in the molecule.⁷⁾ In the ^1H -NMR spectrum, a lone 1H singlet at δ 7.47, which was assignable to H-8, and a D₂O-exchangeable broad signal at δ 5.46 (5-OH) appeared in addition to a chelated hydroxyl signal at δ 13.28 (1-OH). Two pairs of doublets at δ 5.70, 6.42 (each 1H, J =9.9 Hz) and δ 5.58, 6.88 (each 1H, J =9.9 Hz), together with two 6H-singlets at δ 1.51 and 1.46, indicated the presence of two dimethylpyran ring systems in the molecule. Further, the presence of a prenyl moiety was indicated by two 3H singlets (δ 1.80, 1.67), a 2H doublet (δ 3.33, J =7.2 Hz), and a 1H multiplet (δ 5.24) in the ^1H -NMR spectrum, and a fragment ion peak at m/z 405 [$\text{M}^+ - \cdot\text{CH}=\text{C}(\text{CH}_3)_2$] in EI-MS. In an NOE experiment, irradiation of the H-8 signal at δ 7.47 caused an enhancement of the H-1' signal (δ 6.42) indicating the presence of a dimethylpyran ring fused with the 1,3,5,6-tetraoxygenated xanthone nucleus at C-6 and C-7. The structure of **13** was confirmed by HMQC and HMBC experiments as follows. The presence of a prenyl moiety at C-2 was suggested by a significant C-H three- or two-bond correlation between a hydrogen-bonded proton at δ_{H} 13.28 and a carbon at δ_{C} 111.69 (C-2), which was also related to the methylene

protons (H-1', δ_{H} 3.33) on the prenyl moiety, respectively, in the HMBC spectrum. The presence of a dimethylpyran ring fused with the 1,3,5,6-tetraoxygenated xanthone nucleus at C-6 and C-7 was also suggested by a C-H three-bond correlation between a lone deshielded 1H singlet (H-8, δ_{H} 7.47) and a carbon at δ_{C} 121.48 (C-1'') bearing a proton at δ_{H} 6.42 (H-1''). Further, the observation of a C-H three-bond correlation between a 1H-doublet proton (H-1''', δ_{H} 6.88) and a carbon at δ_{C} 158.14 (C-3), which was also related to the methylene protons (H-1', δ_{H} 3.33), indicated the presence of another dimethylpyran ring fused with the 1,3,5,6-tetraoxygenated xanthone nucleus at C-3 and C-4. Other C-H long-range correlations observed are shown by arrows in Fig. 6. On the basis of these results, the structure of latisxanthone-A is proposed to be **13**.

Structure of Latisxanthone-B (14**)** Latisxanthone-B (**14**), [α]_D +5° (CHCl_3), was obtained as a yellow powder. The molecular formula $\text{C}_{28}\text{H}_{28}\text{O}_8$, a difference of O_2 compared with **13**, was established by HR-FAB-MS. The UV spectrum (see Experimental) was similar to that of **13**. The ^1H -NMR spectrum also showed a similar signal pattern to that of **13**, except for the following signals in place of the signals due to a prenyl side chain [$-\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$]. ABC-type signals at δ 2.96 (1H, dd, J =4.4, 13.9 Hz), 3.09 (1H, dd, J =8.8, 13.9 Hz), and 4.39 (1H, dd, J =4.4, 8.8 Hz), two 1H broad singlets at δ 4.94 and 4.95 assignable to *exo*-methylene protons, and a 3H singlet at δ 1.85 due to a vinyl methyl group were observed, as well as the broad singlet at δ 9.07 which disappeared on addition of D₂O. Signals at δ_{H} 4.39, one of the ABC-type protons, and δ_{C} 86.52 (d) in the ^1H - and ^{13}C -NMR spectra, respectively, together with a fragment ion peak at m/z 476 corresponding to [$\text{M}^+ - \cdot\text{O}$] in the EI-MS, suggested the presence of a hydroperoxy moiety in this xanthone. These data, coupled with two significant mass fragment ion peaks at m/z 405 (100%) and 391 (16%) ascribed to ions [$\text{M}^+ - \cdot\text{CH}(\text{OOH})-\text{C}(\text{CH}_3)=\text{CH}_2$] and [$\text{M}^+ - \cdot\text{CH}_2-\text{CH}(\text{OOH})-\text{C}(\text{CH}_3)=\text{CH}_2$], respectively, indicated the structure [$-\text{CH}_2-\text{CH}(\text{OOH})-\text{C}(\text{CH}_3)=\text{CH}_2$] for the side chain. These results suggested the structure of latisxanthone-B to be **14**. The structure **14** was further confirmed by HMQC and HMBC experiments as shown by arrows in Fig. 7.

This is the second example of the isolation of a hydroperoxyoxygenated xanthone from a natural source.⁸⁾

Structure of Latisxanthone-C (15**)** Latisxanthone-C (**15**) was obtained as a pale yellow powder, $\text{C}_{28}\text{H}_{30}\text{O}_6$. The UV absorptions (see Experimental), and IR bands at ν_{max} 3543, 3377 (br) and 1637 cm^{-1} due to hydroxyl and carbonyl groups, respectively, suggested the presence of a 1,3,5,6-tetraoxygenated xanthone chromophore in the molecule.⁷⁾ In the ^1H -NMR spectrum, a lone deshielded 1H singlet [δ 7.48], two broad signals which disappeared with D₂O [δ 5.48, 6.43], and two set of signals due to prenyl moieties [δ 3.46 (2H, d, J =7.3 Hz), 5.29 (1H, m), 1.85 (3H, s), 1.77 (3H, s) and δ 3.60 (2H, d, J =7.0 Hz), 5.32 (1H, m), 1.89 (3H, s), 1.75 (3H, s)] appeared in addition to a chelated hydroxyl signal at δ 13.31. Further, the ^1H -NMR spectrum showed a singlet (6H) at δ 1.53 assignable to geminal dimethyls attached to an oxygenated

Table 5. ^1H -NMR Data for the New Pyranoxanthones in CDCl_3

	13	14	15	16
1-OH	13.28 (s)	13.81 (s)	13.31 (s)	13.32 (s)
H-4				6.42 (s)
5-OH	5.46 (br)	5.42 (br)	5.48 (br)	
H-8	7.47 (s)	7.42 (s)	7.48 (s)	7.43 (s)
H-1'	3.33 (2H, d, $J=7.3$)	2.96 (dd, $J=4.4, 13.9$)	3.46 (2H, d, $J=7.3$)	3.40 (2H, d, $J=7.0$)
		3.09 (dd, $J=8.8, 13.9$)		
H-2'	5.24 (m)	4.39 (dd, $J=4.4, 8.8$)	5.29 ^a (m)	5.24 (m)
3'-CH ₂		4.94 (br s)		
		4.95 (br s)		
3'-CH ₃	1.80 (3H, s)	1.85 (3H, s)	1.85 ^a (3H, s)	1.78 (3H, s)
	1.67 (3H, s)		1.77 ^a (3H, s)	1.71 (3H, s)
H-1''	6.42 (d, $J=9.9$)	6.38 (d, $J=9.9$)	6.44 (d, $J=9.9$)	6.37 (d, $J=10.3$)
H-2''	5.70 (d, $J=9.9$)	5.67 (d, $J=9.9$)	5.72 (d, $J=9.9$)	5.66 (d, $J=10.3$)
3''-CH ₃	1.51 (6H, s)	1.45 (6H, s)	1.53 (6H, s)	1.47 (6H, s)
Others	6.88 (d, $J=9.9$, H-1''')	9.07 (br s, OOH)	6.43 (s, 3-OH)	6.10 (br, OH)
	5.58 (d, $J=9.9$, H-2''')	6.85 (d, $J=9.9$, H-1''')	3.60 (2H, d, $J=7.0$, H-1''')	5.51 (br, OH)
	1.46 (6H, s, 3'''-CH ₃)	5.55 (d, $J=9.9$, H-2''')	5.32 ^a (m, H-2''')	
		1.42 (6H, s, 3'''-CH ₃)	1.89 ^a (3H, s, 3'''-CH ₃)	
			1.75 ^a (3H, s, 3'''-CH ₃)	

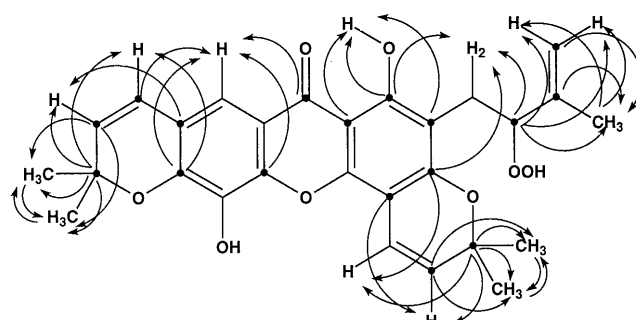
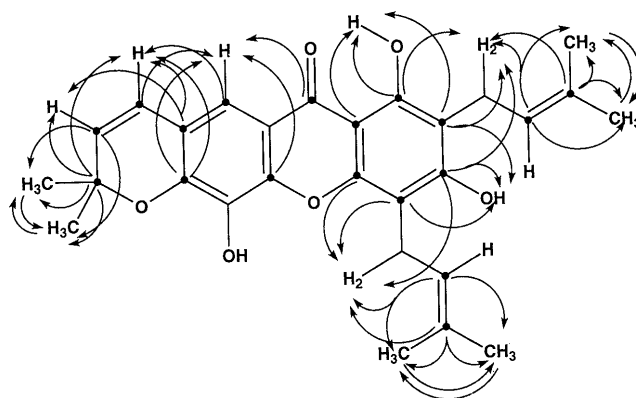
Values in (δ) ppm. The coupling constants (J) in parentheses are in Hz. All signals correspond to 1H, unless otherwise stated. a) Assignments may be reversed.

Table 6. ^{13}C -NMR Data for the New Pyranoxanthones in CDCl_3

	13	14	15	16
C-1	160.25 (s)	160.65 (s)	158.49 (s)	160.47 (s)
C-2	111.69 (s)	108.20 (s)	109.06 (s)	108.81 (s)
C-3	158.14 (s)	158.20 (s)	160.55 (s)	162.18 (s)
C-4	100.97 (s)	99.90 (s)	105.55 (s)	94.48 (d)
C-4a	149.84 (s)	— ^a	152.64 (s)	152.96 (s)
C-5	132.27 (s)	132.31 (s)	132.28 (s)	131.96 (s)
C-6	144.51 (s)	144.75 (s)	144.55 (s)	144.65 (s)
C-7	117.60 (s)	117.76 (s)	117.62 (s)	117.65 (s)
C-8	113.51 (d)	113.48 (d)	113.44 (d)	113.57 (d)
C-8a	114.75 (s)	— ^a	114.50 (s)	114.65 (s)
C-9	180.32 (s)	180.43 (s)	180.68 (s)	180.25 (s)
C-9a	102.82 (s)	102.67 (s)	103.01 (s)	103.28 (s)
C-10a	144.99 (s)	144.99 (s)	145.26 (s)	145.11 (s)
C-1'	21.23 (t)	23.13 (t)	21.62 (t)	21.42 (t)
C-2'	122.14 (d)	86.52 (d)	121.51 (d) ^b	121.36 (d) ^b
C-3'	131.46 (s)	144.30 (s)	135.30 (s)	136.08 (s)
3'-CH ₂		112.84 (t)		
3'-CH ₃	25.81 (q)	19.64 (q)	25.85 (q)	25.82 (q)
	17.91 (q)		17.94 (q)	17.90 (q)
C-1''	121.48 (d)	121.36 (d)	121.85 (d)	121.18 (d) ^b
C-2''	130.86 (d)	130.99 (d)	130.83 (d)	130.93 (d)
C-3''	78.87 (s)	78.98 (s)	78.75 (s)	78.89 (s)
3''-CH ₃	28.20 (q \times 2)	28.17 (q \times 2)	28.48 (q \times 2)	28.46 (q \times 2)
C-1'''	115.52 (d)	115.37 (d)	21.96 (t)	
C-2'''	126.82 (d)	126.76 (d)	121.55 (d) ^b	
C-3'''	77.95 (s)	78.63 (s)	134.00 (s)	
3'''-CH ₃	28.45 (q \times 2)	28.44 (q \times 2)	25.85 (q)	
			17.92 (q)	

Values in (δ) ppm. a) Because of the small quantity obtained, these quaternary carbon signals could not be assigned. b) Assignments may be reversed.

carbon, and AB-type doublets at δ 6.44 and 5.72 (each 1H, $J=9.9$ Hz), indicating the presence of a dimethylpyran ring system in the molecule. In the HMBC spectrum, one of the methylene proton signals of prenyl moieties at δ_{H} 3.46 showed C-H long-range correlations with the carbon signals at δ_{C} 158.49 (C-1), 109.06 (C-2), and 160.55 (C-3). The other one at δ_{H} 3.60 was correlated with carbon signals at δ_{C} 152.64 (C-4a), 105.55 (C-4), and 160.55 (C-3). These results suggested the two prenyl moieties to be located at

Fig. 7. C-H Long-Range Correlations in the HMBC Spectrum of Latisxanthone-B (14) in CDCl_3 Fig. 8. C-H Long-Range Correlations in the HMBC Spectrum of Latisxanthone-C (15) in CDCl_3

C-2 and C-4, respectively. The presence of a dimethylpyran ring fused with the 1,3,5,6-tetraoxygenated xanthone nucleus at C-6 and C-7 was indicated by C-H long-range correlations between a 1H doublet at δ_{H} 6.44 (H-1'') and carbon signals at δ_{C} 113.44 (C-8), 117.62 (C-7), and 144.55 (C-6), together with an NOE enhancement between H-1'' (δ 6.44) and H-8 (δ 7.48) signals. From the aforementioned results and the HMBC results shown by arrows in Fig. 8, the structure of latisxanthone-C was concluded to be 15.

Structure of Latisxanthone-D (16) Latisxanthone-D

(**16**) was isolated as a pale yellow oil, $C_{23}H_{22}O_6$. The UV absorptions and IR bands (see Experimental) suggested the presence of a xanthone skeleton in the molecule. The 1H -NMR spectrum showed a similar signal pattern to that of **15**, except for the appearance of a higher-field sharp 1H singlet at δ 6.42 in place of a set of signals assignable to one of two prenyl side chains $[-CH_2CH=C(CH_3)_2]$ in the spectrum of **15**. In the HMBC spectrum, the presence of a prenyl moiety at C-2 was suggested by a significant C-H three- or two-bond correlation between a hydrogen-bonded proton at δ_H 13.32 and a carbon at δ_C 108.81 (C-2), which was also related to the methylene protons (H-1', δ_H 3.40) on the prenyl moiety. Other long-range correlations observed are shown by arrows in Fig. 9. Based on these results, we assigned structure **16**, corresponding to one of the deprenylated derivatives of **15**, to latisxanthone-D.

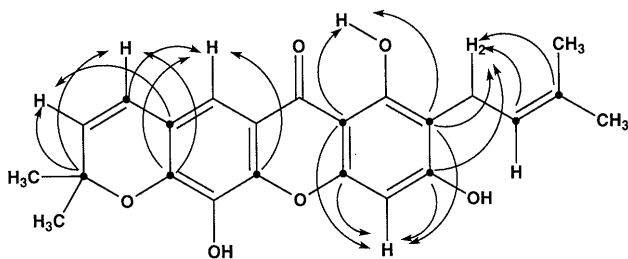
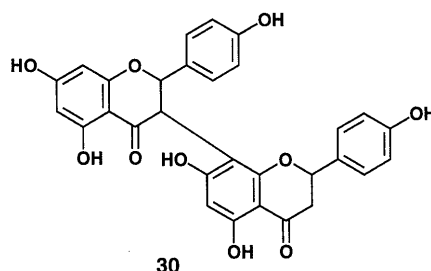
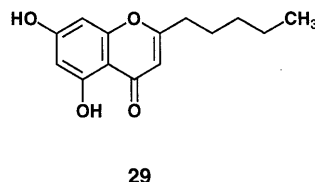
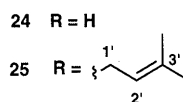
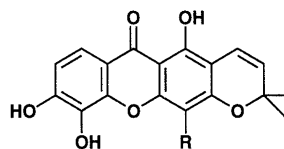
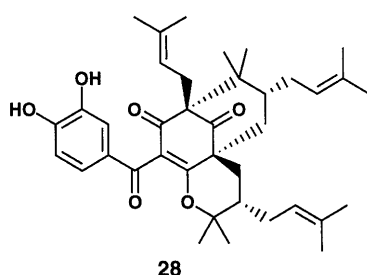
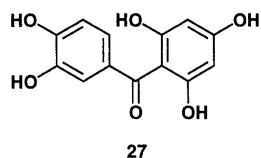
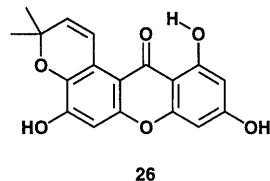
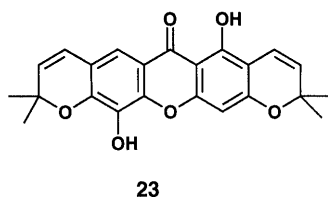


Fig. 9. C-H Long-Range Correlations in the HMBC Spectrum of Latisxanthone-D (**16**) in $CDCl_3$



Other compounds isolated from the EtOH extract were characterized as ugaxanthone (**8**),⁵ 1,3,6,7-tetrahydroxy-8-(3-methylbut-2-enyl)xanthone (**12**),⁶ isoprenylxanthone (**17**),⁹ pancixanthone-A (**18**),² 1,3,5-trihydroxyxanthone (**19**),¹⁰ 1,5-dihydroxyxanthone (**20**),¹¹ gentisein (**21**),¹² 1,3,7-trihydroxy-2-(3-methyl-2-butenyl)xanthone (**22**),¹³ pyranojacareubin (**23**),¹⁴ jacareubin (**24**),⁹ xanthone VI (**25**),¹⁵ toxylloxanthone B (**26**),^{16,17} maclurin (**27**),¹⁸ isogarcinol (**28**),^{19,20} 5-hydroxy-7-methoxy-2-pentylchromone (**29**),²¹ and GB-1a (**30**),²² by comparisons of the 1H -NMR, IR, UV, MS, and $[\alpha]_D$ data with those reported in the literature.^{2,5,6,9-22}

Experimental

Melting points were measured on a micromelting point hot-stage apparatus (Yanagimoto). 1H - and ^{13}C -NMR, HMQC, and HMBC ($J=8$ Hz) spectra were recorded on an A-400 or A-600 (JEOL) spectrometer. Chemical shifts are shown in δ values (ppm) with tetramethylsilane (TMS) as an internal reference. All mass spectra were taken under EI conditions, unless otherwise stated, using an M-80 (Hitachi) spectrometer having a direct inlet system. UV spectra were recorded on a UVIDE-610C double-beam spectrophotometer (JASCO) in MeOH, IR spectra on an IR-230 (JASCO) in $CHCl_3$, and optical rotations on a DIP-370 (JASCO) in $CHCl_3$ at 25 °C. Preparative TLC was done on Kieselgel 60 F₂₅₄ (Merck).

Plant Materials The plant materials used in this study, *Garcinia assigu* LANTB., *Garcinia dulcis* (ROXB.) KURZ., and *Garcinia latissima* MIQ. (Guttiferae) were collected in Central Province of Papua New Guinea. Voucher specimens have been deposited at the herbarium of the University of Papua New Guinea.

Isolation and Separation of Garcinisidone-A (1), Assiguxanthone-A (3),

and -B (9) from *G. assigu* The dried stem bark (560 g) of *G. assigu* was extracted with EtOH under reflux. The EtOH extract was evaporated under reduced pressure to give an oily residue, which was fractionated with hexane, CH_2Cl_2 , EtOAc, CH_2Cl_2 -MeOH (3:1), and MeOH. The hexane-soluble portion was subjected to silica gel chromatography eluted with hexane-acetone (9:1, 17:3, 4:1, 7:3, 1:1), acetone, CH_2Cl_2 -MeOH (3:1), and MeOH, successively. The hexane-acetone (4:1) eluate was further subjected to preparative TLC with hexane-acetone (4:1) and benzene-MeOH (19:1) as developing solvents to obtain garcinisidone-A (**1**) (2.5 mg). The CH_2Cl_2 -soluble portion was subjected to silica gel column chromatography. Successive elution with hexane-EtOAc (9:1, 4:1, 7:3, 3:2, 1:1, 3:7), EtOAc, acetone, CH_2Cl_2 -MeOH (3:1), and MeOH gave ten fractions. Each fraction was further subjected to silica gel column chromatography and preparative TLC with appropriate combinations of hexane, benzene, CHCl_3 , iso- Pr_2O , EtOAc, acetone, and MeOH as developing solvents to give the following compounds. From the hexane-EtOAc (7:3) fraction: toxylanthone B (**26**) (4.0 mg). From the hexane-EtOAc (1:1) fraction: assiguxanthone-A (**3**) (5.3 mg) and 1,3,5-trihydroxyxanthone (**19**) (2.0 mg). From the hexane-EtOAc (3:7) fraction: assiguxanthone-B (**9**) (1.4 mg), 1,3,6,7-tetrahydroxy-8-(3-methylbut-2-enyl)xanthone (**12**) (1.5 mg) and maclurin (**27**) (9.8 mg). The EtOAc-soluble portion was treated in the same manner as the hexane-soluble portion described above. The hexane-acetone (9:1) eluate was subjected to silica gel column chromatography with a gradient of hexane and iso- Pr_2O , and further preparative TLC with hexane-EtOAc (9:1) and hexane- CHCl_3 (1:1) to obtain pancixanthone-A (**18**) (2.6 mg) and 1,5-dihydroxyxanthone (**20**) (4.6 mg).

Garcinisidone-A (1): Pale yellow oil. UV λ_{max} nm: 206, 226 (sh), 280, 315. IR ν_{max} cm^{-1} : 3527, 3300 (br), 1668, 1624, 1267, 1153. MS m/z (%): 426 (M^+ , 100), 370 (56), 355 (24), 339 (14), 327 (16), 315 (38), 311 (13), 299 (13), 273 (14), 219 (16), 217 (21), 191 (15). HR-MS Calcd for $\text{C}_{24}\text{H}_{26}\text{O}_7$: 426.1676. Found: 426.1661. Differential NOE: irradiation of 8-OCH₃ (δ 3.66) gave 3% NOE at H-2' (δ 5.08) and 2% NOE at H-1' (δ 3.33); irradiation of H-4 (δ 6.26) gave 2% NOE at H-6 (δ 6.65); irradiation of H-6 (δ 6.65) gave 1% NOE at H-4 (δ 6.26).

O-Methylation of 1 A mixture of **1** (2.5 mg), anhydrous K_2CO_3 (4.0 mg) and methyl iodide (5.5 μl) in acetone (1.0 ml) was stirred overnight. K_2CO_3 was filtered off and the filtrate was subjected to preparative TLC [hexane-acetone (4:1)] to give a colorless oil (**2**, 2.4 mg). **2:** Colorless oil. UV λ_{max} nm: 210, 223 (sh), 268, 283 (sh). IR ν_{max} cm^{-1} : 1730, 1605, 1257, 1143. MS m/z (%): 468 (M^+ , 100), 453 (51), 437 (31), 397 (11), 371 (60), 247 (31), 221 (31), 205 (57), 191 (51), 175 (40). Differential NOE: irradiation of 3-OCH₃ (δ 3.88) gave 16% NOE at H-4 (δ 6.83) and 1% NOE at 3'-CH₃ (δ 1.68); irradiation of 1-OCH₃ (δ 3.66) gave 3, 2, 2, and 4% NOE at H-2' (δ 5.01), 3'-CH₃ (δ 1.68), 3''-CH₃ (δ 1.56), and 3''-CH₃ (δ 1.74), respectively; irradiation of 7-OCH₃ (δ 3.80)-16% NOE at H-6 (δ 7.02) and 2% NOE at 8-OCH₃ (δ 3.69); irradiation of 8-OCH₃ (δ 3.69)-1, 2, 1, and 1% NOE at 7-OCH₃ (δ 3.80), H-2'' (δ 5.01), H-1'' (δ 3.34), and 3''-CH₃ (δ 1.74), respectively; irradiation of H-4 (δ 6.83) gave 2% NOE at H-6 (δ 7.02) and 8% NOE at 3-OCH₃ (δ 3.88); irradiation of H-6 (δ 7.02) gave 1% NOE at H-4 (δ 6.83) and 8% NOE at 7-OCH₃ (δ 3.80).

Assiguxanthone-A (3): Pale yellow powder. UV λ_{max} nm: 204, 252, 283, 327. IR ν_{max} cm^{-1} : 3545, 3423, 3200 (br), 1647, 1589. MS m/z (%): 328 (M^+ , 40), 313 (100), 298 (19), 285 (24), 273 (17), 260 (20), 257 (11), 138 (18). HR-MS Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_6$: 328.0945. Found: 328.0934.

Assiguxanthone-B (9): Yellow powder. UV λ_{max} nm: 206, 238, 259, 321, 368. IR ν_{max} cm^{-1} : 3200 (br), 1645, 1614. MS m/z (%): 328 (M^+ , 46), 313 (28), 311 (17), 285 (79), 273 (100), 260 (14), 245 (9), 201 (10). HR-MS Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_6$: 328.0945. Found: 328.0944.

O-Methylation of 9 with Diazomethane A large excess of ethereal diazomethane was added to a methanolic solution (20 ml) of **9** (1.4 mg), and the mixture was left overnight at room temperature. The solvent was evaporated, and the residue was purified by preparative TLC with hexane-acetone (4:1) to give **10** almost quantitatively: Colorless oil. UV λ_{max} nm: 205, 244, 262, 298 (sh), 319, 360. IR ν_{max} cm^{-1} : 3200 (br), 1647, 1608, 1581. MS m/z (%): 370 (M^+ , 49), 355 (23), 327 (76), 315 (100), 295 (8), 269 (9), 229 (6), 219 (5), 203 (5). Differential NOE: irradiation of 3-OCH₃ (δ 3.92) gave 23% NOE at H-4 (δ 6.41); irradiation of 6-OCH₃ (δ 4.01) gave 10% NOE at H-5 (δ 6.86); irradiation of 7-OCH₃ (δ 3.99) gave 25% NOE at H-8 (δ 7.58).

Isolation and Separation of Dulxanthone-A (4), -B (6), -C (7), and -D (11) from *G. dulcis* The dried stem bark (1.5 kg) of *G. dulcis* was treated in the same manner as described above. The CH_2Cl_2 -soluble portion

(880 mg) was subjected to silica gel chromatography with hexane-EtOAc (9:1, 17:3, 4:1, 7:3, 3:2, 3:7), EtOAc, CH_2Cl_2 -MeOH (3:1), and MeOH, successively. The hexane-EtOAc (4:1) eluate was further subjected repeatedly to silica gel column chromatographies and preparative TLC with appropriate combinations of hexane, CH_2Cl_2 , acetone, EtOAc, CHCl_3 , and MeOH as developing solvents to obtain dulxanthone-C (**7**) (4.4 mg). The EtOAc-soluble portion (4.82 g) was subjected to silica gel chromatography with hexane-acetone (4:1, 3:1, 7:3, 3:2, 1:1, 3:7), acetone, CH_2Cl_2 -MeOH (3:1), and MeOH, successively. Each fraction was further subjected to silica gel column and preparative TLC with appropriate combinations of hexane, CH_2Cl_2 , acetone, EtOAc, CHCl_3 , and MeOH as developing solvents. From the hexane-acetone (3:1) eluate: dulxanthone-A (**4**) (8.8 mg), dulxanthone-B (**6**) (5.9 mg), dulxanthone-D (**11**) (1.0 mg), xanthone VI (**25**) (9.0 mg), 1,3,7-trihydroxy-2-(3-methyl-2-butenyl)xanthone (**22**) (1.7 mg) and toxylanthone B (**26**) (1.0 mg). From the hexane-acetone (7:3) eluate: uga-xanthone (**8**) (1.9 mg), jacareubin (**24**) (3.9 mg), gentisein (**21**) (2.0 mg). From the hexane-acetone (3:2) eluate: isoprenylxanthone (**17**) (4.6 mg). From the hexane-acetone (1:1) eluate: GB-1a (**30**) (140.3 mg).

Dulxanthone-A (4): Yellow powder. UV λ_{max} nm: 236 (sh), 253, 285, 328. IR ν_{max} cm^{-1} : 3545 (br), 1645, 1589. MS m/z (%): 342 (M^+ , 67), 327 (100), 313 (10), 297 (13), 286 (65), 274 (52), 264 (22), 257 (29), 245 (22), 229 (6), 201 (11), 157 (10), 152 (40). HR-MS Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_6$: 342.1102. Found: 342.1105. Differential NOE: irradiation of the 3-OCH₃ (δ 3.96) gave 4% NOE at H-2 (δ 6.41).

O-Methylation of 4 with Diazomethane A methanolic solution (20 ml) of **4** (2.1 mg) was treated in the same manner as described above for the O-methylation of **9** to give **5** almost quantitatively: Yellow powder. UV λ_{max} nm: 242, 257 (sh), 283, 318, 360. IR ν_{max} cm^{-1} : 3595 (br), 1645, 1599, 1572. MS m/z (%): 370 (M^+ , 98), 355 (100), 339 (10), 315 (21), 302 (64), 299 (5), 293 (5), 278 (8), 272 (12), 269 (7), 257 (11), 227 (6), 177 (6), 165 (5). Differential NOE: irradiation of 3-OCH₃ (δ 3.92) gave 23% NOE at H-2 (δ 6.38); irradiation of 6-OCH₃ (δ 4.01) gave 12% NOE at H-7 (δ 6.98); irradiation of 5-OCH₃ (δ 4.00) gave no NOE at any proton signal.

Dulxanthone-B (6): Yellow oil. UV λ_{max} nm: 236 (sh), 257, 282 (sh), 327. IR ν_{max} cm^{-1} : 3525 (br), 1635, 1593. MS m/z (%): 410 (M^+ , 76), 395 (14), 379 (11), 367 (100), 355 (89), 339 (30), 321 (14), 311 (22), 299 (15), 297 (22), 285 (49), 257 (12). HR-MS Calcd for $\text{C}_{24}\text{H}_{26}\text{O}_6$: 410.1728. Found: 410.1747.

Dulxanthone-C (7): Pale yellow powder. UV λ_{max} nm: 236, 254, 284 (sh), 329. IR ν_{max} cm^{-1} : 3544 (br), 1645, 1622, 1601, 1577. MS m/z (%): 424 (M^+ , 51), 409 (10), 381 (100), 369 (37), 313 (25). HR-MS Calcd for $\text{C}_{25}\text{H}_{28}\text{O}_6$: 424.1883. Found: 424.1881. Differential NOE: irradiation of 3-OCH₃ (δ 3.88) gave 27% NOE at H-2 (δ 6.33); irradiation of 6-OCH₃ (δ 3.98) gave 18% NOE at H-7 (δ 6.72); irradiation of H-1'' (δ 4.00) gave 9% NOE at H-7 (δ 6.72), 1% NOE at H-2'' (δ 5.34), and 1% NOE at 3''-CH₃ (δ 1.74); irradiation of H-1' (δ 3.50) gave 1% NOE at H-2' (δ 5.25), 9% NOE at 3'-CH₃ (δ 1.80).

Dulxanthone-D (11): Yellow powder. UV λ_{max} nm: 241, 252, 312, 350. IR ν_{max} cm^{-1} : 3400 (br), 1647, 1604, 1558. MS m/z (%): 342 (M^+ , 39), 327 (29), 311 (13), 309 (16), 299 (73), 285 (17), 284 (18), 271 (16), 257 (10), 245 (7), 229 (6), 216 (6), 203 (6), 187 (8). HR-MS Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_6$: 342.1102. Found: 342.1109. Differential NOE: irradiation of 7-OCH₃ (δ 3.81) gave 3% NOE at H-1' (δ 4.08).

Isolation and Separation of Latisxanthone-A (13), -B (14), -C (15) and -D (16) from *G. latissima* The dried stem bark (550 g) of *G. latissima* was also treated in the same manner as described above. The hexane-soluble portion (5 g) was subjected to silica gel column chromatography with hexane-acetone (10:1, 4:1, 2:1, 1:1, 1:2), acetone, CH_2Cl_2 -MeOH (3:1), and MeOH, successively. Each fraction was further subjected to silica gel column chromatographies and preparative TLC with appropriate combinations of the same solvents as described above. From the hexane-acetone (4:1) eluate: 5-hydroxy-7-methoxy-2-pentylchromone (**29**) (1.8 mg). From the hexane-acetone (1:1) eluate: latisxanthone-D (**16**) (1.0 mg) and GB-1a (**30**) (6.7 mg). The CH_2Cl_2 -soluble portion (2.2 g) was subjected to silica gel chromatography eluted with hexane-acetone (10:1, 4:1, 2:1, 1:1, 1:2), acetone, CH_2Cl_2 -MeOH (3:1), and MeOH, successively. Each fraction was further subjected to silica gel column chromatographies and preparative TLC with appropriate combinations of the same solvents as described above. From the hexane-acetone (2:1) eluate: latisxanthone-A (**13**) (4.2 mg) and latisxanthone-B (**14**) (1.0 mg). From the hexane-acetone (1:1) eluate: latisxanthone-C (**15**) (1.0 mg) and pyranojacareubin (**23**) (2.3 mg). From

the hexane-acetone (1:2) eluate: isogarcinol (**28**) (15.1 mg).

Latisxanthone-A (**13**): Yellow powder. UV λ_{\max} nm: 282, 337, 371. IR ν_{\max} cm^{-1} : 3539 (br), 1635, 1583. MS m/z (%): 460 (M^+ , 86), 445 (100), 417 (51), 405 (63), 389 (14), 377 (9), 230 (11), 215 (19), 203 (18), 187 (26). HR-MS Calcd for $C_{28}H_{28}O_6$: 460.1884. Found: 460.1877. Differential NOE: irradiation of H-8 (δ 7.47) gave 8% NOE at H-1'' (δ 6.42).

Latisxanthone-B (**14**): Yellow powder. $[\alpha]_D^{25} + 5^\circ$ ($c=0.066$). UV λ_{\max} nm: 224 (sh), 280, 331, 370. IR ν_{\max} cm^{-1} : 3734, 3545, 3384 (br), 1635, 1583. FAB-MS m/z (%): 493 $[M+H]^+$. EI-MS m/z (%): 476 (12), 405 (100), 391 (16), 248 (14), 203 (15). HR-FAB-MS Calcd for $C_{28}H_{28}O_8$: 493.1863 $[M+H]^+$. Found: 493.1852. Differential NOE: irradiation of H-8 (δ 7.42) gave 12% NOE at H-1'' (δ 6.38).

Latisxanthone-C (**15**): Pale yellow powder. UV λ_{\max} nm: 281, 337, 383. IR ν_{\max} cm^{-1} : 3543, 3377 (br), 1637, 1614, 1583. MS m/z (%): 462 (M^+ , 35), 445 (10), 419 (22), 407 (22), 405 (11), 391 (16), 363 (23), 351 (40), 335 (11), 203 (12), 188 (12). HR-MS Calcd for $C_{28}H_{30}O_6$: 462.2040. Found: 462.2036. Differential NOE: irradiation of H-1'' (δ 6.44) gave 10% NOE at H-8 (δ 7.48); irradiation of H-1' (δ 3.46) gave 7% NOE at H-2' (δ 5.29) and 10% NOE at 3'-CH₃ (δ 1.85); irradiation of H-1''' (δ 3.60) gave 1% NOE at 3-OH (δ 6.43), 4% NOE at H-2''' (δ 5.32), and 12% NOE at 3'''-CH₃ (δ 1.89).

Latisxanthone-D (**16**): Pale yellow oil. UV λ_{\max} nm: 261 (sh), 288, 296, 346. IR ν_{\max} cm^{-1} : 3566, 3423 (br), 1635, 1608, 1583. MS m/z (%): 394 (M^+ , 60), 379 (42), 351 (70), 339 (100), 323 (27), 311 (13), 203 (12), 162 (16). HR-MS Calcd for $C_{23}H_{22}O_6$: 394.1414. Found: 394.1398. Differential NOE: irradiation of H-8 (δ 7.43) gave 11% NOE at H-1'' (δ 6.37).

Acknowledgements We are grateful to Mr. Pius Piskaut of the Biology Department, University of Papua New Guinea for identification of the plants. We also thank Mr. K. Masuda of Meijo University for measurements of HR-FAB-MS.

References and Notes

- 1) A part of this paper was presented at the 116th Annual Meeting of the Pharmaceutical Society of Japan, Kanazawa, March 1996.
- 2) Ito C., Miyamoto Y., Rao K. S., Furukawa H., *Chem. Pharm. Bull.*, **44**, 441—443 (1996).
- 3) Rao K. S., *Int. J. Pharmacogn.*, **34**, 223—225 (1996).⁴⁾
- 4) In this paper, as the scientific names of two *Garcinia* species had not been assigned, *Garcinia* species I and II were used tentatively. *Garcinia* species I and II have now been identified as *Garcinia dulcis* (ROXB.) KURZ. and *Garcinia latissima* (MIQ.), respectively.
- 5) Locksley H. D., Moore I., Scheinmann F., *J. Chem. Soc. (C)*, **1966**, 2265—2269.
- 6) Ishiguro K., Nakajima M., Fukumoto H., Isoi K., *Phytochemistry*, **38**, 867—869 (1995).
- 7) Monache G. D., Botta B., de Mello J. F., de Barros Coelho J. S., Menichini F., *J. Nat. Prod.*, **47**, 620—625 (1984).
- 8) Hano Y., Matsumoto Y., Shinohara K., Sun J.-Y., Nomura T., *Planta Med.*, **57**, 172—175 (1991).
- 9) Scheinmann F., Sripong N.-A., *Phytochemistry*, **10**, 1331—1333 (1971).
- 10) Locksley H. D., Murray I. G., *J. Chem. Soc. (C)*, **1971**, 1332—1340.
- 11) Rocha L., Marston A., Kaplan M. A. C., Stoeckli-Evans H., Thull U., Testa B., Hostettmann K., *Phytochemistry*, **36**, 1381—1385 (1994).
- 12) Kitanov G., Achtardjiev C., *Pharmazie*, **34**, 447—448 (1979).
- 13) Harrison L. J., Leong L.-S., Sia G.-L., Sim K.-Y., Tan H. T.-W., *Phytochemistry*, **33**, 727—728 (1993).
- 14) Waterman P. G., Crichton E. G., *Phytochemistry*, **19**, 2723—2726 (1980).
- 15) Botta B., Monache G. D., Monache F. D., Bettolo G. B. M., Menichini F., *Phytochemistry*, **25**, 1217—1219 (1986).
- 16) Chen M.-T., Chen C.-M., *Heterocycles*, **23**, 2543—2548 (1985).
- 17) Ishiguro K., Fukumoto H., Nakajima M., Iso K., *Phytochemistry*, **33**, 839—840 (1993).
- 18) Locksley H. D., Moore I., Scheinmann F., *Tetrahedron*, **23**, 2229—2234 (1967).
- 19) Krishnamurthy N., Lewis Y. S., Ravindranath B., *Tetrahedron Lett.*, **22**, 793—796 (1981).
- 20) Krishnamurthy N., Ravindranath B., Guru Row T. N., Ven Katesan K., *Tetrahedron Lett.*, **23**, 2233—2236 (1982).
- 21) Jimenez C., Marcos M., Villaverde M. C., Riguera R., Castedo L., Stermitz F., *Phytochemistry*, **28**, 1992—1993 (1989).
- 22) Cotterill P. J., Scheinmann F., Stenhouse I. A., *J. Chem. Soc., Perkin Trans. 1*, **1978**, 532—539.