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Xanthones from the heartwood of *Garcinia mangostana*

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Abstract

Twelve xanthones were isolated from the hexane extract of the heartwood of *Garcinia mangostana* from Myanmar. Their structures were determined using 1D and 2D NMR techniques

Keywords: *Garcinia mangostana*; Guttiferae; Xanthones; Isolation; Structure determination

1. Introduction

Garcinia mangostana L., from which the mangosteen fruit is obtained, is commonly encountered in southeast Asia. Most of its metabolites are xanthones (Bennett and Lee, 1989) with α-mangostin (**1**), β-mangostin (**2**), and γ-mangostin (**3**) being the major components. We have previously isolated a number of known triterpenoids and xanthones as well as a new biphenyl, 3,4′,5-dihydroxy-3′,4,5-trimethoxybiphenyl, from the hexane soluble heartwood constituents of *G. mangostana* from Myanmar (Nilar and Harrison, 2002). We now report the isolation of twelve new xanthones, most of which are the result of side-chain modification of the mangostins.

2. Results and discussion

The first novel compound, garciniafuran (**4**), $C_{22}H_{20}O_6$ (*m*/*z* 380.1266), was obtained as a yellow amorphous powder, mp 185–186 °C. Its IR absorptions showed the presence of hydroxyl, chelated carbonyl, and aromatic groups [ν_{max} 3500 cm^{-1} (OH), 1649 cm^{-1} (C=O), and 1604 cm^{-1} (aromatic ring)]. The ^1H and ^{13}C NMR spectra (see Experimental and Table 1) showed the presence of a chelated hydroxyl group [δ_H 14.24 (1H, *s*, 1-OH)], a chelated carbonyl [δ_C 183.8 (*s*, C-9)], two isolated aromatic protons [δ_H 6.95 (1H, *br d*, $J=0.9$ Hz, H-4) and 6.80 (1H, *s*, H-5); δ_C 98.4 (*d*, C-5) and 89.6 (*d*, C-4)], two coupled aromatic protons [δ_H 7.54 (1H, *d*, $J=2.2$ Hz, H-12) and 6.99 (1H, *dd*, $J=0.9$ and 2.2 Hz, H-11); δ_C 144.1 (*d*, C-12) and 104.5 (*d*, C-11)], a 3-methylbut-2-enyl group [δ_H 5.28 (1H, *t sept*, $J=6.6$ and 1.4 Hz, H-14), 4.15 (2H, *br d*, $J=6.6$ Hz, H_2-13), 1.87 (3H, *s*, H_3-17) and 1.69 (3H, *br s*, H_3-16); δ_C 132.1 (*s*, C-15), 123.1 (*d*, C-14), 26.3 (*t*, C-13), 25.9 (*q*, C-16) and 18.2 (*q*, C-17)] and two methoxyl groups [δ_H 3.98 (3H, *s*, 6-OMe) and 3.81 (3H, *s*, 7-OMe); δ_C 61.0 (*q*, 7-OMe) and 56.1 (*q*, 6-OMe)] as well as ten substituted aromatic carbons, six of which were oxygenated. The molecule was therefore tetracyclic. As the molecule contained only one hydroxyl group, this ring must take the form of an ether in order to account for the number of oxygen atoms which were present. Comparison of the ^1H and ^{13}C chemical shifts of **4** with those of dimethylmangostin (**5**) revealed that the same dimethoxy-(3-methylbut-2-enyl) substituted ring was present and that **4** was thus a xanthone derivative. Confirmation of this came from NOE difference spectroscopy. Irradiation of the 7-methoxyl protons enhanced the resonances of the 3-methylbut-2-enyl group [H-14 (2%), H_2-13 (1.3%) and H_3-17 (0.9%)], whilst irradiation of the 6-methoxyl group enhanced the signal due to H-5 (19.6%). The chelated hydroxyl and more shielded aromatic proton (H-4) were therefore attached to the other aromatic ring. The remaining oxygen and two sp^2 carbons must therefore be part of a benzofuran system. The hydroxyl group was placed at C-1 to account for its formation of an intramolecular hydrogen bond with the carbonyl group. The presence of a small coupling ($J=0.9$ Hz) between the more deshielded furan hydrogen and H-4 occurred by a ^5J extended W pathway. H-4 was therefore *ortho* to

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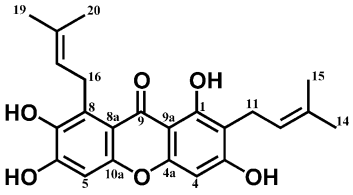

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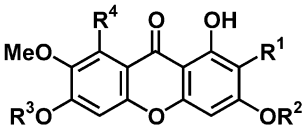

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(8) R^1=A, R^2=R^3=Me, R^4=B
(9) R^1=A, R^2=Me, R^3=H, R^4=B
(10) R^1=B, R^2=Me, R^3=H, R^4=A
(11) R^1=B, R^2=R^3=Me, R^4=A
(12) R^1=B, R^2=H, R^3=Me, R^4=A
(13) R^1=A, R^2=Me, R^3=H, R^4=C
(14) R^1=A, R^2=R^3=Me, R^4=C
(21) R^1=A, R^2=Me, R^3=R^4=H
(22) R^1=A, R^2=R^3=Me, R^4=H
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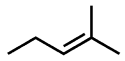
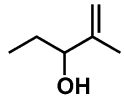
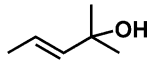
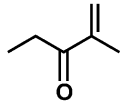
A = 

B = 

C = 

D = 

the furan oxygen. The furan ring was shown to be fused to the xanthone in a linear fashion by the use of ^{1}H-^{13}C correlation spectroscopy. In this case, a selective INEPT (SINEPT) experiment (Lin et al., 1993) involving irradiation of the chelated hydroxyl proton showed no enhancement of the unsubstituted aromatic carbon but did show enhancements of three substituted aromatic carbons. H-4 was therefore *para* to the chelated hydroxyl group. The ^{1}H and ^{13}C NMR assignments for **4** were made by comparison with those of dimethylmangostin **5**.

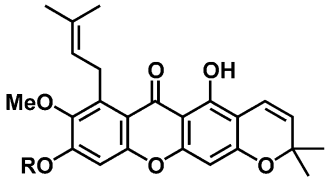
1-Hydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-xanthone (**6**) was obtained as a pale yellow gum, $[\alpha]_D$ +26.0. Its molecular formula, $C_{26}H_{30}O_7$, was established by high-resolution mass spectrometry. Its UV spectrum (λ_{max} 244, 262, 314, and 354 nm) was virtually identical to that of dimethylmangostin. Its IR spectrum exhibited absorptions at 3423 cm^{-1} (OH), 1645 cm^{-1} (C=O) and 1599 cm^{-1} (aromatic ring). The ^{1}H and ^{13}C NMR spectra (see Experimental and Table 1) also compared well with those of dimethylmangostin apart from the absence of signals for the C-8 prenyl substituent. These were replaced by signals which could be ascribed to a 2-hydroxy-3-methylbut-3-enyl group [δ_H 5.11 (1H, *br s*, H-19), 4.90 (1H, *br s*, H-19′), 4.31 (1H, *dd*, J=3.2 and 10.2 Hz, H-17), 3.70 (1H, *dd*, J=10.2 and 12.8 Hz, H-16), 3.54 (1H, *dd*, J=3.2 and 12.8 Hz, H-16) and 1.96 (3H, *s*, H_3-20); δ_C 148.8 (*s*, C-18), 109.9 (*t*, C-19), 77.1 (*d*, C-17), 33.2 (*t*, C-16) and 18.2 (*q*, C-20)]. Proof of the structure as well as the spectral assignments were obtained using a combination of HMQC and HMBC spectroscopy (see Experimental). Compound **6** was therefore 1-hydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-xanthone.

Four other co-metabolites which possessed a 2-hydroxy-3-methylbut-3-enyl group were isolated. The first was 1,6-dihydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**7**). Its ^{1}H and ^{13}C NMR spectra (see Experimental and Table 1) were almost identical to those of **6** and it afforded **6** upon treatment with diazomethane. Since one of the methoxyl groups of **7** was *ortho*-disubstituted (δ_C 61.0), the free hydroxyl group must be at C-3 or C-6. HMBC spectroscopy showed correlations from the prenyl group methylene protons and the second methoxyl group to the same aromatic carbon and established that C-3 was methoxylated. The other correlations were in agreement with the proposed structure.

Compound **8** was isomeric with **7**. Comparison of their ^{13}C NMR spectra revealed only minor differences in the xanthone nucleus resonances, with C-2 being more shielded in the former and C-8 being more shielded in the latter. Similar behaviour was observed for the side-chain methylene protons and carbons suggesting that the positions of the alkyl groups had been interchanged and that **8** was therefore 1,6-dihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-3,7-dimethoxy-8-(3-methylbut-2-enyl)-xanthone. Confirmation of this came from the results of HMBC spectroscopy (see Experimental).

The ^{1}H and ^{13}C NMR spectra (see Experimental and Table 1) of the trimethyl ether (**9**) and the dimethyl ether (**10**) were also similar to those of **8**. It was apparent that **10** was an isomer of **8** whereas **9** was a methyl ether of **8**. As expected, methylation of either **8** or **10** afforded **9**, which was identified as 1-hydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-3,6,7-trimethoxy-8-(3-methyl-but-2-enyl)-xanthone since its ^{1}H NMR spectrum contained a chelated hydroxyl resonance (δ_H 13.78). Compound **10** was therefore 1,3-dihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-6,7-dimethoxy-8-(3-methylbut-2-enyl)-xanthone since its ^{13}C NMR spectrum contained a resonance (δ_C 61.0) characteristic of an *ortho*-disubstituted methoxyl. ^{13}C NMR assignments of **9** and **10** were made by comparison with those of **8**.

The next two compounds differed only by an *O*-methyl group. The more polar, (16*E*)-1,6-dihydroxy-8-(3-hydroxy-3-methylbut-1-enyl)-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**11**) was readily converted to



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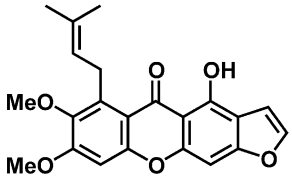

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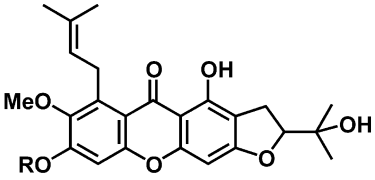

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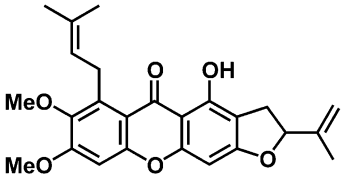

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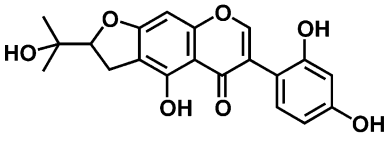

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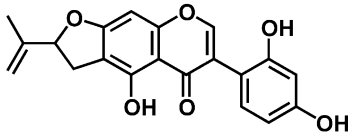

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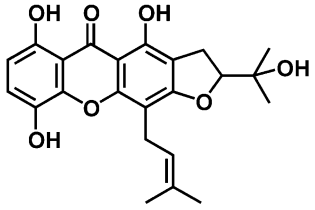

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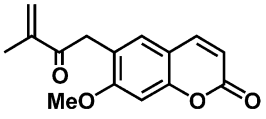

(25)

(16*E*)-1-hydroxy-8-(3-hydroxy-3-methylbut-1-enyl)-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-xanthone (**12**) upon treatment with diazomethane. The ^{1}H and ^{13}C NMR spectra of **11** (see Experimental and Table 1) were similar to those of **8** apart from those signals due to C-8 and the C-8 substituent. The presence of signals for a *trans*-alkene [δ_H 7.34 (^{1}H, *d*, $J=16.6$ Hz, H-16) and 6.25 (^{1}H, *d*, $J=16.6$ Hz, H-17); δ_C 124.7 (*d*, C-16) and 139.5 (*d*, C-17)] and two tertiary methyls [δ_H 1.48 (6H, *s*, H_3-19 and H_3-20); δ_C 25.1 ($2\times q$)] attached to a fully-substituted oxygenated carbon [δ_C 82.3 (*s*, C-18)] were indicative of a 3-hydroxy-3-methylbut-1-enyl substituent. These facts pointed to structure **11** which was confirmed by the results of an HMBC experiment (see Experimental). Compound **12** was therefore the 6-*O*-methyl ether of **11** since it still possessed a chelated hydroxyl group [δ_H 12.88 (1H, *s*, OH)]. ^{13}C NMR assignments of **12** were made by comparison with those of **11**.

Mangostanin (**13**), $C_{24}H_{26}O_7$, (*m*/*z*), also occurred in the extract along with its 6-*O*-methyl ether (**14**). Comparison of its ^{1}H and ^{13}C NMR spectra (see Experimental and Table 1) with those of 1,6-dihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-3,7-dimethoxy-8-(3-methylbut-2-enyl)-xanthone (**8**) showed the presence of a 6-hydroxy-7-methoxy-8-(3-methylbut-2-enyl)-xanthone system. The A ring was trisubstituted as only one aromatic proton was unaccounted for and it was hydroxylated in the *peri* position [δ_H 13.57 (1H, *s*, OH]. A second C_5 unit comprised of a benzylic methylene [δ_H 3.10 (1H, *dd*, $J=8.1$ and 15.4 Hz, H-11) and 3.19 (1H, *dd*, $J=9.4$ and 15.4 Hz, H-11); δ_C 26.9 (*t*, C-11)] which was coupled to an oxygenated methine [δ_H 4.77 (1H, *dd*, $J=8.1$ and 9.4 Hz, H-12); δ_C 91.8 (d, C-12)] as well as two tertiary methyls [δ_H 1.24 (3H, *s*, H_3-14) and 1.36 (3H, *s*, H_3-15); δ_C 23.9 (*q*, C-14) and 25.9 (*q*, C-15)] and an oxygenated fully-substituted carbon [δ_C 72.0 (*s*, C-13)]

Table 1
^{13}C NMR (125 MHz) spectral data of xanthones **4**, **6**–**15**, **19**–**22**

C No.	**4**[a]	**6**[a]	**7**[b]	**8**[b]	**9**[a]	**10**[a]	**11**[b]	**12**[a]	**13**[a]	**14**[a]	**15**[a]	**19**[a]	**20**[a]	**21**[a]	**22**[a]
1	156.9	159.7	160.5	161.3	160.6	161.3	160.3	159.6	158.1	158.1	158.2	159.4	159.4	159.5	159.7
2	112.1	111.9	111.9	108.5	108.8	107.7	112.0	112.1	107.6	107.6	107.2	111.8	111.8	111.5	111.6
3	159.3	164.0	164.7	165.1	163.7	163.2	164.7	163.9	166.3	166.2	164.4	163.9	163.8	163.6	163.6
4	89.6	88.9	89.9	89.9	89.0	94.3	90.0	89.0	88.3	88.1	88.2	89.6	89.5	89.1	88.8
4a	156.0	155.4	156.2	156.5[c]	155.6[c]	155.5	156.3[c]	155.5[c]	155.8[c]	157.1[c]	157.3[c]	152.6[c]	155.4[c]	155.3[c]	155.2[c]
5	98.4	98.9	103.2	102.8	98.3	98.4	103.1	99.0	101.6	98.3	98.3	102.5	99.4	102.6	99.1
6	158.6	158.2	157.4	157.7	158.3	158.1	158.0	158.8	157.2	158.1	158.2	156.3	156.2	155.4	158.0
7	144.1	144.9	145.7	144.7	144.2	144.0	144.1	143.5	142.7	144.1	144.1	144.4	146.7	143.9	144.8
8	137.5	134.4	134.8	138.1	137.5	137.3	133.2	132.4	137.8	137.2	137.2	104.6	104.7	129.7	130.4
8a	111.4	112.9	112.2	112.0	112.1	111.9	112.1	112.7	112.2	111.9	111.9	113.6	113.6	112.2	112.2
9	183.8	183.0	183.0	182.9	182.1	182.1	182.7	181.7	182.2	182.2	182.2	179.9	179.8	181.4	181.5
9a	104.7	104.0	104.2	104.0	104.0	103.5	104.2	104.0	104.2	104.4	104.3	103.4	103.5	103.6	103.8
10a	153.4	155.4	156.2	156.2[c]	155.5[c]	155.5	155.8[c]	154.9[c]	154.6[c]	155.5[c]	155.5[c]	152.4[c]	152.3[c]	154.7[c]	155.4[c]
11	104.5	21.4	21.9	24.9	26.2	28.3	21.9	21.4	26.9	26.9	30.7	21.4	21.4	21.3	21.3
12	144.1	122.2	123.2	88.1	75.9	77.6	123.4	122.0	91.8	91.8	88.2	122.2	122.2	122.3	122.3
13	26.3	131.9	131.5	146.0	147.8	146.8	131.5	131.9	72.0	72.0	143.3	131.9	131.9	131.6	131.7
14	123.1	25.8	25.8	112.9	110.0	110.4	25.9	25.8	25.9	23.9	112.6	25.8	25.8	25.8	25.8
15	132.1	17.8	17.8	18.3	18.2	18.6	17.8	17.8	25.9	25.9	17.0	17.8	17.8	17.8	17.8
16	25.9	33.2	30.0	26.9	29.1	26.2	124.7	124.3	26.6	26.2	23.9			37.4	37.0
17	18.2	77.1	89.4	124.7	123.1	123.3	139.5	137.6	123.2	123.2	123.2			199.7	199.2
18		148.8	146.5	131.5	132.0	131.8	82.3	82.1	132.2	131.9	131.9			144.8	144.9
19		109.9	112.6	25.9	25.9	25.9	25.1	25.5	23.9	25.9	25.9			124.0	123.5
20		18.2	17.9	17.3	18.2	18.2	25.1	25.5	18.2	18.2	18.2			18.0	18.0
3-OMe		55.9	56.5	56.5	56.0[d]		56.6	55.9[d]				55.9[d]	55.9[d]	55.8	55.8
6-OMe	56.1	56.1			56.1[d]	56.0		56.3[d]		56.1	56.1		56.5[d]		56.1
7-OMe	61.0	60.9	61.0	61.3	61.0	61.0	60.5	60.5	62.1	61.0	61.0	56.6[d]	56.4[d]	62.2	61.4

[a] $CDC1_3$.
[b] In $(CD_3)_2CO$.
[c] Interchangeable within a column.
[d] Interchangeable within a column.

was also attached to this ring. However, the molecular formula indicated there to be one unit of unsaturation still unaccounted for which, along with the number of oxygen atoms, suggested that the second C_5 unit formed an ether. This was shown to be part of a benzodihydrofuran since dehydration of the 6-*O*-methyl ether (**14**) yielded a compound (**15**) which possessed an isopropenyl group, thus ruling out other ring systems. The dihydrofuran was shown to be fused to C-2 and C-3 of the xanthone A-ring using SINEPT spectroscopy. Thus, in **13**, the chelated hydroxyl was coupled to three aromatic carbons [δ_C 158.1 (C-1), 107.6 (C-2), and 104.2 (C-9a)] which showed that C-2 must be alkylated. Mangostanin therefore possessed structure **13** and its methyl ether, which possessed a chelated hydroxyl group [δ_H 13.62 (1H, *s*, OH)], was **14**. The chemical shifts of **13**, **14** and **15** agreed well with those reported for lupinisoflavones A (**16**) and B (**17**) (Tahara et al., 1984). Although this modification of a prenyl side-chain is not common in xanthones, it has been found in morusignin E (**18**) from *Morus signis* (Moraceae) (Hano et al., 1991). ^{13}C NMR assignments were made by comparison with those of **1**, **2**, **16** and **17**.

The sole monoalkylated xanthone derivative in the extract was 1,6-dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**19**), $C_{20}H_{20}O_6$, *m*/*z* 370.1416. The UV [244, 258, 318, and 368 nm] and IR [3522 (OH), 1646 (C=O) and 1607 cm^{-1} (aromatic ring) cm^{-1}] spectra suggested that **19** was a xanthone. Methylation of **19** with diazomethane gave a trimethyl ether (**20**) [δ_H 4.01, 3.99 and 3.92 (each 3H, *s*, 7-OMe, 6-OMe and 3-OMe)] establishing the presence of one non-chelated phenolic hydroxyl in the parent compound. In the ^{1}H NMR spectrum, signals for a chelated hydroxyl [δ_H 13.04 (1H, *s*, 1-OH)] and three isolated aromatic protons [δ_H 7.61 (1H, *s*, H-8), 6.94 (1H, *s*, H-5), and 6.43 (1H, *s*, H-4)] were observed in addition to that of an aromatic hydroxyl group [δ_H 6.40 (1H, *br s*, 6-OH)]. The spectrum further showed the presence of a 3-methylbut-2-enyl group [δ_H 5.24 (1H, *t sept*, J = 7.3 and 1.4 Hz, H-12), 3.37 (2H, *br d*, J = 7.3 Hz, H_2-11), 1.80 (3H, *s*, H_3-15) and 1.69 (3H, *br s*, H_3-14)] and two methoxyl groups [δ_H 4.01 (3H, *s*, 7-OMe) and 3.92 (3H, *s*, 3-OMe)]. The ^{13}C NMR spectrum (see Table 1) exhibited 20 carbon resonances due to two methoxyls, two methyls, one methylene, four methines, and eleven quaternary carbons. The presence

of a xanthone nucleus and 3-methylbut-2-enyl group accounted for all of the units of unsaturation. Comparison of its ^{1}H and ^{13}C NMR spectra with those of **2** revealed that the A rings of the two compounds were identical. Irradiation of the 3-methoxyl group showed the expected NOE at H-4 (9.1%). The B ring was therefore substituted at C-6 and C-7 since the remaining aromatic ^{1}H NMR signals were singlets. Irradiation of the remaining methoxyl group enhanced (8.4%) the most deshielded aromatic proton resonance, which must be due to H-8. The compound was therefore 1,6-dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**19**).

The last xanthone was 1,6-dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-8-(2-oxo-3-methylbut-3-enyl)-xanthone (**21**), $C_{25}H_{26}O_7$, *m*/*z* 452.1823. Its UV (λ_{max} 244, 258, 318 and 358 nm) and IR spectra [ν_{max} 3509 (OH), 1646 (chelated C=O) and 1601 (aromatic ring) cm^{-1}] showed typical oxygenated xanthone absorptions as well as indicating the presence of an α,β-unsaturated ketone (ν_{max} 1679 cm^{-1})]. The ^{1}H and ^{13}C NMR spectra (see Experimental and Table 1) showed the presence of a chelated carbonyl [δ_C 181.4 (*s*)], a conjugated ketone [δ_C 199.7 (*s*)], a chelated hydroxyl group [δ_H 13.13 (1H, *s*, 1-OH)], two isolated aromatic protons [δ_H 6.75 (1H, *s*, H-5) and 6.21 (1H, *s*, H-4); δ_C 102.6 (*d*, C-5) and 89.1 (*d*, C-4)], an exomethylene group [δ_H 6.19 (1H, *br s*, H$_2$-19) and 5.86 (1H, *br s*, H$_2$-19); δ_C 124.0 (*t*, C-19)], a deshielded methylene group [δ_H 4.67 (2H, *s*, H$_2$-16); δ_C 37.4 (*t*, C-16)], a 3-methylbut-2-enyl group [δ_H 5.20 (1H, *t sept*, *J* = 7.1 and 1.4 Hz, H-12), 3.31 (2H, *br d*, *J* = 7.1 Hz, H$_2$-11), 1.78 (3H, *s*, H$_3$-15), and 1.67 (3H, *br s*, H$_3$-14); δ_C 122.3 (*d*, C-12), 21.3 (*t*, C-11), 25.8 (*q*, C-14), and 17.8 (*q*, C-15)], a vinyl methyl [δ_H 2.01 (3H, *s*, H$_3$-20); δ_C 18.0 (*q*, C-20)] and two methoxyl groups [δ_H 3.85 (3H, *s*, 3-OMe) and 3.75 (3H, *s*, 7-OMe); δ_C 62.2 (*q*, 7-OMe) and 55.8 (*q*, 3-OMe)] in addition to ten substituted aromatic carbons, six of which were oxygenated. The xanthone nucleus, ketone and 3-methylbut-2-enyl group accounted for all of the units of unsaturation. Methylation afforded a trimethyl ether (**22**) indicating the presence of a free hydroxyl group in the parent molecule. Comparison of the NMR shifts with those of **7** established the presence of a 1-hydroxy-3-methoxy-2-(3-methylbut-2-enyl) substituted xanthone ring and this was confirmed following HMBC spectroscopy (see Experimental).

The ^{1}H chemical shift of the exomethylene protons (δ_H 5.86 and 6.19) showed that they were more deshielded than usual for this type of hydrogen. As the compound also contained an α,β-unsaturated ketone [δ_C 199.7 (*s*)], these two groups were combined along with the third vinyl methyl (δ_H 2.01) and deshielded methylene (δ_H 4.67) to give a 2-oxo-3-methylbut-3-enyl group. This was supported by the observed HMBC correlations (see Experimental). This group must be *para* to the more deshielded aromatic hydrogen since H-5 and the methylene hydrogens have only two HMBC correlations in common. The ^{1}H NMR shift of the methylene hydrogens was greater than in the case of (*R*)-(+)-6-(2′-hydroxy-3′-methyl-3′-butenyl)-7-methoxycoumarin (**23**) (Burke and Parkins, 1979) indicating that the side chain must be *peri* to the xanthone carbonyl. The less deshielded methoxyl group (δ_H 3.75) was positioned *ortho* to this side-chain as an NOE enhancement (1.3%) of the methylene hydrogens was observed upon saturation of the methoxyl protons. The compound was therefore 1,6-dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-8-(2-oxo-3-methylbut-3-enyl)-xanthone (**21**). This is the first report of the xanthone with a 2-oxo-3-methylbut-3-enyl substituent.

3. Experimental

Mps: uncorr. $[\alpha]_D$: $CHCl_3$. IR: $CHCl_3$ unless otherwise specified. UV: EtOH. EIMS: 70 eV. CC: silica gel (Baker, 40 μm); C_{18} (Bakerbond, 40 μm). GPC: Sephadex LH-20 ($CHCl_3$–MeOH 1:1 as eluant). HPLC: Lichrosorb silica, C-18 or DIOL, 10 μm, 4.5×250 mm or 9.0×250 mm, RI detection. NMR spectroscopy: 500 (^{1}H) and 125 MHz (^{13}C) in $CDCl_3$ (unless specified otherwise) relative to TMS at δ 0.0.

Isolation. The heartwood of *Garcinia mangostana* was collected in Yangon, Myanmar in 1995. The plant material was identified by the Singapore Botanic Gardens and a voucher specimen (LJH067) is retained in the National University of Singapore herbarium. After air-drying and grinding, the wood (1.3 kg) was extracted exhaustively with hot hexane (5 l). Concentration of the solution afforded a crude extract (23 g), which was subjected to column chromatography (silica, EtOAc–hexane gradient). A combination of gel permeation chromatography and HPLC of the resulting frs. afforded the following compounds in order of increasing polarity: garciniafuran (**4**) (5 mg), 1-hydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-xanthone (**6**) (2.3 mg), (16*E*)-1-hydroxy-8-(3-hydroxy-3-methylbut-1-enyl)-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-xanthone (**12**) (2 mg) and 1-hydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-3,6,7-trimethoxy-8-(3-methylbut-2-enyl)-xanthone (**9**) (2 mg), β-mangostin (**2**) (54 mg), 1,6-dihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-3,7-dimethoxy-8-(3-methylbut-2-enyl)-xanthone (**8**) (11 mg), (16*E*)-1,6-dihydroxy-8-(3-hydroxy-3-methylbut-1-enyl)-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**11**) (10 mg) and 1,6-dihydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**7**) (11 mg), 1,3-dihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-6,7-dimethoxy-8-(3-methylbut-2-enyl)-xanthone (**10**) (7 mg) and mangostanin (**13**) (30 mg), 6-*O*-methylmangostanin (**14**) (4 mg), 1,6-dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**19**) (8 mg) and 1,6-dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-8-(2-oxo-3-methylbut-3-enyl)-xanthone (**21**) (7 mg).

3.1. Garciniafuran (**4**)

Pale yellow solid, mp 185–186 °C. UV λ_{max} nm (log ε): 238 (4.11), 260 (4.30), 276 (4.33), 306 (3.99), 364 (3.41). IR ν_{max} cm^{-1}: 3500 (OH), 1649 (C=O), 1604 (Ar). EIMS *m/z* (rel. int.): 380 $[M]^+$ (27), 365 (8), 347 (12), 338 (20), 337 (100), 325 (6), 323 (9), 321 (10), 309 (12), 294 (6), 279 (4), 236 (6), 175 (6), 151 (5), 129 (10), 71 (8), 43 (18). HR–EIMS *m/z* 380.1266 ($C_{22}H_{20}O_6$ requires *m/z* 380.1260). ^{1}H NMR: 14.24 (*s*, 1-OH), 7.54 (*d*, *J* = 2.2 Hz, H-12), 6.99 (*dd*, *J* = 0.9, 2.2 Hz, H-11), 6.95 (*br d*, *J* = 0.9 Hz, H-4), 6.80 (*s*, H-5), 5.28 (*t sept*, *J* = 6.6, 1.4 Hz, H-14), 4.15 (*br d*, *J* = 6.6 Hz, H-13), 3.98 (*s*, 6-OMe), 3.81 (*s*, 7-OMe), 1.87 (*s*, H_3-17), 1.69 (*br s*, H_3-16). ^{13}C NMR: see Table 1.

3.2. 1-Hydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-xanthone (**6**)

Pale yellow gum. $[\alpha]_D$ +26 (*c* 0.2 in $CHCl_3$). UV λ_{max} nm (log ε): 244 (4.04), 262 (4.05), 314 (3.87), 354 (3.42). IR ν_{max} cm^{-1}: 3423 (OH), 1645 (C=O), 1599 (Ar), 1457, 1427, 1277, 1118. EIMS *m/z* (rel. int.): 454 $[M]^+$ (10), 438 (11), 436 (19), 399 (13), 395 (16), 393 (44), 384 (75), 381 (39), 359 (51), 365 (19), 353 (10), 349 (26), 341 (78), 329 (100), 313 (28), 285 (19), 270 (7), 202 (9), 181 (26), 97 (19), 81 (32), 71 (32), 55 (54), 43 (48). HR–EIMS *m/z* 454.1989 ($C_{26}H_{30}O_7$ requires *m/z* 454.1992). ^{1}H NMR: 13.21 (*s*, exchangeable with D_2O, 1-OH), 6.82 (*s*, H-5), 6.37 (*s*, H-4), 5.23 (*t sept*, *J* = 7.1, 1.4 Hz, H-12), 5.11 (*br s*, H-19), 4.90 (*br s*, H-19), 4.31 (*dd*, *J* = 3.2, 10.2 Hz, H-17), 3.99 (*s*, 6-OMe), 3.92 (*s*, 3-OMe), 3.87 (*s*, 7-OMe), 3.70 (*dd*, *J* = 10.2, 12.8 Hz, H-16), 3.54 (*dd*, *J* = 3.2, 12.8 Hz, H-16), 3.36 (*br d*, *J* = 7.1 Hz, H-11), 1.96 (*s*, H_3-20), 1.80 (*s*, H_3-15), 1.68 (*br s*, H_3-14). NOE: 3-OMe [H-4]; 6-OMe [H-5]. ^{13}C NMR: see Table 1. HMBC: H-4 [C-2, C-3, C-4a, C-9a]; H-5 [C-6, C-7, C-8a, C-10a]; H-11 [C-1, C-2, C-3, C-12, C-13]; H-12 [C-14, C-15]; H_3-14 [C-12, C-13, C-15]; H_3-15 [C-12, C-13, C-14]; H_2-16 [C-7, C-8, C-8a, C-17]; H-17 [C-18, C-19, C-20]; H_2-19 [C-17, C-20]; H_3-20 [C-17, C-18, C-19]; 1-OH [C-1, C-2, C-9a]; 3-OMe [C-3]; 6-OMe [C-6]; 7-OMe [C-7]. This compound was identical to the product obtained upon treatment of **7** with CH_2N_2.

3.3. 1,6-Dihydroxy-8-(2-hydroxy-3-methylbut-3-enyl)-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (**7**)

Yellow gum. $[\alpha]_D$ +9.1 (*c* 0.66 in MeOH). UV λ_{max} nm (log ε): 244 (4.53), 258 (4.49), 316 (4.25), 356 (4.07). IR ν_{max} cm^{-1}: 3400 (OH), 1646 (C=O), 1602 (Ar). EIMS *m/z* (rel. int.): 440 $[M]^+$ (10), 439 (40), 438 (78), 424 (16), 423 (45), 405 (14), 397 (17), 395 (88), 384 (59), 383 (100), 367 (17), 365 (39), 355 (49), 351 (68), 339 (43), 338 (10), 325 (21), 315 (14), 312 (10), 299 (32), 271 (11), 192 (3), 157 (6), 115 (6), 69 (11), 41 (80). HR–EIMS *m/z* 440.1815 ($C_{25}H_{28}O_7$ requires *m/z* 440.1835). ^{1}H NMR: 13.60 (1H, *s*, 1-OH), 10.38 (1H, *s*, OH), 9.78 (1H, *br s*, OH), 6.89 (1H, *s*, H-5), 6.51 (1H, *s*, H-4), 5.22 (1H, *t sept*, *J* = 7.2 and 1.4 Hz, H-12), 4.70 (2H, *t*, *J* = 6.9 Hz, H_2-17), 4.93 (1H, *br s*, H-19′), 4.89 (1H, *br s*, H-19), 3.97 (3H, *s*, 3-OMe), 3.87 (3H, *s*, 7-OMe), 3.65 (2H, *br d*, *J* = 6.9 Hz, H_2-16), 3.33 (2H, *br d*, *J* = 7.2 Hz, H_2-11), 1.90 (3H, *s*, H_3-20), 1.78 (3H, *br s*, H_3-15), 1.65 (3H, *br s*, H_3-14). ^{13}C NMR: see Table 1. HMBC: H-4 [C-2, C-3, C-4a, C-9a]; H-5 [C-6, C-7, C-8a, C-10a]; H-11 [C-1, C-2, C-3, C-12, C-13]; H-12 [C-14, C-15]; H-14 [C-12, C-13, C-15]; H-15 [C-12, C-13, C-14]; H-16 [C-7, C-8, C-8a, C-17]; H-17 [C-18, C-19, C-20]; H-19 [C-17, C-20]; H-20 [C-17, C-18, C-19, C-20]; 3-OMe [C-3]; 7-OMe [C-7]; 1-OH [C-1, C-2, C-9a].

3.4. 1,6-Dihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-3,7-dimethoxy-8-(3-methylbut-2-enyl)-xanthone (**8**)

Yellow gum. $[\alpha]_D$ +13.6 (*c* 0.22 in MeOH). UV λ_{max} nm (log ε): 244 (4.52), 256 (4.45), 314 (4.27), 354 (4.03). IR ν_{max} cm^{-1}: 3400 (OH), 1645 (C=O), 1602 (Ar). EIMS *m/z* (rel. int.): 440 $[M]^+$ (21), 438 (28), 407 (29), 395 (15), 383 (26), 382 (17), 371 (19), 370 (60), 369 (100), 366 (41), 353 (34), 339 (22), 327 (18), 325 (15), 313 (30), 299 (22), 264 (4), 225 (2), 170 (4), 128 (3), 70 (30), 41 (47). HR–EIMS *m/z* 440.1839 ($C_{25}H_{28}O_7$ requires *m/z* 440.1835). ^{1}H NMR (Me_2CO-d_6): 13.78 (*s*, exchangeable with D_2O, 1-OH), 6.84 (*s*, H-5), 6.46 (*s*, H-4), 5.27 (*t sept*, *J* = 6.5, 1.4 Hz, H-17), 4.76 (*br s*, H-14), 4.70 (*br s*, H-14), 4.60 (*t*, *J* = 7.2 Hz, H-12), 4.11 (*br d*, *J* = 6.5 Hz, H_2-16), 3.95 (*s*, 3-OMe), 3.80 (*s*, 7-OMe), 2.93 (*dd*, *J* = 7.2, 13.3 Hz, H-11), 2.82 (*dd*, *J* = 7.2, 13.3 Hz, H-11), 1.83 (*s*, H_3-15), 1.81 (*br s*, H_3-20), 1.65 (*br s*, H_3-19). NOE: 3-OMe [H-4]; 7-OMe [H_2-16, H-17, H_3-20] ^{13}C NMR (Me_2CO-d_6): see Table 1. HMBC: H-4 [C-2, C-3, C-4a, C-9a]; H-5 [C-6, C-7, C-8a, C-10a]; H_2-11 [C-1, C-2, C-3, C-12, C-13]; H-12 [C-14, C-15]; H_2-14 [C-12, C-13, C-15]; H_3-15 [C-12, C-13, C-14]; H_2-16 [C-7, C-8, C-8a, C-17, C-18]; H-17 [C-16, C-19, C-20]; H_3-19 [C-17, C-18, C-20]; H_3-20 [C-17, C-18, C-19]; 1-OH [C-1, C-2, C-9a]; 3-OMe [C-3]; 7-OMe [C-7].

3.5. 1-Hydroxy-3,6,7-trimethoxy-2-(2-hydroxy-3-methylbut-3-enyl)-8-(3-methylbut-2-enyl)-xanthone (**9**)

Pale yellow gum. $[\alpha]_D$ +30.0 (*c* 0.2 in $CHCl_3$). UV λ_{max} nm (log ε): 246 (4.29), 262 (4.31), 312 (4.15), 348 (3.65). IR ν_{max} cm^{-1}: 3401 (OH), 1644 (C=O), 1599 (Ar), 1467, 1427, 1277, 1120. EIMS *m/z* (rel. int.): 454 $[M]^+$ (21), 436 (31), 421 (28), 383 (100), 365 (23), 341 (20), 327 (42), 149 (19), 57 (22), 55 (26), 43 (23), 41 (51). HR–EIMS *m/z* 454.2011 ($C_{26}H_{30}O_7$ requires *m/z* 454.1992). ^{1}H NMR: 13.78 (1H, *s*, 1-OH), 6.76 (1H, *s*, H-5), 6.37 (1H, *s*, H-4), 5.24 (1H, *t sept*, *J* = 6.6 and 1.4 Hz, H-17), 4.99 (1H, *br s*, H_2-14), 4.82 (1H, *br s*, H_2-14), 4.29 (1H, *br d*, *J* = 5.9 Hz, H-12), 4.13 (2H, *br d*, *J* = 6.6 Hz, H_2-16), 3.97 (3H, *s*, 6-OMe), 3.91 (3H, *s*, 3-OMe), 3.80 (3H, *s*, 7-OMe), 3.03 (1H, *dd*, *J* = 3.8 and 13.9 Hz, H_2-11), 2.93 (1H, *dd*,

$J=8.9$ and 13.9 Hz, H_2-11), 1.86 (3H, *s*, H_3-15), 1.85 (3H, *s*, H_3-20), 1.68 (3H, *br s*, H_3-19). ^{13}C NMR: see Table 1. This compound was identical to the product obtained when **8** or **10** was methylated with CH_2N_2.

3.6. 1,3-Dihydroxy-2-(2-hydroxy-3-methylbut-3-enyl)-6,7-dimethoxy-8-(3-methylbut-2-enyl)-xanthone (*10*)

Yellow gum. $[\alpha]_D$−2.9 (*c* 0.38 in $CHCl_3$). UV λ_{max} nm (log ε): 244 (4.43), 260 (4.41), 314 (4.22), 352 (3.93). IR ν_{max} cm^{-1}: 3233 (OH), 1644 (C=O), 1607 (Ar), 1459, 1427, 1279, 1168, 1113. EIMS *m*/*z* (rel. int.): 440 $[M]^+$ (21), 422 (30), 407 (40), 397 (33), 379 (100), 370 (25), 353 (20), 327 (25), 313 (37), 301 (44), 271 (24), 133 (19), 34 (18), 29 (48). HR–EIMS *m*/*z* 440.1815 ($C_{25}H_{28}O_7$ requires *m*/*z* 440.1835). ^1H NMR: 13.86 (*s*, 1-OH), 9.15 (*br s*, OH), 6.75 (*s*, H-5), 6.36 (*s*, H-4), 5.25 (*t sept*, $J=6.7$ and 1.3 Hz, H-17), 5.00 (*br s*, H-14), 4.88 (*br s*, H-14), 4.41 (*br d*, $J=8.2$ Hz, H-12), 4.12 (*br d*, $J=6.7$ Hz, H_2-16), 3.96 (*s*, 6-OMe), 3.79 (*s*, 7-OMe), 3.19 (*dd*, $J=2.1$ and 15.1 Hz, H-11), 2.88 (*dd*, $J=8.2$ and 15.1 Hz, H-11), 1.88 (*s*, H_3-15), 1.85 (*s*, H_3-21), 1.68 (*br s*, H_3-19). NOE: 6-OMe [H-5, 7-OMe]; 7-OMe [6-OMe, H_2-16, H-17, H_3-19, H_3-20]. ^{13}C NMR: see Table 1.

3.7. (16E)-1,6-Dihydroxy-8-(3-hydroxy-3-methylbut-1-enyl)-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (*11*)

Yellow gum. UV λ_{max} nm (log ε): 246 (4.60), 322 (4.29), 364 (4.10). IR ν_{max} cm^{-1}: 3389 (OH), 1644 (C=O), 1599 (Ar). EIMS *m*/*z* (rel. int.): 440 $[M]^+$ (5), 438 (14), 423 (31), 422 (71), 418 (7), 412 (10), 407 (20), 398 (97), 382 (56), 378 (86), 352 (76), 327 (78), 325 (95), 315 (100), 299 (68), 95 (76), 59 (53), 31 (65). HR–EIMS *m*/*z* 440.1840 ($C_{25}H_{28}O_7$ requires *m*/*z* 440.1835). ^1H NMR (Me_2CO-d_6): 13.34 (*s*, exchangeable with D_2O, 1-OH), 7.34 (*d*, $J=16.6$ Hz, H-16), 6.85 (*s*, H-5), 6.49 (*s*, H-4), 6.25 (*d*, $J=16.6$ Hz, H-17), 5.20 (*t sept* $J=7.3$, 1.3 Hz, H-12), 3.97 (*s*, 3-OMe), 3.73 (*s*, 7-OMe), 3.30 (*br d*, $J=7.3$ Hz, H-11)), 1.77 (*s*, H_3-15), 1.64 (*br s*, H_3-14), 1.48 (*s*, H_3-19), 1.48 (*s*, H_3-20). NOE: 3-OMe [H-4]; 7-OMe [H-16, H-17]. ^{13}C NMR (Me_2CO-d_6): see Table 1. HMBC: H-4 [C-2, C-3, C-4a, C-9a]; H-5 [C-6, C-7, C-8a, C-10a]; H-11 [C-1, C-2, C-3, C-12, C-13]; H-12 [C-14, C-15]; H-14 [C-12, C-13, C-15]; H-15 [C-12, C-13, C-14]; H-16 [C-7, C-17, C-18]; H-17 [C-8, C-18, C-19, C-20]; H-19 [C-17, C-18, C-20]; H-20 [C-17, C-18, C-19]; 1-OH [C-1, C-2, C-9a]; 3-OMe [C-3]; 7-OMe [C-7].

3.8. (16E)-1-Hydroxy-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-8-(3-hydroxy-3-methylbut-1-enyl)-xanthone (*12*)

Pale yellow gum. UV λ_{max} nm (log ε): 246 (4.61), 260 (4.56), 314 (4.42), 354 (3.96). IR ν_{max} cm^{-1}: 3440 (OH), 1644 (C=O), 1596 (Ar), 1457, 1423, 1277, 1120. EIMS *m*/*z* (rel. int.): 454 $[M]^+$ (2), 452 (3), 436 (38), 411 (25), 395 (94), 365 (20), 357 (42), 349 (37), 341 (25), 339 (61), 325 (19), 202 (19), 95 (21), 73 (18), 69 (26), 55 (44), 43 (100). HR–EIMS *m*/*z* 454.2005 ($C_{26}H_{30}O_7$ requires *m*/*z* 454.1992). ^1H NMR: 12.88 (1H, *s*, 1-OH), 9.77 (1H, *s*, 18-OH), 7.20 (1H, *d*, $J=16.5$ Hz, H-16), 6.81 (1H, *s*, H-5), 6.37 (1H, *s*, H-4), 5.97 (1H, *d*, $J=16.5$ Hz, H-17), 5.21 (1H, *t sept*, $J=7.0$ and 1.4 Hz, H-12), 3.99 (3H, *s*, 6-OMe), 3.92 (3H, *s*, 3-OMe), 3.70 (3H, *s*, 7-OMe), 3.35 (2H, *br d*, $J=7.0$ Hz, H_2-11), 1.79 (3H, *s*, H_3-15), 1.68 (3H, *br s*, H_3-14), 1.48 (6H, *s*, H_3-19 and H_3-20). ^{13}C NMR: see Table 1.

3.9. Mangostanin (*13*)

Yellow solid, mp 215–217 °C. $[\alpha]_D$ −0.7 (*c* 1.17 in $CHCl_3$). UV λ_{max} nm (log ε): 246 (4.57), 318 (4.37), 350 (4.11). IR ν_{max} cm^{-1}: 3506 (OH), 1661 (C=O), 1611 (Ar), 1463, 1283, 1171. EIMS *m*/*z* (rel. int.): 426 $[M]^+$ (52), 411 (41), 383 (100), 365 (14), 339 (14), 323 (13), 311 (19), 296 (11), 283 (5), 212 (5), 170 (4), 127 (4), 108 (2), 53 (1). HR–EIMS *m*/*z* 426.1682 ($C_{24}H_{26}O_7$ requires *m*/*z* 426.1679). ^1H NMR: 13.57 (*s*, exchangeable with D_2O, 1-OH), 6.83 (*s*, H-5), 6.41 (*br s*, exchangeable with D_2O, 13-OH), 6.28 (*s*, H-4), 5.27 (*t sept*, $J=6.3$, 1.4 Hz, H-17), 4.77 (*dd*, $J=8.1$, 9.4 Hz, H-12), 4.09 (*br d*, $J=6.3$ Hz, H_2-16), 3.81 (*s*, 7-OMe), 3.19 (*dd*, $J=9.4$, 15.4 Hz, H-11), 3.10 (*dd*, $J=8.1$, 15.4 Hz, H-11), 1.83 (*s*, H_3-20), 1.70 (*br s*, H_3-19), 1.36 (*s*, H_3-15), 1.24 (*s*, H_3-14). ^{13}C NMR: see Table 1.

3.10. 6-O-Methylmangostanin (*14*)

Pale yellow gum. $[\alpha]_D$ +14.0 (*c* 0.43 in $CHCl_3$). UV λ_{max} nm (log ε): 248 (4.30), 314 (4.14), 348 (3.66). IR ν_{max} cm^{-1}: 1662 (C=O), 1608 (Ar), 1460, 1427, 1278, 1102. EIMS *m*/*z* (rel. int.): 440 $[M]^+$ (31), 425 (18), 407 (10), 397 (100), 379 (22), 337 (23), 119 (10), 69 (11), 58 (10), 43 (38). HR–EIMS *m*/*z* 440.1842 ($C_{25}H_{28}O_7$ requires *m*/*z* 440.1835). ^1H NMR: 13.64 (1H, *s*, 1-OH), 6.76 (1H, *s*, H-5), 6.28 (1H, *s*, H-4), 5.25 (1H, *t sept*, $J=6.6$ and 1.3 Hz, H-17), 4.77 (1H, *dd*, $J=8.1$ and 9.4 Hz, H-12), 4.13 (2H, *br d*, $J=6.6$ Hz, H_2-16), 3.96 (3H, *s*, 6-OMe), 3.79 (3H, *s*, 7-OMe), 3.19 (1H, *dd*, $J=9.4$ and 15.4 Hz, H_2-11), 3.10 (1H, *dd*, $J=8.1$ and 15.4 Hz, H_2-11), 1.85 (3H, *s*, H_3-20), 1.68 (3H, *br s*, H_3-19), 1.35 (3H, *s*, H_3-15), 1.24 (3H, *s*, H_3-14). ^{13}C NMR: see Table 1. This compound was identical to the product of methylation of **13** with CH_2N_2.

3.11. Dehydration of 6-O-Methylmangostanin (*14*)

To a stirred, chilled (−10 °C) soln of the alcohol (**14**) (10 mg) in dry pyridine (2 ml) was added freshly distilled $SOCl_2$ (0.5 ml). After the reaction was complete (by TLC), the soln was poured into ice-cold aq. $NaHCO_3$ and extracted with $CHCl_3$. CC of the crude product (silica gel, 3% EtOAc–hexane) gave (**15**) (7 mg). Brown gum. UV λ_{max} nm (log ε): 248 (4.08), 314 (3.93), 352

(3.46). IR ν_{max} cm^{-1}: 1659 (C=O), 1608 (Ar), 1460, 1427, 1278, 1215. EIMS *m/z* (rel. int.): 422 $[M]^+$ (28), 407 (14), 389 (7), 379 (100), 353 (7), 349 (7), 168 (6), 149 (11), 83 (8), 57 (11), 39 (10). HR–EIMS *m/z* 422.1722 ($C_{25}H_{26}O_6$ requires *m/z* 422.1729). ^1H NMR: 13.66 (1H, *s*, 1-OH), 6.77 (1H, *s*, H-5), 6.30 (1H, *s*, H-4), 5.33 (1H, *dd*, *J* = 7.6 and 9.5 Hz, H-12), 5.25 (1H, *t sept*, *J* = 6.5 and 1.4 Hz, H-17), 5.10 (1H, *br s*, H_2-14), 4.94 (1H, *br s*, H_2-14), 4.13 (2H, *br d*, *J* = 6.5 Hz, H_2-16), 3.96 (3H, *s*, 6-OMe), 3.79 (3H, *s*, 7-OMe), 3.37 (1H, *dd*, *J* = 9.5 and 15.5 Hz, H_2-11), 3.02 (1H, *dd*, *J* = 7.6 and 15.5 Hz, H_2-11), 1.85 (3H, *s*, H_3-15), 1.78 (3H, *br s*, H_3-20), 1.68 (3H, *s*, H_3-19). ^{13}C NMR: see Table 1.

3.12. 1,6-Dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-xanthone (*19*)

Pale yellow gum. UV λ_{max} nm (log ε): 244 (4.39), 258 (4.33), 318 (4.04), 368 (4.03). IR ν_{max} cm^{-1}: 3522 (OH), 1646 (C=O), 1607 (Ar), 1481, 1442, 1286, 1167, 1114. EIMS *m/z* (rel. int.): 356 $[M]^+$ (21), 341 (13), 317 (10), 314 (15), 313 (62), 302 (17), 301 (100), 298 (14), 288 (9), 283 (11), 271 (32), 256 (10), 199 (11), 163 (13), 149 (10), 78 (15), 77 (16), 57 (10), 56 (17), 41 (25), 34 (22). HR–EIMS *m/z* 356.1260 ($C_{20}H_{20}O_6$ requires *m/z* 356.1260). ^1H NMR: see Text. ^{13}C NMR: see Table 1.

3.13. 1-Hydroxy-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-xanthone (*20*)

The xanthone (**19**) (5 mg) was methylated with CH_2N_2 to afford **20** as a pale yellow gum. UV λ_{max} nm (log ε): 244 (4.34), 262 (4.41), 318 (4.16), 358 (3.86). IR ν_{max} cm^{-1}: 1647 (C=O), 1608 (Ar), 1483, 1437, 1281, 1115. EIMS *m/z* (rel. int.): 370 $[M]^+$ (34), 328 (13), 327 (67), 316 (20), 315 (100), 311 (6), 302 (7), 285 (15), 170 (10), 149 (6), 71 (8), 57 (10), 55 (8), 43 (6), 41 (10), 30 (6). HR–EIMS *m/z* 370.1416 ($C_{21}H_{22}O_6$ requires *m/z* 370.1416). ^1H NMR: 13.05 (1H, *s*, 1-OH), 7.58 (*s*, H-8), 6.86 (1H, *s*, H-5), 6.41 (1H, *s*, H-4), 5.24 (1H, *t sept*, *J* = 7.1 and 1.4 Hz, H-12), 4.01 (3H, *s*, 7-OMe), 3.99 (3H, *s*, 6-OMe), 3.92 (3H, *s*, 3-OMe), 3.38 (2H, *br d*, *J* = 7.1 Hz, H_2-11), 1.81 (3H, *s*, H_3-15), 1.69 (3H, *br s*, H_3-14). ^{13}C NMR: see Table 1.

3.14. 1,6-Dihydroxy-3,7-dimethoxy-2-(3-methylbut-2-enyl)-8-(2-oxo-3-methylbut-3-enyl)-xanthone (*21*)

Yellow gum. UV λ_{max} nm (log ε): 244 (4.39), 258 (4.28), 318 (4.09), 358 (3.99). IR ν_{max} cm^{-1}: 3509 (OH), 1679 (α,β-unsaturated C=O), 1646 (C=O), 1601 (Ar), 1467, 1287, 1161, 1115. $[\alpha]_D$ +6.76 (*c* 0.74 in $CHCl_3$). EIMS *m/z* (rel. int.): 438 $[M]^+$ (75), 423 (37), 396 (42), 395 (85), 384 (47), 382 (100), 365 (38), 353 (40), 351 (65), 339 (38), 313 (35), 69 (40), 41 (90), 36 (54). HR–EIMS *m/z* 438.1693 ($C_{25}H_{26}O_7$ requires *m/z* 438.1679). ^1H NMR: 13.13 (*s*, exchangeable with D_2O, 1-OH), 6.75 (*s*, H-5), 6.21 (*s*, H-4), 6.19 (*br s*, H-19), 5.86 (*br s*, H-19), 5.20 (*t sept*, *J* = 7.1, 1.4 Hz, H-12), 4.67 (*s*, H_2-16), 3.85 (*s*, 3-OMe), 3.75 (*s*, 7-OMe), 3.31 (*br d*, J = 7.1 Hz, H_2-11), 2.01 (*s*, H_3-20), 1.78 (*s*, H_3-15), 1.67 (*br s*, H_3-14). NOE: 7-OMe [H_2-16]. ^{13}C NMR: see Table 1. HMBC: H-4 [C-2, C-3, C-4a, C-9a]; H-5 [C-6, C-7, C-8a, C-10a]; H_2-11 [C-2, C-12, C-13]; [C-12, C-13, C-15]; H_3-15 [C-12, C-13, C-14]; H_2-16 [C-7, C-8, C-8a, C-17]; H_2-19 [C-17, C-20]; H_3-20 [C-17, C-18, C-19]; 1-OH [C-1, C-2, C-9a]; 3-OMe [C-3]; 7-OMe [C-7].

3.15. 1-Hydroxy-3,6,7-trimethoxy-2-(3-methylbut-2-enyl)-8-(2-oxo-3-methylbut-3-enyl)-xanthone (*22*)

Methylation of the xanthone (**21**) (3 mg) with MeI (0.5 ml) and K_2CO_3 (10 mg) in Me_2CO (1 ml) for 5 h followed by CC of the residue (silica gel, 30% EtOAc–hexane) afforded the trimethyl ether (**22**) (1.5 mg) as a pale yellow gum. UV λ_{max} nm (log ε): 244 (4.28), 260 (4.25), 312 (4.10), 346 (3.62). IR ν_{max} cm^{-1}: 3625 (OH), 1680 (α,β-unsaturated C=O), 1645 (C=O), 1601 (Ar), 1458, 1279, 1218, 1118. EIMS *m/z* (rel. int.): 452 $[M]^+$ (49), 435 (16), 421 (24), 409 (81), 397 (100), 383 (32), 279 (36), 365 (57), 353 (18), 327 (28), 313 (14), 297 (11), 239 (3), 69 (43), 41 (54). HR–EIMS *m/z* 452.1823 ($C_{26}H_{28}O_7$ requires *m/z* 452.1835). ^1H NMR: 13.10 (1H, *s*, 1-OH), 6.75 (1H, *s*, H-5), 6.26 (1H, *s*, H-4), 6.10 (1H, *s*, H_2-19), 5.75 (1H, *s*, H_2-19), 5.13 (1H, *t sept*, *J* = 7.1 and 1.4 Hz, H-12), 4.69 (2H, *s*, H_2-16), 3.91 (3H, *s*, 6-OMe), 3.83 (3H, *s*, 3-OMe), 3.68 (3H, *s*, 7-OMe), 3.25 (2H, *br d*, *J* = 7.1 Hz, H_2-11), 1.92 (3H, *s*, H_3-20), 1.71 (3H, *s*, H_3-15), 1.60 (3H, *s*, H_3-14). ^{13}C NMR: see Table 1.

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