Phytochemistry Letters 13 (2015) 119–122

Contents lists available at ScienceDirect

Phytochemistry Letters

journal homepage: www.elsevier.com/locate/phytol

Geranylated tetraoxygenated xanthones from the pericarp of *Garcinia pedunculata*

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ARTICLE INFO

Article history:
Received 3 April 2015
Received in revised form 17 May 2015
Accepted 20 May 2015
Available online 6 June 2015

Keywords:
Garcinia pedunculata
Guttiferae
Xanthones
Pedunxanthones D-F
Structure determination
Cytotoxicity

ABSTRACT

Three new xanthones, pedunxanthones D-F (**1–3**), along with ten known compounds, were isolated from a chloroform extract of the pericarp of *Garcinia pedunculata*. Their structures were determined using spectroscopic techniques. Cytotoxicity against HeLa and NCI-H460 cells of the isolated compounds using an SRB assay was evaluated with pedunxanthone D (**1**) as the most active compound (IC_{50} 24.9 ± 0.4 and 26.1 ± 1.5 μg/ml, respectively).

1. Introduction

In a previous paper (Vo et al., 2012), we reported the isolation and determination of three new xanthones, pedunxanthones A-C, and five known compounds, 1,5-dihydroxy-3-methoxy-6′,6′-dimethyl-2H-pyrano(2′,3′:6,7)-4-(3-methylbut-2-enyl)xanthone, 1,5-dihydroxy-3-methoxy-4-(3-methylbut-2-enyl)xanthone, dulxanthone A, garbogiol and oleanolic acid, from the bark of *Garcinia pedunculata* (Guttiferae) collected in the Saigon Botanical and Zoological Garden. In this paper, we describe the isolation and characterisation of another three new xanthones, pedunxanthones D-F (**1–3**), together with ten known compounds, from the pericarp of the same species collected in Cat Tien National Park, Viet Nam.

2. Results and discussion

Column chromatography on a chloroform extract of the pericarp of *G. pedunculata* led to the isolation of three new xanthones, named pedunxanthones D-F (**1–3**) (Fig. 1), along with ten known compounds, 1,6-dihydroxy-7-methoxy-8-(3-methyl-2-butenyl)-6′,6′-dimethylpyrano-(2′,3′:3,2)xanthone (Sen et al., 1981), 6-*O*-demethyloliverixanthone (Vo et al., 2012), fuscaxanthone A (Ito et al., 2003), cowanin (Likhitwitayawuid et al., 1998), norcowanin (na-Pattalung et al., 1994), cowanol (Likhitwitayawuid et al., 1998), α-mangostin (Mahabusarakam et al., 1987), mangostanol (Chairungsrilerd et al., 1995), 3-isomangostin (Mahabusarakam et al., 1987), and 1,7-dihydroxyxanthone (Fujita et al., 1992). Except for 1,7-dihydroxyxanthone, all the remaining known compounds were 1,3,6,7-tetraoxygenated xanthones and previously found in the genus *Garcinia*.

Analysis of the ^{1}H and ^{13}C NMR data of compounds **1–3** (Table 1) revealed that they all had a xanthone skeleton characteristic of two benzene rings and a conjugated carbonyl carbon. Of the twelve aromatic carbons, six were oxygenated, showing that the xanthones were tetraoxygenated since two of them were assigned to C-4a and C-10a. In addition, the compounds had almost the same UV spectrum with four maximum absorptions *ca.* 243, 257, 314 and 355 nm (see Section 3), indicating the same 1,3,6,7-tetraoxygenated pattern (Na-Pattalung et al., 1994; Nilar and Harrison, 2002) in the molecules. Moreover, each compound carried a methoxyl group, a modified C_5 unit, and a geranyl group which bore two carbon-carbon double bonds, three methylenes and three vinyl methyls. The highly deshielded shift (δ_H 4.10–4.14) of the benzylic methylene protons (H_2-16) of the geranyl group showed that the group was attached to the *peri* position (C-8) (Silva and Pinto, 2005).

Compound **1** was obtained as a yellow gum, giving a dark green colour with ethanolic ferric chloride. The molecular formula, $C_{29}H_{34}O_6$, was determined by HRESIMS (*m/z* 501.2259 $[M+Na]^+$). The UV spectrum showed four absorption maxima at 243, 258, 317

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http://dx.doi.org/10.1016/j.phytol.2015.05.017
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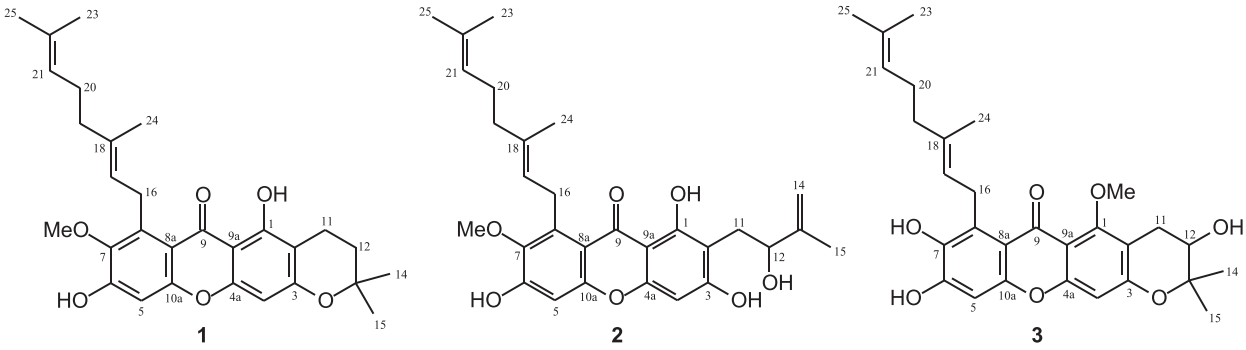

Fig. 1. Structures of **1–3**.

Table 1
1H (500 MHz) and ^{13}C (125 MHz) NMR data for **1–3**.

Position	**1** (in $CDCl_3$)		**2** (in acetone-d_6)		**3** (in acetone-d_6)	
	δ_H	δ_c	δ_H	δ_C	δ_H	δ_C
1		160.7		162.3		144.2
2		111.4		109.0		105.0
3		161.7		164.7		160.6
4	6.33 s	93.9	6.33 s	94.3	6.39 s	94.2
4a		155.9		156.4		157.6
5	6.82 s	101.6	6.83 s	102.8	6.72 s	102.2
6		155.2[a]		157.6		154.9[b]
7		142.7		144.8		144.2
8		137.2		138.3		137.8
8a		112.4		112.1		115.5
9		182.1		182.9		176.1
9a		103.5		103.6		108.0
10a		154.5[a]		156.3		155.4[b]
11	2.79 t (6.8 Hz)	16.2	3.08 dd (14.5 and 3.0 Hz) 2.89 dd (14.5 and 7.8 Hz)	29.9	2.95 dd (16.8 and 5.8 Hz) 2.57 dd (16.8 and 8.0 Hz)	27.2
12	1.80 m	41.4	4.41 dd (7.8 and 3.0 Hz)	76.7	3.82 m	69.2
13		72.5		148.4		78.6
14	1.31 s	29.8	4.94 br s and 4.76 br s	110.4	1.44 s	26.1
15	1.31 s	29.8	1.83 s	18.4	1.30 s	20.6
16	4.10 d (6.5 Hz)	26.6	4.14 d (6.5 Hz)	26.9	4.12 d (6.5 Hz)	26.5
17	5.27 t (6.5 Hz)	123.4	5.28 t (6.5 Hz)	124.9	5.33 t (6.5 Hz)	125.7[c]
18		135.5		135.1		134.5
19	2.00 m	39.8	1.98 m	40.5	1.97 m	40.6
20	2.05 m	26.7	2.07 m	27.4	2.06 m	27.5
21	5.03 t (6.4 Hz)	124.4	5.04 t (6.3 Hz)	125.2	5.05 t (6.5 Hz)	125.3[c]
22		131.2		131.6		131.5
23	1.55 s	17.7	1.52 s	17.7	1.53 s	17.7
24	1.82 d (1.0 Hz)	16.5	1.83 s	16.6	1.83 s	16.6
25	1.60 d (1.0 Hz)	25.6	1.56 s	25.7	1.56 s	25.8
1-OH	13.70 s		14.01 s			
7-OMe	3.80 s	62.1	3.80 s	61.4		
1-OMe					3.78 s	61.3

[a,b,c]Assignments with the same superscript are interchangeable.

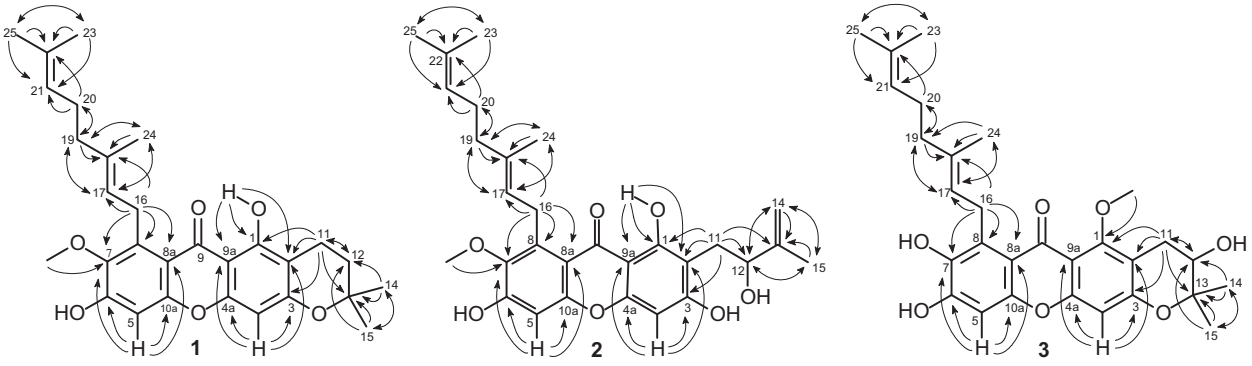

Fig. 2. HMBC correlations for **1–3**.