Available online at www.sciencedirect.com
SCIENCE DIRECT®
Phytochemistry 66 (2005) 2351–2355
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

# Bangangxanthone A and B, two xanthones from the stem bark of *Garcinia polyantha* Oliv.

A. Meli Lannang [a,*], J. Komguem [a], F. Ngounou Ngninzeko [a], J. Gustave Tangmouo [a], D. Lontsi [a], Asma Ajaz [b], M. Iqbal Choudhary [b], Rosa Ranjit [b], Krishna P. Devkota [b], B. Luc Sondengam [a]

[a] *Department of Organic Chemistry, Faculty of Sciences, University of Yaounde I, P.O. Box 812, Yaounde, Cameroon*
[b] *H.E.J. Research Institute of Chemistry, International Center for Chemical Sciences, University of Karachi, Karachi 75270, Pakistan*

Received 1 March 2005; received in revised form 1 June 2005
Available online 3 August 2005

**Abstract**

Two xanthones, bangangxanthone A (**1**) [1,5,8-trihydroxy-6′-methyl-6′-(4-methylpent-3-enyl)- pyrano[2′,3′:3,4]xanthone] and B (**2**) [1,4,8-trihydroxy-2-prenylxanthone], along with two known xanthones, 1,5-dihydroxyxanthone, 2-hydroxy-1,7-dimethoxyxanthone and the pentacyclic triterpenoids, friedelin, oleanolic acid and lupeol were isolated from the chloroform extract of the stem bark of *Garcinia polyantha*. The structures of these compounds were assigned by spectroscopic analysis. Compounds **1**–**4** showed antioxidant DPPH radical scavenging activities.


*Keywords:* *Garcinia polyantha*; Guttiferae; Bangangxanthone A; Bangangxanthone B; Prenylated xanthones; Antioxidant

## 1. Introduction

*Garcinia* is the most important genus of Guttiferae family, widely distributed in tropical Africa, Asia, New Caledonia and Polynesia (Ampofo and Waterman, 1986). The genus *Garcinia* is well known to be rich in a variety of oxygenated and prenylated phenol derivatives (Peres et al., 2000; Bennett and Lee, 1989). Some of them exhibited a wide range of biological activities such as cytotoxic, anti-fungal, anti-microbial, anti-oxidant, anti-inflammatory, anti HIV activities (Hiroyuki et al., 1996; Nkengfack et al., 2002; Hay et al., 2004; Merza et al., 2004). In our search for biologically active substances, we focused our study on *Garcinia polyantha* Oliv.; a ''false chew stick'' tree generally distributed in the lowland tropical rainforest of West, East and Central Africa (Ampofo and Waterman, 1986; Berhaut, 1975). In West and Central Africa, the yellow resinous sap (latex) of the plant is used for making a dressing for wounds (Bouquet, 1969). Previous studies of *G. polyantha* showed the presence of isorheediaxanthone-B (Ampofo and Waterman, 1986). From *Garcinia* species, we now report the phytochemical analysis of the stem bark of *G. polyantha* along with the antioxidant activity of some of the isolated compounds.

## 2. Results and discussion

Extensive column chromatography of the chloroform extract of the stem bark of *G. polyantha* led to the

* Corresponding author. Tel.: +237 776 27 80/753 48 30; fax: +237 222 91 16.
*E-mail addresses:* alainmeli@yahoo.com, ameli@uycdc.uninet.cm (A.M. Lannang).

0031-9422/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2005.06.016

isolation of two new xanthones, bangangxanthone A (**1**) and bangangxanthone B (**2**), as well as two known xanthones; 2-hydroxy-1,7-dimethoxyxanthone (**3**) (Galeffi et al., 1990) and 1,5-dihydroxyxanthone (**4**) (Nkengfack et al., 2002), three pentacyclic triterpenoids, lupeol (**5**) (Wenkert et al., 1978), oleanolic acid (**6**) (Ampofo and Waterman, 1986) and friedelin (**7**) (LeFevre et al., 2001).

Bangangxanthone A (**1**) was isolated as yellow needle crystals, m.p.: 157–158 °C having the $M^+$ at *m/z* 394.1420 in HREIMS indicated the formula $C_{23}H_{22}O_6$ (calcd. 394.1416). The UV spectrum showed absorption band at $\lambda_{max}$ 360, 336, 268, 222, 210 and 201 nm indicated to be a xanthone derivative (Nkengfack et al., 2002). The IR spectrum showed absorption at 3468, 3369, 1659 and 1627 $cm^{-1}$ suggested the xanthone skeleton with a chelated carbonyl group (Federicio et al., 2001). Both the $^1H$ and $^{13}C$ NMR spectra (Table 1) revealed the presence of a prenyl moiety characterized by the signals at $\delta_H$ 5.07 (1H, *t*, 6.8 Hz, H-17), 1.55 (3H, *s*, H-19), 1.64 (3H, *s*, H-20), and $\delta_C$ 132.1 (C-18), 126.8 (C-17), 17.6 (C-19), 25.6 (C-20) and 22.6 (C-16), respectively. The presence of a chromene ring system was indicated by an AX proton system at $\delta_H$ 5.58 (1H, *d*, 10.1 Hz, H-12) and 6.76 (1H, *d*, 10.1 Hz, H-11), further supported by signals at $\delta_C$ 123.5 (C-12), 114.8 (C-11), 81.1 (C-13) and 27.1 (C-14). The lack of one methyl signal, in 6′,6′-dimethylchromene system (Azebaze et al., 2004) and the appearance of additional one methylene signal at $\delta_C$ 41.6 (C-15), suggested that one methyl was substituted by a 4-methylpent-3-enyl group. This fact was further supported by the appearance of an abundant fragment ion at *m/z* 311 ($[M]^+ - 83$) resulting from the loss of the 4-methylpent-3-enyl moiety. The analysis of an aromatic AB type proton at $\delta$ 7.24 (1H, *d*, 8.8 Hz, H-6) and 6.66 (1H, *d*, 8.8 Hz, H-7), suggested the presence of *ortho* protons. A shielded isolated proton at $\delta$ 6.25 (1H, *s*, H-2) was in agreement with a pentasubstituted aromatic ring A. The signals at $\delta_C$ 184.3 (C-9), $\delta_H$ 12.09 (1H, *s*, 1-OH) and 11.22 (1H, *s*, 8-OH), indicated the presence of a conjugated carbonyl and a chelated hydroxyl. The long range correlation (Fig. 1) between $\delta_H$ 12.09 (1-OH) with the signal at $\delta_C$ 162.1 (C-1), 99.8 (C-2) and 102.3 (C-9a), and correlations between at $\delta$ 6.25 (H-2) with $\delta_C$ 162.9 (C-3), 162.1 (C-1), 101.0 (C-4) and 102.3 (C-9a), and that of $\delta$ 5.58 (H-12) with $\delta_C$ 101.0 (C-4) allowed an unequivocal assignment of A ring in the xanthone moiety. In the B ring, the correlation between $\delta_H$ 11.22 (8-OH) with $\delta_C$ 154.2 (C-8), 110.3 (C-7) and 107.3 (C-8a), and the signals at $\delta_H$ 7.24 (H-6) with $\delta_C$ 142.7 (C-10a), 135.5 (C-5) and 154.2 (C-8) established the free hydroxyl position at C-5. All those spectral data, associate with COSY 45° allowed an unequivocal assignment of the ring B and confirmed the structure proposed as 1,5,8-trihydroxy-6′-methyl-6′-(4-methylpent-3-enyl)-pyrano[2′,3′:3,4]xanthone (**1**). No nOe between H-2/H-11 or H-12, no long range correlation between H-2 and C-11 confirmed the pyrano[2′,3′:3,4]-xanthone squeleton (see Fig. 2).

Table 1
$^1H$ and $^{13}C$ NMR data of bangangxanthone A (**1**) (500, 125 MHz) and bangangxanthone B (**2**) (600, 150 MHz) in $CDCl_3$

| Position | **1** | | **2** | |
|---|---|---|---|---|
| | $^1H$ [*m*, *J* (Hz)] | $^{13}C$ | $^1H$ [*m*, *J* (Hz)] | $^{13}C$ |
| 1 | | 162.1 | – | 151.3 |
| 2 | 6.25 (*s*) | 99.8 | – | 123.3 |
| 3 | – | 162.9 | 7.21 (*s*) | 124.4 |
| 4 | – | 101.0 | – | 135.1 |
| 4a | – | 151.0 | – | 141.0 |
| 10a | – | 142.7 | – | 155.7 |
| 5 | – | 135.5 | 6.91 (*d*, 8.4) | 106.8 |
| 6 | 7.24 (*d*, 8.8) | 123.5 | 7.59 (*t*, 8.4) | 137.4 |
| 7 | 6.66 (*d*, 8.8) | 110.3 | 6.79 (*d*, 8.4) | 111.1 |
| 8 | – | 154.2 | – | 161.7 |
| 8a | – | 107.3 | – | 110.6 |
| 9a | – | 102.3 | – | 107.8 |
| 9 | – | 184.3 | – | 186.2 |
| 1′ | – | – | 3.35 (*d*, 7.3) | 26.8 |
| 2′ | – | – | 5.30 (*t*, 7.0) | 121.2 |
| 3′ | – | – | – | 133.9 |
| 4′ | – | – | 1.71 (*s*) | 17.8 |
| 5′ | – | – | 1.75 (*s*) | 25.8 |
| 11 | 6.76 (*d*, 10.1) | 114.8 | – | – |
| 12 | 5.58 (*d*, 10.1) | 123.5 | – | – |
| 13 | – | 81.1 | – | – |
| 14 | 1.44 (*s*) | 27.1 | – | – |
| 15 | 1.80 and 1.68 (*m*) | 41.6 | – | – |
| 16 | 2.09 (*m*) | 22.6 | – | – |
| 17 | 5.07 (*t*, 6.8) | 126.8 | – | – |
| 18 | – | 132.1 | – | – |
| 19 | 1.55 (*s*) | 17.6 | – | – |
| 20 | 1.64 (*s*) | 25.6 | – | – |
| 1-OH | 12.09 | – | 11.35 (*s*) | – |
| 4-OH | – | – | 5.11 (*s*) | – |
| 8-OH | 11.22 | – | 11.94 (*s*) | – |

Bangangxanthone B (**2**), was obtained as yellow needle crystals, m.p.: 199–201 °C. Its formula $C_{18}H_{16}O_5$ was determined by HREIMS ($M^+$ at *m/z* 312.0991, calcd. 312.0998). The compound showed a dark green color with methanolic ferric chloride. The UV spectrum of compound **2** revealed $\lambda_{max}$ at 389, 342, 296, 269 and 237 nm. The IR spectrum exhibited absorption bands

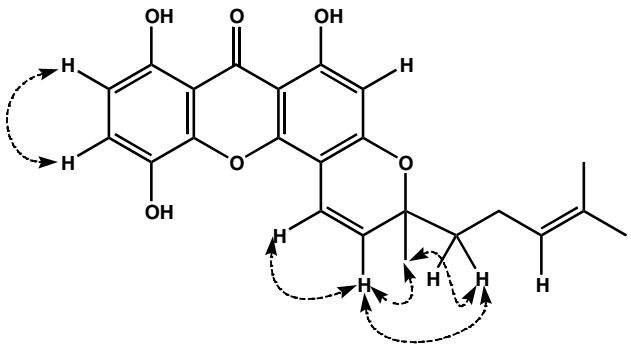


Fig. 1. NOESY correlations of **1**.

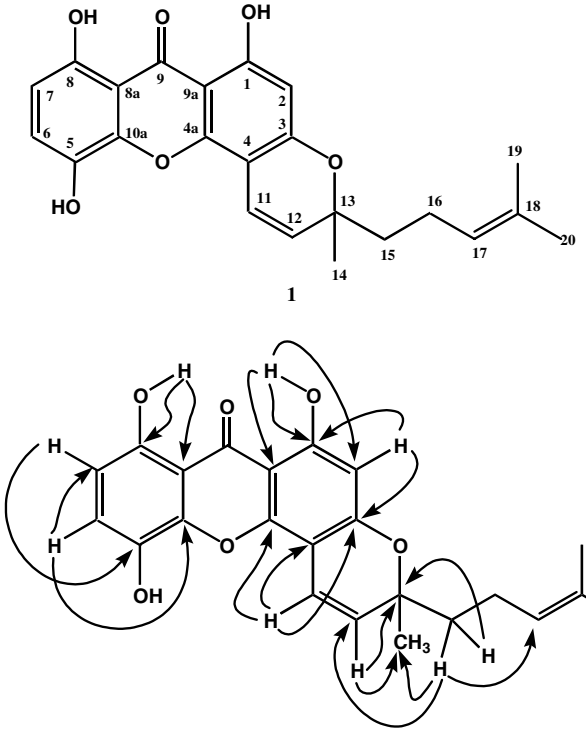

Fig. 2. Key HMBC correlations of **1**.

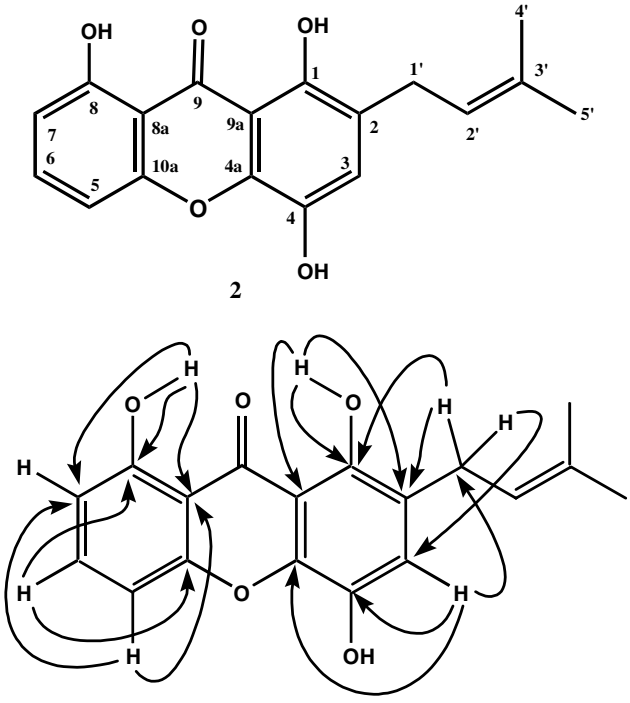

Fig. 3. Key HMBC correlations of **2**.

at 3400 and 1627 $cm^{-1}$ due to a phenolic hydroxyl and a chelated carbonyl. The UV and IR spectral features were similar to those of compound **1**, suggesting a xanthone derivative. The $^1H$ NMR spectrum of compound **2** showed the signals at $\delta$ 5.30 (1H, *t*, $J = 7.0$ Hz, H-2′), 3.35 (2H, *d*, $J = 7.3$Hz, $H_2$-1′), 1.71 (3H, *s*, $H_3$-4′) and 1.75 (3H, *s*, $H_3$-5′) suggested the presence of a prenyl moiety, which was connected to C-2 ($\delta_C$ 123.3) on the basis of the HMBC correlation of $H_2$-1′ with C-1 ($\delta_C$ 151.3), C-2 ($\delta_C$ 123.3) and C-3 ($\delta_C$ 124.4) (Fig. 3). A singlet aromatic proton at $\delta$ 7.21 (1H, *s*, H-3) was attached to the C-3 position, on the basis of HMBC correlation between H-3 with C-2, C-1, C-4a ($\delta_C$ 141.0) and C-1′ ($\delta_C$ 26.8). The signal resonating at $\delta_C$ 186.3 (C-9), $\delta_H$ 11.35 (1H, *s*, 1-OH) and 11.94 (1H, *s*, 8-OH) indicated the presence of a chelated carbonyl group and a chelated hydroxyl in the compound **2**. In the HMBC spectrum of compound **2** $\delta_H$ 11.35 (1-OH) correlated with the signal at $\delta_C$ 107.8 (C-8b), C-1 and C-2, further supported the substitution pattern of the A ring. The signal at $\delta_H$ 11.94 (8-OH) showed a cross peak with a signal at $\delta_C$ 161.7 (C-8), 111.1 (C-7) and 110.6 (C-8a). The aromatic ABC type proton system at $\delta_H$ 6.91 (1H, *br d*, $J = 8.4$ Hz, H-5), 6.79 (1H, *br d*, $J = 8.4$ Hz, H-7) and 7.59 (1H, *t*, $J = 8.4$ Hz, H-6), suggested the presence of three adjacent protons in the same ring. H-5 showed long range correlation with C-8a, C-7, and, this of H-6 correlated with $\delta_C$ 155.7 (C-10a) and C-8. In the interpretation of spectral data, compound **2** was confirmed as a trioxygenated xanthone named bangangxanthone B (1,4,8-trihydroxy-2-prenylxanthone).

### 2.1. Antioxidant activity

Compounds **1**–**4** were screened for DPPH Radical scavenging activity. Compound **1** showed significant activity ($IC_{50} = 87.0$ μM) compared to the standard, 3-*t*-butyl-4-hydroxyanisole ($IC_{50} = 42.0$ μM). Similarly, compound **2** showed weak activity with $IC_{50}$ 482.0 μM, while **3** and **4** showed 47.8% and 39.5% of inhibition, respectively at the concentration of 1 mM.

## 3. Experimental

### 3.1. General procedure

The melting points were recorded on a micro melting point apparatus and are uncorrected. Optical rotations were measured on a digital polarimeter in acetone and chloroform. Ultraviolet spectra were determined in methanol. Infrared spectra were measured on a spectrometer with KBr pellets. The mass spectra were recorded on a double focusing mass spectrometer. Accurate mass measurements were carried out with FAB source using glycerol as matrix, and HR-EIMS were carried out. The $^1H$ NMR spectra were registered on 600 and 500 MHz, while $^{13}C$ NMR spectra were recorded on 150 and 125 MHz, respectively. Methyl, methylene and methine carbons were distinguished by

DEPT experiments. Homonuclear $^{1}H$ connectivities were determined by using the COSY experiment. One-bond $^{1}H$–$^{13}C$ connectivities were determined with HMQC gradient pulse factor selection. Two- and three-bond $^{1}H$–$^{13}C$ connectivities were determined by HMBC experiment. Chemical shifts were reported in $\delta$ (ppm) and coupling constants ($J$) were measured in Hz. Precoated TLC plates (silica gel) were used to check the purity of compounds, and ceric sulphate spraying reagent was used for the staining of compounds on TLC. All reagents used were of analytical grades.

### 3.2. Plant material

The stem bark of *G. polyantha* was collected from Mt Kala, central-province Cameroon in August 2003, and identified by Dr. Tchiengue Bathelemy of the Cameroon Nation Herbarium (Yaoundé), where a voucher specimen (21337/SRF/Cam/Mt Kala) was deposited.

### 3.3. Extraction and isolation

Air dried stem bark of *G. polyantha* (4 kg) was ground and extracted at room temperature successively with hexane, chloroform and ethyl acetate and respective fractions concentrated under reduce pressure to yield 18, 25 and 60 g, respectively. Chloroform extract (15 g) was chromatographed over silica gel ($5 \times 80$ cm) eluted with a mixture of pet. ether/EtOAc to have four fractions (10:1 fraction 1, 10:2 fraction 2, 10:4 fraction 3 and 10:5 fraction 4). After evaporation, fraction 1 was subjected to silica gel column chromatography and eluted with gradient of 11:1 and 10:1 pet. ether/EtOAc to obtain pure compounds **1** (11 mg), **2** (9 mg), **5** (55 mg) and **7** (25 mg). Similarly, compounds **3** (15 mg), **4** (17 mg) and **6** (8 mg) were obtained from fraction 3 on elution of a column with 10:1 and 10:2 pet. ether/EtOAc.

#### 3.3.1. 1,5,8-Trihydroxy-6′-methyl-6′-(4-methylpent-3-enyl)-pyrano[2′,3′:3,4]xanthone (*1*)

Yellow needle crystals: m.p.: 157–158 °C, $[\alpha]_D^{29} = +25^\circ$ ($c$ 0.032, $C_3H_6O$). UV (MeOH) $\lambda_{max}$ ($\log\varepsilon$): 360 (3.92), 336 (4.08), 268 (4.40), 222 (4.12), 210 (4.03) and 201 (4.22) nm. IR ($CHCl_3$) $\nu_{max}$: 3468, 3369, 2920, 2854, 1659, 1627, 1574, 1489 $cm^{-1}$. EIMS: $m/z$ 394 $[M]^+$ (14.7), 311 (100), 83 (26), 78 (23), 69 (6), 63 (23). HR-EIMS: $m/z$ 394.1420 (calcd. 394.1416 for $C_{23}H_{22}O_6$). $^{1}H$ (500 MHz) and $^{13}C$ (125 MHz) NMR, see Table 1.

#### 3.3.2. 1,4,8-Trihydroxy-2-prenylxanthone (*2*)

Yellow needle crystals, m.p.: 199–201 °C. UV $(MeOH)_{max}$ ($\log\varepsilon$): 389 (3.21), 379 (3.14), 342 (3.67), 296 (3.33), 269 (4.17), 237 (4.02) nm. IR ($CHCl_3$) $\nu_{max}$: 3468, 3369, 3080, 2920, 2854, 1659, 1627, 1574, 1489, 1164 $cm^{-1}$. EIMS: $m/z$ 312 $[M]^+$ (95), 297 (64), 295 (22), 294 (5), 279 (11), 269 (31), 258 (18), 244 (6), 241 (7), 149 (16), 85 (29), 83 (42), 69 (5), 63 (76), 55 (6). HR-EIMS: $m/z$ 312.0991 (calcd. 312.0998 for $C_{23}H_{22}O_5$). $^{1}H$ (600 MHz) and $^{13}C$ (150 MHz) NMR, see Table 1.

### 3.4. Determination of the radical scavenging activity

The reaction mixture containing 5 μL of test sample (1 mM in DMSO) and 95 μL of DPPH (Sigma, 300 μM) in ethanol the reaction mixture was taken in a 96-well micro liter plate (Molecular Devices, USA) and incubated at 37 °C for 30 min. The absorbance was measured at 515 nm. Percent radical scavenging activity determined by comparison with a DMSO containing control. $IC_{50}$ values represent concentration of compounds to scavenge 50% of DPPH radicals. 3-*t*-Butyl-4-Hydroxyanisole (BHA) was used as a positive control. All the chemicals used were of analytical grade (Sigma, USA).

## Acknowledgements

One of us, A. Meli Lannang, is thankful to the TWAS for financial support for research and advanced training at the H.E.J Research Institute of Chemistry, International Center of Chemical Sciences. He is also thankful to ECTA-BTP for providing the car for plants collection and Mr. Nana Victor of the Cameroon National Herbarium for the collection and identification of the plant material.

## References

Ampofo, A.S., Waterman, G.P., 1986. Xanthones from three *Garcinia* species. Phytochemistry 25, 2351–2355.

Azebaze, A.G.B., Meyer, M., Bodo, B., Nkengfack, A.E., 2004. Allanxanthone B, a polyisoprenylated xanthone from the stem barks of *Allanblackia monticola* Staner L.C.. Phytochemistry 65, 2561–2564.

Bennett, G.J., Lee, H.H., 1989. Xanthones from guttiferae. Phytochemistry 28, 967–998.

Berhaut, J., 1975. Flore illustré du Sénégal. Gouvernement du Sénégal, ministère du développement rural et de l'hydraulique, direction des eaux et foret, Dakar, pp. 89–90.

Bouquet, A., 1969. Féticheurs et médecines traditionnelles du Congo (Brazzaville). O.R.S.T.O.M., Paris, p. 133.

Federicio, G.C., Jose, T.D.S.N., Maria, L.S.G., 2001. Xanthone and coumarins from *Kielmeyera lathrophyton*. J. Braz. Chem. Soc. 12, 117–122.

Galeffi, C., Federici, E., Msonthi, J.D., Marini Bettolo, G.B., Nicoletti, M., 1990. New xanthones from *Ectiadiopsis oblongifolia* and *Securidaca longipedunculata*. Fitoterapia, LXI 1, 79–81.

Hay, A.E., Aumond, M.D., Mallet, S., Dumontet, V., Litaudon, M., Rondeau, D., Richomme, P., 2004. Antioxydant xanthones from *Garcinia viellardii*. J. Nat. Prod. 67, 707–709.

Hiroyuki, M., Emi, T., Mitsuaki, K., Yoshiyasu, F., 1996. Three xanthones from *Garcinia subelliptica*. Phytochemistry 41, 629–633.

LeFevre, J.W., Kristin, I.M., Janet, L.M., 2001. Isolating friedelin from cork and reducing it to friedelinol and epifriedelinol. A project involving NMR spectrometry and molecular modeling. J. Chem. Educ. 78, 535.

Merza, J., Aumond, M.-C., Rondeau, D., Dumontet, V., Le Ray, A.M., Séraphin, D., Richomme, P., 2004. Prenylated xanthones and tocotrienols from *Garcinia virgata*. Phytochemistry 65, 2915–2920.

Nkengfack, E.A., Mkounga, P., Fomum, T.Z., Meyer, M., Bodo, B., 2002. Globulixanthones A and B, two new cytotoxic xanthones with isoprenoid groups from the root bark of *Symphonia globulifera*. J. Nat. Prod. 65, 734–736.

Peres, V., Nagem, T.J., Oliveira, F.F., 2000. Tetraoxygenated naturally occurring xanthones. Phytochemistry 55, 683–710.

Wenkert, E., Baddeley, G.V., Burfitt, I.R., Moreno, L.N., 1978. Carbon-13 nuclear magnetic resonance spectroscopy of naturally-occurring substances. Org. Magn. Reason. 11, 337–342.