

Polyisoprenylated benzophenones from *Garcinia semseii* (Clusiaceae)

Joseph J. Magadula^{a,*}, Modest C. Kapingu^a, Merhatibeb Bezabih^b, Berhanu M. Abegaz^b

^aInstitute of Traditional Medicine, Muhimbili University of Health and Allied Sciences, P.O. Box 65001, Dar es Salaam, Tanzania

^bChemistry Department, University of Botswana, Private Bag 0047, Gaborone, Botswana

ARTICLE INFO

Article history:

Received 15 September 2008

Received in revised form 8 October 2008

Accepted 8 October 2008

Available online 28 October 2008

Keywords:

Garcinia semseii

Clusiaceae

Benzophenones

Semsinones A–C

Isolation

Characterisation

ABSTRACT

Three novel polyisoprenylated benzophenones, semsinones A–C have been isolated from the stem bark of *Garcinia semseii* together with a known monocyclic triterpene, achilleol A. The structures of the new compounds have been determined by analysis of the spectroscopic data and comparison of the NMR data with those of the closely related compounds previously reported.

© 2008 Published by Elsevier B.V. on behalf of Phytochemical Society of Europe.

1. Introduction

The genus *Garcinia* (Clusiaceae) consists of about 180 species that are mainly encountered in lowland rain forests of the tropical world, particularly in Africa and Southeast Asia (Perry and Metzger, 1980). The genus has been a major source of prenylated xanthenes (Bennet and Lee, 1989; Yang et al., 2007), polyisoprenylated benzophenones (Oliveira et al., 1999; Gustafson et al., 1992), biflavonoids mainly with a 3/8-linkage (Babu et al., 1988; Mbawambo et al., 2006) and triterpenoids (Nyemba et al., 1990). Phenolic constituents from *Garcinia* species have been reported to possess various biological activities, including antibacterial (Permana et al., 2001; Suksamrarn et al., 2003), antimalarial (Hay et al., 2004) and cytotoxic (Shadid et al., 2007), prooxidant (Wu et al., 2008), quinone reductase-inducing (Chin et al., 2008) and HIV-inhibitory activities (Gustafson et al., 1992).

As part of our search for new substances from medicinal plants, we have studied the chemical constituents of *G. semseii* Verdc., an endemic plant growing in the Kihansi Forest Reserve, Morogoro region, Tanzania. Three new polyisoprenylated benzophenones, named semsinones A (**1**), B (**2**) and C (**3**), were isolated from the ethanol extract of the stem bark of *G. semseii*. Their structures were established using spectral data and by comparison with the closely related compounds reported in the literature (Porto

et al., 2000; Cuesta-Rubio et al., 2001; Wu et al., 2008). In addition to compounds **1–3**, the known monocyclic triterpene, achilleol A has been isolated (Akihisa et al., 1999). This is the first report of the isolation of achilleol A from *Garcinia* species. In this paper we report the isolation and structure elucidation of new compounds **1–3** (Fig. 1).

2. Results and discussion

Compound **1** was obtained as a gum. The positive HRESIMS of compound **1** indicated a pseudo-molecular ion at m/z 671.4229 $[M+H]^+$ which was consistent with the molecular formula $C_{43}H_{58}O_6$. The IR spectrum indicated the absorption bands at 3348, 1725, 1641 cm^{-1} attributed to hydroxyl, non-conjugated and conjugated carbonyl groups, respectively. The UV spectrum showed absorption bands due to an aromatic chromophore at 282 and 234 nm due to a conjugated carbonyl group. Examination of the 1H NMR spectrum of this compound in methanol showed duplicate signals for most regions of the spectrum. However, using CD_3OD with 0.1% TFA at 600 MHz it was possible to obtain a clear and a single set of signals (Gustafson et al., 1992). In the aromatic region of the 1H NMR spectrum, three proton ABD signals were observed at $[\delta_H$ 7.10 (1H, d, J = 1.8 Hz, H-12), 7.00 (1H, d, J = 8.5 Hz, H-15) and 7.18 (1H, dd, J = 8.5, 1.8 Hz, H-16)] due to the 1,2,4-trisubstituted benzene ring. Signals representing each of a vinyl proton of the four trisubstituted double bonds were seen at $[\delta_H$ 4.96 (1H, br, t , J = 8.0 Hz, H-18), 5.22 (1H, dd, J = 9.2, 7.0 Hz, H-30), 5.25 (1H, m, H-35), 4.85 (1H, br t , J = 7.9 Hz, H-40)], two tertiary

* Corresponding author. Tel.: +255 22 2150096; fax: +255 22 2150465.

E-mail address: jmagadula@yahoo.co.uk (J.J. Magadula).

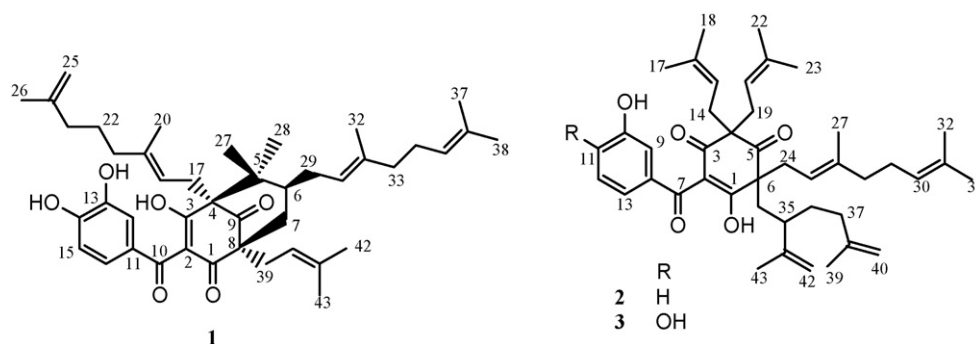


Fig. 1. Chemical structures of compounds isolated from *G. semseii*.

methyl protons [δ_{H} 1.30 (3H, s, H-27) and 1.22 (3H, s, H-28)], one resonance for a terminal alkene at $\delta_{\text{H}\alpha}$ 4.66 and $\delta_{\text{H}\beta}$ 4.69 [2H, d, $J = 1.7$ Hz each, H-25], eight allylic methylene protons at δ_{H} 2.0–2.50 (16H, m) and signals for seven vinylic methyl groups (s, 3H each) at [δ_{H} 1.68 (H-20), 1.72 (H-26), 1.72 (H-32), 1.96 (H-37), 1.99 (H-38), 1.89 (H-42) and 1.91 (H-43)] were observed. Inspection in the ^{13}C NMR spectrum indicated the presence of a conjugated carbonyl group at δ_{C} 196.8 (C-10) and six aromatic carbon signals at δ_{C} 130.1 (C-11), 116.0 (C-12), 158.2 (C-13), 156.7 (C-14), 129.6 (C-15), 127.6 (C-16). The ^{13}C NMR spectrum also showed carbon signals that are characteristic of the bicyclo [3.3.1] nonane ring system of a polyisoprenylated benzophenone at δ_{C} 205.9 (C-9) for a non-conjugated carbonyl, a methine carbon signal at δ_{C} 41.9 (C-6), a methylene carbon signal at δ_{C} 40.6 (C-7) and six quaternary carbon signals at δ_{C} 195.3 (C-1), 115.0 (C-2), 194.9 (C-3), 67.2 (C-4) and 63.7 (C-8) (Gustafson et al., 1992; Lokvam et al., 2000).

The location of the side chains was determined by the use of NOESY and HMBC experiments. The methylene proton signals at [δ_{H} 2.69 (H_{α} -17) and 2.50 (H_{β} -17)] showed correlations in the HMBC spectrum to four quaternary carbon signals at δ_{C} 194.9, 67.2, 53.2, 205.9 ascribed to C-3, C-4, C-5 and C-9, respectively, and a methine carbon signal at δ_{C} 124.2 due to C-18. This allowed the placement of the geranyl group with a terminal alkene at C-4. The correlations of the methylene protons at δ_{H} 2.10 (H-29) to a single quaternary carbon signal at δ_{C} 53.2 (C-5), a methine carbon signal at δ_{C} 41.9 (C-6) and a methylene carbon signal at δ_{C} 40.6 (C-7) required the placement of a geranyl group at C-6. The double doublet proton signals at [δ_{H} 2.49 (H_{α} -39) and 2.40 (H_{β} -39)] showed correlations to three quaternary carbon signals at δ_{C} 195.3, 63.7 and 205.9 attributed to C-1, C-8, and C-9, respectively, and a methylene carbon signal at δ_{C} 40.6 (C-7). This confirmed the placement of a 3-methylbut-2-enyl group at C-8. Further inspection of the HMBC spectrum indicated cross peaks between the proton signals at δ_{H} 1.30 (H-27) and 1.22 (H-28) due to the *gem*-methyl groups and carbon signals at δ_{C} 67.2, 53.2 and 41.9 ascribed to C-4, C-5 and C-6, respectively.

The relative stereochemistry of the side chains of compound **1** was deduced from NOESY experiments, by analysis of coupling constants and by comparing the ^{13}C NMR spectral data of reference compounds. The side chains on the bicyclo [3.3.1] nonane were found to have equatorial orientation at positions C-4 and C-8. In the proton spectra the high coupling constant ($J = 9.8$ Hz) between H-7 α and H-6 suggested an equatorial position of the geranyl group at C-6. The upfield chemical shift of the C-28 (δ_{C} 16.3) signal was caused by the γ -*gauche* interaction with C-29 of the geranyl group at C-6 (Nilar et al., 2005; Cuesta-Rubio et al., 2001). Furthermore, the high vicinal J -values observed were due to the chair conformation for the B-ring of the bicyclo [3.3.1] nonane system of compound **1**. In the NOESY spectrum, the proton signal for H-6 (δ_{H} 1.64) correlated with the proton signal at δ_{H} 2.20

ascribed to H-7 eq together with one of the methylene protons for H-29. Further inspection in the NOESY spectrum indicated a correlation between the H-6 proton signal with the proton signal at δ_{H} 1.22, integrating to three protons attributable to the H-28 protons. The literature search for compound **1** led to a previous report of a compound, aristophenone B (Cuesta-Rubio et al., 2001) isolated from *Garcinia aristata* (Clusiaceae) which has a basic skeleton similar to **1** but with a difference in the side chains. In aristophenone B, all the side chains at positions C-4, C-6 and C-8 were 3-methylbut-2-enyl groups while compound **1** has a (3,7-dimethyloct-2,7-dienyl) group at C-4, a geranyl group at C-6 and a 3-methylbut-2-enyl group at C-8. Thus, **1** was identified as a new polyisoprenylated benzophenone, 5,5-dimethyl-6-geranyl-3-hydroxy-2-(13,14-dihydroxybenzoyl)-4-(3,7-dimethyloct-2,7-dienyl)-8-(3-methylbut-2-enyl)-bicyclo[3.3.1]nonan-2-en-1,9-dione and a trivial name, semsinone A, is proposed for this novel compound.

Compound **2** was obtained as a brownish oil. The high resolution mass (HRESIMS) spectrum showed the pseudo-molecular ion at m/z 655. 4279 [$\text{M} + \text{H}$] $^{+}$ that was consistent with the molecular formula $\text{C}_{43}\text{H}_{58}\text{O}_5$. The UV spectrum indicated absorption bands at 250 and 352 nm. The ^1H NMR spectrum, showed nine singlet methyl proton signals (s, 3H each) at δ_{H} 1.58, 1.76, 1.71, 1.60, 1.67, 1.67, 1.54, 1.65 and 1.64 corresponding to H-17, H-18, H-22, H-23, H-27, H-32, H-33, H-39 and H-43, respectively. Further analysis in the ^1H NMR spectrum, indicated four vinyl proton signals at δ_{H} 4.98 (1H, m, H-15), 5.00 (1H, m, H-20), 4.97 (1H, t, $J = 7.0$ Hz, H-26) and 4.98 (1H, t, $J = 6.1$ Hz, H-30) ascribed to H-15, H-20, H-26 and H-30, respectively. Signals were observed at $\delta_{\text{H}\alpha}$ 4.68 and $\delta_{\text{H}\beta}$ 4.66 [2H, d, $J = 1.9$ Hz each, H-40] and at $\delta_{\text{H}\alpha}$ 4.65 and $\delta_{\text{H}\beta}$ 4.63 [2H, d, $J = 1.8$ Hz each, H-42] due to two terminal alkenes. In the aromatic region, four proton signals were observed at δ_{H} 7.25 (1H, d, $J = 1.5$ Hz), 7.18 (1H, dd, $J = 8.8, 1.5$ Hz), 7.11 (1H, t, $J = 9.0, 7.21$ (1H, dd, $J = 8.8, 1.5$ Hz) attributed to H-9, H-11, H-12 and H-13, respectively, that were consistent with a monosubstituted benzoyl group.

The ^{13}C NMR spectrum showed 43 signals with fifteen quaternary carbon signals, nine methine carbon signals, ten methylene carbon signals and nine methyl carbon signals (Table 1). Comparison of the carbon spectra recorded for **2** with those of **1** showed the absence of signals observed for the quaternary carbon signals at δ_{C} 53.2 (C-5), a methine at δ_{C} 41.9 (C-6) and methylene carbon signal at δ_{C} 40.6 (C-7), that are characteristic of the bicyclo [3.3.1] nonane ring system. Instead, the observed data were consistent with a cyclohex-2-enone skeleton (Porto et al., 2000). In the HMBC spectrum, two methylene proton signals at (δ_{H} 3.11, 3.06, $\text{H}_{\alpha,\beta}$ -14) and (δ_{H} 2.99, 2.89, $\text{H}_{\alpha,\beta}$ -19) both displayed cross peaks with three quaternary carbon signals at δ_{C} 195.4 (C-3), 63.4 (C-4) and 208.6 (C-5), this confirmed the placement of the two prenyl groups at position C-4. Further

Table 1
NMR assignments of compounds **1–3** (CD₃OD with 0.1% TFA, 600 MHz).

C	1	2	3
	δ_H	δ_C	δ_H
1		195.3 (C)	195.2 (C)
2		115.0 (C)	113.2 (C)
3		194.9 (C)	195.4 (C)
4		67.2 (C)	63.4 (C)
5		53.2 (C)	208.6 (C)
6	1.64 (1H, m)	41.9 (CH)	50.9 (C)
7	α 2.20 (1H, dd, $J = 12.9, 2.8$ Hz) β 2.09 (1H, dd, $J = 12.9, 9.8$ Hz)	40.6 (CH ₂)	195.3 (C)
8		63.7 (C)	129.2 (C)
9		205.9 (C)	7.25 (1H, d, $J = 1.5$ Hz)
10		196.8 (C)	116.4 (CH)
11		130.1 (C)	145.2 (C)
12	7.10 (1H, d, $J = 1.8$ Hz)	116.0 (CH)	7.18 (1H, dd, $J = 8.8, 1.5$ Hz)
13		158.2 (C)	7.11 (1H, t, $J = 9.0$ Hz)
14		156.7 (C)	7.21 (1H, dd, $J = 8.8, 1.5$ Hz)
15	7.00 (1H, d, $J = 8.5$ Hz)	129.6 (CH)	α 3.11 (1H, dd, $J = 14.9, 5.1$)
16	7.18 (1H, dd, $J = 8.5, 1.8$ Hz)	127.6 (CH)	β 3.06 (1H, dd, $J = 14.9, 6.0$)
17	α 2.69 (1H, dd, $J = 13.8, 7.7$ Hz) β 2.50 (1H, dd, $J = 7.7, 5.6$ Hz)	26.9 (CH ₂)	4.98 (1H, m)
18	4.96 (1H, br, t, $J = 8.0$ Hz)	124.2 (CH)	1.58 (3H, s)
19		137.3 (C)	17.1 (CH ₃)
20	1.68 (3H, s)	15.5 (CH ₃)	1.76 (3H, s)
21	2.06 (2H, m)	39.9 (CH ₂)	α 2.99 (1H, dd, $J = 14.9, 5.1$)
22	1.51 (2H, m)	24.8 (CH ₂)	β 2.89 (1H, dd, $J = 14.9, 6.0$)
23	1.75 (2H, m)	36.5 (CH ₂)	5.00 (1H, m)
24		144.8 (C)	1.71 (3H, s)
25	α 4.66 (1H, d, $J = 1.7$ Hz) β 4.69 (1H, d, $J = 1.7$ Hz)	109.9 (CH ₂)	1.60 (3H, s)
26	1.72 (3H, s)	21.3 (CH ₃)	2.47 (2H, d, $J = 6.9$ Hz)
27	1.30 (3H, s)	27.5 (CH ₃)	5.00 (1H, m)
28	1.22 (3H, s)	16.3 (CH ₃)	4.97 (1H, t, $J = 7.0$ Hz)
29	2.10 (2H, m)	28.4 (CH ₂)	1.67 (3H, s)
30	5.22 (1H, dd, $J = 9.2, 7.0$ Hz)	124.6 (CH)	1.99 (2H, m)
31		131.3 (C)	1.97 (2H, m)
32	1.72 (3H, s)	16.8 (CH ₃)	4.98 (1H, t, $J = 6.1$ Hz)
33	2.11 (2H, m)	39.6 (CH ₂)	1.67 (3H, s)
34	1.96 (2H, m)	23.6 (CH ₂)	1.54 (3H, s)
35	5.25 (1H, m)	122.8 (CH)	25.1 (CH ₃)
36		131.3 (C)	28.9 (CH ₂)
37	1.96 (3H, s)	16.9 (CH ₃)	39.8 (CH)
38	1.99 (3H, s)	24.9 (CH ₃)	α 1.92 (1H, m)
39	α 2.49 (1H, dd, $J = 14.0, 7.9$ Hz) β 2.40 (1H, dd, $J = 7.9, 6.0$ Hz)	25.5 (CH ₂)	β 2.15 (1H, m)
40	4.85 (1H, br t, $J = 7.9$ Hz)	123.8 (CH)	1.86 (2H, m)
41		133.8 (C)	α 4.68 (1H, d, $J = 1.9$ Hz)
42	1.89 (3H, s)	24.8 (CH ₃)	β 4.66 (1H, d, $J = 1.9$ Hz)
43	1.91 (3H, s)	17.3 (CH ₃)	α 4.65 (1H, d, $J = 1.8$ Hz)
			β 4.63 (1H, d, $J = 1.8$ Hz)
			1.64 (3H, s)
			17.9 (CH ₃)
			1.62 (3H, s)
			17.8 (CH ₃)

correlations were observed in the HMBC between the proton signals at δ_H 2.47 (H-24) and δ_H 1.84 (H-34) and carbon signals at δ_C 195.2, 50.9 and 208.6, ascribed to C-1, C-6 and C-5, respectively. This also confirmed the placement of geranyl and 2-(1-methylethenyl)-5-methylhex-5-enyl groups at position C-6. Hence compound **2** was established as novel 4,4-di(3-methylbut-2-enyl)-6-geranyl-1-hydroxy-2-(10-hydroxybenzoyl)-6-[2-(1-methylethenyl)-5-methylhex-5-enyl]-cyclohex-1-en-3,5-dione and the name semsinone B was adopted.

Compound **3** had a similar UV spectrum with that of **2** (250 and 352 nm), and had similar chromophore groups. The HRESIMS of compound **3** showed a pseudo-molecular ion at m/z 671.4233 $[M + H]^+$ that was consistent with the molecular formula C₄₃H₅₈O₆ indicating the addition of an OH group to the molecular mass of compound **2**. In the ¹H NMR spectrum, proton signals were similar to that of compound **2** except for the signal at δ_H 7.18 (H-11) for **2** that

was missing in compound **3**. Hence, only three proton signals were observed in the benzoyl moiety of compound **3**. Similarly, in the ¹³C NMR spectrum of compound **3** there was the addition of one quaternary carbon at δ_C 150.3 (C-11) as compared to compound **2** (Table 1). The remaining of the carbon and proton signals of **3** were similar to those of compound **2**. Hence compound **3** was characterised as a new 4,4-di(3-methylbut-2-enyl)-6-geranyl-1-hydroxy-2-(10-hydroxybenzoyl)-6-[2-(1-methylethenyl)-5-methylhex-5-enyl]-cyclohex-1-en-3,5-dione, semsinone C (**3**).

3. Experimental

3.1. General experimental procedures

NMR (¹H, ¹³C, COSY, DEPT 135, NOESY, HMBC and HSQC) spectra were recorded in CD₃OD with 0.1% TFA on a Bruker

instrument operating at 600 MHz for ^1H and 150 MHz for ^{13}C nuclei. Chemical shifts (δ) are expressed in ppm with residual solvent peaks as internal references. IR spectra were recorded on a PerkinElmer System 2000 FTIR spectrometer, using NaCl windows with dichloromethane as solvent against an air background. HRESIMS was performed on a Micromass Q-TOF Ultima mass spectrometer. Optical rotations were measured on a PerkinElmer 241 polarimeter. Silica gel type 60 (Merck) particle size 230–400 mesh ASTM were used for column chromatography. Prep.TLC utilized silica gel 60 PF_{254&366} spread on a 20 × 20 cm glass plates, 0.5 mm thick. Analytical TLC was performed on 20 × 20 cm pre-coated plates. 1 g vanillin + 95% MeOH + 5% conc. H_2SO_4 and FeCl_3 were used as spraying reagents. Sephadex® LH-20 was used for the final purifications.

3.2. Plant material

The stem bark of *G. semseii* was collected in July 2002 from Kihansi Forest Reserve, Morogoro region, Tanzania by Mr. Frank Mbago who also confirmed the identity of the plant. A voucher specimen # FM 1629, has been deposited at the Herbarium of the Institute of Traditional Medicine, Muhimbili University of Health and Allied Sciences, Dar es Salaam, Tanzania.

3.3. Extraction and isolation of compounds

The air-dried and powdered stem bark (200 g) of *G. semseii* was macerated with ethanol for 48 h. The extract was concentrated under reduced pressure at 40 °C at which 35 g of the crude extract was obtained. The column was packed using silica gel in petroleum ether, then 15 g of the crude extract was introduced and eluted with 100% petroleum ether, then adding EtOAc in increasing amount up to 100% then followed by increasing amount of MeOH up to 100% from which 40 fractions (each 100 ml) were collected. Fractions 1–5 contained less polar fatty acids as indicated in the TLC analysis and were not followed-up. Fractions 6–14 showed similar compositions hence were combined and fractionated by CC (gravity) on silica gel with Pet ether:EtOAc, 9:1 (250 ml) to give achilleol A (10 mg). Fractions 15–25 were combined and fractionated by CC (gravity) on silica gel with Pet ether:EtOAc, 1:1 (150 ml) followed by prepTLC using EtOAc:Pet ether, 1:4 (200 ml) to afford **1** (25 mg) and **2** (10 mg). Each compound was further purified on CC packed with Sephadex LH-20 and flushed with MeOH (100 ml). Fractions 26–40 were combined and fractionated by CC (gravity) on silica gel eluting with MeOH: CHCl_3 , 1:19 (150 ml) to afford compound **3** (7.5 mg).

5,5-dimethyl-6-geranyl-3-hydroxy-2-(13,14-dihydroxybenzoyl)-4-(3,7-dimethyloct-2,7-dienyl)-8-(3-methylbut-2-enyl)-bicyclo[3.3.1]nonan-2-en-1,9-dione, semsinone A (**1**): colourless oil (25 mg), HRESIMS: m/z 671.4229 $[\text{M} + \text{H}]^+$ (calcd. for $\text{C}_{43}\text{H}_{58}\text{O}_6$, 670.4233); IR: ν_{max} (NaCl) cm^{-1} : 3348, 1725, 1641; UV-vis: λ_{max} (MeOH) nm (log ϵ): 282 (4.9), 320 (4.6); $[\alpha]_D^{20} = +52^\circ$ (c0.1, CHCl_3), ^1H and ^{13}C NMR data, see Table 1.

4,4-di(3-methylbut-2-enyl)-6-geranyl-1-hydroxy-2-(10-hydroxybenzoyl)-6-[2-(1-methylethenyl)-5-methylhex-5-enyl]-cyclohex-1-en-3,5-dione, semsinone B (**2**): Brownish oil (10 mg), HRESIMS: m/z 655.4279 $[\text{M} + \text{H}]^+$ (calcd. for $\text{C}_{43}\text{H}_{58}\text{O}_5$, 654.4284), IR: ν_{max} (NaCl) cm^{-1} : 3350, 1730, 1650; UV-vis: λ_{max} (MeOH) nm (log ϵ): 250 (4.4), 352 (4.1); ^1H and ^{13}C NMR data, see Table 1.

4,4-di(3-methylbut-2-enyl)-6-geranyl-1-hydroxy-2-(10,11-dihydroxybenzoyl)-6-[2-(1-methylethenyl)-5-methylhex-5-

enyl]-cyclohex-1-en-3,5-dione, semsinone C (**3**): yellow gum (7.5 mg), HRESIMS: m/z 671.4265 $[\text{M} + \text{H}]^+$ (calcd. for $\text{C}_{43}\text{H}_{58}\text{O}_5$, 670.4233); IR: ν_{max} (NaCl) cm^{-1} : 3350, 1730, 1650; UV-vis: λ_{max} (MeOH) nm (log ϵ): 250 (4.4), 352 (4.1); ^1H and ^{13}C NMR data, see Table 1).

Acknowledgements

We would like to thank Mr. Frank Mbago for collection and identification of the plant material, Mr. S. Marape for running NMR spectral experiments. This study was supported by the University Science, Humanities and Engineering Partnership in Africa (USHEPIA). JJM thanks USHEPIA for the travel grant to the Department of Chemistry, University of Botswana for the research visit under Prof B.M. Abegaz.

References

- Akihisa, T., Koike, K., Kimura, Y., Sashida, N., Matsumoto, T., Ukiya, M., Nikaido, T., 1999. Acyclic and incompletely cyclized triterpene alcohols in the seed oils of theaceae and gramineae. *Lipids* 34, 1151–1157.
- Babu, V., Ali, S.M., Sultana, S., Ilyas, M., 1988. A biflavonoid from *Garcinia nervosa*. *Phytochemistry* 27, 3332–3335.
- Bennet, G.J., Lee, H.H., 1989. Xanthonenes from Guttiferae. *Phytochemistry* 28, 967.
- Chin, Y.W., Jung, H.A., Chai, H., Keller, W.J., Kinghorn, A.D., 2008. Xanthonenes with quinine reductase-inducing activity from the fruits of *Garcinia mangostana* (Mangosteen). *Phytochemistry* 69, 754–758.
- Cuesta-Rubio, O., Padron, A., Castro, H.V., Cosimo Pizza, C., Rastrelli, L., 2001. Aristophenones A and B. A new tautomeric pair of polyisoprenylated benzophenones from *Garcinia aristata*. *J. Nat. Prod.* 64, 973–975.
- Gustafson, K.R., Blunt, J.W., Munro, M.H.G., Fuller, R.W., McKee, T.C., Cardellina II, J.H., McMahon, J.B., Cragg, G.M., Boyd, M.R., 1992. The Guttiferones, HIV-inhibitory benzophenones from *Symphonia globulifera*, *Garcinia livingstonei*, *Garcinia ovalifolia* and *Clusia rosea*. *Tetrahedron* 48, 10093.
- Hay, A.E., Hélesbeux, J.J.H., Duval, O., Labaied, M., Grellier, P., Richomme, P., 2004. Antimalarial xanthonenes from *Calophyllum caledonicum* and *Garcinia vieillardii*. *Life Sci.* 75, 3077–3085.
- Lokvam, J., Braddock, J.F., Reichardt, P.B., Clausen, T.P., 2000. Two polyisoprenylated benzophenones from the trunk latex of *Clusia grandiflora* (Clusiaceae). *Phytochemistry* 55, 29–34.
- Mbwambo, Z.H., Kapingu, M.C., Moshi, M.J., Machumi, F., Apers, S., Cos, P., Ferreira, D., Marais, J.P.J., Berghe, D.V., Maes, L., Vlietinck, A., Pieters, L., 2006. Antiparasitic Activity of some Xanthonenes and Biflavonoids from the root bark of *Garcinia livingstonei*. *J. Nat. Prod.* 69, 369–372.
- Nilar, Nguyen, L.H.D., Venkatraman, G., Sim, K.Y., Harrison, L.J., 2005. Xanthonenes and benzophenones from *Garcinia griffithii* and *Garcinia mangostana*. *Phytochemistry* 66, 1718–1723.
- Nyemba, A.M., Mpondo, T.N., Connolly, J.D., Rycroft, D.S., 1990. Cycloartane derivatives from *Garcinia lucida*. *Phytochemistry* 29, 994–997.
- Oliveira, C.M.A., Porto, A.L.M., Biurich, V., Marsaioli, A.J., 1999. Two prenylated benzophenones from the floral resins of three *Clusia* species. *Phytochemistry* 50, 1073–1079.
- Permana, D., Lajis, N.H., Mackeen, M.M., Ali, A.M., Aimi, N., Kitajima, M., Takayama, H., 2001. Isolation and bioactivities of constituents of the roots of *Garcinia atrovirens*. *J. Nat. Prod.* 64, 976–979.
- Perry, L.M., Metzger, J. (Eds.), 1980. *Medicinal Plants of East and South-East Asia*. MIT Press, London, p. 175.
- Porto, A.L.M., Machado, S.M.F., Oliveira, C.M.A., Bittrich, V., Amaral, M.C.E., Marsaioli, A.J., 2000. Polyisoprenylated benzophenones from *Clusia* floral resins. *Phytochemistry* 55, 755–768.
- Suksamrarn, S., Suwannapoch, N., Phakhodee, W., Thanuhiranlert, J., Ratananukul, P., Chimnoi, N., Suksamrarn, A., 2003. Antimycobacterial activity of prenylated xanthonenes from the fruits of *Garcinia mangostana*. *Chem. Pharm. Bull.* 51, 857–859.
- Shadid, K.A., Shaari, K., Abas, F., Israf, D.A., Hamzah, A.S., Syakroni, N., Saha, K., Lajis, N.H., 2007. Cytotoxic caged-polyisoprenylated xanthonoids and a xanthone from *Garcinia cantleyana*. *Phytochemistry* 68, 2537–2544.
- Wu, C.C., Lu, Y.H., Wei, B.L., Yang, S.C., Won, S.J., Lin, C.N., 2008. Phloroglucinols with prooxidant activity from *Garcinia subelliptica*. *J. Nat. Prod.* 71, 246–250.
- Yang, N.Y., Han, Q.B., Cao, X.W., Qiao, C.F., Song, J.Z., Chen, S.L., Yang, D.J., Yiu, H., Xu, H.X., 2007. Two new xanthonenes isolated from the stem bark of *Garcinia lancilimba*. *Chem. Pharm. Bull.* 55, 950–952.