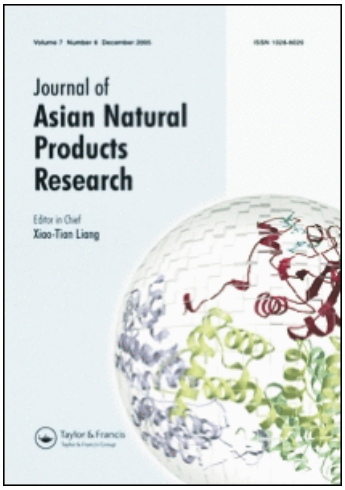

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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To cite this Article Hartati, Sri , Soemiati, Atiek , Wang, Hong-Bing , Kardono, Leonardus B. S. , Hanafi, Muhammad , Kosela, Soleh and Qin, Guo-Wei(2008) 'A novel polyisoprenyl benzophenone derivative from *Garcinia eugeniaefolia*', Journal of Asian Natural Products Research, 10: 6, 509 — 513
To link to this Article: DOI: 10.1080/10286020801966922
URL: http://dx.doi.org/10.1080/10286020801966922

Journal of Asian Natural Products Research
Vol. 10, No. 6, June 2008, 509–513

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A novel polyisoprenyl benzophenone derivative from *Garcinia eugeniaefolia*

Sri Hartati[a,b], Atiek Soemiati[b], Hong-Bing Wang[c], Leonardus B.S. Kardono[a], Muhammad Hanafi[a], Soleh Kosela[b]* and Guo-Wei Qin[c]*

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(*Received 2 February 2007; final version received 8 June 2007*)

A novel polyisoprenyl benzophenone derivative named eugeniaphenone (**1**) was isolated from the stem bark of *Garcinia eugeniaefolia* Wall. Its structure was elucidated by spectroscopic methods, including 1D and 2D NMR techniques, and confirmed by single-crystal X-ray diffraction analysis. It is the first example in which an isoprenyl unit formed a cyclobutane-containing side chain in the polyisoprenyl benzophenone derivatives.

Keywords: *Garcinia eugeniaefolia*; Cluciaceae; eugeniaphenone; polyisoprenyl benzophenone

1. Introduction

Garcinia species (Cluciaceae) are rich in various oxidized and isoprenylated xanthones and benzophenones,[1,2] of which some exhibited a wide range of biological and pharmacological activities including antimalarial,[3] growth inhibition of human leukemia cells, cytopathic inhibition of *in vitro* HIV infection and cytotoxicities.[2,4,5] The polyisoprenyl benzophenones are mostly found in *Garcinia* and its related genera. They are unique in the structures and stereochemistry, possessing a common 2,4,9-triketo-bicycle[3,3,1]nonane moiety with various modified isoprenylated chains in different linkage forms. The biological significance and structural novelties of such compounds have attracted our great interests for further chemical study, which resulted in the isolation of lateriflorone, a cytotoxic spiroxalactone with a novel skeleton from *Garcinia lateriflora* and gaudichaudiic acids F–I, the novel cytotoxic polyprenyl heptacyclic xanthonoids from *Garcinia gaudichaudii*.[5,6] In the course of our continuing study on genus *Garcinia*, we have investigated the species *Garcinia eugeniaefolia* Wall., a tropical plant distributed in Indonesia (Kalimantan and Sumatra Islands), Philippines, Malaysia and India, and its chemical constituents have never been reported previously. In this paper, we describe the isolation and structural elucidation of eugeniaphenone (**1**), a minor component with novel polyisoprenyl benzophenone structure from the stem barks of the plant.

2. Results and discussion

Eugeniaphenone (**1**) revealed a molecular formula $C_{38}H_{50}O_6$ by the EI-MS (*m/z* 602, $[M]^+$) and ^1H and ^{13}C NMR spectral data

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ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020801966922
http://www.informaworld.com

Table 1. ^{1}H and ^{13}C NMR spectral data of **1** (ppm, *J* in Hz)[a].

No.	^{1}H	^{13}C	HMBC (H → C)
1	–	210.4	
2	4.82 s	70.3	C_1, C_{10}, C_3, C_{11}
3	–	210.4	
4	–	77.5	
5	–	51.5	
6	1.42 m	48.3	C_5, C_8, C_{24}, C_{25}
7	2.52 m; 2.69 m	27.6	C_1
8	–	61.7	
9	–	210.4	
10	–	196.8	
11	–	118.8	
12	7.20 d (1.9)	115.8	C_{10}, C_{14}, C_{16}
13	–	146.8	
14	–	153.1	
15	6.71 d (8.3)	117.7	C_{13}, C_{16}
16	7.03 dd (8.3; 1.9)	121.6	C_{10}, C_{12}, C_{14}
17	1.70 m; 2.09 m	30.7	C_3, C_9
18	4.87 m	126.1	C_{17}, C_{19}
19	–	134.2	
20	1.20 s	31.2	C_{18}
21	1.51 s	18.7	C_{18}
22	1.22 s	23.9	C_4, C_5
23	0.99 s	27.8	C_6
24	1.71 m; 2.08 m	30.8	C_{25}
25	5.10 m	125.5	C_{26}
26	–	136.4	
27	1.62 s	23.6	C_{25}
28	1.64 s	18.8	C_{25}, C_{26}
29	1.62 m; 1.96 m	33.9	C_1, C_{30}
30	1.78 m	40.4	C_{29}
31	–	44.3	
32	2.25 m	51.5	C_{36}
33	2.02 m; 2.18 m	42.1	C_{30}, C_{31}
34	0.84 s	16.9	C_{32}
35	1.72 s	26.9	C_{30}
36	–	147.2	
37	1.68 s	26.5	C_{38}
38	4.52 s; 4.74 s	110.2	C_{32}

[a] In CD_3OD, at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR spectra.

analyses. In the EI-MS, the fragmentation peaks at *m/z* 137 and 69 suggested the presence of a 3,4-dihydroxybenzoyl group ($C_7H_5O_3$) and isoprenyl substituents (C_5H_9), respectively. The IR spectrum exhibited absorption bands for hydroxyl (3550 and 3303 cm^{-1}) and both conjugated and non-conjugated carbonyl (1720 and 1634 cm^{-1}) groups. The ^{1}H NMR spectrum showed the signals for nine methyl (four aliphatic and five olefinic), four olefinic protons (two isolated and two terminal) and a 1,3,4-trisubstituted benzene (Table 1). The ^{13}C NMR spectrum revealed 38 carbons including nine methyl (five olefinic), six methylene (one olefinic), nine methine (three aromatic, two olefinic), and 14 quaternary (two oxygenated aromatic and one non-oxygenated aromatic, four carbonyl and three olefinic) carbons. This ^{1}H and ^{13}C NMR

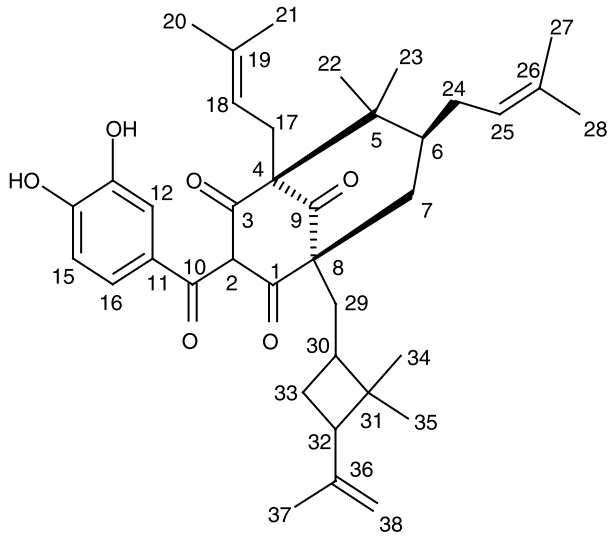

Figure 1. Structure of eugeniaphenone (**1**).

spectral feature suggested that **1** (Figure 1) was a polyisoprenyl benzophenone derivative containing a 3,4-dihydroxybenzoyl group, a bicyclic[3,3,1]nonane-2,4,9-trione moiety and four isoprenyl substituents, like camboginol isolated from other *Garcinia* species[7].

Further comparison of the NMR spectral data of **1** with those of other polyisoprenyl benzophenone derivatives suggested that **1** possessed a special side chain consisting of eight carbons, in which two isoprenyl units formed a four-membered ring. The HMBC correlations (Figure 2) confirmed the proposed structure as a polyisoprenyl benzophenone derivative with a cyclobutane-containing side chain. Due to the stereochemical complexity of this compound, **1** was submitted for X-ray crystallographic analysis. The results (Figure 3) showed that compound **1** possessed a similar

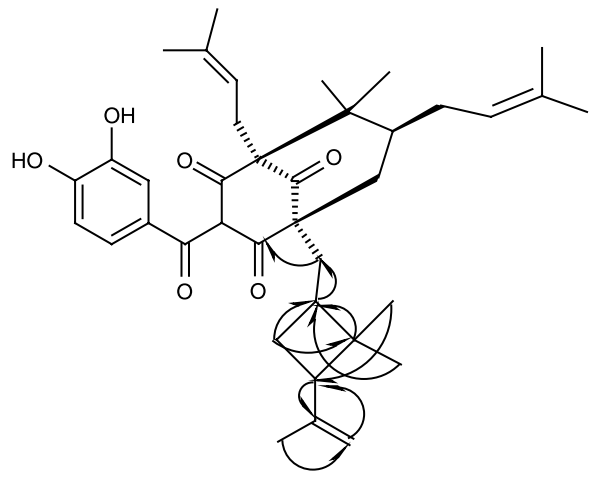

Figure 2. Key HMBC correlations of **1**.

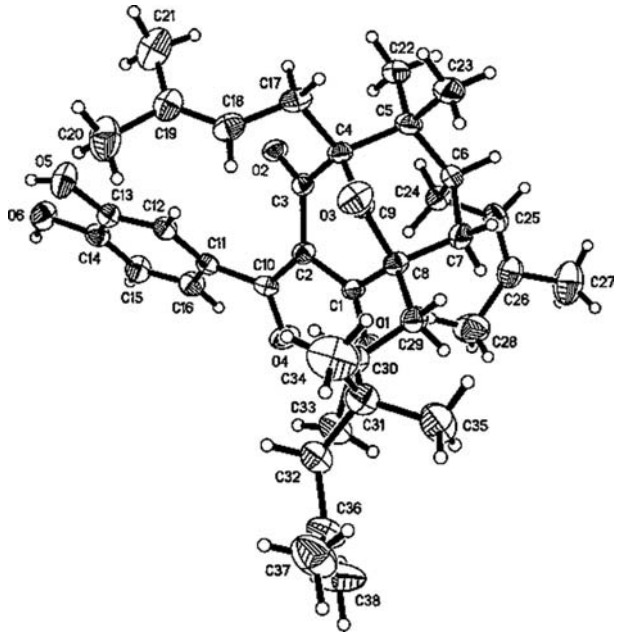

Figure 3. Crystal structure of **1**.

stereochemical structure to that of camboginol, a known polyisoprenyl benzophenone derivative, but having a different side chain. The C_8-cyclobutane-containing side chain, which was formed by the rearrangement of isoprenyl units, is unique and first discovered in the polyisoprenyl benzophenone derivatives.

3. Experimental

3.1 General experimental procedures

Melting point was determined on a SGW X-4 micro-melting point apparatus and uncorrected. The IR spectrum was measured on a Nicolt–Magna 750 spectrophotometer. The mass spectrum was recorded using a MAT-241 mass spectrometer. The NMR spectra were recorded on Bruker AM-400 spectrometers. X-ray analysis was run on Bruker SMART CCD area-detector diffractometer.

3.2 Plant material

The stem bark of *Garcinia eugeniaefolia* was collected from Riau Islands forest of Indonesia in July 2003 and identified at Herbarium Bogoriense. A voucher specimen (No. 20030701) is deposited in Herbarium Bogoriense, Indonesia.

3.3 Extraction and isolation

The dried stem bark (2 kg) of *G. eugeniaefolia* was extracted with *n*-hexane at room temperature to give a hexane extract (10.4 g). The hexane extract was separated by repeated flash column chromatography to afford euginiophenon **1** (300 mg). The residue was further extracted with acetone to give an acetone extract (150. 1 g). The acetone extract (20 g) was separated by repeated flash column chromatography also to afford 122 mg of euginiophenon **1**.

*3.3.1 Eugeniaphenone **1***

Yellow needles, mp 156–157°C; IR (KBr) ν_{max} (cm^{-1}): 3550, 3303 (OH), 1720, 1634 (C═O); ^1H and ^{13}C NMR spectral data (Table 1); EI-MS *m/z*: 602 $[M]^+$(8), 465 (100), 341 (65), 231 (56), 137 (48), 69 (44).

3.4 The crystallographic data of 1

A yellow crystal with dimensions $0.501 \times 0.137 \times 0.126\,mm^3$; empirical formula $C_{38}H_{50}O_6$; molecular weight 601.77; crystal system orthorhombic; space group *P2*; unit cell dimension: $a = 8.999$ (8), $b = 18.3452$ (17), $c = 23.760$ (2) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$; volume 3922.5(6) A^3; $Z = 4$; $F(000) = 1300$. The intensity data within the θ range of 1.40–25.50° were collected at 273 K and the completeness to $\theta(25.50)$ is 100%. A total of 20,885 reflections were collected, of which 7292 reflections were observed on the basis of $I > 2\sigma(I)$. The final R and R_w were 0.0853 and 0.2033, respectively, with goodness of fit of 0.992. The structure was solved using Fourier transformation techniques and refined by a full-matrix least-squares calculation on F^2.

References

[1]Y.J. Xu, S.G. Cao, X.H. Wu, Y.H. Lai, B.H.K. Tan, J.T. Pereira, S.H. Goh, G. Venkatraman, L.J. Harrison, and K.Y. Sim, *Tetrahedron Lett.* **39**, 9103 (1998).

[2]S.G. Cao, H.L. Valerie, X.H. Wu, K.Y. Sim, B.H.K. Tan, J.T. Piriera, and S.H. Goh, *Tetrahedron* **54**, 10915 (1998).

[3]K. Likhitayawuid, T. Padungcharoen, and J. Krungkrai, *Planta Med.* **64**, 69 (1998).

[4]K. Matsmoto, Y. Akao, E. Kobayashi, K. Ohguchi, T. Ito, T. Tanaka, M. Inuma, and Y. Nojawa, *J. Nat. Prod.* **66**, 1124 (2003).

[5]Y.J. Xu, S.C. Yip, S. Kosela, E. Fitri, M. Hanafi, S.H. Goh, and K.Y. Sim, *Organic Lett.* **2**, 3945 (2000).

[6]S. Kosela, S.G. Cao, X.H. Wu, J.J. Vittal, T. Sukri, Masdianto, S.H. Goh, and K.Y. Sim, *Tetrahedron Lett.* **40**, 157 (1999).

[7]A.V.R. Rao, G. Venkatswamy, and A.D. Pendse, *Tetrahedron* **21**, 1975 (1980).