A XANTHONE FROM THE STEM BARK OF MANGGIS HUTAN (*Garcinia bancana*)

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ABSTRACT

A xanthone, 1,5-dihidroxy-3,6-dimethoxy-2,7-bis-(3-methylbutenyl)xanthone had been isolated from the stem bark of Garcinia bancana *Miq. The structure of this compound was elucidated by analysis of spectroscopic data, especially using 1D and 2D NMR spectroscopic data.*

Keywords : Xanthone, 1,5-dihidroxy-3,6-dimethoxy-2,7-bis-(3-methylbutenyl)xanthone, G. bancana

INTRODUCTION

Garcinia is the most important genus of the Guttiferae family, widely distributed in tropical Asia, Africa, and Polynesia [1]. The genus is known to be rich in oxygenated xanthone [2], prenylated xanthone [3], and polyisoprenylated benzophenones [4,5]. Some of them exhibit various biological activities such as antimicrobacterial, antioxidant, cytotoxic and anti malaria activities [6-9]. *Garcinia bancana* Miq. is distributed throughout Southern Thailand, Malaysia and Indonesia. In our continuing phytochemical investigation of *Garcinia* plants found in Indonesia, we have examined the stem bark of *G. bancana*. This plant is locally named *manggis hutan* [1,10]. In this paper we described the isolation and structure elucidation of compound **(**1,5-dihidroxy-3,6-dimethoxy-2,7-bis-(3-methyl-butenyl)xanthone, from the methanol extract of the stem bark of *G. bancana*. This is the first report on the isolation of compound from this plant. The structure of this compound was determined based on their UV, IR, and NMR 1D and 2D spectroscopic data.

EXPERIMENTAL SECTION

General Experimental Procedure

UV and IR spectra were measured with spectrophotometers Beckman DU-700 and Shimadzu FTIR 8400. ^{1}H and ^{13}C NMR spectra was recorded JEOL JNM ECA-500 500 MHz (^{1}H) and 125 MHz (^{13}C) using internal standard TMS. Vacuum liquid chromatography (VLC) was carried out using Merck Si gel 60 GF_{254} (230-400 Mesh) and column chromatography using Si gel Merck G 60 (70-230 Mesh), thin layer chromatography (TLC) analysis was performed on precoated Si Gel plates (Merck Kiesel gel 60 GF_{254}, 0.25 mm 20 x 20 cm.

Plant material

Sample of the stem bark of *G. bancana* was collected on April 2006 from the Sarasah Bonta Payah kumbuh, Sumatera Barat. The plant was identified by the staff at the Herbarium Anda, Andalas University, Padang and a voucher specimen had been deposited at the herbarium.

Extraction and isolation

The powdered of the stem bark G *.bancana* (3 Kg) was extracted by maceration technique three times with hexane, dichloromethane and methanol respectively for 5 days at room temperature. Evaporation of each extract (n-hexane, dichloro-methane and methanol) to dryness *in vacuo*, afford

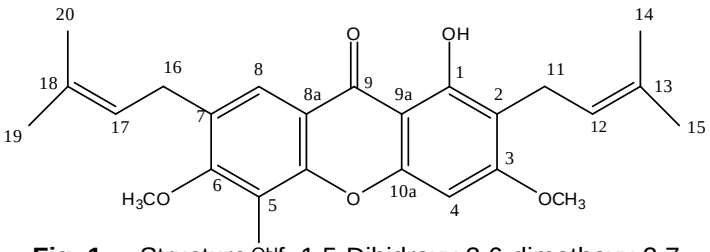

Fig 1. Structure of 1,5-Dihidroxy-3,6-dimethoxy-2,7-bis-(3-methyl-butenyl)xanthone

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Table 1. ^{1}H NMR and 13C NMR data (chloroform-d_1) for 1,5-dihidroxy-3,6-dimethoxy-2,7-bis-(3-methyl-butenyl)xanthone

Posisi	δ_H (mult., J_{Hz})	δ_C	DEPT
1	12.98 (*s*)	159.7	C
2		112.2	C
3		164.3	C
3-OMe	3.92 (s)	56.2	CH_3
4	6.53 (*s*)	89.9	CH
4[a]		157.0	C
5	5.58 (*br s*)	136.7	C
6		150.0	C
6-OMe	3.97 (*s*)	61.3	CH_3
7		131.5	C
8	7.62 (*s*)	116.7	CH
8[a]		114.1	C
9		180,6	C
9[a]		100,1	C
10[a]		154.0	C
11	3.36 (*d*, 7.5)	21.6	CH_2
12	5.23 (*t*, 7.5)	121.9	CH
13		132.2	C
14	1.80	18.0	CH_3
15	1.68	26.2	CH_3
16	3.42 (*d*, 7.3)	28.6	CH_2
17	5.30 (*t*, 7.3)	1221	CH
18		133.8	C
19	1.76	26.0	CH_3
20	1.74	17.9	CH_3

Table 2. NMR correlations data for 1,5-dihidroxy-3,6-dimethoxy-2,7-bis-(3-methylbutenyl)xanthone

Position H	HMQC	HMBC	COSY
1	C-1		
3-OMe	C-3-OMe	C-3	
4	C-4	C-4a	
5-OH	C-5		
6-OMe	C-6-OMe	C-6,	
8	C-8	C-10a	
H-11	C-11	C-2,C-3, C-13	H-12, H-14, H-15
H12	C-12	C-2	H-11, H-14, H-15
14	C-14	C-12, C-13, C-15	
15	C-15	C-12, C-13, C-14	
16	C-16	C-6, C-7, C-18	H-17, H-19, H-20
17	C-17		H-16, H-19, H-20
19	C-19	C-17, C-18, C-20	
20	C-20	C-17, C-18, C-19	

n-hexana extract (30 g), dicloromethane (55 g) and methanol (30 g). Methanol extract was subjected to vacum liquid chromatography eluted with a gradient system (*n*-hexana, *n*-hexana: EtOAc = 9:1; 8:2; 7:3; 6:4 and EtOAc) to afford 5 fractions A1 – A5. Fraction 2 was further purified column chromatography (eluted with gradient system *n*-hexana, *n*-hexana : EtOAc = 9:1; 8:2; 7:3 and EtOAc) to afford 4 subfraction. Subfraction 2 after purification with recrystalization gave a pure compound (7 mg).

This compound obtained as a yellow crystal, UV: λ_{max} absorption at 261, 312 and 368 nm. IR (KBr) V_{maks} cm^{-1} 3444 (OH), 2962, 2920 (C-H alifatic), 1651(carbonil chelating), 1600, 1569 dan 1465 $cm^{-}1$ (benzena derivated) and 1172 (C-O ether). ^{1}H NMR (chloroform-d_1, 500 MHz) δ_H ppm, ^{13}C NMR (chloroform-d_1, 125 MHz) δ_C ppm see Table 1, and correlation H-C HMQC, HMBC dan H-H COSY spectrum see Table 2.

RESULT AND DISCUSSION

The methanol extract of the stem bark of *G. bancana* was subjected to chromatographic purification to afford one xanthone compound. The structure was elucidating using 1D and 2D NMR spectroscopic data. The ^{13}C NMR signals were assigned from DEPT, HMQC, HMBC and COSY spectras. The ^{1}H and ^{13}C spectra data also compared with those reported in the literature.

The pure compound was obtained as a yellow crystal. The UV spectrum showed λ_{max} absorption at 261, 312 and 368 nm characteristic to xanthone nucleus [11]. The IR spectrum exhibited absorptions for hydroxyl (3444), C-H aliphatic (2920, 2962), carbonyl (1651), aromatic (1600, 1569 and 1465 cm^{-1}) and ether (1172 cm^{-1}). The ^{1}H NMR and ^{13}C HNMR spectra of compound (Table 1) showed characteristic signals for prenylated xanthone derivated [12]. ^{1}H NMR Spectrum showed peaks for one prenyl group at [δ_H 3.36 (2H, d, *J*= 7.5), δ_H 5.23 (1H, t, *J*=7.5), δ_H 1.80 (3H, s) and δ_H 1.68 (3H, s)], prenyl group others at [δ_H 3.42 (2H, d, *J*=7.3), δ_H 5.30 (1H, d, *J*=7.3), δ_H 1.36 (3H, s) and δ_H 1.74 (3H, s)], two methoxyl group at δ_H 3.97 (3H, s) and δ_H 3.92 (3H, s), two hydroxyl group at δ_H 12.98 (1H, s) and δ_H 5.58 (1H, br s) and two proton aromatic at δ_H 6.53 (1H ,s) and δ_H 7.62 (1H, s). DEPT spectrum showed six carbon methyl at δ_C 164.3 (C-3-OMe), 150.0 (C-6-OMe), 18.0 (C-14), 26.2 (C-15), 26.0 (C-19) and δ_C 17.9 (C-20) ppm, two carbon methylene at δ_C 21.5 (C-11), and δ_C 28.6 (C-16), four carbon methyne at δ_C 89.9 (C-4), 116.7 (C-8) 121.9 (C-12) and δ_C 122.1 (C-17) and thirteen carbon

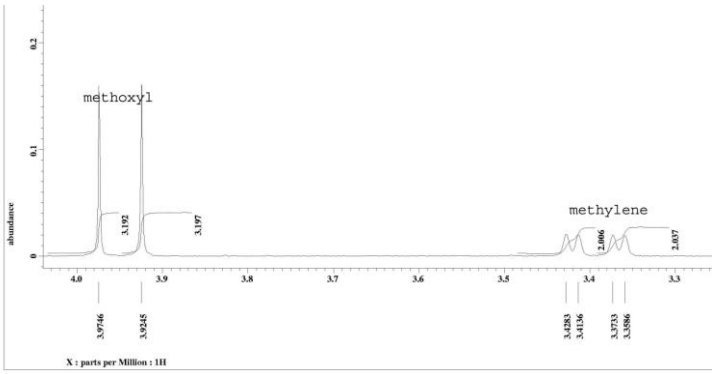

Fig 2. ^{1}H NMR spectrum

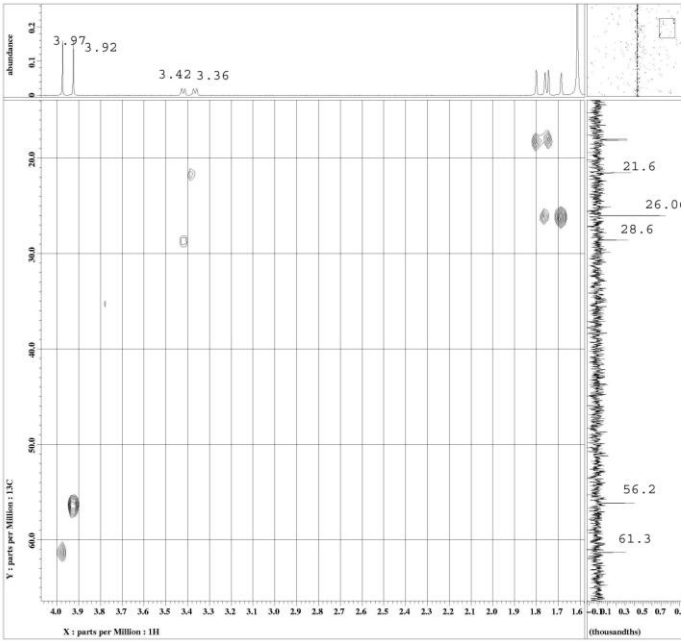

Fig 3. HMQC spectrum

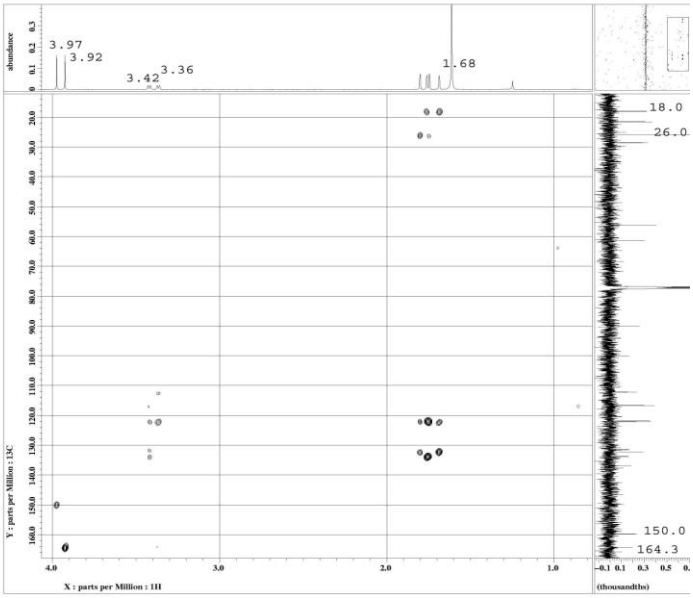

Fig 4. HMBC spectrum

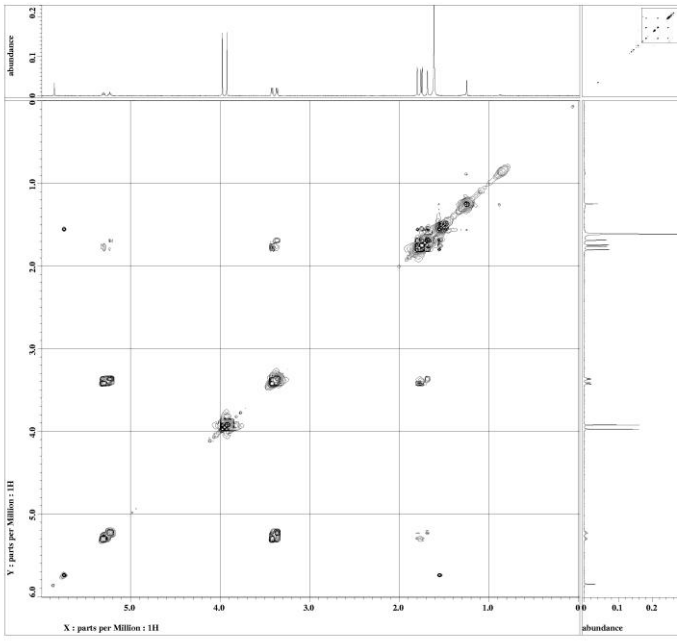

Fig 5. COSY spectrum

Fig 6. HMBC correlations from two prenyl group

quaternary at δ_C 159.7 (C-1), 112.2 (C-2), 164.3 (C-3), 157.0 (C-4a), 136.7 (C-5), 150.0 (C-6), 131.5 (C-7), 114.1 (C-8a), 180.6 (C-9), 100.1 (C-9a), 154.0 (C-10a), 132.2 (C-13), and δ_C 133.8 (C-18) ppm.

From HMQC, the methylene proton signal δ_H 3.36 ppm showed a connection to a carbon signal at δ_C 21.5 ppm and HMBC showed correlations between the methylene protons at δ_H 3.36 (2H, H-11) and quaternary carbons at δ_C 112.2 (C-2), 164.3 (C-3) and δ_C 132.2 (C-13). In the COSY spectrum showed that proton at δ_H 3.36 (H-11) coupled with a methyne group at δ_H 5.23 ppm (H-12) as well as with two methyl groups at δ_H 1.80 (H-14) and δ_H 1.68 (H-15). Signal at δ_H 3.42 (2H-16) connected to a carbon δ_C 28.58 and long correlations with carbons signal at δ_C 150.0 (C-6), δ_C 131.5 (C-7) and δ_C 133.8 (C-18). In the COSY spectrum showed that proton coupled with a methylen proton at δ_H 5.30 (H-17), and methyl proton at δ_H 1.76 (H-19) and δ_H 1.74 (H-20). Furthermore, the position of the prenyl group at C-2 and C-7 were deduced from HMBC long range correlations between proton at 3,36 (H-11) with carbon at 112,2 (C-2) and 164,3 (C-3) and proton at 3.42 with carbon at 116,7 (C-8) and 131,4 (C-7). HMBC correlations from two prenyl group can see at Fig 6.

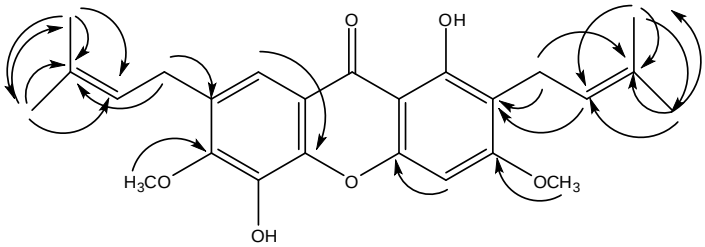

Fig 7. HMBC correlations in 1,5-Dihidroxy-3,6-dimethoxy-2,7-bis-(3-methyl-butenyl)xanthone.

In the HMQC spectrum also showed the proton methyl from methoxyl group at δ_H 3.92 connected to carbon signal at δ_C 56.2, proton at δ_H 3.97 connected to carbon at δ_C 61.9. In HMBC spectrum proton at δ_H 3.92 showed long correlation with carbon signal at 164,50 (C-3), and proton at δ_H 3,97 long range correlation to carbon at δ_C 150 (C-6) The methoxyl group were placed at C-3 and C-6, adjacent to the prenyl group due to its HMBC correlation with C-3 and C-6. In HMQC spectrum showed proton at δ_H 7.62 connected to carbon at δ_C 116.7 (C-8) and long correlation to carbon at δ_C 154 (C-10a), proton at δ_H 6.53 connected to carbon at δ_C 89.9 (C-4) and long correlation to carbon at δ_C 157 (C-4a). The position of the hydroxyl group were determined to be at δ_C 159,7 (C-1) and δ_C 136,7 (C-5). Correlation at HMBC spectrum can see at Fig 7.

Therefore was determined as 1,5-Dihidroxy-3,6-dimethoxy-2,7-bis-(3-methyl-butenyl)xanthone. This is the first report on the isolation of compound from this plant.

CONCLUSION

Xanthone, prenylated xanthone type: 1,5-Dihidroxy-3,6-dimetoxy-2,7-bis-(3-methyl-butenyl)-xanthone, had been isolated from methanol extract of stem bark *G. bancana*. The structure of this compound was determined based on NMR data.

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