A diprenylated xanthone, 1,5-dihydroxy-3-methoxy-4,7-diprenylxanthone (1) had been isolated for the first time from the dichloromethane extract of the stem bark of Garcinia griffithii, together with 1,7-dihydroxyxanthone (2) and polyisoprenylated benzophenone, guttiferone I (3). The structure of these compounds were determined on the basis of spectroscopic data including UV, IR, $^1$H NMR, $^{13}$C NMR, HMQC, HMBC and COSY. 

Keywords: diprenylated xanthone, 1,5-dihydroxy-3-methoxy-4,7-diprenylxanthone, Garcinia griffithii

INTRODUCTION

The genus Garcinia (Guttiferae) is known to produce a variety of biologically active metabolites such as polyisoprenylated benzophenone and xanthone [1,2]. Some of them exhibited a wide range of biological activities such as cytotoxic, antifungal, antimicrobial, antioxidant, antiinflammatory, and antiHIV activities [3,4]. Garcinia griffithii T. Anders. is a medium-sized tree found in South East Asia [5]. No medicinal uses are recorded for this species although it has been used as a fruit tree [6]. As part of a phytochemical study of our research, we have previously reported the presence of 1,7-dihydroxyxanthone (2) [7] and guttiferone I (3) [8] and now describe the isolation and structural elucidation of further constituent of the stem bark of G. griffithii collected in West Sumatra.

EXPERIMENTAL SECTION

Materials

Vacuum Liquid Chromatography (VLC) was carried out using Merck Si Gel 60 GF254 (230-400 Mesh), column chromatography using Si Gel 60 (70-230 mesh), TLC analysis was performed on Si Gel plates (Merck kieselger 60 GF254, 0.25 mm, 20x20 cm). Solvents were of technical grade and were distilled before use.

Instrumentation

Melting point was determined on a micromelting point apparatus UV and IR spectra were measured with Cary Varian 100 Conc. and Shimadzu FTIR 8400 spectrophotometers, respectively. The $^1$H and $^{13}$C NMR spectra were recorded using JEOL JNM ECA-500 FTNMR spectrometer, operating at 500 MHz ($^1$H) and
125 MHz (13C) with TMS as an internal reference and CDCl3 as a solvent.

**Plant material**

Stem bark of *G. griffithii* was collected on April 2006 from the Sarasah Bonta, Lembah Arau, Kabupaten Lima Puluh Kota, West Sumatra. The plant was identified by the staff at the Andalas University Herbarium (ANDA), Padang and voucher specimen had been deposited at the Herbarium.

**Extraction and isolation of the compounds**

Powdered stem bark (1 kg) of the plant was successively extracted into three fractions with hexane (35.2 g of dry weight), dichloromethane (23.5 g), and methanol (125.4 g). A portion (20 g) of the total dichloromethane extract was fractionated by VLC eluted with hexane- dichloromethane of increasing polarity and dichloromethane-methanol (9:1, 8:2, and 7:3) to given six fractions F1–F6 (2.61; 2.23; 1.71; 7.98; 4.04; and 5.80 g respectively). The first fraction, F1 (2.50 g) was further fractionated by column chromatography eluted with hexane-ethylacetate of increasing polarity to given five fractions F1.1–F1.5. Purification at the third fractions, F1.3 by column chromatography eluted with hexane-ethylacetate (8:2) afforded compound 1 (6 mg). Fraction F4 (4.91 g) was further fractionated by column chromatography eluted with hexane-ethylacetate (8:2) afforded compound 1 (6 mg). Fraction F4.1 (20 g) was further fractionated by column chromatography eluted with hexane-ethylacetate of increasing polarity to given five fractions F4.1–F5.5. Fraction F4.1 had been recrystalization afforded compound 2 (10 mg). Fraction F4.4 had been recolumn chromatography eluted with hexane-dichloromethane (4:6) afforded compound 3 (5 mg).

**RESULT AND DISCUSSION**

The dichloromethane extract from the stem bark of *Garcinia griffithii* had been isolated a diprenylated xanthone, 1,5-dihydroxy-3-methoxy-4,7-diprenylxanthone (1) as a yellow solid, m.p. 153-155°C. The UV spectrum showed absorptions at \( \lambda_{\text{max}} \) 236 and 255 nm revealed aromatic and conjugated carbonyl chromophores. Some bathochromic shifts of absorption bands in the spectrum (\( \lambda_{\text{max}} \) 205, 368 nm) suggested the presence of xanthone skeleton [9]. The IR spectrum exhibited bands for hydroxyl (3375.4 cm\(^{-1}\)), alifatic C-H (2923.9 and 2854.5 cm\(^{-1}\)), carbonyl (1643.2 cm\(^{-1}\)), aromatic C=C (1600.8, 1581.5, 1481.2 cm\(^{-1}\)) and C-O eter (1115 cm\(^{-1}\)).

The \(^1H\)-NMR spectrum (Fig 1) revealed the presence of three singlet aromatic signal at \( \delta_H \) 6.14, 6.37, and 7.59 ppm, one methoxy group at \( \delta_H \) 3.90 ppm (3H, s), two hydroxyl and two prenyl group. The presence of a chelated hydroxyl and another one hydroxyl group showed by the signal at \( \delta_H \) 13.13 ppm (1H, s), 5.67 ppm (1H, s). One of prenyl group characterized by the signal at \( \delta_H \) 3.50 ppm (2H, d, J=7.3, H-1'), 5.21 ppm (1H, t, J=7.3, H-2'), 1.85 ppm (3H, s, H-4'), 1.70 ppm (3H, s, H-5') respectively. The other of prenyl group characterized by the signal at \( \delta_H \) 3.42 ppm (2H, d, J=7.4, H-1''), 5.34 ppm (1H, t, J=7.4, H-2''), 1.75 ppm (3H, s, H-4''), 1.77 ppm (3H, s, H-5'') respectively. The \(^13\)C NMR spectrum revealed the presences of 24 carbon resonances due to a carbonyl carbon, 12 aromatic carbon, one methoxyl group and 10 carbon of two prenyl group.

The position of the side chains were assigned from the HMBC spectrum (Table 1). The methylen...
Table 1. $^1$H (500 MHz), $^{13}$C (125 MHz), HMBC and COSY data for 1 in CDCl$_3$

<table>
<thead>
<tr>
<th>No.</th>
<th>C</th>
<th>$^1$H (ppm)</th>
<th>$^{13}$C (ppm)</th>
<th>HMBC</th>
<th>COSY</th>
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<tr>
<td>1</td>
<td></td>
<td>162.3</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td></td>
<td>6.37 (1H,s)</td>
<td>94.5</td>
<td>103.1, 107.5, 162.3</td>
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</tr>
<tr>
<td>3</td>
<td></td>
<td>163.8</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td></td>
<td>107.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td></td>
<td>153.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>6.14 (1H,s)</td>
<td>113.5</td>
<td>125.5, 147.9</td>
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</tr>
<tr>
<td>6</td>
<td></td>
<td>147.9</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>7</td>
<td></td>
<td>125.5</td>
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<td>8</td>
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<td>7.59 (1H,s)</td>
<td>117.2</td>
<td>143.9, 147.9, 180.9</td>
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<tr>
<td>8a</td>
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<td>103.1</td>
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</tr>
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<td>10a</td>
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<td>143.9</td>
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<td>1'</td>
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<td>3.50 (2H,d,J=7.3)</td>
<td>21.9</td>
<td>107.5, 123.0, 131.9, 153.9, 163.8</td>
<td>5.21, 1.70</td>
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<tr>
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<tr>
<td>3'</td>
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<tr>
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<td></td>
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<td>25.8, 123.0, 131.9</td>
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<td>3.42 (2H,d,J=7.4)</td>
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<td>121.2</td>
<td></td>
<td>3.42</td>
</tr>
<tr>
<td>3''</td>
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<td></td>
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<tr>
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<td></td>
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<td>163.8</td>
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<td>5.67 (1H,s)</td>
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</table>

protons at $\delta_H$ 3.50 (H-1') showed five correlations [$^2$J: C-4 (107.5), C-2' (123.0); $^2$J: C-3' (131.9), C-4a (153.9), C-3 (163.8)] which required the placemen of one of the 3-methylbut-2-enyl groups at C-4. The methylene protons at $\delta_H$ 3.42 (H-1") showed five correlations [$^2$J: C-7 (125.5), C-2" (121.2); $^2$J: C-3" (134.5), C-6 (147.9), C-8 (117.2) which required the placemen of the other 3-methylbut-2-enyl groups at C-7. The methoxy proton at $\delta_H$ 3.90 showed correlation with $^2$J: C-3, which required the placemen of one methoxy groups at C-3.

Three aromatic proton at $\delta_H$ 6.37 showed three correlations [$^2$J: C-1 (162.3); $^2$J: C-4 (107.5), C-9a (103.1)]. $\delta_H$ 6.14 showed two correlations [$^2$J: C-6 (147.9); $^2$J: C-7 (125.5)] and $\delta_H$ 7.59 showed three correlations [$^2$J: C-6 (147.9), C-9 (180.9), and C-10a (143.9)] which required the placemen of three aromatic proton at C-2, C-5 and C-8, respectively. The hydroxyl proton at $\delta_H$ 13.13 showed correlation with $^2$J: C-2 (94.5) and the other hydroxyl proton at $\delta_H$ 5.67 correlation with $^2$J: C-6 (147.9), which required the placemen of two hydroxyl groups at C-1 and C-6, respectively. Correlation $^1$H-$^{13}$C HMBC (Fig 2 and Fig 3).

The allylic methylene proton at $\delta_H$ 3.50 (H-1') a COSY cross-peak to methine and methyl protons at $\delta_H$ 5.21 (H-2') and 1.70 (H-5') respectively, $\delta_H$ 5.21 (H-2')
Figure 3. HMBC spectrum of 1: correlation of H-1'; H-2'' and 3-OCH₃ (CDCl₃, 500 MHz).

Fig 4. Arrows denote key HMBC correlations and bold lines indicate COSY cross peak for 1

cross-peak to 3.50 (H-1'), and δH 1.70 (H-5') cross-peak to 3.50 (H-1'). The alillic methylen proton at δH 3.42 (H-1'') a COSY cross-peak to methine and methyl protons at δH 5.34 (H-2'') and 1.77 (H-5'') respectively, δH 5.34 (H-2'') cross-peak to 3.42 (H-1''), δH 1.70 (H-5'') crosspeak to 3.42 (H-1'').The methoxy protons at δH 3.90 /δC 56.3 correlated with C-3 (163.8). The HMBC and COSY correlation of 1 (Fig 4).

CONCLUSION

A diprenylated xanthone, 1,5-dihydroxy-3-methoxy-4,7-diprenylxanthone had been isolated from the dichloromethane extract of the stem bark of Garcinia griffithii, together with 1,7-dihydroxyxanthone (2) and polyisoprenylated benzophenone, guttiferone I (3). Existence of compound 1 owning important meaning at chemotaxonomy from Garcinia genus and add kinds of xanthone which have been found at G. griffithii.

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REFERENCES