GARCIDUOLS A AND B, NEW BENZOPHENONE-XANTHONE DIMERS, FROM *GARCINIA DULCIS*

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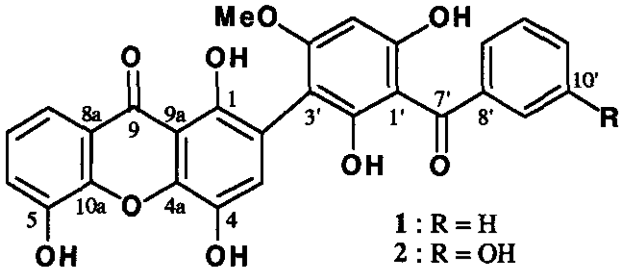
Abstract — From the roots of *Garcinia dulcis* (Guttiferae), two new compounds, garciduols A and B, were isolated. The skeleton was a dimer composed of a xanthone and a benzophenone.

In continuation of our phytochemical studies[1-5] on Guttiferaeous plants oriented to search for biological active principles, the chemical constituents (xanthones, benzophenones, anthrones *etc.*) isolated from some plants of *Garcinia*,[1,2] *Calophyllum*,[3] *Harngna*[4] and *Mammea*[5] were characterized. In a preceding paper, the structures of some xanthones with C_5 and/or C_{10} units in the bark or the roots of *Garcinia dulcis* Kurz. were revealed.[6] Further investigation into an acetone extract of the roots of the plant resulted in isolation of two compounds. This communication deals with the structural determination of garciduols A and B with a new skeleton of benzophenone-xanthone dimer.

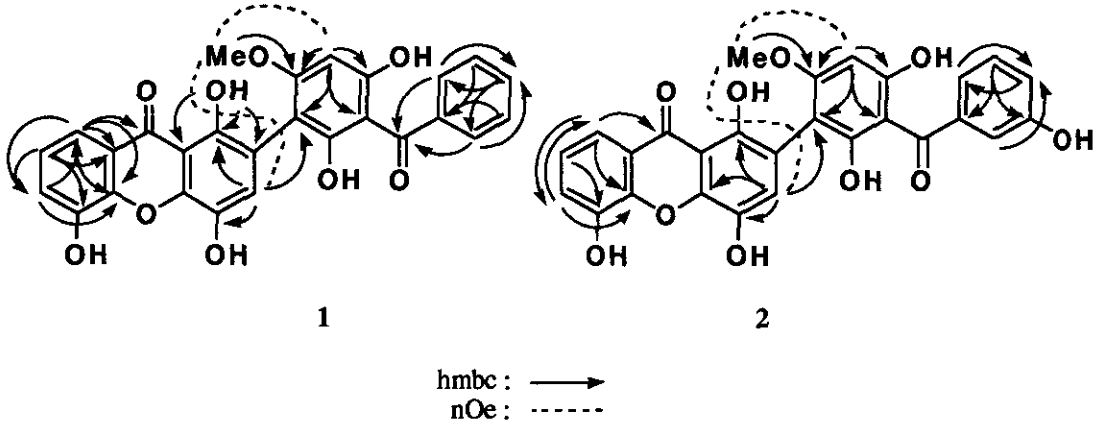
Garciduol A (**1**),[7] a yellow amorphous powder, gave positive to $FeCl_3$ and Gibbs reagent. The $[M]^+$ at *m/z* 486.0959 in the high-resolution eims corresponds to $C_{27}H_{18}O_9$. The ^1H nmr spectrum showed ten aromatic protons, five hydroxyls including a chelated one and a methoxyl group. Eight aromatic protons among them were the hydrogens assigned to a 1,2,3-trisubstituted and a monosubstituted benzene ring by their coupling constants and the other two were allotted to the isolated hydrogens. In the ^{13}C nmr spectrum, two carbonyl carbons (δ 183.3 and 200.0) were observed. The hmbc spectrum (Figure 2) showed the correlations between one of protons at δ 7.74 (H-8) on the 1,2,3-trisubstituted benzene ring and the carbonyl carbon at δ 183.3 (C-9) and a carbon at δ 145.8 (C-10a), and between another proton at δ 7.34 (H-7) on the same ring and a carbon with *O*-function at δ 147.1 (C-5), which indicated that a partial structure of 1 was composed of a 5-hydroxyxanthone moiety. The hmbc spectrum further exhibited the correlations between the chelated hydroxyl group at C-1 and three quaternary carbons (C-1, C-2 and C-9a), the former carbon was additionally correlated to an aromatic proton (H-3). In addition to the above results, the chemical shifts of the aromatic carbons with *O*-function attributable to C-1, C-4 and C-4a showed that the structure of the xanthone moiety could be expanded to a 1,4,5-trihydroxyxanthone, which was supported by comparison of the ^{1}H and ^{13}C nmr spectral data with those of authentic sample[1]. On the other hand, two protons (H-9' and H-13') on the monosubstituted benzene ring were correlated to another carbonyl carbon at δ 200.0 in the hmbc spectrum, indicating the presence of a benzoyl moiety. As the chemical shifts of the other unassigned six aromatic carbons (δ 92.4, 105.7, 106.0, 160.3, 163.1 and 164.7) were allotted to a benzene ring with a phloroglucinol substitution[8], the benzoyl moiety was a part of 2',4',6'-trioxygenated benzophenone. In the ^{1}H nmr spectrum, nOes were observed between the methoxyl signal and two aromatic signals in singlet (H-3 and H-5') (Figure 2). These results indicated the methoxyl group was located at C-4'. Finally, the aromatic proton (H-3) was correlated to the carbon (C-3') which was additionally correlated to the aromatic proton (H-5'), indicating that two partial structures were connected at C-2 and C-3', that is, at C-2 of a 1,4,5-trihydroxyxanthone and at C-3' of a 2',6'-hydroxy-4'-methoxybenzophenone. Thus, the total structure of garciduol A was characterized as **1**.



1 : R = H
2 : R = OH

Figure 1

Garciduol B (**2**),[9] a yellow amorphous powder, had a molecular formula $C_{27}H_{18}O_{10}$ determined by the high-resolution eims. The spectral data of **2** were similar to those of **1** except for the presence of a 1,3-disubstituted benzene ring instead of a monosubstituted benzene ring composed of the benzophenone moiety. Therefore garciduol B was a derivative with a hydroxyl group at C-10' in **1**, which was supported by an nOe experiment and the correlations observed in the hmbc spectrum (Figure 2).



1 **2**

Figure 2 Hmbc spectrum ($J = 10$ Hz) and nOe experiment of **1** and **2**

In this communication, we described the structural characterization of garciduols A and B, which is a first presentation to introduce naturally occurring benzophenone-xanthone dimer. The results of further phytochemical research of this plant and the biological activities of the two compounds will be reported elsewhere.

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7. **1**: A yellow amorphous; hreims: $[M]^+$ *m/z* 486.0959 (Calcd 486.0951 for $C_{27}H_{18}O_9$); $[\alpha]_D^{24}$ 0° (*c* 0.1, acetone); uv λ (nm, MeOH): 212, 230sh, 250, 265sh, 311, 400, + NaOMe: 215, 255, 320,

+AlCl$_3$: 213, 231, 250, 266, 327, +AlCl$_3$/HCl: 204, 212, 250, 265sh, 320, +NaOAc: 222, 262, 312, 315, 415, +NaOAc/H$_3$BO$_3$: 223, 303; ir ν (cm^{-1}, KBr): 3365, 3184, 1624, 1587; ^{1}H nmr (400 MHz, acetone-d_6) δ: 3.80 (3H, s, OMe), 6.27 (1H, s, H-5'), 7.25 (1H, s, H-3), 7.34 (1H, t, J = 7.8 Hz, H-7), 7.39 (1H, dd, J = 7.8, 2.0 Hz, H-6), 7.43 (2H, m, H-10', 12'), 7.50 (1H, m, H-11'), 7.70 (2H, m, H-9', 13'), 7.74 (1H, dd, J = 7.8, 2.0 Hz, H-8), 8.82 (2H, br s, OH x 2), 9.85, 10.35 (1H, each br s, OH), 12.32 (1H, s, C-1-OH); ^{13}C nmr (100 MHz, acetone-d_6) δ: 56.2 (OMe), 92.4 (C-5'), 105.7 (C-3'), 106.0 (C-1'), 109.4 (C-9a), 115.5 (C-2), 116.6 (C-8), 122.0 (C-6), 122.1 (C-8a), 125.3 (C-7), 128.2 (C-3), 128.5 (C-10', 12'), 129.2 (C-9', 13'), 131.9 (C-11'), 137.5 (C-4), 142.5 (C-8'), 143.7 (C-4a), 145.8 (C-10a), 147.1 (C-5), 153.2 (C-1), 160.3 (C-2'), 163.1 (C-6'), 164.7 (C-4'), 183.3 (C-9), 200.0 (C-7').

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9. **2**: A yellow amorphous; hreims: $[M]^+$ m/z 502.0916 (Calcd 502.0900 for C$_{27}$H$_{18}$O$_{10}$); $[\alpha]_D^{24}$ 0° (c 0.1, acetone); uv λ (nm, MeOH): 207, 250, 268sh, 314, 400sh, + NaOMe: 214, 245; +AlCl$_3$: 205, 250, 267, 285sh, 325, 395, +AlCl$_3$/HCl: 205, 250, 263sh, 322, 395, +NaOAc: 212, 262, 315, +NaOAc /H$_3$BO$_3$: 213, 249, 260sh, 310; ir ν (cm^{-1}, KBr): 3400, 2927, 2855, 1704, 1617, 1596; ^{1}H nmr (400 MHz, acetone-d_6) δ: 3.79 (3H, s, OMe), 6.26 (1H, s, H-5'), 6.97 (1H, ddd, J = 7.9, 2.4, 1.2 Hz, H-11'), 7.19 (2H, m, H-9', 13'), 7.24 (1H, s, H-3), 7.25 (1H, t, J = 7.9 Hz, H-12'), 7.32 (1H, t, J = 7.8 Hz, H-7), 7.38 (1H, dd, J = 7.8, 2.0 Hz, H-6), 7.71 (1H, dd, J = 7.8, 2.0 Hz, H-8), 9.65, (1H, br s, OH), 12.36 (1H, s, C-1-OH); ^{13}C nmr (100 MHz, acetone-d_6) δ: 56.3 (OMe), 92.5 (C-5'), 105.9 (C-3'), 106.3 (C-1'), 109.6 (C-9a), 116.0 (C-2). 116.2 (C-9'), 116.4 (C-8), 119.2 (C-11'), 120.6 (C-13'), 122.1 (C-8a), 122.2 (C-6), 125.4 (C-7), 128.3 (C-3), 129.8 (C-12'), 137.9 (C-4), 143.87* (C-8'), 143.93* (C-4a), 146.1 (C-10a), 147.8 (C-5), 153.1 (C-1), 157.9 (C-10'), 160.1 (C-2'), 163.0 (C-6'), 164.6 (C-4'), 183.5 (C-9), 199.9 (C-7') (*: interchangeable).

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