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 studies1-5 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 Harnigna4 and Mammea5 were characterized. In a preceding paper, the structures of some xanthones with C5 and/or C10 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 FeCl3 and Gibbs reagent. The [M]+ at m/z 486.0959 in the high-resolution eims corresponds to C27H18O9. 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 13C 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 1H and 13C nmr spectral data with those of authentic sample1. 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 substitution8, the benzoyl moiety was a part of 2',4',6'-trioxygenated benzophenone. In the 1H 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.

Garciduol B (2),9 a yellow amorphous powder, had a molecular formula C27H18O10 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

![Figure 1](image_url)
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).

![Figure 2 Hmbc spectrum (J = 10 Hz) and nOe experiment of 1 and 2](image)

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.

REFERENCES AND NOTES

7. 1: A yellow amorphous; hreims: [M]+ m/z 486.0959 (Calcd 486.0951 for C27H18O9); [α]D24 0° (c 0.1, acetone); uv λ (nm, MeOH): 212, 230sh, 250, 265sh, 311, 400, + NaOMe: 215, 255, 320,
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+AlCl₃: 213, 231, 250, 266, 327, +AlCl₃/HCl: 204, 212, 250, 265sh, 320, +NaOAc: 222, 262, 312, 315, 415, +NaOAc/H₃BO₃: 223, 303; ir ν (cm⁻¹, KBr): 3365, 3184, 1624, 1587; ¹H nmr (400 MHz, acetone-ᵈ) 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); ¹³C nmr (100 MHz, acetone-d₆) δ: 56.2 (OMe), 92.4 (C-S), 105.9 (C-3'), 106.3 (C-1'), 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').


9. 2: A yellow amorphous; hreims: [M]+ m/z 502.0916 (Calcd 502.0900 for C₂₇H₁₈O₁₀); [α]D²⁴ 0° (c 0.1, acetone); uv λ (nm, MeOH): 207, 250, 268sh, 314, 400sh, + NaOMe: 214, 245; +AlCl₃: 205, 250, 267, 285sh, 325, 395, +AlCl₃/HCl: 205, 250, 263sh, 322, 395, +NaOAc: 212, 262, 315, +NaOAc /H₃BO₃: 213, 249, 260sh, 310; ir ν (cm⁻¹, KBr): 3400, 2927, 2855, 1704, 1617, 1596; ¹H nmr (400 MHz, acetone-ᵈ) 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); ¹³C nmr (100 MHz, acetone-ᵈ) 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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