

A PRENYLATED XANTHONE FROM THE BARK OF *SYMPHONIA GLOBULIFERA*

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Abstract—One new prenylated xanthone, ananixanthone, was isolated from the bark of *Symphonia globulifera*. The structure was determined by NMR spectroscopy including 2D techniques. © 1998 Elsevier Science Ltd. All rights reserved

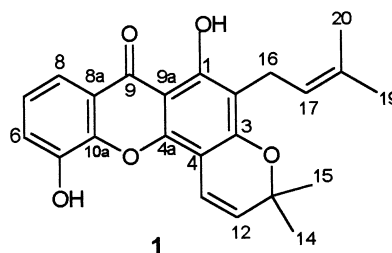
INTRODUCTION

Symphonia globulifera is a tree of North of Brazil where it is known as ‘anani’ and is used as a medicinal plant as laxative for pregnant women and a general tonic. Previous studies [1–4] of this plant reported the isolation of eight xanthones. In our search for biologically active compounds from amazonian plants we reexamined *S. globulifera* and now report the isolation and structural determination of a new polyoxygenated xanthone.

RESULTS AND DISCUSSION

The bark of *S. globulifera* collected in Belém, Pará, Brazil was dried, ground, and extracted with EtOAc. The EtOAc extract was chromatographed on silica-gel (chloroform-methanol elution with increasing polarity) and preparative TLC gave the xanthone **1**.

Compound **1** (ananixanthone), obtained as a pale colourless amorphous material, showed in the EI mass spectrum the $[M]^+$ at m/z 378, corresponding to $C_{23}H_{22}O_5$. The IR spectrum exhibited bands due to hydroxyl groups (3377 cm^{-1}) and a conjugated carbonyl group (1648 cm^{-1}). The UV absorptions indicated **1** to be a xanthone derivative. The ^1H NMR spectrum showed the presence of a 1,2,3-trisubstituted benzene ring [δ 7.75 and 7.30 (1H each, *dd*, $J = 7.8$ and 1.8 Hz), 7.24 (1H, *t*, $J = 7.8$ Hz)], a 3,3-dimethylallyl group [δ 5.24 (1H, *br t*, $J = 6.7$ Hz), 3.50 (2H, *d*, $J = 6.7$ Hz), 1.87 (3H, *s*) and 1.72 (3H, *s*)] and a dimethylchromene ring [δ 1.48 (6H, *s*), 6.75 and 5.62 (1H each, *d*, $J = 10$ Hz)], in addition to two hydroxyl



groups, including a chelated one [δ 5.69 (1H, *s*) and 13.08 (1H, *s*, chelated OH)]. In the HMBC spectrum, one of the ABX system protons, which appeared at δ 7.75, gave cross peaks with the carbonyl carbon (δ 181.2), one CH aromatic carbon (δ 120.6) and one aromatic carbon with a O-function (δ 144.6 or 144.8). These results proved that one aromatic proton (δ 7.75) was located at a *peri*-position (C-8) to the carbonyl group and that the C-5 position was substituted by OH or 3,3-dimethylallyl group. As the other aromatic proton, which showed a triplet signal (δ 7.24) attributed to H-7, gave a cross peak with a oxygenated aromatic carbon (δ 144.6 or 144.8), the C-5 position must be substituted by OH group. The substitution of the other ring of the xanthone nucleus was confirmed as follows. In the HMBC spectrum the chelated OH proton (δ 13.08) caused cross peaks with two aromatic carbons at δ 103.6 and 112.6, indicating that the C-2 position was not substituted by a group possessing O-function. Furthermore the C-2 carbon (δ 112.6) was correlated to methylene protons (δ 3.50) of the 3,3-dimethylallyl group. The last protons were also correlated to the two oxygenated aromatic carbons at δ 160.9 and 159.0, one of which (δ 159.0) was correlated to the *cis*-olefinic proton (δ 6.75) of the chromene ring. The spectral evidence indicated that 3,3-dimethylallyl

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group was located at the C-2 position and the chromene ring was fused in an angular form at C-4 through an oxygen at C-3. The structure of ananixanthone was thus characterized as **1**, which was supported by the other correlations in the HMBC spectrum. Assignment of the ^{13}C NMR spectral data are shown in Experimental.

EXPERIMENTAL

Plant material

Bark of *Symphonia globulifera* was collected in July, 1996 in Belém, Pará, Brazil. The plant material was identified by Dr. Irenice A. Rodrigues, Departamento de Botânica and a voucher specimen is deposited in the Herbarium of Centro de Pesquisa Agro-Florestal da Amazonia Oriental (CPATU) under No. 164390.

Extraction and isolation

Dried and ground bark (500g) was extracted with EtOAc (2 l) at room temp. Evapn of the solvent gave a gummy syrup (30g). The EtOAc extract (2g) was subjected to a silica gel vacuum liquid chromatography (VLC) eluted with CHCl_3 -MeOH system. Further purification of fr. 17 (120 mg) were performed on preparative TLC (n-hexane-EtOAc 85:15) followed by crystallization from MeOH to give **1** (12 mg).

Compound 1 (ananixanthone). Pale colourless amorphous, mp 170–171° (MeOH). EI-MS m/z (rel. int.): 378 $[\text{M}]^+$ (45), 363 (100), 335 (15), 323 (24), 295 (12), 194 (23), 177 (18), 97 (17), 83 (19), 69 (22). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ) 253.3 (4.19), 269.6 (4.19), 332.8 (3.74); $\lambda_{\text{max}}^{\text{MeOH} + \text{NaOH}}$ 269.6 (4.23), 285 (4.13) sh, 348 (3.62); $\lambda_{\text{max}}^{\text{MeOH} + \text{NaOAc}}$ 269.6 (4.27), 285 (4.15) sh, 338.3

(3.67); $\lambda_{\text{max}}^{\text{MeOH} + \text{AlCl}_3}$ unchanged. IR ν^{KBr} cm^{-1} 3377, 2919, 2852, 1648 ^1H NMR (300 MHz, CDCl_3): δ 1.48 (6H, s, H-14, H-15), 1.72 (3H, s, H-20), 1.87 (3H, s, H-19), 3.50 (2H, d, $J = 6.7$ Hz, H-16), 5.24 (1H, t, $J = 6.7$ Hz, H-17), 5.26 (1H, d, $J = 10$ Hz, H-12), 5.69 (1H, s, C-6-OH), 6.75 (1H, d, $J = 10$ Hz, H-11), 7.24 (1H, t, $J = 7.8$ Hz, H-7), 7.30 (1H, dd, $J = 7.8$ and 1.8 Hz, H-6), 7.75 (1H, dd, $J = 7.8$ and 1.8 Hz, H-8), 13.08 (1H, s, C-1-OH).

^{13}C NMR (300 MHz, CDCl_3): δ 160.9 (C-1, s), 112.6 (C-2, s), 159.0 (C-3, s), 101.1 (C-4, s), 149.7 (C-4a, s), 144.8^a (C-5, s), 120.6 (C-6, d), 124.3 (C-7, d), 117.8 (C-8, d), 121.6 (C-8a, s), 181.2 (C-9, s), 103.6 (C-9a, s), 144.6^a (C-10a, s), 115.4 (C-11, d), 127.7 (C-12, d), 78.5 (C-13, s), 28.6 (C-14, q), 28.6 (C-15, q), 21.6 (C-16, t), 122.3 (C-17, d), 132.1 (C-18, s), 26.2 (C-19, q), 18.3 (C-20, q). ^aInterchangeable.

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