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A XANTHONE FROM *GARCINIA ATROVIRIDIS*

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Key Word Index—*Garcinia atroviridis*; Guttiferae; tetraoxygenated xanthone; atroviridin.

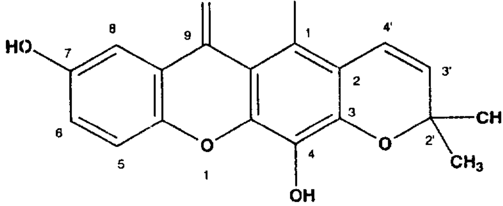
Abstract—A new xanthone, atroviridin, was isolated from the stem bark of *Garcinia atroviridis* (Guttiferae). Its structure elucidation and unambiguous NMR spectral assignment were achieved by the aid of the combination of 1D and 2D NMR techniques. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Garcinia atroviridis Griff. (Guttiferae), a lofty tree, is known locally in Thai as 'Som Khaek' or 'Som ma won'. A decoction of the leaves and root is dropped into the ear to treat earache. The acid fruit is used in curry [1]. Previous works have reported the presence of xanthones from other *Garcinia* species [2]. As part of a chemical study on the genus *Garcinia*, the present paper deals with the isolation and the structure elucidation of a new tetraoxygenated xanthone named atroviridin (**1**) from the stem bark of *G. atroviridis*.

RESULTS AND DISCUSSION

Purification of a chloroform extract of the stem bark of *Garcinia atroviridis* with silica gel column chromatography resulted in the isolation of a new tetraoxygenated xanthone (**1**). Compound **1**, m.p. 257–259°, was obtained as a yellow amorphous powder. The molecular formula of **1** was deducted to be $C_{18}H_{14}O_6$ (Calcd 326.0789 amu) from its $[M]^+$ at *m/z* 326.0781 in the high resolution mass spectrum. The xanthone chromophore was evident from its UV absorption at 298 nm (log ε 4.75) [3], and the pyrone-carbonyl stretching frequency was found in the region 1655 cm^{-1} of the IR spectrum [4, 5]. The ^1H NMR spectrum of **1** indicated the presence of three aromatic protons of ABX-type signals at δ 7.50 (*d*, $J = 9.2$ Hz), 7.40 (*d*, $J = 2.9$ Hz) and 7.29 (*dd*, $J = 9.2$, 2.9 Hz), and two D_2O exchangeable signals at δ 9.29 (7-OH) and 8.73 (4-OH) appeared in addition to a chelated hydroxyl signal at δ 12.70 (1-OH). The appearance of a pair of doublets at δ 5.76, 6.61 (each 1H, $J = 9.9$ Hz) together with a 6H-singlet at δ 1.45 indicated the presence of a dimethylpyran ring system in the molecule. The structure of **1** was confirmed by ^1H-detected heteronuclear multiple quantum coherence (HMQC) and ^1H-detected multiple bond connectivity (HMBC) spectroscopies. The presence of a dimethylpyran ring fused with the 1,3-dioxygenated xanthone nucleus at C-2 and C-3 was suggested by the appearance of a C-H three bond correlation between the hydrogen bonded proton at δ_H 12.70 and a carbon at δ_C 103.48 (C-2), which was also related to the aromatic protons (H-3′, δ_H 5.76) on the dimethylpyran ring, respectively, in the HMBC sprectum. A hydroxyl group at δ_H 8.73 showed C-H long-range correlations with the carbon signals at δ_C 148.46 (C-3), 125.35 (C-4), 145.10 (C-4a). Furthermore, another hydroxyl proton at δ_H 9.99 was correlated with carbon signals at δ_C 107.90 (C-8), 153.91 (C-7), 124.68 (C-6). These results strongly support the proposed structure of **1** as a new tetraoxygenate xanthone named atroviridin.



EXPERIMENTAL

General. ^1H and ^{13}C NMR, HMQC and HMBC ($J = 8$ Hz) spectra were recorded on a A-600 (JEOL) spectrometer in DMSO-d_6 and chemical shifts are given on a δ(ppm) scale with TMS as int. standard. MS were recorded at 70 eV using a direct inlet system on a Hitachi M-80 spectrometer. UV:MeOH. IR:KBr

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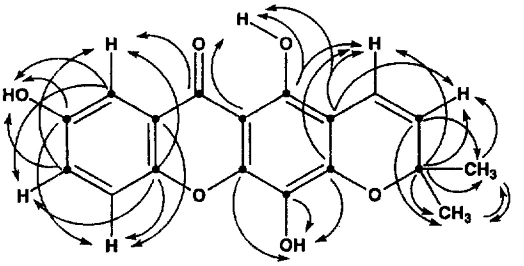

Fig. 1. ^{13}C-^1H long-range correlations observed in the HMBC spectrum of **1**.

disc. Mps are uncorr. Merck silica gel 60 F_{254} plates were used for analyt. TLC, and kieselgel 60 for CC.

Plant material. The stem bark of *Garcinia atroviridis* Griff. was collected from Chumphorn province Thailand in December 1995 and was identified by one of us (N.R.). A voucher specimen is deposited in the herbarium of the Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bankok, Thailand.

Extraction and isolation of **1**. The minced fresh stem bark (12 kg) was extracted with $CHCl_3$ (10 and 5 l) for 3-day-periods each and filtered. The combined filtrates were evapd *in vacuo* until dryness to yield a syrupy mass residue (84 g). The residue (14 g) was chromatographed on silica gel CC (8 × 12 cm) using $CHCl_3$ as eluent and collected 50 ml frs. The column was initially eluted with $CHCl_3$ and then the $CHCl_3$–EtOH with an increasing concn of EtOH. Those frs containing homogeneous components, as judged by TLC, were combined and the solvent removed. Elution with $CHCl_3$–EtOH (19:1) gave a fr. that mainly contained compound **1** along with a trace of minor components. The sepn and purification of **1** was achieved by rechromatograph on silica gel CC (2 × 15 cm) using hexane–EtOAc (3:1) as eluent to yield 25 mg (2.08×10^{-4}%) of **1**.

Compound **1**. Mp 257–259°; UV λ_{max}^{MeOH} nm (log ε): 205(4.48), 235(4.46), 262(4.41), 288(4.71), 298(4.75), 356(3.80), 404(3.83). IR ν_{max} cm^{-1}: 3590–3100, 1655, 1579, 1482, 1381, 1356, 1232, 1171. ^1H and ^{13}C NMR: Table 1. EIMS 70 eV (Probe) *m/z* (rel. int.): $326[M]^+$(47), 311(100), 282(3), 189(4), 163(3), 138(13), 105(6). 83(8), 56(16).

Table 1. The ^1H and ^{13}C NMR Spectra of a New Xanthone

	1	
	δ_H	δ_C
1		148.74 (*s*)
1-OH	12.70 (1H, *s*)	
2		103.48 (*s*)
3		148.46 (*s*)
4		125.35 (*s*)
4-OH	8.73 (1H, *s*)	
4a		145.10 (*s*)
5	7.50 (1H, *d*, $J = 9.2$ Hz)	119.11 (*d*)
6	7.29 (1H, *dd*, $J = 9.2, 2.9$ Hz)	124.68 (*d*)
7		153.91 (*s*)
7-OH	9.99 (1H, *s*)	
8	7.40 (1H, *d*, $J = 2.9$ Hz)	107.90 (*d*)
8a		120.13 (*s*)
9		180.38 (*s*)
9a		102.28 (*s*)
10		149.08 (*s*)
2′-CH_3	1.45 (6H, *s*)	27.76 ($q \times 2$)
2′		77.94 (*s*)
3′	5.76 (1H, *d*, $J = 9.9$ Hz)	128.54 (*d*)
4′	6.61 (1H, *d*, $J = 9.9$ Hz)	114.91 (*d*)

Values in (δ_H and δ_C) ppm. ^1H and ^{13}C NMR spectra was recorded at 600 MHz and 150 MHz, respectively, in DMSO-d_6.

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