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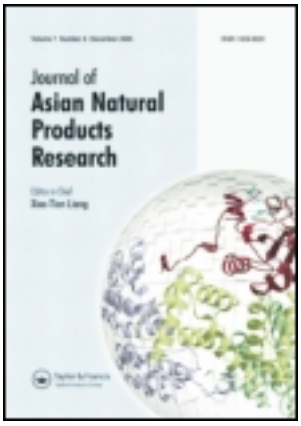

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Triterpenes and xanthones from the stem bark of *Garcinia tetralata*

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Triterpenes and xanthones from the stem bark of *Garcinia tetralata*

Yong-En Guo[a]*, Li-Li Wang[b], Zhan-Lin Li[b], Sheng-Li Niu[b], Xiao-Qiu Liu[b], Hui-Ming Hua[b1], Hong Chen[c2], Jie Chu[d] and Tong-Cun Zhang[a3]

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A new compound, 3β,18,19β-trihydroxylupane, was isolated from *Garcinia tetralata*, along with five known compounds, garcinexanthone B, morolic acid acetate, toxyloxanthone A, 6,11-dihydroxy-2,2-dimethylpyrano[3,2-*c*]xanthen-7(2*H*)-one, and 1,4-dihydroxy-5,6-dimethoxy-xanthone. The structure of the new compound was established by extensive spectroscopic techniques.

Keywords: Guttiferae; *Garcinia tetralata*; 3β,18,19β-trihydroxylupane

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1. Introduction

The plants of the genus *Garcinia* (Guttiferae) are well known as rich natural sources of xanthones, benzophenones, and biflavonoids [1,2]. Due to various biological properties including antibacterial activity, antimalarial activity, and cytotoxicity [2,3], *Garcinia* plants have attracted the interests of many natural medicinal chemists. *Garcinia tetralata* C.Y. Wu is distributed uniquely in Yunnan Province of China. No previous phytochemical investigation was focused on *G. tetralata*. To identify biologically active compounds from *Garcinia* plants, the chemical constituents of *G. tetralata* were investigated. Herein, the isolation and characterization of one new compound together with five known compounds from the stem bark of *G. tetralata* are reported.

2. Results and discussion

The 95% ethanol extract of the stem bark of *G. tetralata* was suspended in water and partitioned with $CHCl_3$ and *n*-butanol, successively. The $CHCl_3$ fraction was subjected to repeated silica gel column chromatographies, as well as octadecyl silane (ODS) column chromatography, to afford a new compound **1** and five known compounds **2**–**6** which were identified as garcinexanthone B (**2**), morolic acid acetate (**3**), toxyloxanthone A (**4**), 6,11-dihydroxy-2,2-dimethylpyrano[3,2-*c*]xanthen-7(2*H*)-one (**5**), and 1,4-dihydroxy-5,6-dimethoxyxanthone (**6**), respectively, by comparison of their spectral data with those reported in the literatures [4–8] (Figure 1).

Compound **1** was obtained as colorless needles, and its molecular formula was determined as $C_{30}H_{52}O_3$ on the basis of the HR-ESI-MS (*m/z* 443.3860 $[M-H_2O+H]^+$) combined with the

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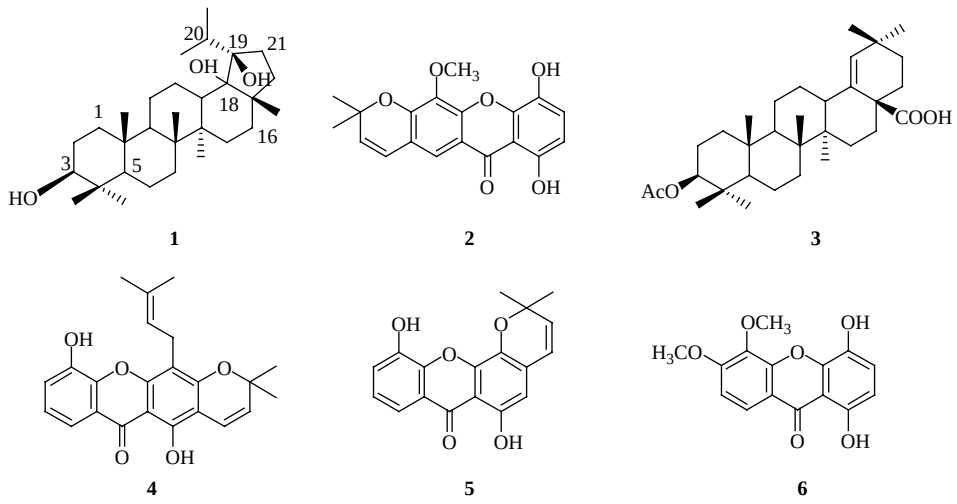

Figure 1. The structures of compounds **1**–**6** from *G. tetralata*.

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NMR spectral data in Table 1. The IR (KBr) absorption of compound **1** at 3490 cm^{-1} revealed the presence of a hydroxyl group. The ^1H NMR spectrum showed two secondary methyl groups at δ 0.95, 1.06 (each 3H, d, $J = 6.0$ Hz); six tertiary methyl groups at δ 0.76, 0.83, 0.83, 0.98, 1.03, and 1.05 (each 3H, s); and one oxygenated methine proton at δ 3.20 (1H, dd, $J = 4.6$, 11.6 Hz). The ^{13}C NMR spectrum revealed 30 carbon signals, including three oxygenated carbon signals at δ_C 78.6, 76.0, and 75.0. On the basis of the above data, compound **1** was assumed to be a lupane-type triterpene [9]. The ^1H and ^{13}C NMR spectral data were assigned by the ^1H–^1H COSY, HSQC, and HMBC spectra in Table 1. In the HMBC spectrum, the long-range correlations between the methyl protons at δ 0.98 (H-23), 0.76 (H-24), and the oxygenated methine at δ_C 78.6 implied that one hydroxyl group was located at C-3. The locations of two oxygenated quaternary carbons at C-18 and C-19 were determined by the long-range correlations between C-18 at δ_C 76.0 and H-21, H-22, H-28, and the correlations between C-19 at δc 75.0 and H-20, H-22, H-30. On the basis of the chemical shifts of C-18 (δ_C 76.0) and C-19 (δ_C 75.0), the 18,19-dihydroxy instead of 18,19-epoxy group was determined. The β-orientation of 3-hydroxy group was determined by the coupling constants of the methine proton at δ 3.20 (1H, dd, $J = 4.6$, 11.6 Hz, H-3) and comparing the ^{13}C NMR spectral data with those of the known compound lupeol [9]. The correlations between CH_3-28β at δ 0.83 and H-21β at δ 1.62, H-21α at δ 1.33 and H-20 at δ 1.71, in the NOESY spectrum indicated 19-isopropyl as an α-orientation, which confirmed that the 19-hydroxy group had a β-orientation. Thus, compound **1** was assigned as 3β,18,19β-trihydroxylupane.

3. Experimental

3.1 General experimental procedures

Melting points (°C, uncorrected) were determined on a Yanaco MP-S3 apparatus. Optical rotation was measured with a Perkin Elmer 241 polarimeter. The UV spectrum was conducted on a Shimadzu UV-2201 spectrometer. The FT-IR spectra were obtained on a Perkin IFS-55 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-300 NMR spectrometer using TMS as an internal

Table 1. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and HMBC spectral data of compound **1** ($CDCl_3$).

Position	δ_H (J in Hz)	δ_C	HMBC ($^{1}H \rightarrow {}^{13}C$)
1	1.71, m	38.4, t	C-2, C-5, C-9, C-10, C-25
	0.94, m		
2	1.62, m	27.0, t	C-3, C-4, C-10
	1.54, m		
3	3.20, dd (4.6, 11.6)	78.6, d	C-1, C-23, C-24
4		38.5, s	
5	0.69, m	54.8, d	C-1, C-3, C-6, C-7, C-9, C-10, C-23, C-24
6	1.54, m	18.0, t	C-7
	1.41, m		
7	1.41, m	32.9, t	C-5, C-6, C-9, C-26
	1.33, m		
8		41.4, s	
9	1.27, m	50.1, d	C-7, C-8, C-10, C-11, C-12, C-14, C-25
10		36.7, s	
11	1.54, m	20.6, t	C-8, C-10, C-12, C-13
	1.33, m		
12	1.71, m	22.8, t	C-11, C-13, C-14
	1.41, m		
13	1.82, dd (1.5, 4.8)	43.0, d	C-8, C-11, C-12, C-17, C-27
14		41.7, s	
15	1.71, m	28.8, t	C-13, C-16
	1.27, m		
16	2.04, m	19.8, t	C-15
	1.33, m		
17		42.9, s	
18		76.0, s	
19		75.0, s	
20	1.71, m	28.1, d	C-19, C-29, C-30
21	1.62, m	22.9, t	C-18, C-22
	1.33, m		
22	1.14, m	34.2, t	C-17, C-18, C-19, C-28
	1.04, m		
23	0.98, s	27.6, q	C-3, C-4, C-5, C-24
24	0.76, s	15.0, q	C-3, C-4, C-5, C-23
25	0.83, s	15.5, q	C-1, C-5, C-9, C-10
26	1.03, s	16.2, q	C-7, C-8, C-9, C-14
27	1.05, s	15.5, q	C-8, C-13, C-14, C-15
28	0.83, s	17.5, q	C-17, C-18, C-22
29	0.95, d (6.0)	18.7, q	C-19, C-20, C-30
30	1.06, d (6.0)	17.9, q	C-19, C-20, C-29

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standard. The HSQC, HMBC, $^{1}H-^{1}H$ COSY, and NOESY spectra were measured on a Bruker AV-600 NMR spectrometer. EI-MS was conducted on Shimadzu GCMS-QP5050A and ESI-MS on an Agilent 1100 ion trap spectrometer. HR-ESI-MS was recorded on a Varian QFT-ESI instrument. The chromatographic silica gel (200–300 mesh) was purchased from Qingdao Ocean Chemical Factory (Qingdao, China), and ODS (50 μm) was purchased from YMC Co. Ltd (Kyoto, Japan).

3.2 Plant materials

The stem barks of *G. tetralata* were collected from Mengla County, Yunnan Province, China in 2006. The material was identified by Prof. Qi-Shi Sun, Shenyang

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Pharmaceutical University, Shenyang, China. The voucher sample (SZTH-2006) has been deposited in the Department of Natural Products Chemistry, Shenyang Pharmaceutical University.

3.3 Extraction and isolation

The dried stem bark of *G. tetralata* (5 kg) was extracted three times (2, 2, and 1 h) with 95% EtOH under reflux. After the removal of the solvent, the residue (780 g) was suspended in water (1000 ml) and partitioned successively with $CHCl_3$ (3×1000 ml) and *n*-BuOH (3×1000 ml). The $CHCl_3$ soluble fraction (150 g) was chromatographed over silica gel using a gradient of petroleum ether (60–90°C)-acetone (100:0–0:100) to give 11 fractions (Fr. 1–Fr. 11). Fr. 1 (2.5 g) was separated by a silica gel column eluting with petroleum ether (60–90°C)-acetone (100:4) to afford compounds **1** (6.0 mg) and **3** (5.0 mg).

Fr. 3 (5.5 mg) was chromatographed on silica gel with petroleum ether (60–90°C)–acetone (100:5) and then purified by ODS with MeOH–H_2O (80:20) to furnish compound **4** (2.3 mg). Fr. 4 (2.0 g) was separated by a silica gel column eluting with petroleum ether (60–90°C)-acetone (100:7) and then purified by opening ODS column chromatography [MeOH–H_2O (80:20)] to yield compound **5** (2.6 mg). Fr. 6 (2.5 g) was subjected to silica gel column chromatography eluting with petroleum ether (60–90°C)-acetone (100:9) and then purified by opening ODS column chromatography [MeOH–H_2O (80:20)] to yield compound **2** (2.0 mg). Fr. 8 (2.0 g) was separated by a silica gel column eluting with petroleum ether (60–90°C)–acetone (100:15), and then purified by preparative TLC with a developing solvent system of petroleum ether (60–90°C)–acetone (3:2) to obtain compound **6** (1.7 mg).

3.3.1 3β,18,19β-Trihydroxylupane (*1*)

Mp 190–192°C. $[\alpha]_D^{20} + 6.0$ ($c = 1.30$, $CHCl_3$). FT-IR (KBr): ν_{max} 3490 (OH), 2942, 2867, 1380 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectral data, see Table 1. EI-MS (70 ev): *m/z* 442 $[M-H_2O]^+$. HR-ESI-MS: *m/z* 443.3860 $[M-H_2O+H]^+$ (calcd for $C_{30}H_{51}O_2$, 443.3889).

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References

[1] I. Sort-Diserens, A. Martin, M. Hamburger, C. Rogers, K. Hostettmann, and C. Rogers, *Helv. Chim. Acta* **72**, 1001 (1989).

[2] O. Chantarasriwong, A. Batova, W. Chiavari, and E.A. Theodorakis, *Chem. Eur. J.* **16**, 9944 (2010).

[3] K. Likhitwitayawuid, W. Chanmahasathien, N. Ruangrungsi, and J. Krungkrai, *Planta Med.* **64**, 281 (1998).

[4] Y. Chen, F.-F. Zhong, H.-W. He, Y. Hu, D. Zhu, and G.-Z. Yang, *Magn. Reson. Chem.* **46**, 1180 (2008).

[5] A.G. González, B.M. Fraga, P. González, M.G. Hernandez, and A.G. Ravelo, *Phytochemistry* **20**, 1919 (1981).

[6] V.H. Deshpande, A.V.R. Rao, M. Varadan, and K. Venkataraman, *Indian J. Chem.* **11**, 518 (1973).

[7] I. Sordat-Diserens, C. Rogers, B. Sordat, and K. Hostettmann, *Phytochemistry* **31**, 313 (1992).

[8] T.R. Govindachari, T.R. Pai, and P.S. Subramaniam, *Tetrahedron* **23**, 243 (1967).

[9] S.B. Mahato and S.B. Kundu, *Phytochemistry* **37**, 1517 (1994).