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Megastigmane glycosides and triterpenoids from *Vitis quinguangularis* Rehd

Hai-Jian Cong, Shu-Wei Zhang, Yi-Ping Wang, Li-Jiang Xuan*

State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 501 Haike Road, Zhangjiang Hi-Tech Park, Shanghai 201203, PR China

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ABSTRACT

A new megastigmane glucoside (**1**), and a novel cycloartane nortriterpenoid compound (**2**), along with four megastigmane glucosides (**3–6**), and one cycloartane triterpenoid (**7**) were isolated from the leaves of *Vitis quinguangularis* Rehd. Their structures were determined on the basis of spectroscopic methods including MS, 1D and 2D NMR.

1. Subject and source

Vitis quinguangularis Rehd (Vitaceae) is a perennial liana growing in mainland China. As a traditional Chinese medicine, the leaves and stems have been used for the treatment of arthritis, fever, carbuncles and inflammatory conditions (State Administration of Traditional Chinese Medicine of the People's Republic of China, 1999). The leaves of *V. quinguangularis* Rehd were collected from Nanning, Guangxi Province, R.P. China, in September 2010, and authenticated by Prof. *Heming Yang*. A voucher specimen (No.SIMMVQ001) is deposited at the Herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences, P. R. China.

2. Previous work

Previous phytochemical studies on the stems of *V. quinguangularis* focused on stilbene derivatives (Li et al., 1996).

3. Present study

3.1. Extraction and isolation

The leaves (5 kg) were extracted with 70% acetone (3 × 25 L, 48 h respectively). After concentration *in vacuo*, the gummy residue was suspended in H_2O, and then extracted with $CHCl_3$ and n-BuOH, successively, to give H_2O, n-BuOH and $CHCl_3$

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* Corresponding author. Tel./fax: +86 21 20231968.
E-mail addresses: ljxuan@mail.shcnc.ac.cn, ljxuan@hotmail.com (L.-J. Xuan).

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fractions. The n-BuOH fraction was submitted to column chromatography on MCI gel CHP 20P, Chromatorex C_{18}, Toyopearl HW-40F, and Sephadex LH-20, respectively, to give **1** (15 mg), **3** (10 mg)**,** **4** (15 mg), **5** (20 mg) and **6** (25 mg). The $CHCl_3$ fraction was submitted to silica gel column chromatography to give **2** (200 mg) and **7** (50 mg).

3.2. Identification of constituents

Separation and purification of the extract of *V. quinguangularis* by repetitive chromatography led to the isolation of a new megastigmane glucoside (**1**), a novel cycloartane nortriterpenoid (**2**), four megastigmane glucosides (**3–6**) and one cycloartane triterpenoid (**7**). Compounds **3–7** were identified as actinidioionoside (Otsuka et al., 2003), (6S, 9R)-roseoside (Yamano and Ito, 2005), Icariside B_5 (Miyase et al., 1988), Icariside B_1 (Hisamoto et al., 2004) and cycloart-23-ene-3β, 25-diol (Khan et al., 2006) (Fig. 1) by comparing their NMR data with those of the literature. The structures of compounds **1**–**2** were determined on the basis of spectroscopic methods including MS, 1D and 2D NMR.

Compound **1**, $[\alpha]_D^{22}$ -16.0 (*c* 0.3, MeOH), was isolated as an amorphous powder. Its elemental composition was determined to be $C_{19}H_{36}O_9$ (*m/z* 431.2255 $[M + Na]^+$, $C_{19}H_{36}O_9Na^+$; calc. 431.2252) by HRESIMS. IR (KBr): 3407, 2933 cm^{-1}. The ^1H- and ^{13}C NMR spectra (Table 1) of compound **1** showed six carbon resonances assignable to a β-glucopyranose unit, which was identified from the anomeric proton at δ_H 4.34 (1H, d, $J = 7.8$ Hz), anomeric carbon at δ_C (102.7), and some other characteristic NMR resonances. The glucose unit obtained after β-cellulose hydrolysis gave a positive optical rotation, $[\alpha]_D^{22}$ +45.0 (*c* 0.1, H_2O), indicating that it was D-glucose. The remaining 13 signals comprised three singlet and one doublet methyls, four methylenes, two methines with hydroxyl substituent, and three quaternary carbons, two of which bearing a hydroxyl substituent, which must form a megastigmane skeleton (Naves, 1964). The functionalities and their relative arrangement on the six-membered ring, available from the results of 1D and 2D NMR spectroscopy, were the same as actinidioionoside (**3**). The ^1H- and ^{13}C NMR of **1** were very similar with those of actinidioionoside (**3**) (Fig. 2), except for the signals of two aliphatic methylenes, which substituted those of the olefin group in the megastigmane moiety. The β-glucopyranosyl unit was deduced to be linked to C-9 as evidenced by an HMBC correlation between the anomeric proton at δ_H 4.34 and C-9 at δ_C 77.6. The stereochemistry at C-9 was assigned as R on the basis of a diagnostic chemical shift of C-9 signal (δ_C 77.6) in the ^{13}C NMR spectrum (Sueyoshi et al., 2006). The absolute configuration of C-3, C-5, C-6 was decided as

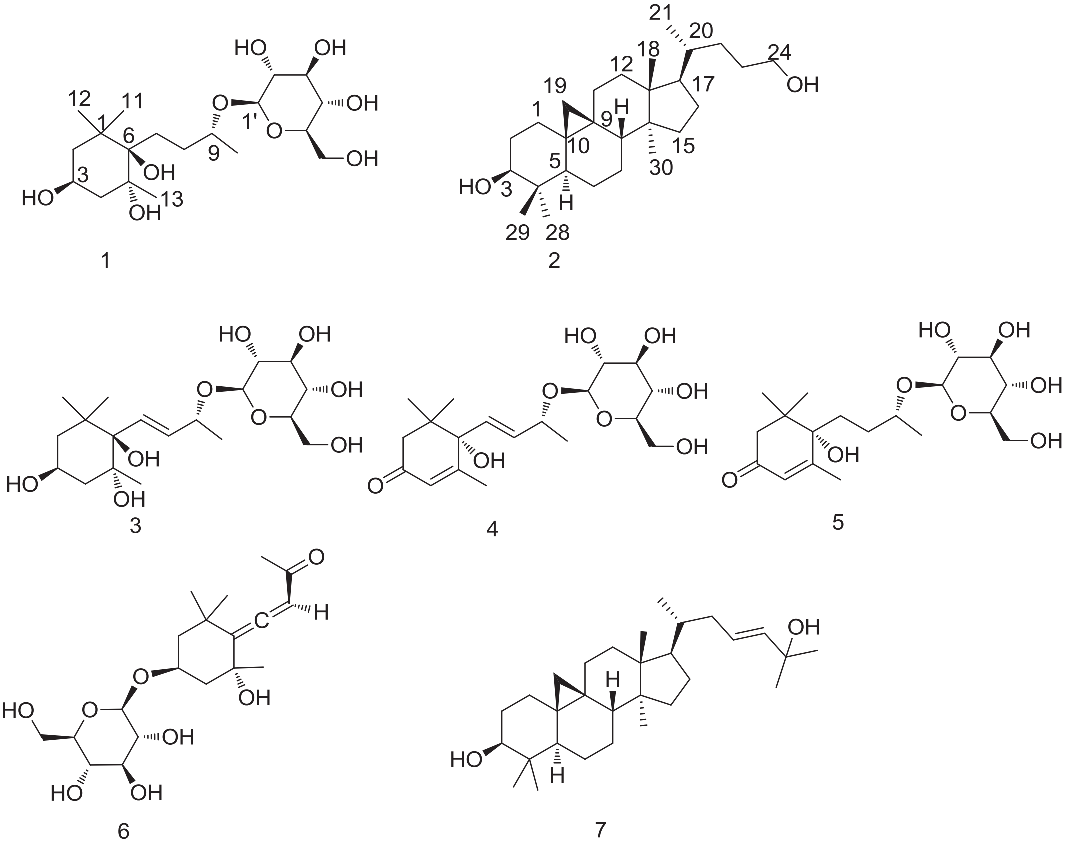

Fig. 1. The structure of compounds **1–7**.