

CHEMICAL CONSTITUENTS OF *Zanthoxylum armatum*. I

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The genus *Zanthoxylum* (Rutaceae) is a common medicinal and edible plant and comprises 250 species distributed in the tropical and subtropical zones of Asia, Africa, America, and Oceania [1]. *Zanthoxylum armatum* DC., a common wild species in the genus, is cultivated in some areas of China [2, 3]. *Z. armatum* is very well known for its diversified chemistry, particularly by the presence of alkaloids, aromatic and aliphatic amides, and phenylpropanoids [4]. Most of the previous phytochemical investigations have focused on petroleum ether, ethyl acetate, and *n*-butanol fractions of *Z. armatum* extract, while the water fraction of its extract was rarely reported. As part of our systematic investigations on the chemical constituents of *Z. armatum*, the present study investigated the water fraction of the ethanol extract of *Z. armatum*, resulting in the isolation of seven compounds.

The roots and stems of *Z. armatum* were collected from Nanning, Guangxi Province of China in 2014. Dried stems of *Z. armatum* (20 kg) were extracted with 95% ethanol (50 L × 3) at room temperature. The combined EtOH extract was filtered and concentrated under reduced pressure to give 680 g of residue. The residue was then suspended in water and partitioned successively with petroleum ether, EtOAc, and *n*-BuOH. The phytochemical investigation of the water-soluble extract (83 g) has resulted in the isolation of seven compounds (1–7), among which compound 5 was firstly isolated from Rutaceae. Compounds 2, 4, and 6 were obtained from the genus *Zanthoxylum* for the first time. Compounds 1, 3, and 7 were isolated from *Z. armatum* for the first time. The structures of all isolated compounds were determined by a combination of spectroscopic methods (MS, ¹H NMR and ¹³C NMR) and comparison with literature data.

Candicine (1), white needle crystals, C₁₁H₁₈NO⁺ [5].

2-Methoxyhydroquinone-4-β-D-glucopyranoside (2), white powder, C₁₃H₁₈O₈ [6].

2,6-Dimethoxy-4-hydroxyphenol-1-O-glucoside (3), white powder, C₁₄H₂₀O₉ [7].

Adenosine (4), white powder, C₁₀H₁₃N₅O₄ [8].

8'-Hydroxyabscisic acid β-D-glucoside (5), white powder, C₂₁H₃₀O₁₀. ¹H NMR (400 MHz, D₂O, δ, ppm, J/Hz): 7.16 (1H, d, J = 16.1, H-4), 6.05 (1H, s, H-3'), 5.97 (1H, d, J = 16.2, H-5), 5.81 (1H, s, H-2), 4.25 (1H, d, J = 7.9, H-1''), 3.91 (1H, d, J = 10.3, H-8'b), 3.85 (1H, dd, J = 11.3, 2.0, H-6''b), 3.67 (1H, dd, J = 11.3, 5.6, H-6''a), 3.59 (1H, d, J = 10.3, H-8'a), 3.43–3.28 (3H, m, H-3'', 4'', 5''), 3.19 (1H, dd, J = 9.2, 8.0, H-2''), 2.60 (1H, d, J = 17.8, H-5'a), 2.50 (1H, d, J = 17.7, H-5'b), 1.91 (3H, s, H-6), 1.87 (3H, s, H-7'), 1.05 (3H, s, H-9'). ¹³C NMR (100 MHz, D₂O, δ, ppm): 202.4 (C-4'), 166.9 (C-1), 139.8 (C-2'), 130.9 (C-3), 129.4 (C-5), 126.8 (C-4), 126.3 (C-3'), 102.8 (C-2), 79.5 (C-1''), 75.8 (C-1'), 75.5 (C-4''), 73.6 (C-5''), 73.1 (C-2''), 69.6 (C-8'), 60.6 (C-3''), 60.4 (C-6''), 45.3 (C-6'), 43.5 (C-5'), 19.4 (C-6'), 18.9 (C-9'), 18.8 (C-7'). ESI-MS *m/z* 465.2 [M + Na]⁺ (calcd for C₂₁H₃₀O₁₀Na) [9].

Guanosine (6), white powder, C₁₀H₁₂N₄O₅ [10].

Chlorogenic acid (7), white crystals, C₁₆H₁₈O₉ [11].

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