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CHEMICAL CONSTITUENTS OF *Zanthoxylum armatum*. II

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Zanthoxylum armatum DC., a common wild species in the genus *Zanthoxylum*, is distributed mainly in southeast and southwest of China and cultivated in some areas of China. *Z. armatum* is a famous traditional Chinese medicine (TCM) for treatment of acute appendicitis and abdominal pain. Its whole plant has the smell of *Z. bungeanum* (called Huajiao in China). The hemp, bitter, and spicy parts of *Z. armatum* are more powerful than that of *Z. bungeanum*. Among fruit, leaf, peel, and stem of *Z. armatum*, the spicy taste of peel is the strongest. The fruit of *Z. armatum* is also widely used as seasoning in East Asia and as a substitute for *Z. bungeanum* at Jiangsu, Jiangxi, Hunan, Guangxi in China. Modern pharmacological studies demonstrated that *Z. armatum* possessed antispasmodic [1], analgesic and anti-inflammatory [2], antimicrobial, antioxidant, antidiabetic [3], antitumor [4], hepatoprotective [5], and anthelmintic [6] activities. Previous phytochemical investigations has led to the isolation of various compounds [7–9] such as amides, alkaloids, flavonoids, coumarins, lignans, triterpene, and phenylpropanoid glycoside.

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 solvent 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 EtOAc-soluble extract (9.4 g) resulted in the isolation of seventeen compounds. The structures of all isolated compounds were determined by a combination of spectroscopic methods (MS, ^{1}H and ^{13}C NMR) and comparison with the literature. The compounds were identified as isodecarine (**1**), phillygenin (**2**), syringaresinol (**3**), de-4′-*O*-methylyangambin (**4**), eudesmin (**5**), allocryptopine (**6**), escholidine perchlorate (**7**), (+)-pinoresinol-di-3,3-dimethylallyl ether (**8**), planispine A (**9**), dictamnine (**10**), (–)-fargesin (**11**), (+)-fargesin (**12**), kobusin (**13**), 6-acetonyldihydrochelerythrine (**14**), 8-acetonyldihydrofagaridine (**15**), 1,2-methylenedioxy-4-(1,2,3-trihydroxypropyl)-benzene (**16**), and demethylchelerythrine (**17**). All the isolated compounds consisted of nine lignans, seven alkaloids, and one phenol. Among them, compounds **2**, **7**, and **16** were first isolated from Rutaceae. Compounds **6**, **8**, **14**, and **15** were first isolated from *Z. armatum*.

Phillygenin (2). White crystals, $C_{21}H_{24}O_6$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.93–6.83 (6H, m, H-2, 2′, 5, 5′, 6, 6′), 4.87 (1H, d, J = 5.3, H-7), 4.44 (1H, d, J = 5.3, H-7′), 4.13 (1H, dd, J = 9.4, 1.2, H-9′a), 3.91 (3H, s, 3-OMe), 3.90 (3H, s, 3′-OMe), 3.88 (3H, s, 4-OMe), 3.85 (2H, m, H-9b, 9′b), 3.33 (2H, m, H-8, 9a), 2.91 (1H, m, H-8′). ESI-MS *m/z* 395.2 $[M + Na]^+$ (calcd for $C_{21}H_{24}O_6Na$) [10].

Allocryptopine (6). Light yellow crystals, $C_{21}H_{23}NO_5$ [11].

Escholidine Perchlorate (7). Light yellow crystals, $C_{20}H_{22}NO_4^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.16 (1H, s, H-1), 7.14 (1H, s, H-4), 6.97 (1H, d, J = 8.5, H-11), 6.73 (1H, d, J = 8.1, H-12), 6.52 (1H, d, J = 12.6, H-8a), 6.41 (1H, d, J = 12.6, H-8b), 5.94 (2H, s, OCH_2O), 5.58 (1H, d, J = 12.7, H-14), 3.78 (2H, m, H-6), 3.76 (3H, s, OMe), 3.62 (1H, m, H-13), 3.47 (1H, t, J = 7.2, H-13), 3.01 (3H, s, NCH_3), 2.81 (2H, s, H-5). ESI-MS *m/z* 341.0 $[M + H]^+$ (calcd for $C_{20}H_{23}NO_4$) [12].

(+)-Pinoresinol-di-3,3-dimethylallyl Ether (8). Colorless oil, $C_{30}H_{38}O_6$ [13].

6-Acetonyldihydrochelerythrine (14). Yellow needle crystals, $C_{24}H_{23}NO_5$ [14].

8-Acetonyldihydrofagaridine (15). Light yellow crystals, $C_{23}H_{21}NO_5$ [15].

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1,2,3-Trihydroxy-1-(3,4-methylenedioxyphenyl)propane (16). White solid, $C_{10}H_{12}O_5$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.85 (1H, d, J = 1.4, H-2′), 6.81 (1H, dd, J = 7.9, 1.4, H-6′), 6.78 (1H, d, J = 7.9, H-5′), 5.95 (2H, s, OCH_2O), 4.71 (1H, d, J = 3.7, H-1), 4.23 (1H, dd, J = 8.8, 6.7, H-3a), 3.87 (1H, dd, J = 9.1, 3.3, H-3b), 3.05 (1H, m, H-2). ESI-MS *m/z* 213.1 $[M + H]^+$ (calcd for $C_{10}H_{13}O_5$) [16].

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