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LIGNANS AND PHENYLPROPANOIDS FROM *Fagopyrum tataricum* ROOTS

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The genus *Fagopyrum* (Polygonaceae) consists of 15 species and is mainly distributed in the North Temperate Zone. Eight species occur in China, including some common crops and medicinal plants, such as *Fagopyrum tataricum* (L.) Gaertn. (tartary buckwheat), *Fagopyrum esculentum* Moench. (buckwheat), and *Fagopyrum dibotrys* (D. Don) Hara [1]. Tartary buckwheat roots were traditionally used in folk medicine in Shanxi, China, to treat some chronic and incurable diseases [2, 3]. Several kinds of chemical compounds have been isolated from the seeds and sprouts of this plant, including flavonoids, steroids, and phenols [4, 5]. The present work led to the isolation of four lignans and two phenylpropanoids, all of which were isolated from the genus *Fagopyrum* for the first time. Lignans **1–4** were first isolated from the family Polygonaceae.

The roots of *Fagopyrum tataricum* were collected from Jiande, Zhejiang Province, China in August 2010 and was identified by Prof. Han-chen Zheng. A voucher specimen (#20100816) was deposited in the Herbarium of the Department of Pharmacognosy, Second Military Medical University, Shanghai, P. R. China.

The dried and powdered material (4 kg) was extracted three times with 95% ethanol under reflux. After removal of the solvent by evaporation, the extracts were suspended in water and partitioned with petroleum ether (PE), CH_2Cl_2, EtOAc, and *n*-BuOH, successively. The CH_2Cl_2 extract (8 g) was subjected to a series of chromatographies, using a silica gel column and Sephadex LH-20, to yield four lignans and two phenylpropanoids. These compounds were identified as syringaresinol (**1**) [6], schizandrin (**2**) [7], 4-ketopinoresinol (**3**) [8], graminone B (**4**) [9], sinapaldehyde (**5**) [10], and *cis*-*p*-coumaric acid ethyl ester (**6**) [11]. The structures of these compounds were confirmed by ^{1}H NMR and ^{13}C NMR methods. The spectroscopic data of all compounds were in good agreement with the literature data.

Syringaresinol (1), $C_{22}H_{26}O_8$, white powder, mp 171–173°C, EI-MS *m/z* 418 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.09 (2H, m, H-1, 5), 3.89 (6H, s, 4 × OCH_3), 4.74 (2H, d, J = 4.4, H-2, 6), 4.29 (4H, dd, J = 6.8, 9.2, H-4, 8), 6.59 (4H, s, H-2′, 2″, 6′, 6″). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 54.2 (C-1, 5), 56.3 (4 × OCH_3), 71.7 (C-4, 8), 85.9 (2, 6), 102.6 (C-2′, 2″), 102.6 (6′, 6″), 131.9 (C-1′, 1″), 134.2 (C-4′, 4″), 147.1 (C-3′, 3″), 147.1 (5′, 5″).

Schizandrin (2), $C_{24}H_{32}O_7$, yellowish amorphous powder, EI-MS *m/z* 432 $[M]^+$. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.82 (3H, d, J = 7.8, H-17), 1.26 (3H, s, H-18), 1.28 (1H, m, H-8), 2.38 (2H, d, J = 13.2, H-9), 2.67 (2H, d, J = 13.2, H-6), 6.54 (1H, s, H-11), 6.62 (1H, s, H-4), 3.59 (6H, 2 × OMe), 3.90 (12H, 4 × OMe). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.8 (C-1), 140.7 (C-2), 152.0 (C-3), 110.4 (C-4), 131.8 (C-5), 40.8 (C-6), 71.8 (C-7), 41.8 (C-8), 34.2 (C-9), 133.8 (C-10), 109.9 (C-11), 152.3 (C-12), 140.2 (C-13), 151.5 (C-14), 122.7 (C-15), 124.1 (C-16), 15.8 (C-17), 29.7 (C-18).

4-Ketopinoresinol (3), $C_{20}H_{20}O_7$, white amorphous powder, EI-MS *m/z* 372 $[M]^+$. ^{1}H NMR (400 MHz, $CDC1_3$, δ, ppm, J/Hz): 3.45 (1H, dd, J = 7.8, 4.0, H-5), 3.23 (1H, m, H-1), 3.89 (6H, s, OCH_3), 4.03 (1H, dd, J = 10.0, 4.8, H-8a), 4.33 (1H, dd, J = 7.8, 3.2, H-8b), 5.33 (1H, d, J = 6, H-6), 5.65 (1H, d, J = 2.8, H-2), 6.80–6.89 (6H, complex, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 49.9 (C-1), 53.3 (C-5), 56.0 (2 × OMe), 72.7 (C-8), 83.3 (C-6), 84.6 (C-2), 107.8, 108.1 (C-2′, 2″), 114.4, 114.7 (C-5′, 5″), 118.0, 118.4 (C-6′, 6″), 131.1, 132.3 (C-1′, 1″), 145.3 (C-3′, 3″), 146.0, 146.9 (C-4′, 4″), 176.9 (C-4).

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Graminone B (4), $C_{21}H_{22}O_8$, white amorphous powder, EI-MS *m/z* 402.13 $[M]^+$. ^1H NMR (400 MHz, $CDC1_3$, δ, ppm, J/Hz): 3.22 (1H, m, H-5), 3.44 (1H, dd, J = 9.2, 3.7, H-1), 3.88 (6H, s, 2 × OMe), 3.89 (3H, s, OMe), 4.03 (1H, dd, J = 9.8, 4.3, H-8), 4.33 (1H, dd, J = 9.8, 6.7, H-8), 5.30 (1H, d, J = 3.7, H-6), 5.33 (1H, d, J = 3.7, H-2), 5.55 (1H, br.s, OH), 5.60 (1H, br.s, OH), 6.48 (1H, s, Ar-H), 6.90–6.95 (4H, complex, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 50.3 (C-1), 53.2 (C-5), 56.1 (OMe), 56.6 (2 × OMe), 72.6 (C-8), 83.5 (C-6), 84.8 (C-2), 102.1 (C-4′), 108.3 (C-2″), 114.5 (C-2′), 118.1 (C-6′, 6″), 130.4 (C-1′), 132.2 (C-1″), 135.1 (C-4″), 145.3 (C-3″), 146.8 (C-3′), 147.5 (C-5′, 5″), 176.9 (C-4).

Sinapaldehyde (5), yellow powder, $C_{11}H_{12}O_4$, mp 108–110°C, ESI-MS *m/z* 209 $[M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.95 (6H, s, 2 × OCH_3), 5.92 (1H, s, 4′-OH), 6.61 (1H, dd, J = 15.8, 7.7, H-2), 6.82 (2H, s, H-2′, H-6′), 7.38 (1H, d, J = 15.8, H-3), 9.66 (1H, d, J = 7.7, H-1). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 125.6 (C-1′), 105.6 (C-2′, C-6′), 147.4 (C-3′, C-5′), 138.1 (C-4′), 153.1 (C-3), 126.8 (C-2), 193.4 (C-1), 56.4 (2 × OCH_3).

***cis-p*-Coumaric acid ethyl ester (6)**, $C_{11}H_{12}O_3$, white amorphous powder, EI-MS *m/z* 192 $[M]^+$. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.27 (3H, t, J = 7.1, CH_3), 4.14 (2H, q, J = 7.1, CH_2), 5.93 (1H, br.s, OH), 6.84 (2H, d, J = 8.5, H-3′, 5′), 6.86 (1H, d, J = 16.0, H-2), 7.43 (2H, d, J = 8.5, H-2′, 6′), 7.64 (1H, d, J = 16.0, H-3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.3 (CH_3), 60.5 (OCH_2), 115.5 (C-3′, 5′), 115.9 (C-2), 127.1 (C-1′), 130.0 (C-2′, 6′), 144.5 (C-3), 157.9 (C-4′), 167.7 (C-1).

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