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# CHEMICAL CONSTITUENTS OF BARK OF *Phellodendron chinense*

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*Phellodendron chinense* C.K. Schneid. (Rutaceae) is distributed mainly in Southwest of China and cultivated in some areas of China [1]. *P. chinense* is one of the 50 fundamental herbs of traditional Chinese medicine [2]. Its taste is very bitter, chewy sticky. Modern pharmacological studies demonstrated that *P. chinense* possessed immunomodulation, antitumor, and antibacterial activities [3]. In this study we investigated the water fraction of the acetone extract from the root bark of *P. chinense*, resulting in the isolation of 11 compounds, including phenylpropanoid glycosides, phenylethanoid glycosides, and phenol glycosides. Among which, except compounds **1** (9.3 mg), **2** (4.7 mg), and **10** (4.5 mg), the other compounds including **3** (15.0 mg), **4** (10.0 mg), **5** (6.2 mg), **7** (4.4 mg), **8** (6.8 mg), **9** (12.4 mg), and **11** (24.2 mg), were firstly isolated from the Rutaceae family, and compound **6** (18.3 mg) were firstly obtained from the plant.

The bark of *P. chinense* was purchased from Shanghai of China in 2015. The Bark of *P. chinense* (20 kg) was extracted thrice with 60% acetone (10 L × 3) 20–26°C. The combined acetone extract was filtered and concentrated under reduced pressure to give 962 g of residue. The residue was then suspended in water and partitioned successively with petroleum ether and *n*-BuOH. The phytochemical investigation of the water-soluble extract (820 g) resulted in the isolation of 11 compounds.

**Syringin (1)**, white powder, $C_{17}H_{24}O_9$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 6.65 (2H, s, H-2, 6), 6.45 (1H, d, J = 15.9, H-7), 6.23 (1H, dt, J = 15.8, 5.5, H-8), 4.77 (1H, d, J = 7.6, H-1′), 4.12 (2H, dd, J = 5.5, 1.4, H-9), 3.76 (6H, s, 2 × OMe), 3.52–3.21 (4H, m, H-2′, 3′, 4′, 5′), 3.76 (1H, dd, J = 12.1, 2.2, H-6′b), 3.66 (1H, dd, J = 12.1, 4.0, H-6′a). ESI-MS *m/z* 395.0 $[M + Na]^+$ (calcd for $C_{17}H_{24}O_9Na$) [4].

**Coniferin (2)**, colorless crystals, $C_{16}H_{22}O_8$ [5].

**Ligusinenoside A (3)**, white amorphous powder, $C_{21}H_{30}O_{12}$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 7.16 (s, H-2), 7.10 (1H, d, J = 8.4, H-5), 7.03 (1H, d, J = 10.0, H-6), 6.57 (1H, d, J = 16.1, H-7), 6.33 (1H, dt, J = 15.7, 5.2, H-8), 5.02 (1H, d, J = 3.1, H-1″), 5.02 (1H, d, J = 3.1, H-1′), 4.22 (2H, d, J = 5.2, H-9), 4.01 (1H, d, J = 4.2, H-2″), 3.90 (2H, d, J = 3.1, H-4″), 3.86 (3H, s, MeO), 3.59–3.53 (1H, m, H-3′, 4′, 5′), 3.61–3.56 (2H, m, H-6′), 3.56 (2H, s, H-5″), 3.47 (1H, dd, J = 9.2, 3.1, H-2′). ESI-MS *m/z* 474.0 $[M]^+$ (calcd for $C_{21}H_{30}O_{12}$) [6].

**Sinapaldehyde glucoside (4)**, white powder, $C_{17}H_{22}O_9$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 9.53 (1H, d, J = 7.8, H-9), 7.51 (1H, d, J = 15.8, H-7), 6.93 (1H, s, H-2), 6.66 (1H, dd, J = 15.8, 7.7, H-8), 6.65 (1H, s, H-6), 4.94 (1H, d, J = 7.5, H-1′), 3.79 (3H, s, MeO), 3.66 (1H, d, J = 12.0, H-2′), 3.54 (1H, dd, J = 12.0, 5.3, H-3′), 3.37 (1H, d, J = 7.7, H-4′), 3.31 (2H, dd, J = 11.8, 7.0, H-6′). ESI-MS *m/z* 370.0 $[M]^+$ (calcd for $C_{17}H_{22}O_9$) [7].

**Coniferaldehyde glucoside (5)**, yellow solid, $C_{16}H_{20}O_8$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 9.23 (1H, d, J = 7.3, H-9), 7.12 (1H, d, J = 7.9, H-2), 7.10 (1H, d, J = 1.7, H-5), 7.02 (1H, dd, J = 8.4, 1.6, H-6), 6.46 (1H, d, J = 16.1, H-7), 6.33 (1H, dt, J = 15.7, 5.2, H-8), 5.02 (1H, d, J = 3.1, H-1′), 3.67 (1H, d, J = 12.0, H-2′), 3.58 (1H, dd, J = 12.0, 5.3, H-3′), 3.61–3.56 (2H, m, H-6′). ESI-MS *m/z* 340 $[M]^+$ (calcd for $C_{16}H_{20}O_8$) [8].

**(–)-(7*R*,8*S*)-Guaiacylglycerol 8-*O*-*β*-D-glucopyranoside (6)**, white powder, $C_{16}H_{24}O_{10}$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 7.03 (1H, s, H-2), 6.81 (1H, d, J = 6.8, H-5), 6.73 (1H, d, J = 8.1, H-6), 4.49 (1H, d, J = 7.7, H-1′), 3.85 (3H, s, MeO), 3.65 (1H, dd, J = 11.0, 5.1, H-6′a), 3.56 (1H, dd, J = 11.0, 2.7, H-6′b), 3.49–3.30 (4H, m, H-2′, 3′, 4′, 5′). ESI-MS *m/z* 399.6 $[M + Na]^+$ (calcd for $C_{16}H_{24}O_{10}Na$) [9].

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**Threo-3-methoxy-5-hydroxy-phenylpropanetriol-8-*O*-*β*-D-glucopyranoside (7)**, white powder, $C_{16}H_{24}O_{10}$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 6.94 (1H, s, H-1), 6.82 (1H, s, H-5), 6.81 (1H, s, H-3), 4.69 (1H, d, J = 6.8, H-8), 4.38 (1H, d, J = 7.8, H-1′), 3.89 (1H, m, H-7), 3.76 (3H, s, MeO), 3.65 (1H, dd, J = 11.0, 5.1, H-6′a), 3.56 (1H, dd, J = 11.0, 2.7, H-6′b), 3.55 (1H, dd, J = 12.3, 3.3, H-9a), 3.49–3.30 (4H, m, H-2′, 3′, 4′, 5′), 3.30 (1H, m, H-9b). HR-ESI-MS *m/z* 399.1261 $[M + Na]^+$ (calcd for $C_{16}H_{24}O_{10}Na$, 399.1261) [10].

**2-(4-Hydroxylphenyl)ethyl *O*-*α*-D-apiofuranosyl-(1–6)-*O*-*β*-D-glucopyranoside (8)**, amorphous powder, $C_{19}H_{28}O_{11}$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 7.17 (2H, d, J = 8.4, H-2, 6), 7.07 (2H, d, J = 8.4, H-3, 5), 4.89 (1H, d, J = 3.3, H-1′), 4.25 (1H, d, J = 8.0, H-1″), 3.91 (1H, d, J = 12.4, H-6′a), 3.74–3.65 (1H, m, H-6′b), 3.53–3.39 (2H, m, H-3′, 5′), 3.53–3.39 (2H, m, H-2′, 4′). ESI-MS *m/z* 455.1 $[M + Na]^+$ (calcd for $C_{19}H_{28}O_{11}Na$) [11].

**Benzoic acid, 4-[(*β*-D-glucopyranosyloxy)methyl]-methyl ester (9)**, colorless crystals, $C_{15}H_{20}O_8$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 7.91 (2H, d, J = 8.8, H-2, 6), 6.87 (2H, d, J = 8.7, H-3, 5), 4.92 (1H, d, J = 3.7, H-1′), 4.42 (1H, d, J = 7.4, H-7a), 4.28 (1H, d, J = 7.4, H-7b), 3.95–3.82 (2H, m, H-2′, 3′), 3.81 (3H, s, MeO), 3.64–3.55 (2H, m, H-4′, 5′), 3.43 (1H, d, J = 6.3, H-6′a), 3.22 (1H, dd, J = 9.7, 6.3, H-6′b). ESI-MS *m/z* 351.0 $[M + Na]^+$ (calcd for $C_{15}H_{20}O_8Na$) [12].

***α*-D-Glucopyranoside, 2-(4-hydroxyphenyl)ethyl (10)**, colorless crystals, $C_{14}H_{20}O_7$ [13].

**3-Hydroxy-3,5-dimethoxyphenyl *β*-D-glucopyranoside (11)**, white amorphous powder, $C_{14}H_{20}O_9$. $^1$H NMR (400 MHz, $D_2O$, δ, ppm, J/Hz): 6.55 (2H, s, H-2, 6), 5.06 (1H, d, J = 8.5, H-1′), 3.71 (6H, s, MeO), 3.54 (1H, dd, J = 9.0, 7.2, H-2′), 3.53–3.41 (3H, m, H-3′, 4′, 5′), 4.08 (1H, d, J = 11.0, H-6′a), 3.65 (1H, dd, J = 11.0, 4.7, H-6′b). ESI-MS *m/z* 355.0 $[M + Na]^+$ (calcd for $C_{14}H_{20}O_9Na$) [14].

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