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CONSTITUENTS FROM CHARRED *Cirsium japonicum*

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Cirsium japonicum DC. (Compositae), distributed in China, Korea, and Japan [1], is widely used in traditional herbal medicine for the treatment of hemorrhage, hepatitis, hypertension, or circulatory problems [2]. In order to find the bioactive constituents from *Cirsium japonicum* DC., MTT-guided isolation and identification of the ethanol extracts of *Cirsium japonicum* DC. have been carried out, and here we report the isolation of eight compounds.

The aerial parts of *Cirsium japonicum* DC. were collected from Zhang Shu (Jiang Xi, China) during June 2006 and identified by Dr. Q. F. Gong. Charred *Cirsium japonicum* DC. was processed by us according to the procedures of the Pharmacopoeia of the People′s Republic of China (2005 version). A voucher specimen (20060608) has been deposited in the Department of Chemistry of Nanchang University (Jiang Xi, China).

The air-dried powdered parts (2 kg) of charred *Cirsium japonicum* DC. were extracted under reflux by alcohol (3 × 70%). The solvent was evaporated in vacuum and then the concentrated extract was successively partitioned with chloroform and *n*-butanol. The chloroform fraction was successively purified on silica gel (200–300 mesh) with $CHCl_3$–MeOH gradient and on Sephadex LH-20 with $CHCl_3$–MeOH (1:1) to yield compounds **1–6**. The *n*-butanol extract was purified using silica gel (200–300 mesh) with $CHCl_3$–MeOH gradient as eluent and on RP-ODS with MeOH–H_2O to furnish compounds **7–8**. All of these compounds were isolated for the first time from charred *Cirsium japonicum* DC., and compounds **4** and **6** were obtained from the genus *Cirsium* for the first time.

The compounds were identified using UV, IR, mass, and NMR spectral data and determined as pectolinarigenin (**1**), acacetin (**2**), diosmetin (**3**), pilosin (**4**), quercetin (**5**), pyrocatechol (**6**), pectolinarin (**7**), and linarin (**8**) [3–9].

Pectolinarigenin (1): yellow crystal (methanol), $C_{17}H_{14}O_6$. UV (MeOH, λ_{max}, nm): 336, 273. ESI-MS *m/z* 313 $[M - H]^-$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.86 (1H, s, H-3), 6.61 (1H, s, H-8), 8.02 (2H, d, J = 8.8, H-2′, 6′), 7.10 (2H, d, J = 8.8, H-3′, 5′), 12.97 (1H, s, 5-OH), 10.78 (1H, s, 7-OH), 3.94 (3H, s, 6-OCH_3), 3.86 (3H, s, 4′-OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.8 (C-2), 103.5 (C-3), 182.6 (C-4), 153.2 (C-5), 131.8 (C-6), 157.8 (C-7), 94.7 (C-8), 152.9 (C-9), 104.6 (C-10), 123.3 (C-1′), 128.7 (C-2′, 6′), 114.9 (C-3′, 5′), 162.7 (C-4′), 60.4 (6-OCH_3), 55.9 (4′-OCH_3).

Acacetin (2): yellow crystal (methanol), $C_{16}H_{12}O_5$. UV (MeOH, λ_{max}, nm): 335, 267. ESI-MS *m/z* 283 $[M - H]^-$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.83 (3H, s, 4′-OCH_3), 6.20 (1H, d, J = 2.0, H-6), 6.50 (1H, d, J = 2.0, H-8), 6.86 (1H, s, H-3), 7.10 (2H, d, J = 8.8, H-3′, 5′), 8.03 (2H, d, J = 8.8, H-2′, 6′), 10.84 (1H, s, 7-OH), 12.92 (1H, s, 5-OH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.3 (C-2), 103.5 (C-3), 181.8 (C-4), 157.3 (C-5), 98.9 (C-6), 164.2 (C-7), 94.0 (C-8), 161.3 (C-9), 103.8 (C-10), 122.8 (C-1′), 128.3 (C-2′, 6′), 114.6 (C-3′, 5′), 162.3 (C-4′), 55.6 (4′-OCH_3).

Diosmetin (3): yellow crystal (methanol), $C_{16}H_{12}O_6$. UV (MeOH, λ_{max}, nm): 339, 269. ESI-MS *m/z* 299 $[M - H]^-$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.92 (3H, s, 4′-OCH_3), 6.25 (1H, d, J = 2.0, H-6), 6.52(1H, d, J = 2.0, H-8), 6.80 (1H, s, H-3), 7.13 (1H, d, J = 8.4, H-5′), 7.48 (1H, d, J = 2.0, H-2′), 7.59 (1H, dd, J = 2.0, 8.4, H-6′), 9.50 (1H, s, 3′-OH), 10.89 (1H, s, 7-OH), 12.98 (1H, s, 5-OH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 163.3 (C-2), 103.6 (C-3), 181.4 (C-4), 157.2 (C-5), 98.7 (C-6), 164.2 (C-7), 93.6 (C-8), 161.4 (C-9), 103.4 (C-10), 118.5 (C-1′), 112.7 (C-2′), 146.6 (C-3′), 151.0 (C-4′), 112.1 (C-5′), 123.1 (C-6′), 55.6 (4′-OCH_3).

Pilosin (4): yellow crystal (methanol), $C_{17}H_{14}O_7$. UV (MeOH, λ_{max}, nm): 332, 287. ESI-MS *m/z* 329 $[M - H]^-$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.88 (1H, s, H-3), 7.03 (2H, d, J = 8.9, H-3′, 5′), 7.96 (2H, d, J = 8.9, H-2′, 6′), 13.22 (1H, s, 5-OH), 10.13 (1H, s, 7-OH), 3.83 (3H, s, 6-OCH_3), 3.72 (3H, s, 4′-OCH_3).

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Pyrocatechol (6): white crystal (acetone), $C_6H_6O_2$, ESI-MS *m/z* 109 $[M - H]^-$. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.72 (2H, dd, J = 3.6, 6, H-4, 5), 6.59 (2H, dd, J = 3.6, 6, H-3, 6), 8.84 (2H, s, 1,2-OH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 114.9 (C-4,5), 120.6 (C-3,6), 142.1 (C-1,2).

Pectolinarin (7): yellow amorphous powder, $C_{29}H_{34}O_{15}$. UV (MeOH, λ_{max}, nm): 335, 271. ESI-MS *m/z* 621 $[M - H]^-$. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.55 (3H, d, J = 6.1, CH_3), 3.69 (3H, s, 4′-OCH_3), 4.04 (3H, s, 6-OCH_3), 5.48 (1H, d, J = 1.1, H-1‴), 5.75 (1H, d, J = 7.4, H-1″), 6.86 (1H, s, H-3), 7.25 (2H, d, J = 9.0, H-3′, 5′), 7.32 (1H, s, H-8), 8.04 (2H, d, J = 8.9, H-2′, 6′), 12.97 (1H, s, 5-OH). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 164.8 (C-2), 102.7 (C-3), 183.2 (C-4), 153.2 (C-5), 135.2 (C-6), 157.8 (C-7), 95.3 (C-8), 154.2 (C-9), 107.3 (C-10), 122.8 (C-1′), 128.9 (C-2′,6′), 115.2 (C-3′,5′), 163.1 (C-4′), 104.4 (C-1″), 74.7 (C-2″), 78.5 (C-3″), 71.4 (C-4″), 77.8 (C-5″), 67.7 (C-6″), 102.4 (C-1‴), 72.1 (C-2‴), 72.9 (C-3‴), 74.1 (C-4‴), 69.9 (C-5‴), 18.6 (C-6‴), 55.5 (4′-OCH_3), 60.9 (6-OCH_3).

Linarin (8): yellow amorphous powder, $C_{28}H_{32}O_{14}$. UV (MeOH, λ_{max}, nm): 331, 265. ESI-MS *m/z* 591 $[M - H]^-$. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.07 (3H, d, J = 6.2, CH_3), 3.85 (3H, s, 4′-OCH_3), 4.55 (1H, br.s, H-1‴), 5.05 (1H, d, J = 7.3, H-1″), 6.25 (1H, d, J = 2.2, H-6), 6.76 (1H, d, J = 2.2, H-8), 6.93 (1H, s, H-3), 7.12 (2H, d, J = 9.0, H-3′, 5′), 8.03 (2H, d, J = 7.0, H-2′, 6′), 12.90 (1H, s, 5-OH).

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