FLAVONOIDS FROM *Salix caprea*

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Salix caprea L. (Salicaceae) is widely used in folk medicine for rheumatoid arthritis, malaria, various hemorrhages, gout, neuralgia, and intestinal diseases as an antipyretic, analgesic, anti-inflammatory, antibacterial, hemostatic, sedative, and antihelminthic agent [1, 2].

Carbohydrates [3], tanning agents [4], steroids [5], phenolglucosides [6], alkaloids, vitamins [7], phenolcarboxylic acids and their derivatives [8], flavonoids chultenin [3], kaempferol, luteolin, apigenin, naringenin, quercetin, isorhamnetin [9], luteolin 7-*O*-*β*-D-glucopyranoside, baccoside, salicaprin [10-12], diosmetin, caperoside, salicaperoside [13, 14], astragalin, quercemeritrin, and quercetin 3,7-di-*O*-glucoside [15] were isolated from *S. caprea.*

Ground air-dried flowers of *S. caprea* (1000 g) that were collected in Hotan district of Xinjiang Autonomous Region, P. R. China, were extracted exhaustively with EtOH (70%) at room temperature. The combined extracts were evaporated *in vacuo*. The condensed residue was diluted with water and treated successively with petroleum ether, ether, EtOAc, and *n*-BuOH.

The EtOAc fraction was separated by HPLC over a Phenomenex ODS-C_{18} column (250 × 4.6 mm, 5 μm) with a C_{18} pre-column. Solvents were filtered through a 0.45 μm filter before use. The mobile phase was MeOH:H_2O (40:60, v/v) at flow rate 1 mL/min. UV detection was carried out at λ 210, 260, 280, and 360 nm (at various recording scales I, II, III, IV). Four compounds (**1**–**4**) were eluted from the column with retention times of 15, 43, 64, and 70 min, respectively.

Pure compounds were identified using UV, IR, PMR, and ^{13}C NMR spectra as astragalin (**1**) [15, 16], quercimeritrin (**2**) [15, 17], isorhamnetin-7-*O*-*β*-D-glucoside (**3**) [18], and isoquercitrin (**4**) [19].

Astragalin (1), $C_{21}H_{20}O_{11}$, mp 177–179°C. UV spectrum (MeOH, λ_{max}, nm): 268, 301, 360; +$AlCl_3$: 272, 304, 398; +$AlCl_3$/HCl: 277, 302, 350, 398; +CH_3COONa: 278, 370.

Acid hydrolysis of astragalin produced kaempferol and D-glucose.

Quercimeritrin (2), $C_{12}H_{20}O_{12}$, mp 251–253°C. UV spectrum (MeOH, λ_{max}, nm): 260, 370; +CH_3COONa: 260, 371.

Acid hydrolysis of **2** produced quercetin and D-glucose.

Isorhamnetin-7-*O*-*β*-D-glucoside (3), $C_{22}H_{22}O_{12}$, mp 255–257°C. UV spectrum (MeOH, λ_{max}, nm): 257, 372; +CH_3COONa: 257, 374.

IR spectrum (KBr, ν, cm^{-1}): 3308, 2929, 1656, 1604, 1511, 1456, 1432, 1358, 1291, 1262, 1205, 1183, 1126, 1025, 994.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz, 0 = HMDS): 3.20-3.78 (6H, Glc), 3.83 (3H, s, OMe), 5.58 (1H, d, J = 7.6, Glc H-1″), 6.20 (1H, d, J = 1.6, H-6), 6.43 (1H, d, J = 1.6, H-8), 6.90 (1H, d, J = 8.4, H-5′), 7.52 (1H, dd, J = 1.6, 8.8, H-6′), 7.95 (1H, d, J = 1.6, H-2′), 12.60 (1H, s, 5-OH).

^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 156.46 (C-2), 132.97 (C-3), 177.30 (C-4), 162.18 (C-5), 98.82 (C-6), 164.65 (C-7), 93.81 (C-8), 156.20 (C-9), 103.83 (C-10), 121.12 (C-1′), 113.48 (C-2′), 149.32 (C-3′), 146.87 (C-4′), 115.17 (C-5′), 122.01 (C-6′), 100.80 (C-1″), 74.27 (C-2″), 76.31 (C-3″), 69.73 (C-4″), 77.43 (C-5″), 60.73 (C-6″), 55.68 (OMe).

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Acid hydrolysis of **3** formed isorhamnetin and D-glucose.

Isoquercitrin (4), $C_{21}H_{20}O_{12}$, mp 248–250°C. UV spectrum (MeOH, λ_{max}, nm): 268, 366; +$NaOCH_3$: 273, 326, 408; +NaAc: 371; +H_3BO_3/NaAc: 374; +$AlCl_3$/HCl: 390.

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz, 0 = HMDS): 3.8–4.18 (H-Glc), 5.37 (1H, d, J = 7.2, Glc H-1″), 6.16 (1H, d, J = 1.8, H-6), 6.37 (1H, d, J = 1.8, H-8), 6.81 (1H, d, J = 8.8, H-5′), 7.54 (1H, dd, J = 2.4, 8.8, H-6′), 7.75 (1H, d, J = 2.4, H-2′), 12.58 (1H, s, 5-OH).

Acid hydrolysis of **4** produced quercetin and D-glucose.

Isorhamnetin-7-*O*-β-D-glucoside and isoquercitrin were isolated for the first time from *S. caprea*.

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