

FLAVONOIDS OF *Saxifraga umbellulata*

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There are about 203 species of *Saxifraga* growing in China [1]. *Saxifraga umbellulata* grows mainly in high, cold areas such as southwest of China and Qinghai, Gansu Province. *S. umbellulata* is an important herb medicine that has been used as a traditional folk medicine for the treatment of hepatitis, cholecystitis, influenza, fever, sore heat, and so on [2]. As part of our continuous research on *Saxifraga umbellulata* [3], seven flavonoids were isolated from *Saxifraga umbellulata* for the first time.

The air-dried whole plants of *Saxifraga umbellulata* were bought from Kumbum Monastery, Tibetan Hospital in Qinghai Province of China in October of 2009 and identified by Prof. Guo Liang Zhang, Lanzhou University. The powdered *S. umbellulata* (3.0 kg) was extracted by ethanol refluxing (12 L \times 2, extraction 2 h for the first time, 1 h for the second time). The EtOH extract was concentrated under reduced pressure to give a residue (320 g), it was sequentially partitioned with PE (90–100°C) (0.5 L \times 4), EtOAc (0.5 L \times 4), and *n*-BuOH (0.5 L \times 4). The EtOAc fraction (45 g) was chromatographed on a silica gel column (4.0 \times 120 cm), eluted with PE–acetone (50:1–0:1) gradually to yield 10 fractions (Fr. 1–10) according to TLC analysis. Fraction 10 was subjected to a series of chromatographic techniques using a silica gel column (mesh 200–300), Sephadex LH-20, and MCI (75–150 μ m). Four flavonoids (**1–4**) were isolated. The *n*-BuOH fraction (75 g) was chromatographed on a silica gel column (5.0 \times 150 cm) eluted with CHCl₃–MeOH (15:1–0:1) gradually to yield 10 fractions (Fr. 1–10) according to TLC analysis. Fractions 4 (1.0 g) and 7 were re-treated on an LH-20 (20–150 μ m) column to obtain three flavonoids (**5–7**). All these flavonoids were identified by NMR, MS, and IR spectra.

Quercetin (**1**), yellow needles, C₁₅H₁₀O₇ [4].

Myricetin (**2**), yellow powder, C₁₅H₁₀O₈ [5].

Syringetin (**3**), yellow powder, C₁₇H₁₄O₈ [6].

Quercetin-3-*O*- β -D-glucopyranoside (**4**), yellow powder, C₂₁H₂₀O₁₂ [7].

Quercetin-3-*O*- β -D-galactopyranoside (**5**), yellow needles, C₂₁H₂₀O₁₂ [8].

Quercetin-3-*O*- β -D-glucuronopyranoside-6''-butyl ester (**6**), yellow powder, C₂₅H₂₆O₁₃. ESI-MS *m/z* 557.2 [M + Na]⁺.

¹H NMR (400 MHz, TMS, DMSO-d₆, δ , ppm, J/Hz): 7.59 (1H, dd, J = 8.4, 2.0, H-6'), 7.51 (1H, d, J = 2.0, H-2'), 6.84 (1H, d, J = 8.4, H-5'), 6.40 (1H, br.s, H-8), 6.20 (1H, br.s, H-6), 5.46 (1H, d, J = 8.0, H-1'), 3.97 (2H, t, J = 8.0, H-1'''), 3.66 (1H, d, J = 9.6, H-5''), 3.3–3.0 (m, sugar protons), 1.41 (2H, pentet-like, J = 8.0, H-2''), 1.15 (2H, sextet-like, J = 8.0, H-3'''), 0.74 (3H, t, J = 8.0, H-4'''). ¹³C NMR (100 MHz, TMS, DMSO-d₆, δ , ppm): 156.5 (C-2), 133.5 (C-3), 177.6 (C-4), 161.7 (C-5), 99.3 (C-6), 163.8 (C-7), 94.0 (C-8), 156.0 (C-9), 104.0 (C-10), 122.1 (C-1'), 115.6 (C-2'), 145.0 (C-3'), 149.0 (C-4'), 116.0 (C-5'), 121.0 (C-6'), 101.6 (C-1''), 74.2 (C-2''), 76.3 (C-3''), 71.6 (C-4''), 75.9 (C-5''), 168.0 (C-6''), 64.5 (C-1'''), 30.3 (C-2'''), 18.7 (C-3'''), 13.8 (C-4''') [9].

Quercetin-3-*O*- β -D-[2''-(*E*)-feruloyl]glucopyranosyl]-7,4'-*O*- β -D-diglucopyranoside (**7**), yellow powder, C₄₃H₄₈O₂₅. FAB-MS *m/z* 987.0 [M + Na]⁺. ¹H NMR (400 MHz, TMS, DMSO-d₆, δ , ppm, J/Hz): 6.41 (1H, s, H-6), 6.78 (1H, s, H-8), 7.67 (1H, br.s, H-2'), 7.22 (1H, d, J = 8.8, H-5'), 7.64 (1H, m, H-6'), 5.68 (1H, d, J = 8.0, H-1'), 4.90 (1H, m, H-2''), 5.08 (1H, d, J = 7.6, H-1'''), 4.98 (1H, d, J = 7.2, H-1'''), 7.34 (1H, br.s, H-2'''), 6.84 (1H, d, J = 7.6, H-5'''), 7.12 (1H, d, J = 8.0, H-6'''), 7.58 (1H, d, J = 15.6, H-7'''), 6.42 (1H, d, J = 16.0, H-8'''), 3.83 (3H, s, H-OMe). ¹³C NMR (100 MHz, TMS, DMSO-d₆, δ , ppm): 156.8 (C-2), 133.6 (C-3), 177.8 (C-4), 160.7 (C-5), 99.2 (C-6), 162.7 (C-7), 94.0 (C-8), 156.6 (C-9), 104.9 (C-10),

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124.0 (C-1'), 116.6 (C-2'), 146.3 (C-3'), 147.6 (C-4'), 115.4 (C-5'), 121.5 (C-6'), 98.3 (C-1''), 74.7 (C-2''), 74.1 (C-3''), 70.3 (C-4''), 77.0 (C-5''), 61.4 (C-6''), 99.2 (C-1'''), 73.7 (C-2'''), 76.3 (C-3'''), 68.9 (C-4'''), 77.9 (C-5'''), 61.1 (C-6'''), 101.2 (C-1'''), 74.8 (C-2'''), 78.0 (C-3'''), 69.4 (C-4'''), 76.9 (C-5'''), 60.6 (C-6'''), 124.5 (C-1'''), 111.0 (C-2'''), 148.0 (C-3'''), 148.9 (C-4'''), 116.6 (C-5'''), 123.0 (C-6'''), 145.2 (C-7'''), 114.6 (C-8'''), 165.8 (C-9'''), 56.4 (C-OMe) [10].

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