

FLAVONES FROM *Artemisia rupestris*^a

F. He,^{1,2} H. A. Aisa,^{1*} and Kh. M. Shakhidoyatov³

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The medicinal plant *Artemisia rupestris* L. is used in traditional Chinese medicine to treat flu [1, 2]. We studied the chemical components of antifungal fractions of this plant that contained flavones and isolated seven flavones. The plant material was collected in June 2008 in the town of Khami, Uyghur Autonomous Region, Xinjiang, China and was determined by Prof. S.-M. Duan (Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences).

Air-dried aerial part of *A. rupestris* (15 kg) was extracted by percolating CH₂Cl₂ (10 × 40 mL) at room temperature. The solvent was vacuum distilled to afford a resin of extracted substances (1.1 kg) that was separated by column chromatography over silica gel with elution by a petroleum ether:EtOAc gradient (from 15:1 to 0:1) and MeOH to produce seven fractions. The third and fourth fractions were separated by column chromatography over silica gel and Sephadex LH-20 with elution by various solvent systems to isolate seven flavones. The spectral characteristics of all obtained compounds 1–7 agreed well with the literature. Compounds 3–6 were isolated for the first time from *A. rupestris*.

Chrysosplenetin (1), C₁₉H₁₈O₈, yellow powder. ESI-MS *m/z* 373 [M – H][–]. PMR spectrum (400 MHz, DMSO-d₆, δ, ppm, J/Hz): 12.64 (1H, 5-OH), 9.96 (1H, 4'-OH), 7.68 (1H, d, J = 2.4, H-2'), 7.64 (1H, dd, J = 8.8, 2.4, H-6'), 6.97 (1H, d, J = 8.4, H-5'), 6.94 (1H, s, H-8), 3.93 (3H, s, OCH₃), 3.88 (3H, s, OCH₃), 3.82 (3H, s, OCH₃), 3.74 (3H, s, OCH₃). ¹³C NMR spectrum (100 MHz, DMSO-d₆, δ, ppm): 178.2 (C-4), 158.6 (C-7), 155.8 (C-9), 151.7 (C-2), 151.6 (C-5), 149.9 (C-3'), 147.5 (C-4'), 138.7 (C-3), 131.4 (C-6), 122.2 (C-1'), 115.6 (C-5'), 112.1 (C-2'), 104.9 (C-10), 91.4 (C-8), 60.0 (OCH₃), 59.7 (OCH₃), 56.5 (OCH₃), 55.8 (OCH₃) [3, 4].

Artemetin (2), C₂₀H₂₀O₈, yellow needle-like crystals (MeOH). ESI-MS *m/z* 387 [M – H][–]. PMR spectrum (400 MHz, DMSO-d₆, δ, ppm, J/Hz): 12.60 (1H, 5-OH), 7.75 (1H, dd, J = 8.8, 2.4, H-6'), 7.67 (1H, d, J = 2.0, H-2'), 7.17 (1H, d, J = 8.8, H-5'), 6.95 (1H, s, H-8), 3.94 (3H, s, OCH₃), 3.87 (6H, s, OCH₃), 3.83 (3H, s, OCH₃), 3.74 (3H, s, OCH₃). ¹³C NMR spectrum (100 MHz, DMSO-d₆, δ, ppm): 178.3 (C-4), 158.7 (C-7), 155.5 (C-9), 151.8 (C-2), 151.6 (C-5), 151.3 (C-4'), 148.5 (C-3'), 138.1 (C-3), 131.6 (C-6), 122.1 (C-1', 6'), 111.6 (C-5'), 111.2 (C-2'), 105.6 (C-10), 91.5 (C-8), 60.0 (OCH₃), 59.8 (OCH₃), 56.5 (OCH₃), 55.7 (OCH₃ × 2) [4, 5].

Acacetin (3), C₁₆H₁₂O₅, yellow powder. ESI-MS *m/z* 283 [M – H][–]. PMR spectrum (400 MHz, DMSO-d₆, δ, ppm, J/Hz): 12.87 (1H, 5-OH), 10.76 (1H, 7-OH), 8.01 (2H, d, J = 8.8, H-2', 6'), 7.09 (2H, d, J = 8.8, H-3', 5'), 6.81 (1H, H-3), 6.48 (1H, d, J = 2, H-8), 6.19 (1H, d, J = 2, H-6), 3.85 (3H, s, OCH₃). ¹³C NMR spectrum (100 MHz, DMSO-d₆, δ, ppm): 181.6 (C-4), 164.1 (C-7), 163.2 (C-2), 162.2 (C-4'), 161.4 (C-9), 157.2 (C-5), 128.2 (C-2', 6'), 122.8 (C-1'), 114.5 (C-3'), 114.5 (C-5'), 103.7 (C-10), 103.5 (C-3), 98.8 (C-6), 93.9 (C-8), 55.4 (OCH₃) [6].

3,5,4'-Trihydroxy-6,7,3'-trimethoxyflavone (4), C₁₈H₁₆O₈, yellow needle-like crystals (MeOH). ESI-MS *m/z* 359 [M – H][–]. PMR spectrum (400 MHz, DMSO-d₆, δ, ppm, J/Hz): 12.44 (1H, 5-OH), 9.78 (1H, 4'-OH), 9.60 (1H, 3-OH), 7.79 (1H, d, J = 2.0, H-2'), 7.76 (1H, dd, J = 8.8, 2.4, H-6'), 6.95 (1H, d, J = 8.8, H-5'), 6.93 (1H, s, H-8), 3.93 (3H, s, OCH₃), 3.86 (3H, s, OCH₃), 3.74 (3H, s, OCH₃). ¹³C NMR spectrum (100 MHz, DMSO-d₆, δ, ppm): 176.1 (C-4), 158.5 (C-7), 151.5 (C-9), 151.0 (C-5), 149.0 (C-3'), 147.4 (C-4'), 147.1 (C-2), 135.9 (C-3), 131.2 (C-6), 121.9 (C-1', 6'), 115.5 (C-5'), 111.7 (C-2'), 104.3 (C-10), 91.3 (C-8), 60.1 (OCH₃), 56.4 (OCH₃), 55.8 (OCH₃) [7].

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1) Key Laboratory of Plant Resources and Chemistry in Arid Regions, Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi 830011, P. R. China, fax: +86 991 38 356 79, e-mail: haji@ms.xjb.ac.cn; 2) Graduate School of the Chinese Academy of Sciences, Beijing 100039, P. R. China; 3) S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences, Republic of Uzbekistan, Tashkent, fax: (99871) 120 64 75, Translated from *Khimiya Prirodnykh Soedinenii*, No. 4, July–August, 2012, pp. 612–613. Original article submitted March 5, 2012.

Retusin C (quercetin-3,3',4',7'-tetramethyl ether) (5), $C_{19}H_{18}O_7$, yellow needle-like crystals (MeOH). ESI-MS m/z 359 $[M + H]^+$, 381 $[M + Na]^+$. PMR spectrum (400 MHz, DMSO- d_6 , δ , ppm, J/Hz): 12.64 (1H, 5-OH), 7.74 (1H, dd, $J = 8.4, 2.4$, H-6'), 7.67 (1H, d, $J = 2.0$, H-2'), 7.18 (1H, d, $J = 8.8$, H-5'), 6.81 (1H, d, $J = 2.4$, H-8), 6.40 (1H, d, $J = 2$, H-6), 3.88 (3H, s, OCH₃), 3.87 (3H, s, OCH₃), 3.86 (3H, s, OCH₃), 3.83 (3H, s, OCH₃). ^{13}C NMR spectrum (100 MHz, DMSO- d_6 , δ , ppm): 178.0 (C-4), 165.1 (C-7), 160.8 (C-5), 156.2 (C-9), 155.4 (C-2), 151.2 (C-4'), 148.4 (C-3'), 138.2 (C-3), 122.0 (C-1', 6'), 111.5 (C-5'), 111.1 (C-2'), 105.2 (C-10), 97.8 (C-6), 92.4 (C-8), 59.7 (OCH₃), 56.0 (OCH₃), 55.6 (OCH₃ $\times$ 2) [8].

Pachypodol (quercetin-3,3',7'-trimethyl ether) (6), $C_{18}H_{16}O_7$, yellow needle-like crystals (MeOH). ESI-MS m/z 343 $[M - H]^-$. PMR spectrum (400 MHz, DMSO- d_6 , δ , ppm, J/Hz): 12.68 (1H, 5-OH), 9.98 (1H, 4'-OH), 7.68 (1H, s, H-2'), 7.64 (1H, d, $J = 8.0$, H-6'), 6.97 (1H, d, $J = 8.0$, H-5'), 6.80 (1H, s, H-8), 6.38 (1H, s, H-6), 3.87 (6H, s, OCH₃), 3.82 (3H, s, OCH₃). ^{13}C NMR spectrum (100 MHz, DMSO- d_6 , δ , ppm): 178.0 (C-4), 165.1 (C-7), 160.9 (C-9), 156.3 (C-5), 155.8 (C-2), 150.0 (C-3'), 147.5 (C-4'), 138.0 (C-3), 122.3 (C-1'), 120.6 (C-6'), 115.7 (C-5'), 112.0 (C-2'), 105.2 (C-10), 97.8 (C-6), 92.4 (C-8), 59.7 (OCH₃), 56.1 (OCH₃), 55.8 (OCH₃) [6].

Isokaempferide (kaempferol-3-methyl ether) (7), $C_{16}H_{12}O_6$, colorless crystals. ESI-MS m/z 299 $[M - H]^-$. PMR spectrum (400 MHz, DMSO- d_6 , δ , ppm, J/Hz): 12.79 (1H, 5-OH), 10.85 (1H, 7-OH), 7.33 (2H, d, $J = 8.8$, H-2', 6'), 7.07 (2H, d, $J = 9.0$, H-3', 5'), 6.36 (1H, d, $J = 2.4$, H-8), 6.21 (1H, d, $J = 2.4$, H-6), 5.04 (1H, 4'-OH), 3.80 (3H, s, OCH₃) [4].

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REFERENCES

1. G. S. Xu, X. Y. Chen, and D. Q. Yu, *Acta Pharm. Sin.*, **23**, 122 (1988).
2. X. Y. Chen and S. H. Wang, *J. Chin. Tradit. Herb. Drugs*, **12**, 25 (1981).
3. A. Rahman, D. Ahmed, and M. I. Choudhary, *Planta Med.*, **54**, 173 (1988).
4. W. X. Song, T. F. Ji, Y. K. Si, and Y. L. Su, *China J. Chin. Mater. Med.*, **31**, 1790 (2006).
5. E. Wenkert and H. E. Gottlieb, *Phytochemistry*, **16**, 1811 (1977).
6. M. H. Gao, H. Li, L. Zhang, and S. X. Xiao, *China J. Chin. Mater. Med.*, **31**, 763 (2008).
7. T. G. Waddell and S. K. Elkins, *J. Nat. Prod.*, **48**, 463 (1985).
8. L. Lin, M. S. Liu, and J. H. Wang, *Chin. J. Med. Chem.*, **19**, 371 (2009).