

## FLAVONOIDS FROM THE AERIAL PART OF *Vicia subvillosa*

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Plants of the *Vicia* L. (Fabaceae) genus are rich sources of flavonoids, anthocyanins, carotenoids, and vitamins. Certain of them are used in folk medicine for ascites, paralysis, epilepsy, and flu. The seeds are used as feed for pets and birds [1, 2].

*Vicia subvillosa* (Ledeb.) Trautv. is a perennial that grows on steppes and rarely on alkaline soils and in the foothills of Central Asia [3].

Ground air-dried raw material (1.0 kg) that was collected during flowering (April 24, 1997) near the Alimtau mountains (Chimkent district, Republic of Kazakhstan) was exhaustively extracted with ethanol. The combined extract was evaporated in vacuo. The condensed residual was diluted with water and treated successively with  $\text{CHCl}_3$ , ethylacetate, and *n*-butanol. The solvents were removed to afford  $\text{CHCl}_3$  (20.5 g), ethylacetate (14.0 g), and butanol (25.0 g) fractions.

The ethylacetate fraction was chromatographed over a silica-gel column using  $\text{CHCl}_3$ : $\text{CH}_3\text{OH}$  (97:3-85:15) to afford **1-4**.

The compounds were identified using UV, IR, mass, and PMR spectral data in addition to chemical transformations and comparison with authentic specimens.

**Apigenin (1)** (5,7,4'-trihydroxyflavone),  $\text{C}_{15}\text{H}_{10}\text{O}_5$ , 270  $[\text{M}]^+$ , mp 347-348°C. UV spectrum (EtOH,  $\lambda_{\text{max}}$ , nm): 270, 311.

PMR spectrum (100 MHz,  $\delta$ , ppm, J/Hz,  $\text{C}_5\text{D}_5\text{N}$ ): 6.61 (1H, d, J = 2.0, H-6), 6.73 (1H, d, J = 2.0, H-8), 6.81 (1H, s, H-3), 7.08 (2H, d, J = 9.0, H-3',5'), 7.85 (2H, d, J = 9.0, H-2',6'), 13.67 (1H, br.s, 5-OH) [4, 5].

**Luteolin (2)** (5,7,3',4'-tetrahydroxyflavone),  $\text{C}_{15}\text{H}_{10}\text{O}_6$ , 286  $[\text{M}]^+$ , mp 328-330°C (dec.). UV spectrum (EtOH,  $\lambda_{\text{max}}$ , nm): 260, 270, 356.

IR spectrum: 3450-3300  $\text{cm}^{-1}$  (OH), 1658 ( $\gamma$ -pyrone carbonyl), 1612, 1584 (aromatic C=C).

PMR spectrum (100 MHz,  $\delta$ , ppm, J/Hz,  $\text{C}_5\text{D}_5\text{N}$ ): 6.58 (1H, d, J = 2.0, H-6), 6.69 (1H, d, J = 2.0, H-8), 6.78 (1H, s, H-3), 7.09 (1H, d, J = 8.0, H-5'), 7.53 (1H, br.s, H-2'), 7.60 (1H, dd, J = 2.0, J = 8.0, H-6').

Acetylation of luteolin by acetic anhydride with pyridine produced the tetraacetate with mp 224-226°C, 454  $[\text{M}]^+$  [4, 6].

**Quercetin (3)** (3,5,7,3',4'-pentahydroxyflavone),  $\text{C}_{15}\text{H}_{10}\text{O}_7$ , 302  $[\text{M}]^+$ , mp 313-314°C. UV spectrum (EtOH,  $\lambda_{\text{max}}$ , nm): 257, 268, 371; + $\text{CH}_3\text{COONa}$ , 270, 406.

PMR spectrum (100 MHz,  $\delta$ , ppm, J/Hz,  $\text{C}_5\text{D}_5\text{N}$ ): 6.54 (1H, d, J = 2.5, H-6), 6.60 (1H, d, J = 2.5, H-8), 7.25 (1H, d, J = 8.5, H-5'), 7.95 (1H, dd, J = 8.5, J = 2.5, H-6'), 8.45 (1H, d, J = 2.5, H-2'), 11.78 (1H, br.s, 3-OH), 13.75 (1H, br.s, 5-OH) [4, 6].

**Cinaroside (4)** (luteolin-7-O- $\beta$ -D-glucopyranoside),  $\text{C}_{21}\text{H}_{20}\text{O}_{11}$ , mp 240-242°C (dec.). UV spectrum (EtOH,  $\lambda_{\text{max}}$ , nm): 256, 268, 350.

IR spectrum: 3480-3300  $\text{cm}^{-1}$  (OH), 1665 ( $\gamma$ -pyran carbonyl), 1560, 1510 (aromatic C=C), 1095, 1030 (glycoside C-O).

PMR spectrum (100 MHz,  $\delta$ , ppm, J/Hz,  $\text{C}_5\text{D}_5\text{N}$ ): 3.92-4.07 (sugar protons), 5.54 (1H, d, J = 7.0, H-1', D-glucose anomeric proton), 6.68 (1H, d, J = 2.5, H-6), 6.79 (1H, s, H-3), 6.83 (1H, d, J = 2.5, H-8), 7.15 (1H, d, J = 8.0, H-5'), 7.40 (1H, dd, J = 8.0, J = 2.5, H-6'), 7.72 (1H, d, J = 2.5, H-2').

Acid hydrolysis of **4** produced luteolin and D-glucose. Acetylation of **4** with acetic anhydride and pyridine gave the heptaacetyl derivative  $\text{C}_{35}\text{H}_{34}\text{O}_{18}$ , 742  $[\text{M}]^+$ , mp 121-123°C [4, 6, 7].

Compounds **1-4** were isolated from *V. subvillosa* for the first time.

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