Chemistry of Natural Compounds, Vol. 46, No. 6, 2011

CHEMICAL CONSTITUENTS OF THE AERIAL PART OF *Astragalus bungeanus*

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UDC 547.913:547.918:547.926

Astragalus bungeanus (Fabaceae L.) is endemic to the flora of Georgia. Purified total extracts of the aerial parts exhibited high leukopoietic and anti-oxidant activity in biological tests [1]. In continuation of the study of the chemical composition of aerial parts of this plant, another five constituents **1**–**5** were isolated in addition to the previously isolated flavonoids [2, 3], triterpene glycoside giganteoside D [4], and a glycoside of coniferyl alcohol [5].

The examined compounds were identified as flavonoids and cycloartanes according to IR, PMR, and ^{13}C NMR spectral data.

Compound 1, $C_{15}H_{10}O_5$, mp 340–342°C. UV spectrum (EtOH, λ_{max}, nm): 325, 296sh, 268. IR spectrum (KBr, ν_{max}, cm^{-1}): 3400-3300 (OH), 1650, 1660 (γ-pyrone C=O), 1510, 1570 (>C=C<).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz): 7.10 (1H, s, H-3), 7.01 (1H, d, J = 2.0, H-6), 7.18 (1H, d, J = 2.0, H-8), 7.55 (2H, d, J = 8.0, H-2′,6′), 7.41 (2H, d, J = 8.0, H-3′,5′).

^{13}C NMR spectrum (100 MHz, C_5D_5N, δ, ppm): 165.2 (C-2), 104.3 (C-3), 183.1 (C-4), 162.1 (C-5), 100.2 (C-6), 164.9 (C-7), 95.6 (C-8), 158.7 (C-9), 105.1 (C-10), 122.7 (C-1′), 129.8 (C-2′,6′), 117.4 (C-3′,5′), 161.8 (C-4′).

Compound **1** was characterized as apigenin by comparison with an authentic sample and literature data [2].

Compound 2, MW 786, $C_{41}H_{70}O_{14}$, mp 280–285°C (MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3550–3300 (OH), 3060 (cyclopropane CH_2).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz): 1.63, 1.29 (2H, dd, J = 13.2, 4.5, H-1), 2.38, 1.99 (2H, m, H-2), 3.52 (1H, dd, J = 11.2, 5, H-3), 1.94 (1H, ddd, J = 12.9, 9.4, 5.3, H-5), 3.81 (1H, ddd, J = 5, 7.1, 8.4, H-6), 2.25, 1.89 (2H, ddd, J = 8.4, 5, 12.9, H-7), 1.99 (1H, dd, J = 5.3, 9.4, H-8), 1.83, 1.30 (2H, ddd, J = 14.7, 9.3, 6.9, H-11), 1.64, 1.41 (2H, m, H-12), 1.85, 2.40 (2H, dd, J = 12.9, 8.0, 6.9, H-15), 4.71 (1H, m, H-16), 1.82 (1H, d, J = 7.1, H-17), 1.41 (3H, s, CH_3-18), 0.59, 0.21 (2H, d, ^{2}J = 4, H-19), 2.40 (1H, m, H-20), 1.09 (3H, d, J = 6.3, CH_3-21), 2.31, 1.48 (2H, m, H-22), 1.99, 1.84 (2H, d, H-23), 3.95 (1H, s, H-24), 1.44 (3H, s, CH_3-26), 1.48 (3H, s, CH_3-27), 2.04 (3H, s, CH_3-28), 1.38 (3H, s, CH_3-29), 0.99 (3H, s, CH_3-30).

^{13}C NMR spectrum (100 MHz, C_5D_5N, δ, ppm): 32.2 (C-1), 30.2 (C-2), 88.6 (C-3), 42.7 (C-4), 52.5 (C-5), 78.8 (C-6), 34.3 (C-7), 45.6 (C-8), 21.4 (C-9), 28.7 (C-10), 26.3 (C-11), 33.1 (C-12), 45.8 (C-13), 46.9 (C-14), 47.8 (C-15), 72.0 (C-16), 57.1 (C-17), 18.5 (C-18), 28.2 (C-19), 28.6 (C-20), 18.4 (C-21), 33.0 (C-22), 27.9 (C-23), 77.1 (C-24), 72.5 (C-25), 25.9 (C-26), 26.4 (C-27), 28.6 (C-28), 16.7 (C-29), 19.8 (C-30), 107.7 (C-1′), 75.6 (C-2′), 78.6 (C-3′), 71.3 (C-4′), 67.1 (C-5′), 105.2 (C-1″), 75.6 (C-2″), 79.1 (C-3″), 71.8 (C-4″), 78.1 (C-5″), 63.1 (C-6″).

Acid hydrolysis of **2** produced the genin, MW 492 (4.2), $C_{30}H_{52}O_5$, mp 192–195°C.

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz): 1.60, 1.27 (2H, dd, J = 13.2, 4.5, H-1), 2.31, 1.93 (2H, m, H-2), 3.49 (1H, dd, J = 11.2, 5, H-3), 1.89 (1H, ddd, J = 12.9, 9.4, 5.3, H-5), 3.80 (1H, ddd, J = 5, 7.1, 8.4, H-6), 2.18, 1.90 (2H, ddd, J = 8.4, 5, 12.9, H-7), 1.85 (1H, dd, J = 5.3, 9.4, H-8), 1.82, 1.23 (2H, ddd, J = 14.7, 9.3, 6.9, H-11), 1.65, 1.41 (2H, m, H-12), 1.80, 2.16 (2H, dd, J = 12.9, 8.0, 6.9, H-15), 4.76 (1H, m, H-16), 1.82 (1H, d, J = 7.1, H-17), 1.41 (3H, s, CH_3-18), 0.60, 0.22 (2H, d, ^{2}J = 4, H-19), 2.39 (1H, m, H-20), 1.07 (3H, d, J = 6.3, H-21), 2.30, 1.46 (2H, m, H-22), 2.01, 1.84 (2H, d, H-23), 3.93 (1H, s, H-24), 1.45 (3H, s, CH_3-26), 1.47 (3H, s, CH_3-27), 2.03 (3H, s, CH_3-28), 1.37 (3H, s, CH_3-29), 0.98 (3H, s, CH_3-30).

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^{13}C NMR spectrum (100 MHz, C_5D_5N, δ, ppm): 32.2 (C-1), 30.2 (C-2), 78.0 (C-3), 42.7 (C-4), 52.5 (C-5), 68.04 (C-6), 38.3 (C-7), 45.6 (C-8), 21.4 (C-9), 28.7 (C-10), 26.3 (C-11), 33.1 (C-12), 45.8 (C-13), 46.9 (C-14), 47.8 (C-15), 72.0 (C-16), 57.1 (C-17), 18.05 (C-18), 28.2 (C-19), 28.6 (C-20), 18.4 (C-21), 33.0 (C-22), 27.9 (C-23), 77.1 (C-24), 72.5 (C-25), 25.9 (C-26), 26.4 (C-27), 28.6 (C-28), 16.7 (C-29), 19.8 (C-30).

The genin dissolved in acetone in the presence of H_2SO_4 and formed an acetonide, mp 222–225°C, indicating the presence of an α-diol in the side chain and, therefore, identifying it as cyclocanthogenin [6]. D-Glucose and D-xylose in a 1:1 ratio were found by PC and HPLC analysis of the carbohydrate part of the hydrolysate [9, 10].

Enzymatic hydrolysis of the glycoside by *Helix plectotropis* gastric juice [11] formed D-glucose and a monoside with mp 153–154°C (EtOAc) that was identified as cyclocanthoside A [8].

A comparison of ^{13}C NMR spectra of **2** and its aglycon showed that the carbohydrate moieties were located on C-3 and C-6 of the genin. The SSCC of the monosaccharide anomeric protons were consistent with the β-configuration and the pyranose form of D-xylose and D-glucose.

The acid-hydrolysis products and HMBC spectra established that D-xylose was bonded to C-3; D-glucose, C-6.

Thus, glycoside **2**, which was isolated from *A. bungeanus* for the first time, was 24*S*-cycloartan-3β,6α,16β,24,25-pentaol 3-*O*-β-D-xylopyranoside-6-*O*-β-D-glucopyranoside or cyclocanthoside E [8, 13].

Compound 3, MW 492, $C_{30}H_{52}O_5$, mp 191–194°C. The physicochemical properties and IR, PMR, and ^{13}C NMR spectral data were identical to those of the genin of **2** and identified it as cyclocanthogenin [6].

Compound 4, MW 490, $C_{30}H_{50}O_5$, mp 185–196°C (MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3460-3200 (OH), 3040 (cyclopropane CH_2). Mass spectrum (*m*/*z*, I_{rel}, %): 490 (1.8) $[M]^+$, 475 (8.6), 472 (17.2), 457 (15.6), 454 (23.4), 439 (14.1), 431 (4.7), 421 (8.6), 413 (23.4), 395 (37.5), 377 (14.8), 289 (17.9), 271 (56.3), 143 (100), 125 (87.5).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz): 3.55 (1H, q, ^{3}J = 11.2, 4.8, H-3), 3.69 (1H, sx, J = 9.4, 9.6, 3.6, H-6), 4.70 (1H, m, Σ^3J = 21, H-16), 1.40 (3H, s, CH_3-18), 0.25, 0.52 (2H, d, ^{2}J = 4.2, H-19), 1.24 (3H, s, CH_3-21), 3.83 (1H, t, J = 15, H-24), 1.18 (3H, s, CH_3-26), 1.57 (3H, s, CH_3-27), 0.89 (3H, s, CH_3-28), 1.78 (3H, s, CH_3-29), 1.17 (3H, s, CH_3-30).

^{13}C NMR spectrum (100 MHz, C_5D_5N, δ, ppm): 32.8 (C-1), 31.4 (C-2), 78.3 (C-3), 42.4 (C-4), 54.0 (C-5), 68.4 (C-6), 38.8 (C-7), 47.3 (C-8), 20.9 (C-9), 29.9 (C-10), 26.3 (C-11), 33.4 (C-12), 45.1 (C-13), 46.2 (C-14), 46.8 (C-15), 72.9 (C-16), 58.4 (C-17), 21.6 (C-18), 31.0 (C-19), 86.7 (C-20), 28.6 (C-21), 34.9 (C-22), 26.1 (C-23), 85.0 (C-24), 70.3 (C-25), 27.1 (C-26), 28.2 (C-27), 20.2 (C-28), 23.4 (C-29), 16.0 (C-30).

The compound was identified as cyclogalegigenin [12].

Compound 5, MW 664, $C_{37}H_{60}O_{10}$, mp 225–227° ($CHCl_3$:MeOH, 1:1). IR spectrum (KBr, ν_{max}, cm^{-1}): 3530–3300 (OH), 3050 (cyclopropane CH_2), 1755, 1245 (ester).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz): 3.52 (1H, q, ^{3}J = 4.8, 11.2, H-3), 3.70 (1H, sx, ^{3}J = 3.6, 9.6, 9.6, H-6), 4.68 (2H, m, ^{3}J = 8, H-1′, H-16), 0.39, 0.56 (1H, d, J = 4, H-19), 3.83 (1H, t, J = 15, H-24), 0.86 (3H, s, CH_3), 1.14 (3H, s, CH_3), 1.15 (3H, s, CH_3), 1.21 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.52 (3H, s, CH_3), 1.63 (3H, s, CH_3), 1.97 (3H, s, CH_3–COO), 5.41 (1H, t, J = 15, H-2′).

^{13}C NMR spectrum (100 MHz, C_5D_5N, δ, ppm): 32.8 (C-1), 31.4 (C-2), 78.3 (C-3), 42.4 (C-4), 54.0 (C-5), 68.4 (C-6), 38.8 (C-7), 47.3 (C-8), 20.9 (C-9), 29.9 (C-10), 26.3 (C-11), 33.4 (C-12), 45.1 (C-13), 46.2 (C-14), 46.8 (C-15), 72.9 (C-16), 58.4 (C-17), 21.6 (C-18), 31.0 (C-19), 86.7 (C-20), 28.6 (C-21), 34.9 (C-22), 26.1 (C-23), 85.0 (C-24), 70.3 (C-25), 27.1 (C-26), 28.2 (C-27), 20.2 (C-28), 23.4 (C-29), 16.0 (C-30), 21.1 ($\underline{C}H_3$–COO), 169.8 (CH_3–$\underline{C}$OO), 104.9 (C-1′), 75.0 (C-2′), 76.4 (C-3′), 71.3 (C-4′), 67.1 (C-5′).

The compound was characterized as cyclogaleginoside A [13].

Compound 6, MW 622, $C_{35}H_{58}O_9$, mp 254–255°C ($CHCl_3$:MeOH, 1:1). IR spectrum (KBr, ν_{max}, cm^{-1}): 3600–3200 (OH), 3045 (cyclopropane CH_2), 1755, 1245 (ester).

PMR spectrum (400 MHz, C_5D_5N, δ, ppm, J/Hz): 0.47, 0.59 (2H, d, ^{2}J = 4, H-19), 0.87 (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.22 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.52 (3H, s, CH_3), 1.83 (3H, s, CH_3), 4.70 (2H, m, H-1′, H-16).

The compound was identical to cyclogaleginoside B [12].

All compounds were isolated and described for the first time from *A. bungeanus*.

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