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CHEMICAL CONSTITUENTS FROM THE ROOTS OF *Cephalaria kotschyi*

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Cephalaria kotschyi Boiss. et Hoh. (Dipsacaceae) is an endemic plant of the Caucasus region growing in Azerbaijan. Earlier phytochemical studies reported the isolation of triterpene saponins, flavonoids, and gentianine type alkaloids from the roots and flowers of *C. kotschyi* [1–7]. In our previous study we described the isolation of the iridoid glycosides loganin and gentiopicroside from the roots of this plant [8].

Herein we report, together with the gentiopicroside and loganin described previously, the isolation of three iridoid and secoiridoid glycosides: loganic acid [9], swertiamarin [10], and cantleyoside [11]; two furofuranic lignans: prinsepiol glycoside [12] and 8-hydroxypinoresinol-4′-*O*-*β*-D-glucoside [13]; and two triterpene saponins: giganteoside J′ [14] and dipsacoside B [15], from an investigation of the chemical constituents of the roots of *C. kotschyi*. The plant was collected in the Lerik region of Azerbaijan in September 2005. A voucher specimen (C 8131005) was deposited at the herbarium of the Botanical Institute, Academy of Science, Azerbaijan.

Air-dried roots (100 g) were extracted by percolation at room temperature with MeOH (1 L for 24 h), and the obtained solution was concentrated under vacuum. The MeOH extract (5 g) was submitted to flash column chromatography on polyamide MN SC 6 Macherey Nagel® (70 μm), using a step gradient of H_2O–MeOH of 90:10, 50:50, and 0:100, to give 3 main fractions (F1–F3). Fraction F1 was further purified by low-pressure liquid chromatography on Prepamatic Chromatospac 10 (Jobin Yvon) with Lichroprep RP18 Merck® (25–40 μm). A step gradient of H_2O–MeOH (100:0; 90:10; 80:20; 70:30; 67:33; 65:35; 62:38; 60:40; 50:50; and 0:100, 1 L for each) allowed us to obtain 20 fractions, Sp1–Sp20. Fractions Sp2, Sp5, Sp7, Sp9, and Sp16 afforded respectively loganic acid (18 mg), swertiamarin (73 mg), gentiopicroside (250 mg), loganin (75 mg), and cantleyoside (230 mg). Purification of fractions Sp12 and Sp13 by means of preparative high-performance liquid chromatography on a Symmetry C18 column (5 μm, 250 × 4.6, waters®), using H_2O–MeOH (75:25), yielded prinsepiol glycoside (20 mg) and 8-hydroxypinoresinol glycoside (18 mg) respectively. Fraction F2 (1 g) was fractionated by silica gel CC using CH_2Cl_2–MeOH–H_2O (50:16:3) and (30:13:3) successively as eluent to give dipsacoside B (30 mg) and giganteoside J′ (30 mg). The structural elucidations of the obtained compounds were performed by spectroscopic analysis, including 2D NMR data, and confirmed by comparison with the previously reported data. NMR spectra were recorded in CD_3OD (δ, ppm) on a Bruker DRX 500 spectrometer operating at 500.13 MHz and 125.13 MHz.

All the isolated compounds, except loganin and gentiopicroside, have been reported for the first time from *C. kotschyi*. The iridoid glycosides loganin, loganic acid, and cantleyoside of *Cephalaria* and other genus of the Dipsacaceae family [16–20] have been previously reported. These compounds are used as chemosystematic markers for plants of the Dipsacaceae family. The secoiridoid swertiamarin has been previously isolated from Dipsacaceae [17]. The prinsepiol glycoside of *C. ambrosioides* has already been reported [20]. The 8-hydroxypinoresinol glycoside is reported for the first time from Dipsacaceae family.

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Loganic Acid. $C_{16}H_{24}O_{10}$, white amorphous powder. ^{1}H NMR (400.13 MHz, CD_3OD, δ, ppm, J/Hz): 7.20 (1H, s, H-3), 5.20 (1H, d, J = 4.2, H-1), 4.66 (1H, d, J = 7.9, H-1′), 4.05 (1H, br.t, J = 4.2, H-7), 3.90 (1H, d, J = 11.5, H-6′), 3.68 (1H, dd, J = 11.5, 5.0, H-6′), 3.39 (1H, t, J = 9.0, H-3′), 3.33 (2H, m, H-4′, H-5′), 3.21 (1H, dd, J = 8.9, 7.8, H-2′), 3.13 (1H, br.q, J = 7.7, H-5), 2.24 (1H, dd, J = 7.8, 3.7, H-6), 1.99 (1H, td, J = 9.0, 4.3, H-9), 1.89 (1H, m, H-8), 1.70 (1H, ddd, J = 13.7, 7.7, 4.2, H-6), 1.10 (3H, d, J = 6.9, H-10).

^{13}C NMR (100.62 MHz, $CDCl_3$, δ, ppm): 99.88 (C-1′), 97.21 (C-1), 78.29 (C-5′), 78.01 (C-3′), 75.25 (C-7), 74.80 (C-2′), 71.62 (C-4′), 62.75 (C-6′), 46.83 (C-9), 42.74 (C-6), 42.09 (C-8), 32.93 (C-5), 13.54 (C-10), C-3, C-4, C-11: no observed.

Swertiamarin. $C_{16}H_{22}O_{10}$, yellowish amorphous powder. ^{1}H NMR (400.13 MHz, CD_3OD, δ, ppm, J/Hz): 7.65 (1H, s, H-3), 5.70 (1H, s, H-1), 5.46 (1H, dt, J = 17.0, 9.5, H-9), 5.38 (1H, dd, J = 17.0, 2.0, H-10), 5.31 (1H, dd, J = 9.8, 2.0, H-10), 4.78 (1H, ddd, J = 13.0, 10.8, 2.4, H-7), 4.66 (1H, d, J = 7.9, H-1′), 4.36 (1H, br.dd, J = 10.8, 4.8, H-7), 3.92 (1H, dd, J = 12.0, 1.4, H-6′), 3.68 (1H, dd, J = 12.0, 5.8, H-6′), 3.39 (1H, t, J = 9.0, H-3′), 3.34 (1H, m, H-5′), 3.30 (1H, t, J = 9.0, H-4′), 3.21 (1H, dd, J = 8.9, 7.8, H-2′), 2.94 (1H, d, J = 9.4, H-8), 1.93 (1H, td, J = 13.9, 5.1, H-6), 1.76 (1H, br.d, J = 13.9, H-6).

^{13}C NMR (100.62 MHz, $CDCl_3$, δ, ppm): 168.0 (C-11), 154.78 (C-3), 133.84 (C-8), 121.18 (C-10), 108.88 (C-4), 100.23 (C-1′), 99.09 (C-1), 78.53 (C-5′), 77.80 (C-3′), 74.43 (C-2′), 71.41 (C-4′), 65.95 (C-7), 64.27 (C-5), 62.57 (C-6′), 51.94 (C-9), 33.73 (C-6).

Cantleyoside. $C_{33}H_{46}O_{19}$, white amorphous powder. ^{1}H NMR (400.13 MHz, CD_3OD, δ, ppm, J/Hz): 9.40 (1H, s, H-7″), 7.55 (1H, d, J = 1.4, H-3″), 7.44 (1H, br.s, H-3), 5.53 (1H, d, J = 4.7, H-1″), 5.29 (1H, d, J = 4.9, H-1), 5.28 (1H, dd, J = 17.2, 1.0, H-10″), 5.25 (1H, dd, J = 10.3, 1.0, H-10″), 5.20 (1H, t, J = 5.0, H-7), 4.71 (1H, d, J = 7.8, H-1‴), 4.68 (1H, d, J = 7.9, H-1′), 3.92 (2H, dd, J = 11.9, 1.8, H-6′ and 6‴), 3.71 (3H, s, OCH_3), 3.68 (2H, dd, J = 11.9, 6.0, H-6′ and 6‴), 3.48 (1H, q, J = 6.0, H-5″), 3.39 (2H, t, J = 8.9, H-3′ and 3‴), 3.28 (4H, m, H-4′, 5′, 4‴ and 5‴), 3.21 (2H, dd, J = 8.9, 7.8, H-2′ and 2‴), 3.10 (1H, q, J = 8.0, H-5), 2.77 (1H, m, H-9″), 2.74 (1H, m, H-6″), 2.55 (1H, dd, J = 17.5, 6.3, H-6″), 2.29 (1H, dd, J = 14.5, 7.5, H-6), 2.14 (1H, m, H-8 and 8″), 2.07 (1H, td, J = 8.7, 5.0, H-9), 1.75 (1H, ddd, J = 14.5, 7.7, 5.0, H-6), 1.07 (1H, d, J = 6.8, H-10).

^{13}C NMR (100.62 MHz, $CDCl_3$, δ, ppm): 203.13 (C-7″), 169.35 (C-11), 167.97 (C-11″), 153.90 (C-3″), 152.61 (C-3), 134.94 (C-8″), 120.54 (C-10″), 113.11 (C-4), 110.26 (C-4″), 100.20 (C-1‴), 100.03 (C-1′), 97.57 (C-1), 97.44 (C-1″), 78.42[a] (C-5′), 78.38[a] (C-7), 78.34 (C-5‴), 77.98 (C-3′ and 3‴), 74.71[b] (C-2′), 74.63[b] (C-2‴), 71.59[c] (C-4‴), 71.55[c] (C-4′), 62.77 (C-6′ and 6‴), 51.76 (OCH_3), 47.09 (C-9), 45.63 (C-6″), 45.37 (C-9″), 41.08 (C-8), 32.69 (C-5), 27.78 (C-5″), 13.85 (C-10). Superscripts [a, b, c] indicate that the assignments may be interchanged.

Prinsepiol Glycoside. $C_{26}H_{32}O_{13}$, white amorphous powder. ^{1}H NMR (400.13 MHz, CD_3OD, δ, ppm, J/Hz): 7.16 (1H, d, J = 8.2, H-5′), 7.13, (1H, br.s, H-2′), 7.06 (1H, br.s, H-2), 6.96 (1H, br.d, J = 8.2, H-6′), 6.86 (1H, br.d, J = 8.0, H-6), 6.79 (1H, d, J = 8.0, H-5), 5.03 (1H, s, H-7′), 4.99 (1H, s, H-7), 4.90 (1H, d, J = 7.8, H-1″), 4.14 (1H, dd, J = 9.4, H-9′), 4.13 (1H, d, J = 9.4, H-9), 4.00 (2H, dd, J = 9.4, H-9 and 9′), 3.90 (3H, s, OCH_3-3′), 3.88 (3H, s, OCH_3-3), 3.87 (1H, m, H-6″), 3.51 (1H, dd, J = 8.9, 7.8, H-2″), 3.41 (2H, m, H-3″ and 4″), 3.47 (1H, m, H-5″), 3.70 (1H, dd, J = 11.5, 5.0, H-6″).

^{13}C NMR (100.62 MHz, $CDCl_3$, δ, ppm): 150.42 (C-3′), 148.66 (C-3), 147.66[a] (C-4′), 147.50[a] (C-4), 133.24 (C-1′), 129.52 (C-1), 121.61 (C-6), 121.38 (C-6′), 117.44 (C-5′), 115.59 (C-5), 113.51 (C-2′), 112.83 (C-2), 102.79 (C-1″), 89.28 (C-8), 89.13 (C-7 and 8′), 88.80 (C-7′), 78.22 (C-5″), 77.84 (C-3″), 76.80 (C-9′), 76.72 (C-9), 74.91 (C-2″), 71.34 (C-4″), 62.51 (C-6″), 56.70 (OCH_3-3′), 56.37 (OCH_3-3). The superscript[a] indicates that the assignments may be interchanged.

8-Hydroxypinoresinol Glycoside. $C_{26}H_{32}O_{12}$, white amorphous powder. ^{1}H NMR (400.13 MHz, CD_3OD, δ, ppm, J/Hz): 7.17 (1H, d, J = 8.3, H-5′), 7.14 (1H, d, J = 1.8, H-2′), 7.06 (1H, d, J = 1.7, H-2), 6.99 (1H, dd, J = 8.3, 1.8, H-6′), 6.86 (1H, dd, J = 8.1, 1.7, H-6), 6.80 (1H, d, J = 8.1, H-5), 4.91 (1H, d, J = 7.8, H-1″), 4.90 (1H, d, J = 8.3, H-7′), 4.69 (1H, s, H-7), 4.49 (1H, dd, J = 9.2, 6.3, H-9′), 4.07 (1H, dd, J = 9.3, H-9), 3.89 (3H, s, OCH_3-3′), 3.88 (3H, s, OCH_3-3), 3.87 (2H, m, H-9 and 6″), 3.79 (1H, dd, J = 9.2, 6.3, H-9′), 3.70 (1H, dd, J = 11.5, 5.0, H-6″), 3.49 (1H, dd, J = 8.9, 7.8, H-2″), 3.44 (1H, m, H-3″), 3.42 (1H, m, H-4″ and 5″), 3.04 (1H, ddd, J = 8.5, 6.1, 4.2, H-8′).

^{13}C NMR (100.62 MHz, $CDCl_3$, δ, ppm): 150.93 (C-3′), 148.69 (C-3), 147.56[a] (C-4 or 4′), 147.50[a] (C-4 or 4′), 137.23 (C-1′), 129.01 (C-1), 121.55 (C-6), 120.19 (C-6′), 117.93 (C-5′), 115.64 (C-5), 112.73 (C-2), 111.90 (C-2′), 102.79 (C-1″), 92.79 (C-8), 89.28 (C-7), 87.33 (C-7′), 78.20 (C-5″), 77.83 (C-3″), 76.17 (C-9), 74.89 (C-2″), 72.06 (C-9′), 71.32 (C-4″), 62.51 (C-8′ and 6″), 56.71 (OCH_3-3′), 56.37 (OCH_3-3). The superscript[a] indicates that the assignments may be interchanged.

Giganteoside J′. $C_{65}H_{106}O_{31}$, white amorphous powder. ^{1}H NMR (400.13 MHz, CD_3OD, δ, ppm): Aglycone: 5.28 (1H, m, H-12), 3.64 (1H, m, H-3), 3.52 (1H, m, H-23), 3.37 (1H, m, H-23), 2.85 (1H, m, H-18), 2.04 (1H, m, H-16), 1.90 (2H,

m, H-11), 1.88 (1H, m, H-2), 1.77 (1H, m, H-2), 1.74 (1H, m, H-15), 1.72 (2H, m, H-16 and 22), 1.68 (1H, m, H-19), 1.63 (2H, m, H-9 and 22), 1.62 (1H, m, H-1), 1.59 (1H, m, H-7), 1.49 (1H, m, H-6), 1.38 (1H, m, H-21), 1.34 (1H, m, H-6), 1.27 (1H, m, H-7), 1.25 (1H, m, H-5), 1.23 (1H, m, H-21), 1.18 (1H, m, H-19), 1.17 (3H, s, H-27), 1.10 (1H, m, H-15), 0.99 (1H, m, H-1), 0.97 (3H, s, H-25), 0.94 (3H, s, H-30), 0.91 (3H, s, H-29), 0.79 (3H, s, H-26), 0.70 (3H, s, H-24); Sugars: 28-*O*-Glc1: 5.39 (1H, m, H-1), 4.15 (1H, m, H-6), 3.81 (1H, m, H-6), 3.55 (1H, m, H-5), 3.52 (1H, m, H-4), 3.47 (1H, m, H-3), 3.40 (1H, m, H-2); Glc-2: 4.36 (1H, m, H-1), 3.87 (1H, m, H-6), 3.71 (1H, m, H-6), 3.42 (1H, m, H-3), 3.36 (1H, m, H-4), 3.30 (1H, m, H-5), 3.27 (1H, m, H-2); 3-*O*-Ara: 4.54 (1H, m, H-1), 3.87 (1H, m, H-5), 3.83 (1H, m, H-4), 3.70 (1H, m, H-3), 3.68 (1H, m, H-2), 3.55 (1H, m, H-5); Rha1: 5.14 (1H, m, H-1), 4.26 (1H, m, H-2), 3.91 (1H, m, H-5), 3.90 (1H, m, H-3), 3.59 (1H, m, H-4), 1.29 (3H, m, H-6); Glc3: 4.56 (1H, m, H-1), 3.90 (1H, m, H-6), 3.72 (1H, m, H-6), 3.55 (1H, m, H-3), 3.39 (1H, m, H-4), 3.44 (2H, d, H-2 and 5); Rha 2: 5.17 (1H, m, H-1), 4.00 (2H, m, H-2 and 5), 3.75 (1H, m, H-3), 3.42 (1H, m, H-4), 1.28 (3H, d, H-6).

^{13}C NMR (100.62 MHz, $CDCl_3$, δ, ppm): Aglycone: 178.00 (C-28), 144.30 (C-13), 123.20 (C-12), 82.60 (C-3), 64.20 (C-23), 48.30 (C-9), 47.80 (C-5), 47.60 (C-17), 46.70 (C-19), 43.40 (C-4), 42.50 (C-14), 42.00 (C-18), 40.00 (C-8), 39.10 (C-1), 37.20 (C-10), 34.50 (C-21), 33.30 (C-29), 32.80 (C-7), 32.60 (C-22), 31.10 (C-20), 28.30 (C-15), 26.20 (C-27), 26.00 (C-2), 24.10 (C-11), 23.80 (C-30), 23.60 (C-16), 18.40 (C-6), 17.40 (C-26), 16.30 (C-25), 13.40 (C-24); Sugars: 28-*O*-Glc1: 95.10 (C-1), 77.30 (C-3), 76.90 (C-5), 73.10 (C-2), 70.10 (C-4), 69.00 (C-6); Glc2: 103.90 (C-1), 77.20 (C-5), 77.10 (C-3), 74.30 (C-2), 70.70 (C-4), 62.00 (C-6); 3-*O*-Ara: 104.00 (C-1), 76.50 (C-2), 72.90 (C-3), 68.70 (C-4), 64.80 (C-5); Rha1: 101.20 (C-1), 82.10 (C-3), 71.80 (C-4), 70.40 (C-2), 69.80 (C-5), 17.80 (C-6); Glc3: 104.90 (C-1), 83.40 (C-3), 77.20 (C-5), 77.00 (C-4), 73.30 (C-2), 62.00 (C-6); Rha2: 102.00 (C-1), 71.60 (C-2 and 3), 69.60 (C-5), 69.20 (C-4), 17.60 (C-6).

Dipsacoside B. C_{53} H_{86} O_{22}, white amorphous powder. 1H NMR (400.13 MHz, CD_3OD, δ, ppm, J/Hz): Aglycone: 5.41 (1H, t, J = 2.9, H-12), 4.16 (1H, m, H-23), 4.29 (1H, m, H-3), 3.75 (1H, m, H-23), 3.18 (1H, dd, J = 13.0, 3.3, H-18), 2.31 (1H, m, H-15), 2.21 (1H, m, H-2), 2.01 (1H, m, H-16), 1.99 (1H, m, H-2), 1.93 (1H, m, H-11), 1.92 (1H, m, H-16), 1.40 (1H, m, H-6), 1.91 (1H, m, H-22), 1.77 (1H, m, H-22), 1.76 (1H, m, H-9), 1.73 (1H, m, H-5), 1.72 (1H, m, H-19), 1.70 (1H, m, H-6), 1.60 (1H, m, H-7), 1.55 (1H, m, H-1), 1.31 (1H, m, H-21), 1.22 (1H, m, H-19), 1.17 (3H, s, H-27), 1.14 (3H, s, H-26), 1.10 (1H, m, H-21), 1.09 (3H, s, H-24), 1.09 (1H, m, H-15), 1.06 (1H, m, H-1), 0.98 (3H, s, H-25), 0.87 (3H, s, H-30), 0.86 (3H, s, H-29); Sugars: 28-*O*-Glc1: 6.29 (1H, d, J = 8.1, H-1), 4.74 (1H, m, H-6), 4.39 (1H, m, H-6), 4.37 (1H, m, H-4), 4.25 (1H, m, H-3), 4.15 (1H, m, H-2), 4.13 (1H, m, H-5); Glc2: 5.06 (1H, d, J = 7.8, H-1), 4.51 (1H, dd, J = 12.1, 2.4, H-6), 4.38 (1H, m, H-6), 4.24 (1H, m, H-4), 4.22 (1H, m, H-3), 4.03 (1H, t, J = 8.4, H-2), 3.91 (1H, m, H-5); 3-*O*-Ara: 5.12 (1H, d, J = 6.4, H-1), 4.60 (1H, dd, J = 8.6, 8.0, H-2), 4.28 (1H, m, H-5), 4.20 (1H, m, H-4), 4.13 (1H, m, H-3), 3.72 (1H, m, H-5); Rha: 6.28 (1H, d, J = 1.3, H-1), 4.76 (1H, m, H-2), 4.71 (1H, m, H-5), 4.67 (1H, dd, J = 9.2, 3.5, H-3), 4.32 (1H, m, H-4), 1.65 (3H, d, J = 6.2, H-6).

^{13}C NMR (100.62 MHz, $CDCl_3$, δ, ppm): Aglycone: 176.90 (C-28), 144.40 (C-13), 123.30 (C-12), 81.40 (C-3), 64.30 (C-23), 48.50 (C-9), 48.10 (C-5), 47.40 (C-17), 46.50 (C-19), 43.80 (C-4), 42.50 (C-14), 42.00 (C-18), 40.20 (C-8), 39.40 (C-1), 37.20 (C-10), 34.30 (C-21), 33.40 (C-29), 33.10 (C-7), 32.90 (C-22), 31.10 (C-20), 28.70 (C-15), 26.60 (C-2), 26.40 (C-27), 24.20 (C-11), 24.00 (C-30), 23.70 (C-16), 18.60 (C-6), 17.90 (C-26), 16.50 (C-25), 14.30 (C-24); Sugars: 28-*O*-Glc1: 96.00 (C-1), 79.10 (C-3), 78.30 (C-5), 74.30 (C-2), 71.30 (C-4), 69.70 (C-6); Glc2: 105.70 (C-1), 78.80 (C-5 and 3), 75.50 (C-2), 71.80 (C-4), 63.00 (C-6); 3-*O*-Ara: 104.70 (C-1), 76.20 (C-2), 75.10 (C-3), 69.70 (C-4), 66.00 (C-5); Rha: 102.10 (C-1), 74.50 (C-4), 72.90 (C-3), 72.70 (C-2), 70.10 (C-5), 18.90 (C-6).

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