FLAVONOIDS AND COUMARINS FROM *Allium rotundum*

M. R. Maisashvili,[1] L. N. Gvazava,[2] and J. K. Kuchukhidze[1] UDC 547.972

Allium rotundum L. is widely distributed over all of Georgia, is readily cultivated, and can provide an industrial base for preparing drugs.

We identified seven sapogenins and saponins in *A. rotundum* [1, 2] and isolated and studied phenolic compounds, in particular, flavonoids and coumarins. Herein we report results from a study of them.

We studied the aerial parts of *A. rotundum* collected during flowering near Tbilisi in Kojori village.

Air-dried ground material (500 g) was extracted exhaustively with hot methanol (80°). The solvent was vacuum distilled. The resulting thick aqueous residue was diluted with water and extracted successively with $CHCl_3$ and EtOAc. Solvents were distilled off to afford $CHCl_3$ (9.8 g) and EtOAc (8.5 g) fractions.

The EtOAc fraction was purified of lipophilic substances over a column of Sephadex G-25. The purified extract was chromatographed over a column of polyamide sorbent (eluent C_2H_5OH:$CHCl_3$ in various ratios). Combined fractions were rechromatographed over a column of silica gel using $CHCl_3$:CH_3OH (97:3 and 85:15) [3].

The $CHCl_3$ extract was separated by partition chromatography over a column of silica gel with elution by petroleum ether:benzene (8:2) and then $CHCl_3$. The resulting fractions were monitored by paper chromatography (PC) using *n*-BuOH:AcOH:H_2O (4:1:2, 1) and THF:$CHCl_3$:$HCONH_2$ [50:50:6.5, paper saturated with $HCONH_2$:$(CH_3)_2CO$, 2]. A total of eight compounds were isolated and identified based on UV, IR, and PMR spectra and certain chemical transformations and by direct comparison with authentic samples and the literature.

Quercetin (3,5,7,3′,4′-pentahydroxyflavone), $C_{15}H_{10}O_7$, $[M]^+$ 302; bright yellow needle-like crystals, mp 312-313°C (CH_3OH). PC (Filtrak FN 7, GDR): R_f 0.77 (system 1); UV spectrum (EtOH, λ_{max}, nm): 257, 268, 371; +CH_3COONa: 270, 406.

Luteolin (5,7,3′,4′-tetrahydroxyflavone), $C_{15}H_{10}O_6$, $[M]^+$ 286, mp 328-329°C. UV spectrum (EtOH, λ_{max}, nm): 261, 272, 355. The IR spectrum contained absorption bands for hydroxyls (3450-3300 cm^{-1}), γ-pyrone carbonyl (1659), and aromatic C=C bonds (1612, 1585).

PMR spectrum (C_5D_5N, δ, ppm, J/Hz): 7.60 (1H, dd, J = 2.2, 8.1, H-6′), 7.51 (1H, br.s, H-2′), 7.09 (1H, d, J = 8.1, H-5′), 6.79 (1H, s, H-3), 6.70 (1H, d, J = 2.1, H-8), 6.59 (1H, d, J = 2.1, H-6).

Luteolin was acetylated by acetic anhydride in the presence of pyridine to give the tetraacetate, mp 222-223°C, $[M]^+$ 454.

Apigenin (5,7,4′-trihydroxyflavone), $C_{15}H_{10}O_5$, $[M]^+$ 270, mp 347-348°C. UV spectrum (EtOH, λ_{max}, nm): 270, 312.

PMR spectrum (C_5D_5N, δ, ppm, J/Hz): 13.69 (1H, br.s, 5-OH), 7.87 (2H, d, J = 9.2, H-2′, H-6′), 7.09 (2H, d, J = 9.2, H-3′, H-5′), 6.82 (1H, s, H-3), 6.75 (1H, d, J = 2.1, H-8), 6.61 (1H, d, J = 2.1, H-6).

Hyperin (quercetin-3-*O*-β-D-galactopyranoside), $C_{21}H_{20}O_{12}$, yellow crystals (EtOH), mp 235-236°C, $[\alpha]_D^{20}$ –60.2° (*c* 0.1, EtOH). PC: R_f 0.71 (system 1). UV spectrum (CH_3OH, λ_{max}, nm): 260, 362; +CH_3COONa: 276, 395; +CH_3ONa: 276, 405; +CH_3COONa + H_3BO_3: 272, 375. The IR spectrum (KBr, ν, cm^{-1}) contained absorption bands at 3300 (OH), 1665 (C=O), 1615, 1565, 1515 (C=C), 1095, 1030 (C–O).

PMR spectrum (CD_3OD, δ, ppm, J/Hz): 7.74 (1H, dd, J = 9, 2, H-6′), 7.32 (1H, d, J = 2, H-2′), 6.79 (1H, d, J = 9, H-5′), 6.42 (1H, d, J = 2, H-8), 6.15 (1H, d, J = 2, H-6). The anomeric proton of β-D-galactose resonated at 5.61 ppm, J = 7.8 Hz.

Acid and enzymatic hydrolysis produced the aglycon quercetin (mp 309-310°C, $C_{15}H_{10}O_7$) and D-galactose.

1) Tbilisi State Medical University, 0108, Tbilisi, ul. G. Akhvlediani, 22; 2) I. Kutatelidze Institute of Pharmaceutical Chemistry, e-mail: liligvazava@yahoo.com. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 77-78, January-February, 2009. Original article submitted June 2, 2008.

0009-3130/09/4501-0087

Cinaroside (luteolin-7-*O*-β-D-glucopyranoside), $C_{21}H_{20}O_{11}$, mp 239-240°C, $[\alpha]_D^{20}$ –58° (*c* 0.52, CH_3OH:Py, 3:2). PC: R_f 0.38 (system 1). UV spectrum (EtOH, λ_{max}, nm): 257, 269, 352. The IR spectrum (KBr, ν, cm^{-1}) contained absorption bands at 3480-3300 (OH), 1665 (C=O), 1560, 1510 (C=C), 1095, 1030 (C–O).

PMR spectrum (C_5H_5N, δ, ppm, J/Hz): 7.73 (1H, d, J = 2.7, H-2′), 7.43 (1H, dd, J = 8.0, 2.6, H-6′), 7.16 (1H, d, J = 8.1, H-5′), 6.85 (1H, d, J = 2.5, H-8), 6.80 (1H, s, H-3), 6.70 (1H, d, J = 2.5, H-6), 6.01 (1H, d, J = 7.2, H-1′, D-glucose anomeric proton), 3.94-4.08 (sugar protons). Acid hydrolysis produced luteolin and D-glucose.

Apigenin-7-*O*-β-D-glucopyranoside, $C_{21}H_{20}O_{10}$, mp 227-228°C. UV spectrum (CH_3OH, λ_{max}, nm): 256, 268 sh, 350; +$AlCl_3$: 278, 350 sh, 385; +$AlCl_3$ + HCl: 279, 346 sh, 384. The IR spectrum (KBr, ν, cm^{-1}) contained absorption bands at 3380, 3257, 3245 (OH), 1652 (γ-pyrone CO), 1573, 1510, 835 (C=C), 1093, 1045 (C–O).

PMR spectrum (CD_3OD, δ, ppm, J/Hz): 7.91 (2H, d, J = 8.6, H-2′, H-6′), 6.98 (2H, d, J = 8.8, H-3′, H-5′), 6.83 (1H, d, J = 2.5, H-8), 6.63 (1H, s, H-3), 6.54 (1H, d, J = 2.5, H-6), 5.16 (1H, d, J = 7.2, Glc-H-1), 3.35-3.93 (glucose protons). Acid hydrolysis produced apigenin and D-glucose.

Scopoletin (6-methoxy-7-hydroxycoumarin), $C_{10}H_8O_4$, $[M]^+$ 192, colorless or yellowish crystals, mp 202-204°C. PC: R_f 0.61 (system 2). UV spectrum (CH_3OH, λ_{max}, nm): 233, 255, 295, 347. The IR spectrum (KBr, ν, cm^{-1}) contained absorption bands at 3349 (OH), 3047, 1712-1705 (α-pyrone C=O), 1650, 1611, 1572 (C=C), 2932 (OCH_3).

Umbelliferone (7-hydroxycoumarin), $C_9H_6O_3$, colorless prisms or needles, mp 234-235°C. PC: R_f 0.29 (system 2). UV spectrum (EtOH, λ_{max}, nm): 320, 255. The IR spectrum (KBr, ν, cm^{-1}) contained absorption bands at 1720 (γ-pyrone), 3300 (OH), 1614, 1571, 1520 (C=C).

All compounds were isolated from *A. rotundum* for the first time.

Phytochemical studies of the plant are continuing.

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