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FLAVONOIDS FROM THE PLANTS *Polygonatum polyanthemum* AND *P. glaberrimum*

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In continuation of studies of plants of the genus *Polygonatum* (Convallariaceae), we studied the flavonoid compositions of roots from the two species *P. polyanthemum* (Bieb.) A. Dietr and *P. glaberrimum* C. Koch [1]. The plants were collected in May–June in Georgia (Kodzhori, Saguramo).

Total flavonoids (400 g) were obtained from dried and ground rhizomes of each plant by extraction (3×) with MeOH (80%) for 1 h under reflux. The alcohol extracts were evaporated to an aqueous residue and worked up with $CHCl_3$. The purified aqueous extract was extracted exhaustively with EtOAc, which was evaporated. Total flavonoids were precipitated with $CHCl_3$.

Pure compounds were isolated by preparative chromatography over a column of polyamide that was formed in $CHCl_3$. The column was eluted by $CHCl_3$ and $CHCl_3$:EtOH in various ratios. The separation was monitored by paper chromatography using *n*-BuOH:HOAc:H_2O (4:1:2), C_6H_6:EtOAc:HOAc:H_2O (50:50:1:1), and formamide:EtOH (1:3).

Similar fractions were combined, evaporated to dryness, and recrystallized from MeOH. Fractions containing a mixture of compounds were rechromatographed over a column of polyamide. The resulting compounds **1–7** were additionally purified by recrystallization from MeOH.

The isolated compounds were identified by physicochemical methods (UV, IR, PMR spectroscopy). A comparison of the results with the literature and with data for authentic samples identified **1** as quercetin [2, 3]; **2**, isoquercitrin [4, 5]; **3**, hyperin [6]; **4**, rutin [5, 7]; **5**, kaempferol [3, 6]; **6**, astragalin [3, 5]; and **7**, kaempferol-3-*O*-α-D-arabinopyranoside [6, 8].

All aforementioned flavonoids were isolated from *P. polyanthemum*. The flavonoid composition of *P. glaberrimum* was qualitatively and quantitatively much poorer. Only **1**, **2**, **5**, and **6** were observed in it.

Quercetin (3,5,7,3′,4′-pentahydroxyflavone) (1), $C_{15}H_{10}O_7$, bright yellow needle-like crystals, mp 312–314°C (MeOH), $[M]^+$ 302. UV spectrum (EtOH, λ_{max}, nm): 257, 372; +CH_3COONa: 270, 406. IR spectrum (KBr, ν, cm^{-1}): 3450–3200 (OH), 1665 (γ-pyrone C=O), 1615, 1565, 1515 (C=C). PMR spectrum (300 MHz, Py-d_5, δ, ppm, J/Hz): 13.83 (br.s, 5-OH), 11.72 (br.s, 3-OH), 8.46 (1H, d, J = 2.3, H-2′), 7.95 (1H, dd, J = 2.3, 8.4, H-6′), 7.23 (1H, d, J = 8.4, H-5′), 6.64 (1H, d, J = 2.5, H-8), 6.58 (1H, d, J = 2.5, H-6).

Quercetin-3-*O*-β-D-glucopyranoside (isoquercitrin) (2), $C_{21}H_{20}O_{12}$, yellow crystals, mp 225–227°C (MeOH), $[M]^+$ 464. UV spectrum (MeOH, λ_{max}, nm): 255, 265, 360. IR spectrum (KBr, ν, cm^{-1}): 3200–2900 (OH), 1650 (C=O), 1615–1450 (C=C), 1085, 1055, 1010, 890. PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.44 (1H, br.s, 5-OH), 7.64 (1H, dd, J = 2.4, 8.8 H-6′), 7.60 (1H, d, J = 2.4, H-2′), 6.86 (1H, d, J = 8.8, H-5′), 6.42 (1H, d, J = 2.0, H-8), 6.21 (1H, d, J = 2.0, H-6), 5.62 (1H, d, J = 7.6, glucose H-1″), 3.2–4.8 (m, glucose 6H).

Quercetin-3-*O*-β-D-galactopyranoside (hyperin) (3), $C_{21}H_{20}O_{12}$, yellow crystals, mp 235–236°C (MeOH), $[M]^+$ 464. UV spectrum (MeOH, λ_{max}, nm): 260, 362; +CH_3COONa: 276, 395; +CH_3ONa: 276, 405; +CH_3COONa + H_3BO_3: 272, 375. IR spectrum (KBr, ν, cm^{-1}): 3300 (OH), 1665 (C=O), 1615, 1565, 1515 (C=C), 1095, 1030 (C–O). PMR spectrum (300 MHz, CD_3OD, δ, ppm, J/Hz): 7.56 (1H, dd, J = 2.0, 8.9, H-6′), 7.44 (1H, d, J = 2.0, H-2′), 6.79 (1H, d, J = 8.9, H-5′), 6.42 (1H, d, J = 2.0, H-8), 6.15 (1H, d, J = 2.0, H-6), 5.61 (1H, d, J = 7.8, galactose H-1″), 3.30–4.6 (m, galactose 6H).

Quercetin-3-*O*-[(α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside (rutin) (4), $C_{27}H_{30}O_{16}$, yellow powder, mp 215–216°C, $[M]^+$ 610, $[\alpha]_D^{20}$ –11.9° (*c* 0.08, EtOH). UV spectrum (MeOH, λ_{max}, nm): 258, 360. IR spectrum (KBr, ν, cm^{-1}): 3450, 1650, 1610, 1520. PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.58 (1H, d, J = 2.0, 8.5, H-6′), 7.50 (1H,

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d, J = 2.0, H-2′), 6.84 (1H, d, J = 8.5, H-5′), 6.40 (1H, d, J = 2.0, H-8), 6.20 (1H, d, J = 2.0, H-6), 5.45 (1H, d, J = 7.6, glucose H-1″), 4.36 (1H, br.s, rhamnose H-1‴), 3.1-4.0 (m, protons of two sugars), 0.99 (3H, d, J = 6.0, rhamnose CH_3).

Kaempferol (3,5,7,4′-tetrahydroxyflavone) (5), $C_{15}H_{10}O_6$, $[M]^+$ 286, yellow needle-like crystals (MeOH), mp 270–272°C. UV spectrum (EtOH, λ_{max}, nm): 266, 367. IR spectrum (KBr, ν, cm^{-1}): 3420–3300 (OH), 1650 (γ-pyrone C=O), 1590, 1540 (C=C). PMR spectrum (300 MHz, CD_3OD, δ, ppm, J/Hz): 8.04 (2H, dd, J = 2.0, 8.1, H-2′,6′), 6.90 (2H, dd, J = 2.0, 8.5, H-3′,5′), 6.40 (1H, d, J = 2.0, H-8), 6.18 (1H, d, J = 2.0, H-6).

Kaempferol-3-*O*-β-D-glucopyranoside (astragalin) (6), $C_{21}H_{20}O_{11}$, yellow crystals, mp 191–193°C (MeOH), $[M]^+$ 448. UV spectrum (EtOH, λ_{max}, nm): 262, 357. PMR spectrum (300 MHz, CD_3OD, δ, ppm, J/Hz): 12.60, 10.85, 10.18 (br.s, OH), 8.05 (2H, d, J = 8.9, H-2′,6′), 6.92 (2H, d, J = 8.9, H-3′,5′), 6.48 (1H, d, J = 2.4, H-8), 6.24 (1H, d, J = 2.4, H-6), 5.42 (1H, d, J = 7.6, glucose H-1″), 4.9–3.1 (m, glucose 6H).

Kaempferol-3-*O*-α-D-arabinopyranoside (7), $C_{20}H_{18}O_{10}$, yellow powder, mp 203–206°C, $[M]^+$ 418. PMR spectrum (300 MHz, CD_3OD, δ, ppm, J/Hz): 7.94 (2H, d, J = 8.4, H-2′,6′), 6.78 (2H, d, J = 8.4, H-3′,5′), 6.28 (1H, d, J = 2.0, H-8), 6.12 (1H, d, J = 2.0, H-6), 5.05 (1H, d, J = 8.0, arabinose H-1″), 3.80–3.10 (m, arabinose 5H). The size of the arabinose oxide ring was determined from the ^{13}C chemical shifts of the carbohydrate part of the molecule (75 MHz, CD_3OD, δ, ppm): 104.8 (C-1″), 74.2 (C-2″), 72.9 (C-3″), 69.2 (C-4″), 66.9 (C-5″). The lack of a resonance with chemical shift in the range 80.0–88.0 indicated that the arabinose had the pyranose form [6, 9].

All studied flavonoids were isolated for the first time from the title plants.

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