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FLAVONOIDS FROM *Lotus ucrainicus* AND *L. arvensis*

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The genus *Lotus* L. (Fabaceae) numbers up to 200 species, the majority of which is concentrated in Mediterranean countries [1]. Over 30 *Lotus* species grow in the CIS [2]; of these, 10 in Ukraine [3]. The plants are used in folk medicine as a wound-healer, emollient, analgesic, sedative, and general tonic [4].

Our goal was to study the flavonoid composition of *Lotus ucrainicus* L. and *L. arvensis* L. herbs collected during flowering in Ivano-Frankovsk Oblast′.

The herb (1000 g of each species) was extracted exhaustively with EtOH (70%), combining maceration (24 h) with subsequent extraction at 85–90°C. The aqueous alcohol extracts were evaporated in vacuo to a thick residue (~700 mL) and left for 10–12 h at 5–10°C. The dark green resinous solid was separated by filtration, treated with hot water (300 mL), cooled, and filtered. The filtrate was combined with the aqueous solution, evaporated to 700 mL, treated with EtOH (1.5 L, 96%) with vigorous shaking, and filtered after settling. The purified aqueous solution was extracted successively with $CHCl_3$, EtOAc, and *n*-BuOH.

The EtOAc extract was evaporated in vacuo to a thick residue. The condensed extract was dried onto polyamide. The resulting powder was placed on a layer of polyamide formed in $CHCl_3$. The chromatographic column was eluted with $CHCl_3$ and $CHCl_3$:EtOH in various ratios. The separation was monitored by paper chromatography using *n*-BuOH:CH_3CO_2H:H_2O (4:1:2), CH_3CO_2H (15%), C_6H_6:EtOAc:CH_3CO_2H:H_2O (50:50:1:1), and formamide:EtOH (1:3).

Homogeneous fractions were combined, evaporated to dryness, and crystallized from EtOH or MeOH. Fractions containing a mixture of compounds were rechromatographed over polyamide columns. The resulting compounds **1**–**13** were additionally purified by recrystallization from aqueous EtOH or MeOH.

The isolated compounds were identified using physicochemical (UV, IR, PMR spectroscopy), chemical, and biochemical analytical methods. Comparison of the results with literature data and authentic samples identified **1** as kaempferol [5]; **2**, quercetin [6]; **3**, astragalin [6]; **11**, hyperoside [6]; and **13**, isorhamnetin [7].

Kaempferol-7-*O*-*β*-D-glucopyranoside (4): $C_{21}H_{20}O_{11}$, mp 270–272°C (MeOH), $[\alpha]_D^{20}$ −46°. UV spectrum (λ_{max}, nm): 270, 368. IR spectrum (KBr, ν_{max}, cm^{-1}): 3303 (OH), 1660 (C=O), 1610, 1570, 1520 (C=C), 890 (*β*-glycoside).

Kaempferol-3-*O*-*β*-D-glucopyranosyl-7-*O*-*β*-D-glucopyranoside (5): $C_{27}H_{30}O_{16}$, mp 198–200°C (70% MeOH), $[\alpha]_D^{20}$ −69°. UV spectrum (λ_{max}, nm): 267, 353. IR spectrum (KBr, ν_{max}, cm^{-1}): 3100 (OH), 1650 (C=O), 1610, 1450 (C=C), 1100–1010, 890 (*β*-glycoside). PMR spectrum (100 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.85 (2H, d, J = 8.0, H-2′,6′), 6.67 (2H, d, J = 8.0, H-3′,5′), 6.30 (1H, d, J = 2.5, H-8), 5.97 (1H, d, J = 2.0, H-6), 5.94 (1H, d, J = 7.0, Glc H-1), 5.33 (1H, d, J = 7.0, Glc H-1).

Kaempferol-3-*O*-*β*-D-galactopyranoside (6): $C_{21}H_{20}O_{11}$, mp 215–217°C (MeOH), $[\alpha]_D^{20}$ −48°. UV spectrum (λ_{max}, nm): 268, 355. IR spectrum (KBr, ν_{max}, cm^{-1}): 3300–2700 (OH), 1660 (C=O), 1610, 1580, 1515 (C=C), 1095, 1075, 1025, 890 (*β*-glycoside). PMR spectrum (100 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.44 (s, 5-OH), 7.96 (2H, d, J = 8.5, H-2′,6′), 6.79 (2H, d, J = 8.5, H-3′,5′), 6.26 (1H, d, J = 2.5, H-8), 6.13 (1H, d, J = 2.5, H-6), 5.65 (1H, d, J = 7.0, Gal H-1).

Quercetin-3-*O*-*β*-D-glucopyranoside (7): $C_{21}H_{20}O_{12}$, mp 229–231°C (MeOH), $[\alpha]_D^{20}$ −12.5°. UV spectrum (λ_{max}, nm): 255, 265, 360. IR spectrum (KBr, ν_{max}, cm^{-1}): 3200–2900 (OH), 1650 (C=O), 1612-1450 (C=C), 1080, 1050, 1010, 890 (*β*-glycoside). PMR spectrum (100 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.40 (s, 5-OH), 7.82 (1H, d, J = 2.5, H-6′), 7.31 (1H, d, J = 2.5, H-2′), 6.74 (2H, d, J = 2.0, H-3′,5′), 6.25 (1H, d, J = 2.5, H-8), 6.12 (1H, d, J = 2.5, H-6), 5.97 (1H, d, J = 7.0, Glc H-1) [6].

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Quercetin-3-*O*-β-L-rhamnopyranoside (8): $C_{21}H_{20}O_{11}$, mp 182–185°C (MeOH), $[\alpha]_D^{20}$ −12.5°. UV spectrum (λ_{max}, nm): 255, 300, 350. IR spectrum (KBr, ν_{max}, cm^{-1}): 3200 (OH), 2800 ($-CH_3$ rhamnose), 1615 (C=O), 1565 (C=C), 1100-1030, 890 (β-glycoside).

Morin (3,5,7,2′,4′-pentahydroxyflavone) (9): $C_{15}H_{10}O_7$, mp 303–305°C (MeOH). UV spectrum (λ_{max}, nm): 265, 395. IR spectrum (KBr, ν_{max}, cm^{-1}): 3232 (OH), 1658 (C=O), 1640, 1608, 1580, 1506 (aromatic C=C).

Morin-3-*O*-β-D-galactopyranoside (10): $C_{21}H_{22}O_{12}$, mp 233–237°C (MeOH). UV spectrum (λ_{max}, nm): 260, 370. IR spectrum (KBr, ν_{max}, cm^{-1}): 3200–2800 (OH), 1660 (C=O), 1610, 1570, 1520, 1090, 1025, 1000, 890 (β-glycoside). PMR spectrum (400 MHz, DMSO-d_6–CCl_4, δ, ppm, J/Hz): 12.65 (s, 5-OH), 1076 (s, 7-OH), 9.40 (s, 2′-OH), 9.40 (s, 4′-OH), 6.35 (1H, dd, J = 8.4, 2.4, 5′-H), 6.40 (1H, d, J = 2.0, 3′-H), 7.24 (1H, d, J = 8.0, 6′-H), 6.32 (1H, d, J = 2.0, 8-H), 6.18 (1H, d, J = 2.0, 6-H), 5.38 (1H, d, J = 7.0, Gal H-1).

3-Methylquercetin (5,7,3′,4′-tetrahydroxy-3-methoxyflavone) (12): $C_{16}H_{12}O_7$, mp 258–260°C (MeOH). UV spectrum (λ_{max}, nm): 257, 358. IR spectrum (KBr, ν_{max}, cm^{-1}): 3390 (OH), 2920 ($-CH_3$), 1640 (C=O), 1605, 1490 (aromatic C=C).

Compounds **1**–**13** were isolated for the first time from *L. ucrainicus* and *L. arvensis*. The flavonoid contents were determined by spectrophotometry and were 1.66 ± 0.03% for *L. ucrainicus* and 1.28 ± 0.03% for *L. arvensis*.

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