FLAVONOIDS FROM *Eurotia ceratoides*

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Phytochemical studies of the aerial part of *Eurotia ceratoides* L. (Chenopodiaceae) collected during flowering in Almaty Oblast (Ili River) in 2005-2007 have been initiated [1].

Qualitative and quantitative analysis showed that this plant contains 1.00% flavonoids [2, 3]. Column chromatography over silica gel and polyamide (eluents $CHCl_3$:EtOAc, H_2O:C_2H_5OH, $CHCl_3$:CH_3OH in various ratios) isolated from the H_2O:C_2H_5OH (70%) extract flavonoids **1-7**.

The isolated flavonoids **1-7** were identified based on chemical (acid hydrolysis, alkaline cleavage) and spectral (UV, IR, mass, PMR, ^{13}C NMR spectroscopy) methods and comparison with the literature.

3,5,7,4′-Tetrahydroxyflavone (1), mp 277-278°C (CH_3OH). UV spectrum (CH_3OH, λ_{max}, nm): 260, 367; CH_3COONa: 262, 371; CH_3COONa + H_3BO_3: 260, 367; CH_3ONa: 256, 326; $AlCl_3$: 263, 430; $AlCl_3$/HCl: 262, 427.

PMR spectrum (CD_3OD, δ, ppm, J/Hz): 8.10 (2H, d, J = 8.8, H-2′, H-6′), 6.93 (2H, d, J = 8.8, H-3′, H-5′), 6.40 (1H, d, J = 2.0, H-8), 6.18 (1H, d, J = 2.0, H-6).

Mass spectrum (EI, 70 eV, *m*/*z*): 286 (67.3), 257 (4), 229 (1), 152 (10), 134 (20), 121 (13), 52 (90) [4].

3,5,7,4′-Tetrahydroxy-3′-methoxyflavone (2), mp 305-307°C (CH_3OH). UV spectrum (CH_3OH, λ_{max}, nm): 255, 369; CH_3COONa: 270, 380; CH_3COONa + H_3BO_3: 256, 370; CH_3ONa: 275, 423; $AlCl_3$: 265, 428; $AlCl_3$/HCl: 264, 428.

PMR spectrum (C_5D_5N, δ, ppm, J/Hz): 8.53 (1H, d, J = 2.0, H-2′), 8.13 (1H, dd, J_1 = 2.0, J_2 = 8.0, H-6′), 7.12 (1H, d, J = 8, H-5′), 6.78 (1H, d, J = 2.0, H-8), 6.73 (1H, d, J = 2.0, H-6), 3.90 (3H, s, OCH_3).

^{13}C NMR spectrum: 157.54 (C-2), 138.38 (C-3), 177.44 (C-4), 162.46 (C-5), 99.27 (C-6), 165.64 (C-7), 94.35 (C-8), 157.54 (C-9), 104.51 (C-10), 125.60 (C-1′), 112.12 (C-2′), 148.06 (C-3′), 147.13 (C-4′), 116.41 (C-5′), 120.44 (C-6′), 55.89 (OCH_3).

Mass spectrum (EI, 70 eV, *m*/*z*): 316 (15), 301 (100), 286 (21.78), 273 (81.07), 229 (4), 167 (3.4), 152 (6), 137 (15.2), 118 (7.2), 82.9 (27.13), 57 (78.4) [5, 6].

3,5,7,3′,4′-Pentahydroxyflavone (3), mp 311-313°C (CH_3OH). UV spectrum (CH_3OH, λ_{max}, nm): 255, 372; CH_3COONa: 280, 390; CH_3COONa + H_3BO_3: 272, 390; CH_3ONa: 246, 330; $AlCl_3$: 266, 428; $AlCl_3$/HCl: 265, 427.

PMR spectrum (C_5D_5N, δ, ppm, J/Hz): 8.63 (1H, d, J = 2.0, H-2′), 8.12 (1H, dd, J_1 = 2.5, J_2 = 8.5, H-6′), 7.39 (1H, d, J = 8.5, H-5′), 6.76 (1H, d, J = 2.5, H-8), 6.72 (1H, d, J = 2.5, H-6).

Mass spectrum (EI, 70 eV, *m*/*z*): 302 (100), 273 (7), 245 (7), 229 (5), 153 (8), 137 (9.2), 127 (10), 127 (10), 83 (5), 68 (17) [7].

5,7,3′,4′-Tetrahydroxyflavone 3-*O*-β-D-glucopyranoside (4), mp 233-235°C (H_2O:CH_3OH); $[\alpha]_D$ −70.1° (*c* 0.14, H_2O:CH_3OH).

UV spectrum (CH_3OH, λ_{max}, nm): 258, 360; CH_3COONa: 272, 380; CH_3COONa + H_3BO_3: 265, 378; CH_3ONa: 262, 434; $AlCl_3$: 273, 400; $AlCl_3$/HCl: 260, 400.

PMR spectrum (C_5D_5N, δ, ppm, J/Hz): 7.70 (1H, d, J = 2.0, H-2′), 7.60 (1H, d, J = 8.0, H-6′), 7.30 (1H, d, J = 8.0, H-5′), 6.66 (1H, d, J = 2.0, H-8′), 6.46 (1H, d, J = 2.0, H-6), 5.62 (1H, d, J = 8.0, H-1″).

Mass spectrum (EI, 70 eV, *m*/*z*): 466 $[M - 1]^+$, 465 (10), 303 (8), 277 (11), 259 (6), 185 (100), 152 (30), 136 (15), 52 (10) [8].

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5,7,3′,4′-Tetrahydroxyflavone 3-*O*-α-L-rhamnopyranoside (5), mp 187-189°C (H_2O:CH_3OH), $[\alpha]_D$ −83.0 (*c* 0.12, H_2O:CH_3OH). UV spectrum (CH_3OH, λ_{max}, nm): 256, 355; CH_3COONa: 268, 365; $CH_3COONa + H_3BO_3$: 262, 367; CH_3ONa: 262, 390; $AlCl_3$: 265, 400; $AlCl_3$/HCl: 266, 390.

PMR spectrum (C_5D_5N, δ, ppm, J/Hz): 8.00 (1H, d, J = 2.0, H-2′), 7.69 (1H, d, J = 2.0, 8.5, H-6′), 7.27 (1H, d, J = 8.0, H-5′), 6.67 (1H, d, J = 2.0, H-8), 6.26 (1H, d, J = 2, H-6), 5.06 (1H, d, J = 2.0, H-1″), (3H, d, J = 7.8, CH_3).

Mass spectrum (EI, 70 eV, *m*/*z*): 448 $[M + 1]^+$, 303 (10), 277 (30), 259 (9), 207 (40), 185 (100), 167 (20), 152 (15), 137 (10), 50 (8) [8].

3,5,7,4′-Tetrahydroxy-3′-methoxyflavone 3-*O*-β-D-glucopyranosyl(1→6)-α-L-rhamnopyranoside (6), mp 177-179°C.

UV spectrum (C_2H_5OH, λ_{max}, nm): 254, 366; CH_3COONa: 266, 376; $CH_3COONa + H_3BO_3$: 254, 364; C_2H_5ONa: 258, 410; $ZrOCl_2$: 270, 420; $ZrOCl_2$ + citric acid: 254, 368.

PMR spectrum (CD_3OD, δ, ppm, J/Hz): 7.93 (1H, d, J = 1.8, H-2′), 7.60 (1H, dd, J = 8.2, 1.8, H-6′), 6.80 (1H, d, J = 8.2, H-5′), 6.39 (1H, d, J = 1.8, H-8), 6.18 (1H, d, J = 1.8, H-6), 5.23 (1H, d, J = 7.3, H-1″), 4.5 (1H, s, J = 2.0, H-1‴), 1.1 (3H, s, CH_3-rhamnose).

Mass spectrum (EI, 70 eV, *m*/*z*): 642 $[M]^+$, 641 (22) $[M - 1]^+$, 316 (15) $[M - Gl - Rh]^+$, $C_{28}H_{32}O_{16}$ [9].

5,7,4′-Trihydroxyflavone 3-*O*-α-L-rhamnopyranoside (7), mp 167-169°C (H_2O:CH_3OH); $[\alpha]_D$ −106° (*c* 0.1, H_2O:CH_3OH).

UV spectrum (CH_3OH, λ_{max}, nm): 265, 340; CH_3COONa: 265, 344; $CH_3COONa + H_3BO_3$: 265, 340; CH_3ONa: 272, 390; $AlCl_3$: 273, 389; $AlCl_3$/HCl: 274, 389.

PMR spectrum (CD_3OD, δ, ppm, J/Hz): 7.79 (2H, d, J = 8.8, H-2′, H-6′), 6.95 (2H, d, J = 8.8, H-3′, H-5′), 6.38 (1H, d, J = 2.0, H-8), 6.21 (1H, d, J = 2, H-6), 5.37 (1H, d, J = 2.0, H-1″), 0.92 (3H, d, J = 6, CH_3).

Mass spectrum (EI, 70 eV, *m*/*z*): 432 $[M]^+$, 431 (10) $[M - 1]^+$, 285 (10), 275 (15), 256 (7), 184 (100), 152 (20), 118 (10), 51 (10) [10].

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