

POLYPHENOLS FROM SEVERAL PSAMMOPELITOPHYTES

G. A. Seitimova,¹ B. K. Eskalieva,^{1*} G. Sh. Burasheva,¹
M. Iqbal Choudhary,² and Achyut Adhikari²

The plants *Climacoptera obtusifolia* and *Kochia prostrata* are psammopelitolophytes that are typically highly tolerant to the soil mechanical composition and have significant resources in Kazakhstan [1, 2]. Therefore, phytochemical research on the aerial part of the Kazakhstan variety of *K. prostrata* was initiated and studies of the chemical composition of *C. obtusifolia* were continued [3, 4].

Fractional extraction and adsorption-distribution and gel chromatography isolated pure phenolic compounds **1–8** (**1–4** from *C. obtusifolia*; **5–8**, *K. prostrata*). The compounds were identified using chemical and spectral analyses and comparison with the literature and authentic samples. Compounds **5–8** were observed for the first time in plants of the genus *Kochia*. Compounds **2–4** were isolated for the first time from plants of the family Chenopodiaceae.

Quercetin 3-O-β-D-Glucopyranosyl-(6→1)-α-L-rhamnopyranoside (rutin) (1). C₂₇H₃₀O₁₆, light-yellow crystals, mp 214–216°C. UV spectrum (MeOH, λ_{max}, nm): 270, 370. ESI-MS mass spectrum, *m/z* 611 [M + H]⁺ [5].

Tamarixetin 3-O-β-D-glucopyranosyl-(2→1)-α-L-rhamnopyranoside (tamaraxetin 3-O-neohesperidoside) (2). C₂₈H₃₂O₁₆, yellow amorphous powder, mp 180–190°C. UV spectrum (MeOH, λ_{max}, nm): 254, 286, 373. Mass spectrum ESI-MS, *m/z* 625 [M + H]⁺. ¹H NMR spectrum (400 MHz, CD₃OD, δ, ppm, J/Hz): 1.09 (3H, d, J = 6.4, H-6''), 3.94 (3H, s, 4'-OCH₃), 4.55 (1H, br.s, H-1''), 5.23 (1H, d, J = 7.2, H-1''), 6.21 (1H, d, J = 1.2, H-6), 6.41 (1H, d, J = 1.2, H-8), 6.91 (1H, d, J = 8.4, H-5'), 7.62 (1H, d, J = 1.2, H-2'), 7.93 (1H, dd, J = 8.4, 1.2, H-6'). ¹³C NMR spectrum (100 MHz, CD₃OD, δ, ppm): 17.87 (C-6''), 56.79 (OCH₃), 62.0 (C-6''), 68.54 (C-5''), 69.78 (C-4''), 72.09 (C-2''), 72.29 (C-3''), 73.85 (C-4''), 75.92 (C-2''), 77.39 (C-5''), 78.19 (C-3''), 94.93 (C-8), 99.99 (C-1''), 100.0 (C-6), 102.52 (C-1''), 104.41 (C-10), 114.59 (C-2'), 116.11 (C-5'), 123.03 (C-1'), 124.01 (C-6'), 135.47 (C-3), 148.34 (C-3'), 150.87 (C-4'), 158.53 (C-9), 158.89 (C-2), 163.03 (C-5), 166.13 (C-7), 179.35 (C-4) [6].

Tamarixetin-3,7-di-O-β-D-glucopyranoside (3). C₂₈H₃₂O₁₇, yellow powder, mp 224–226°C. UV spectrum (MeOH, λ_{max}, nm): 255, 265, 352. Mass spectrum ESI-MS, *m/z* 641 [M + H]⁺. ¹H NMR spectrum (400 MHz, C₅D₅N, δ, ppm, J/Hz): 3.92 (3H, s, 4'-OCH₃), 5.79 (1H, d, J = 7.2, H-1''), 6.53 (1H, d, J = 7.6, H-1''), 6.76 (1H, d, J = 1.6, H-6), 7.01 (1H, d, J = 1.6, H-8), 7.19 (1H, d, J = 8.8, H-5'), 7.35 (1H, d, J = 2.2, H-2'), 7.74 (1H, dd, J = 8.8, 2.2, H-6'), 8.44 (1H, s, 3'-OH), 13.14 (1H, br.s, 5-OH). ¹³C NMR spectrum (125 MHz, C₅D₅N, δ, ppm): 55.74 (OCH₃), 60.4 (C-6''), 60.7 (C-6''), 69.3 (C-4''), 69.6 (C-4''), 72.8 (C-2''), 73.8 (C-2''), 76.0 (C-3''), 76.1 (C-3''), 76.9 (C-5''), 77.3 (C-5''), 94.4 (C-8), 99.3 (C-6), 99.6 (C-1''), 100.5 (C-1''), 105.6 (C-10), 111.2 (C-2'), 115.7 (C-5'), 121.4 (C-1'), 122.4 (C-6'), 133.8 (C-3), 145.6 (C-3'), 150.0 (C-4'), 156.0 (C-9), 156.4 (C-2), 160.5 (C-5), 162.7 (C-7), 178.67 (C-4) [7].

Tamarixetin 3-O-β-D-galactopyranosyl-(6→1)-α-L-rhamnopyranoside (tamaraxetin 3-O-robinobioside) (4). C₂₈H₃₂O₁₆, yellow powder, mp 186–188°C. UV spectrum (MeOH, λ_{max}, nm): 269, 275, 334. Mass spectrum ESI-MS, *m/z* 625 [M + H]⁺. ¹H NMR spectrum (300 MHz, C₅D₅N, δ, ppm, J/Hz): 1.46 (3H, d, J = 5.4, H-6''), 3.90 (3H, s, 4'-OCH₃), 5.33 (1H, s, H-1''), 6.24 (1H, d, J = 7.2, H-1''), 6.68 (1H, d, J = 1.8, H-6), 6.71 (1H, d, J = 1.8, H-8), 7.28 (1H, d, J = 8.4, H-5'), 7.90 (1H, dd, J = 8.4, 1.8, H-6'), 8.37 (1H, d, J = 1.8, H-2'), 13.19 (1H, br.s, 5-OH). ¹³C NMR spectrum (125 MHz, C₅D₅N, δ, ppm): 18.48 (C-6''), 56.04 (OCH₃), 68.29 (C-6''), 69.67 (C-4''), 71.63 (C-4''), 72.11 (C-3''), 72.56 (C-2''), 73.86 (C-2''), 76.20 (C-5''), 77.68 (C-3''), 78.58 (C-5''), 94.69 (C-8), 99.81 (C-6), 100.3 (C-1''), 102.63 (C-1''), 103.99 (C-10), 114.30 (C-2'), 116.31 (C-5'), 123.51 (C-1'), 123.79 (C-6'), 135.8 (C-3), 148.00 (C-3'), 151.24 (C-4'), 157.69 (C-9), 157.73 (C-2), 162.79 (C-5), 165.90 (C-7), 178.64 (C-4) [8].

1) Al-Farabi Kazakh National University, Faculty of Chemistry and Chemical Engineering, Almaty, Republic of Kazakhstan, e-mail: balakyz@mail.ru; 2) Research Institute of Chemistry, International Center of Chemical and Biological Sciences, University of Karachi, Karachi, Pakistan. Translated from *Khimiya Prirodnykh Soedinenii*, No. 2, March–April, 2017, pp. 314–315. Original article submitted June 24, 2016.

3,5-Dimethoxy-6,7-methylenedioxyflavone (5). $C_{18}H_{14}O_6$, white needles, mp 198–200°C. UV spectrum (MeOH, $\lambda_{\max}$, nm): 269, 313. Mass spectrum EI-MS, m/z 325 $[M - H]^-$. 1H NMR spectrum (500 MHz, $CDCl_3$, δ , ppm): 3.86 (3H, s, 3-OCH₃), 4.13 (3H, s, 5-OCH₃), 6.05 (2H, s, OCH₂O), 6.67 (1H, s, H-8), 7.48 (3H, m, H-3', 4', 5'), 8.03 (2H, m, H-2', 6'). ^{13}C NMR spectrum (125 MHz, $CDCl_3$, δ , ppm): 60.18 and 61.41 (OCH₃), 93.10 (C-8), 102.22 (OCH₂O), 119.6 (C-10), 128.2 (C-2', 6'), 128.5 (C-3', 5'), 130.4 (C-4'), 130.8 (C-1'), 134.8 (C-3), 141.1 (C-6), 141.4 (C-5), 152.9 (C-9), 153.0 (C-2), 153.85 (C-7), 174.15 (C-4) [9].

5-Methoxy-6,7-methylenedioxyflavone (6). $C_{17}H_{12}O_5$, yellow compound, mp 278–280°C. UV spectrum (MeOH, $\lambda_{\max}$, nm): 215, 270, 307. Mass spectrum EI-MS, m/z 295 $[M - H]^-$. 1H NMR spectrum (600 MHz, C_5D_5N , δ , ppm): 4.14 (3H, s, 5-OCH₃), 6.07 (2H, s, OCH₂O), 6.93 (1H, s, H-3), 6.98 (1H, s, H-8), 7.46 (3H, m, H-3', 4', 5'), 7.92 (2H, m, H-2', 6'). ^{13}C NMR spectrum (175 MHz, C_5D_5N , δ , ppm): 61.29 (OCH₃), 94.16 (C-8), 103.00 (OCH₂O), 108.80 (C-3), 126.37 (C-5'), 129.35 (C-3', 4'), 131.51 (C-2', 6'), 131.95 (C-1'), 141.45 (C-6), 152.93 (C-5), 153.32 (C-9), 154.92 (C-7), 160.74 (C-2), 176.85 (C-4) [10].

4'-Hydroxyacetophenone (7). $C_8H_8O_2$, white needles, mp 109–111°C. UV spectrum (MeOH, $\lambda_{\max}$, nm): 237. Mass spectrum EI-MS, m/z 136 $[M]^+$. 1H NMR spectrum (500 MHz, CD_3OD , δ , ppm, J/Hz): 2.51 (3H, s, H-2), 6.83 (2H, d, J = 8.8, H-3', 5'), 7.87 (2H, d, J = 8.8, H-2', 6'). ^{13}C NMR spectrum (125 MHz, CD_3OD , δ , ppm): 26.27 (C-2), 116.23 (C-3', 5'), 130.18 (C-1'), 132.13 (C-2', 6'), 164.00 (C-4'), 199.49 (C-1) [11].

3',4'-Dihydroxy-5'-methoxyacetophenone (8). $C_9H_{10}O_4$, white needles, mp 159–160°C. UV spectrum (MeOH, $\lambda_{\max}$, nm): 215, 299. Mass spectrum EI-MS, m/z 182 $[M]^+$. 1H NMR spectrum (400 MHz, CD_3OD , δ , ppm, J/Hz): 2.56 (3H, s, H-2), 3.87 (3H, s, 5'-OCH₃), 5.88 (1H, d, J = 2.4, H-6'), 5.96 (1H, d, J = 2, H-2'). ^{13}C NMR spectrum (100 MHz, CD_3OD , δ , ppm): 31.04 (C-2), 54.17 (OCH₃), 90.13 (C-6'), 94.91 (C-2'), 163.33 (C-4'), 164.83 (C-5'), 166.34 (C-3'), 202.26 (C-1) [12].

REFERENCES

1. N. I. Akzhigitova, *Halophilic Flora of Central Asia and Its Signatures* [in Russian], Fan, Tashkent, 1982, pp. 26-30.
2. *Flora of Kazakhstan* [in Russian], Vol 3, Academy of Sciences of the Kazakh SSR, Alma-Ata, 1960, pp. 179–226, 231–234.
3. B. Yeskaliyeva, M. A. Mesaik, A. Abbaskhan, A. Kulsoom, G. Sh. Burasheva, Zh. A. Abilov, M. I. Choudhary, and Atta-ur-Rahman, *Phytochemistry*, **67**, 2392 (2006).
4. G. A. Seitimova, B. K. Eskalieva, G. Sh. Burasheva, and M. I. Choudhary, *Chem. Nat. Compd.*, **50**, 537 (2014).
5. A. K. Kipchakbaeva, R. A.-A. Khamid, B. K. Eskalieva, G. Sh. Burasheva, Zh. A. Abilov, S. R. Numonov, and H. A. Aisa, *Chem. Nat. Compd.*, **52**, 322 (2016).
6. B. P. Silva, R. R. Bernardo, and J. P. Parente, *Phytochemistry*, **53**, 87 (2000).
7. Q. Xiong, D. Shi, and M. Mizuno, *Phytochemistry*, **39**, 723 (1995).
8. A. F. Barrero, A. Haidour, M. Munoz-Dorado, M. Akssira, A. Sedqui, and I. Mansour, *Phytochemistry*, **48**, 1237 (1998).
9. C. A. Buschi, A. B. Pomilio, and E. G. Gros, *Phytochemistry*, **18**, 1249 (1979).
10. N. A. Ser, *Phytochemistry*, **27**, 3708 (1988).
11. H. C. Kwon and K. R. Lee, *Arch. Pharm. Res.*, **24**, 194 (2001).
12. C. J. Baker, B. D. Whitaker, D. P. Roberts, N. M. Mock, C. P. Rice, K. L. Deahl, and A. A. Aver'yanov, *Physiol. Mol. Plant Pathol.*, **66**, 90 (2005).