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PHENOLIC COMPOUNDS FROM *Euphorbia canescens* AND *E. franchetii*

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Our study of the polyphenol composition of *Euphorbia canescens* L. and *E. franchetii* B. Fedtsch. has been completed [1]. The previously developed method [2] was used to extract ground aerial organs of *E. canescens* with $CHCl_3$ and aqueous acetone. The latter extract was concentrated *in vacuo*. The aqueous residue was treated with EtOAc. The condensed EtOAc extract was treated with $CHCl_3$. The resulting precipitates were filtered off to afford total phenolic compounds in 6.3% yield of the air-dried raw material. Two-dimensional paper chromatography using BuOH:AcOH:H_2O (system 1, 40:12:28) and AcOH (system 2, 2%) showed that the plant polyphenols consisted of 14 compounds.

Total polyphenols were separated preliminarily by chromatography over a column of hide powder with elution by Et_2O, H_2O, and aqueous acetone [3, 4]. Paper chromatography of the resulting fractions found that the Et_2O fraction contained two; the aqueous fraction, five; and the aqueous acetone fraction, seven compounds. Column chromatography of the Et_2O fraction over silica gel isolated gallic (**1**) and ellagic (**2**) acids. The phenolic compounds in the aqueous fraction were chromatographed over a column of polyamide with elution by a $CHCl_3$:MeOH gradient with an increasing MeOH content. This afforded several fractions containing pure compounds that were additionally purified and recrystallized.

The compounds were identified from their physicochemical properties as quercetin (**3**), kaempferol (**4**), quercetin-3-rutinoside (**5**), quercetin-3-*O*-*β*-D-galactopyranoside (hyperoside) (**6**), and kaempferol-3-glucopyranoside (astragalin) (**7**). Chromatography of the aqueous acetone fraction over silica gel with elution by Et_2O:EtOAc and pure EtOAc isolated seven pure compounds that were identified from their physicochemical properties as 1-*O*-galloyl-4,6-hexahydroxydiphenoyl-*β*-D-glucose (**8**), geraniin (**9**), 2,3-di-*O*-galloyl-*β*-D-glucose (**10**), 1,4,6-tri-*O*-galloyl-*β*-D-glucose (**11**), 1,2,6-tri-*O*-galloyl-*β*-D-glucose (**12**), and 1,2,3-tri-*O*-galloyl-*β*-D-glucose (**13**) [1–3].

Compound 14. $C_{48}H_{33}O_{31}$, MW 1105, mp 253–254°C (dec.), brown amorphous powder, R_f 0.12 (system 1). The acid hydrolysis products (HCl, 5%) contained glucose and gallic and valoneic acids. The phenol:sugar ratio was 4:1. UV spectrum (EtOH, λ_{max}, nm): 225, 290. IR spectrum (KBr, ν, cm^{-1}): 3400–3300 (OH), 1620–1610, 1450 (Ar), 1320 (–C–OH), 1250, 1045 (–C–O–C), 1080–1070 (C–O), 1040, 1010 (sugar). PMR spectrum (200 MHz, acetone-d_6, δ, ppm, J/Hz): 4.87 (1H, d, J = 8, Glc-1), 3.62 (1H, dd, J = 8, 10, Glc-2), 5.51 (1H, t, J = 10, Glc-3), 5.34 (1H, t, J = 10, Glc-4), 4.12 (1H, dd, J = 7, 13, Glc-5), 4.40 (2H, dd, J = 7, 13, Glc-6), 7.18, 7.15, 7.10, 7.04, 7.00 (H, galloyl), 6.15, 6.13, 6.09, 6.06 (H, valoneyl). ^{13}C NMR spectrum (50 MHz, acetone-d_6, δ, ppm): 94.2 (glucose C-1), 70.9 (C-2), 65.3 (C-3), 67.2 (C-4), 64.3 (C-5), 65.4 (C-6); galloyl: 125.9 (C-1), 110.9 (C-2), 145.8 (C-3), 136.0 (C-4), 145.8 (C-5), 110.9 (C-6), 167.0 (C-7); valoneyl: 119.0 (C-1), 124.8 (C-2), 111.4 (C-3), 144.7 (C-4), 136.5 (C-5), 144.7 (C-6), 167.0 (C-7), 119.5 (C-1′), 123.1 (C-2′), 113.0 (C-3′), 143.5 (C-4′), 138.1 (C-5′), 143.0 (C-6′), 167.0 (C-7′), 114.8 (C-1″), 138.9 (C-2″), 134.6 (C-3″), 136.6 (C-4″), 138.9 (C-5″), 111.0 (C-6″), 172.0 (C-7″). The structure of **14** was determined based on the results as 1,4,6-tri-*O*-galloyl-2,3-valoneyl-*β*-D-glucose. It is a new compound that has not been described before.

The total polyphenols isolated from the aerial part of *E. franchetii* contained 11 compounds. Column chromatography over silica gel with elution by $CHCl_3$:MeOH (17:3, 17:4, and 17:5, successively) separated the total polyphenols into three fractions [1]. The first fraction contained a single compound with R_f 0.51 (system 2, *n*-BuOH:AcOH:H_2O, 4:1:5). The second fraction contained five flavonols with R_f 0.80, 0.75, 0.38, 0.79, and 0.62 (system 1). Rechromatography of it over a column of polyamide with elution by $CHCl_3$:MeOH (9:1 and 8:2) isolated the pure compounds (**15**, **3**, **16**, **4**, **17**).

Rechromatography over a column of silica gel of the third fraction with elution by MeOH solvents (MeOH 60% → MeOH 70%), MeOH:acetone:H_2O (7:2:1 → 6:2:2 → 5:3:2) isolated five pure compounds (**18**, **9**, **10**, **19**, **20**) [1]. Compounds

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1–9 were identified from their physicochemical properties as gallic acid (**1**), quercetin-3-*O*-rhamnoside (quercitrin) (**15**), quercetin (**3**), kaempferol-3-*O*-glucoside (**16**), kaempferol (**4**), quercetin-3-galactoside (**17**), 3-*O*-galloyl-4,6-hexahydroxydiphenoyl-*β*-D-glucose (**18**), geraniin (**9**), and 2,3-di-*O*-galloyl-*β*-D-glucose (**10**) [1–4].

1-*O*-Galloyl-2,3-hexahydroxydiphenoyl-4,6-valoneyl-*β*-D-glucose (19). $C_{48}H_{32}O_{31}$, MW 1104, mp 257–258°C (dec.), yellow amorphous powder, R_f 0.28 (system 1). The acid hydrolysis products (HCl, 5%) contained glucose and gallic, ellagic, and valoneic acids. The phenol:sugar ratio was 3:1. Stepwise hydrolysis produced 1-*O*-galloylglucose, 2,3-hexahydroxydiphenoylglucose, and 4,6-valoneylglucose.

UV spectrum (EtOH, λ_{max}, nm): 220, 280. IR spectrum (KBr, ν, cm^{-1}): 3300–3400 (OH), 1620–1610, 1450 (Ar), 1320 (–C–OH), 1250, 1045 (–C–O–C), 1080–1070 (C–O), 1040, 1010 (sugar). PMR spectrum (200 MHz, acetone-d_6, δ, ppm, J/Hz): 6.39 (1H, d, J = 4.0, Glc-1), 5.66 (1H, dd, J = 4, 10, Glc-2), 6.06 (1H, t, J = 10, Glc-3), 5.70 (1H, t, J = 10, Glc-4), 4.60 (1H, m, J = 7, 13, Glc-5), 4.45 (2H, dd, J = 13, Glc-6), 7.57, 7.55, 7.10, 6.98, 6.57, 6.56 (H, valoneyl), 6.75, 6.73, 6.68, 6.63 (H, galloyl), 6.84, 6.70 (H, hexahydroxydiphenoyl). ^{13}C NMR spectrum (100 MHz, acetone-d_6, δ, ppm): glucose: 94.2 (C-1), 70.9 (C-2), 65.3 (C-3), 67.2 (C-4), 64.3 (C-5), 65.4 (C-6); galloyl: 125.9 (C-1), 110.9 (C-2), 145.8 (C-3), 136.0 (C-4), 145.8 (C-5), 110.9 (C-6), 167.0 (C-7); hexahydroxydiphenoyl: 119.0 (C-1), 124.8 (C-2), 111.4 (C-3), 144.7 (C-4), 136.65 (C-5), 144.7 (C-6), 167.0 (C-7), 119.0 (C-1′), 144.7 (C-2′), 136.5 (C-3′), 144.7 (C-4′), 111.4 (C-5′), 124.8 (C-6′), 167.0 (C-7′); valoneyl: 119.0 (C-1), 124.8 (C-2), 111.4 (C-3), 144.7 (C-4), 136.5 (C-5), 114.7 (C-6), 167.0 (C-7), 119.5 (C-1′), 123.1 (C-2′), 113.0 (C-3′), 143.5 (C-4′), 138.1 (C-5′), 143.0 (C-6′), 167.0 (C-7′), 114.8 (C-1″), 138.9 (C-2″), 134.6 (C-3″), 136.6 (C-4″), 138.9 (C-5″), 111.0 (C-6″), 172.0 (C-7″).

1,4-Di-*O*-galloyl-*β*-D-xylose (20). $C_{19}H_{18}O_{13}$, MW 454, white amorphous powder, R_f 0.12 (system 1), mp 182–183°C. The acid hydrolysis products (HCl, 5%) contained xylose and gallic acid in a 1:2 ratio. UV spectrum (EtOH, λ_{max}, nm): 214, 286. IR spectrum (KBr, ν, cm^{-1}): 3500–3200 (OH), 2935, 1495 (–CH–, $–CH_2$), 1625, 1545, 1510, 1435 (Ar), 1270–1040 (=C–O–C). PMR spectrum (200 MHz, acetone-d_6, δ, ppm, J/Hz): xylose: 3.63 (1H, d, J = 1.4, H-1), 3.32 (1H, m, J = 2.1, H-2), 3.07 (1H, m, J = 7.7, H-3), 3.30 (1H, m, J = 2.0, H-4), 3.58 (1H, m, J = 8.5, H-5), 6.97, 7.02, 7.08, 7.09 (H, galloyl). ^{13}C NMR spectrum (50 MHz, acetone-d_6, δ, ppm): xylose: 93.6 (C-1), 70.9 (C-2), 61.6 (C-3), 77.0 (C-4), 87.5 (C-5); galloyl: 125.9 (C-1), 110.9 (C-2), 145.8 (C-3), 136.0 (C-4), 145.8 (C-5), 110.9 (C-6).

Thus, 25 compounds of phenolic nature, three of which were new and not previously described in the literature, were isolated from two plants of the family Euphorbiaceae.

REFERENCES

1. R. N. Rakhimov, N. G .Abdulladzhanova, and S. M. Mavlyanov, in: *Proceedings of the International Conference Phenolic Compounds from Euphorbia canescens L.* [in Russian], Tashkent, 2010, pp. 89, 90.
2. S. M. Mavlyanov, N. G. Abdulladzhanova, and D. N. Dalimov, *Khim. Prir. Soedin.*, 167 (2001).
3. S. M. Mavlyanov, Sh. Yu. Islambekov, A. K. Karimdzhanov, and A. I. Ismailov, *Khim. Prir. Soedin.*, 124 (1997).
4. S. M. Mavlyanov, Sh. Yu. Islambekov, A. K. Karimdzhanov, and A. I. Ismailov, *Khim. Prir. Soedin.*, 124 (1994).