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BRIEF COMMUNICATIONS

STILBENE GLYCOSIDES FROM *Euphorbia armena* ROOTS

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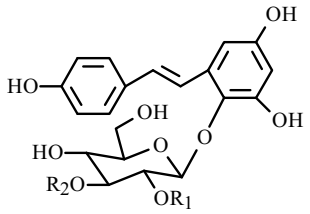
Plants of the genus *Euphorbia* are widely distributed around the whole world. About 45 of the more than 800 known species are indigenous to Georgia [1]. The chemical composition of many plants of this genus has been well studied [2, 3] and includes compounds such as triterpenes, steroids, sesquiterpenes, phenolic compounds, etc.

We have previously studied the chemical compositions of *E. armena* Prokh. and *E. glareosa* Pall. ex Bieb., plants of the Georgian flora. We isolated and characterized flavonoids [4] in addition to the new hydrolyzed tannins glareins A, B, and C [5].

In continuation of the study of the chemical composition of *E. armena*, we isolated total phenolic compounds, which contained stilbenes, from the plant roots.

Roots of *E. armena* were collected in various regions of eastern Georgia. Raw material (500 g of air-dried roots) was extracted three times by refluxing in MeOH (80%) for 1 h. Solvent was removed. The remaining aqueous phase was treated with hexane to remove lipophilic substances and then extracted with EtOAc. The EtOAc fraction was chromatographed over a column of Sephadex LH-20 with gradient elution by H_2O:MeOH with an increasing alcohol concentration to produce six fractions. Fractions 5 and 6 contained stilbenes and were combined and rechromatographed over an analogous column with elution by EtOH to isolate three pure compounds. Compound **1** (0.089 g, 0.018% calcd for raw material weight), **2** (0.076 g, 0.015%), and **3** (0.061 g, 0.012%).



1 - 3

1: $R_1 = R_2 = H$; **2:** $R_1 = –COC_6H_2(OH)_3$, $R_2 = H$
3: $R_1 = H$, $R_2 = –COC_6H_2(OH)_3$

Compound **1**, yellowish powder, $[\alpha]_D^{20}$ +75° (*c* 0.69, Me_2CO). IR spectrum (KBr, ν_{max}, cm^{-1}): 3420 (OH), 1615 (benzene ring). PMR spectrum (δ, ppm, J/Hz): 7.76 and 6.98 (1H each, d, J = 15.8, *trans*-olefinic protons), 7.45 and 6.82 (2H each, d, J = 8.8, H-2′,6′ and H-3′,5′, respectively), 6.68 and 6.31 (1H each, d, J = 2.9, H-6 and H-4, respectively), 4.57 (1H, d, J = 7.8, glucose H-1″), 3.84-3.42 (6H, br.m, glucose protons). From this and ^{13}C NMR data (Table 1), **1** was identified as 2-*O*-β-D-glucopyranosyl-2,3,5,4′-tetrahydroxystilbene [6].

Compound **2**, light brown crystals, mp 184–185°C, $[\alpha]_D^{20}$ –30.5° (*c* 0.25, Me_2CO). IR spectrum (KBr, ν_{max}, cm^{-1}): 3300 (OH), 1710 (ester carbonyl). PMR spectrum (δ, ppm, J/Hz): 7.24 (2H, s, gallic acid protons), 7.19 and 6.66 (2H each, d, J = 8.8, H-2′,6′ and H-3′,5′, respectively), 7.12 and 6.86 (1H, d, J = 16.6, *trans*-olefinic protons), 6.60 and 6.32 (1H each, d, J = 3, H-6 and H-4, respectively), 5.32 (1H, t, J = 8.9, H-2″), 5.02 (1H, d, J = 8.9, glucose H-1″), 4.0–3.4 (5H, br.m, glucose protons). Compound **2** was identified as 2-*O*-[β-D-glucopyranosyl-(2″-*O*-galloyl)]-2,3,5,4′-tetrahydroxystilbene [6].

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TABLE 1. ^{13}C NMR Spectrum of Stilbene Glycosides **1**–**3** (Me_2CO-d_6, δ, ppm, 0 = TMS)

C atom	**1**	**2**	**3**
C-1	121.3	118.8	120.8
C-2	137.3	134.9	136.8
C-3	151.5	151.3	151.0
C-4	103.2	103.2	103.2
C-5	155.3	155.0	155.2
C-6	107.3	103.4	107.0
C-1′	129.2	134.5	129.5
C-2′,6′	128.6	128.5	128.6
C-3′,5′	116.0	116.2	116.0
C-4′	157.6	157.5	157.5
C-α,β	130.0, 132.9	129.0, 132.3	129.7, 132.9
	D-Glucose		
C-1″	102.0	102.8	102.2
C-2″	74.9	75.1	73.1
C-3″	77.5	75.1	78.5
C-4″	70.6	70.3	68.4
C-5″	77.5	77.4	77.3
C-6″	62.1	61.3	61.3
	Gallic acid		
C-1	–	121.1	121.1
C-2,6	–	110.1	109.9
C-3,5	–	145.7	145.5
C-4	–	138.9	138.7
-COO-	–	166.7	167.0

Compound **3**, light brown amorphous powder, $[\alpha]_D^{20}$ +12.0° (*c* 0.15, Me_2CO). IR spectrum (KBr, ν_{max}, cm^{-1}): 3350 (OH), 1700 (ester carbonyl), 1610 (benzene ring). PMR spectrum (δ, ppm, J/Hz): 7.25 and 6.94 (1H each, d, J = 15.8, *trans*-olefinic protons), 7.46 and 6.82 (2H each, d, J = 8.8, H-2′,6′ and H-3′,5′, respectively), 7.18 (2H, s, gallic acid protons), 6.70 and 6.32 (1H each, d, J = 3, H-6 and H-4, respectively), 5.28 (1H, t, J = 8.9, H-3″), 4.76 (1H, d, J = 8.8, glucose H-1″), 4.1–3.38 (5H, m, glucose protons). Compound **3** was identified as 2-*O*-[β-D-glucopyranosyl-(3″-*O*-galloyl)]-2,3,5,4′-tetrahydroxystilbene [6].

All studied stilbene glycosides were isolated and described for the first time from plants of the genus *Euphorbia*.

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