CYCLOARTANE GLYCOSIDES FROM *Euphorbia glareosa*

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We have previously reported the isolation from various species of *Euphorbia* growing in Georgia of flavonoids [1] and polyphenols [2]. We also found that all studied species contained in addition to the aforementioned classes of compounds triterpene glycosides of the cycloartane series. Herein we communicate results from a study of the structure of cycloartane glycosides isolated from *E. glareosa* (Euphorbiaceae).

Triterpene glycosides were obtained by exhaustive extraction (2 × 5 L) of ground air-dried roots (0.8 kg) at room temperature. The MeOH extract was evaporated and worked up by the literature method [3] to afford triterpenoids (20.5 g total) that were separated over a column of silica gel (L 40/100, Czech Rep.) using $CHCl_3$:CH_3OH (1, 15:1), $CHCl_3$:CH_3OH:H_2O (2, 70:23:4), C_6H_6:EtOAc (3, 2:1 and 1:1), and $CHCl_3$:C_6H_{14}:EtOAc (4, 1:1:1) [3]. We isolated eight compounds designated in order of increasing polarity as **1**–**8**. Compounds **1** and **2** were the genins cyclosiversigenin and asgenin; the others, their glycosides.

Compound **1**, cyclosiversigenin, $C_{30}H_{50}O_5$ (cycloastragenol, astramembrangenin [4]), yield 0.036% (here and henceforth of the weight of air-dried raw material), mp 238–240°C, $[\alpha]_D^{20}$ +50.4° (*c* 2.0, MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3500–3350 (OH), 3040, 1760, 1750, 1260–1250. PMR spectrum (Py-d_5, δ, ppm, J/Hz, 0 = HMDS): 4.90 (1H, q, J = 7.0, H-16), 3.78 (1H, br.q, H-24), 3.57 (2H, m, H-3, H-6), 0.51 (d, J = 4.0) and 0.23 (br.s, 2H-19); CH_3 groups 1.76, 1.46, 1.35, 1.25, 1.21, 1.18, 0.92 [3].

Compound **2**, cycloasgenin, $C_{30}H_{48}O_6$, yield 0.011%, mp 234–235°C, $[\alpha]_D^{20}$ +130.4° (*c* 0.8, MeHO). IR spectrum (KBr, ν_{max}, cm^{-1}): 3450–3350 (OH), 3060 (cyclopropane CH_2), 1706–1695 (C=O). PMR spectrum (Py-d_5, δ, ppm, J/Hz, 0 = HMDS): 4.92 (1H, q, J = 7.3, H-16), 4.20 (1H, dd, J = 9.8, 2.5, H-11), 3.72 (1H, m, H-6), 1.64 (d, J = 4.0) and 0.46 (br.s, 2H-19), 3.75 (1H, dd, J = 8.8, 5.6, H-24), CH_3 groups 1.70, 1.44, 1.41, 1.39. 1.21, 1.16, 0.84 [3].

A study of the acid hydrolysis products of the glycosides [5] showed that they all contained cyclosiversigenin as the genin. The structures of the carbohydrate parts of the glycosides were established using chemical transformations (Hakomori methylation [6] with subsequent methanolysis and GC of the sugars) and IR and PMR spectral data.

Compound **3**, cyclosiversigenin 3,6-*O*-*β*-D-dixylopyranoside, $C_{40}H_{66}O_{13}$, 0.008%, mp 218–221°C (MeOH), $[\alpha]_D^{20}$ +29.0° (*c* 0.71, MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3200-3600 (OH), 3040–3060 (cyclopropane CH_2). PMR spectrum (Py-d_5, δ, ppm, J/Hz): 4.56 and 4.42 (d, J = 7.2, H′ and H″), 1.70, 1.44, 1.25, 0.95 (eath 3H, s, CH_3), 1.16 (9H, s, $CH_3 \times 3$), 0.46 (1H, br.s, H_a-19) [7, 8].

Compound **4**, cyclosiversigenin 3-*O*-[*β*-D-xylopyranoside-(2′-*O*-acetyl)]-6-*O*-*β*-D-xylopyranoside, $C_{42}H_{68}O_{14}$, 0.03%, mp 253–254°C (MeOH), $[\alpha]_D^{20}$ +31° (*c* 0.90, MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3360–3500 (OH), 1750, 1260 (ester). PMR spectrum (Py-d_5, δ, ppm, J/Hz): 5.32 (1H, br.t, H-2′), 4.68 (1H, d, J = 6.2) and 4.55 (1H, d, J = 7.5); anomeric protons of two xyloses: 1.90 (3H, s, CH_3CO), 1.52, 1.41, 1.26, 1.18, 1.15, 1.07, 0.95, (each 3H, s, CH_3), 0.45 (1H, d, J = 4.0, H_a-19) [8, 9].

Compound **5**, cyclosiversigenin 3-*O*-*β*-D-xylopyranoside-6-*O*-*β*-D-glucopyranoside, $C_{41}H_{68}O_{14}$, 0.009%, mp 247–249°C (MeOH), $[\alpha]_D^{20}$ +37.0° (*c* 0.5, MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3300–3500 (OH), 3040 (cyclopropane CH_2). PMR spectrum (Py-d_5, δ, ppm, J/Hz): 4.78 (1H, d, J = 7.8, H-1″), 4.52 (1H, d, J = 7.4, H-1′), 1.82, 1.40, 1.26, 0.80, (each 3H, s, CH_3), 1.16 (9H, s, CH_3), 0.44 (1H, d, J = 3.9, H_a-19) [10].

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Compound **6**, cyclosiversigenin 3-*O*-[β-D-xylopyranoside-(2′-*O*-acetyl)]-6-*O*-β-D-glucopyranoside, $C_{43}H_{70}O_{15}$, 0.014%, mp 266–268°C, $[\alpha]_D^{20}$ +47.0° (*c* 0.85, MeOH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3300–3500 (OH), 1750, 1250 (ester). PMR spectrum (Py-d_5, δ, ppm, J/Hz): 2.04 (3H, s, CH_3CO), 1.82, 1.58, 1.40, 1.27, 0.95 (each 3H, s, CH_3), 1.32 (6H, s, CH_3), 0.54 (1H, d, J = 4.2, H_a-19), 0.22 (1H, d, J = 4.2, H_b-19) [8, 11].

All studied glycosides were described from *E. glareosa* for the first time. The study of the structures of the cycloasgenin glycosides is continuing.

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