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Triterpenoid saponins from the roots of two *Gypsophila* species

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ABSTRACT

Two triterpenoid saponins with two known ones have been isolated from the roots of *Gypsophila arrostii* var. *nebulosa*, and two new ones from the roots of *Gypsophila bicolor*. Their structures were established by extensive NMR and mass spectroscopic techniques as 3-*O*-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosylquillaic acid 28-*O*-β-D-xylopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-β-D-fucopyranosyl ester (**1**), 3-*O*-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosylgypsogenin 28-*O*-β-D-xylopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→4)]-β-D-fucopyranosyl ester (**2**), 3-*O*-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosylgypsogenin 28-*O*-β-D-xylopyranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-[(4-*O*-acetyl)-β-D-quinovopyranosyl-(1→4)]-β-D-fucopyranosyl ester (**3**), gypsogenic acid 28-*O*-β-D-glucopyranosyl-(1→3)-{6-*O*-[3-hydroxy-3-methylglutaryl]-β-D-glucopyranosyl-(1→6)}-β-D-galactopyranosyl ester (**4**). Three compounds were evaluated against one human colon cancer cell line SW480 and one rat cardiomyoblast cell line H9c2.

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Introduction

The genus *Gypsophila* (Caryophyllacae) represented by small perennial herbs comprises more than 150 species and some of these species have long been used as pharmaceutical and ornamental plants (Nie et al., 2010a). Some of them are a rich source of saponins having a pharmaceutical and commercial importance as medicines, detergents, adjuvants, and cosmetics (Jia et al., 2002). A great diversity of saponins has been reported in several species such as *Gypsophila pilulifera* (Arslan et al., 2012), *Gypsophila oldhamania* (Luo et al., 2008), *Gypsophila repens* (Elbandy et al., 2007) and *Gypsophila arrostii* (Frechet et al., 1991; Hostettmann and Marston, 1995). In our continuing study on saponins from *Gypsophila* genus (Elbandy et al., 2007), we have examined the saponin fraction of the roots of *G. arrostii* var. *nebulosa* (Boiss. & Heldr.) Bark. and *Gypsophila bicolor* (Freyn & Sint.) Grossh collected in the Southwestern of Turkey. In the present paper, we report the isolation and structure elucidation of two new triterpenoid saponins (**1**, **2**) together with two known ones from *G. arrostii* var. *nebulosa*, and two new triterpenoid saponins (**3**, **4**) from *G. bicolor*. The cytotoxicity of **1**, **3**, and 3-*O*-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosylgypsogenin 28-*O*-β-D-glucopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranosyl ester was evaluated against a human colon cancer cell line (SW 480) and a rat cardiomyoblast cell line (H9c2). Their structures were elucidated by spectroscopic methods including 600 MHz 1D and 2D NMR experiments (^{1}H, ^{13}C, COSY, TOCSY, NOESY, HSQC, HMBC) in combination with HR-ESI-MS and by comparaison of their physical and spectral data with literature values.

Results and discussion

The *n*-BuOH fractions obtained from the MeOH/H_2O (7:3) extract of the roots of *G. arrostii* var. *nebulosa* and *G. bicolor*, Ga and Gb respectively, were fractionated by vacuum-liquid chromatography (VLC) and purified by repeated medium-pressure liquid chromatography (MPLC) on normal- and RP18 silica gel yielding compounds **1**, **2** from Ga and **3**, **4** from Gb (Fig. 1). Their structures

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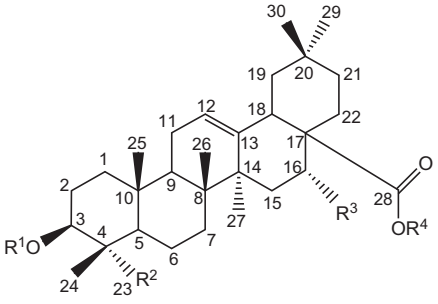

	R^1	R^2	R^3	R^4
1	S1	CHO	OH	S2
2	S1	CHO	H	S2
3	S1	CHO	H	S3
4	H	COOH	H	S4

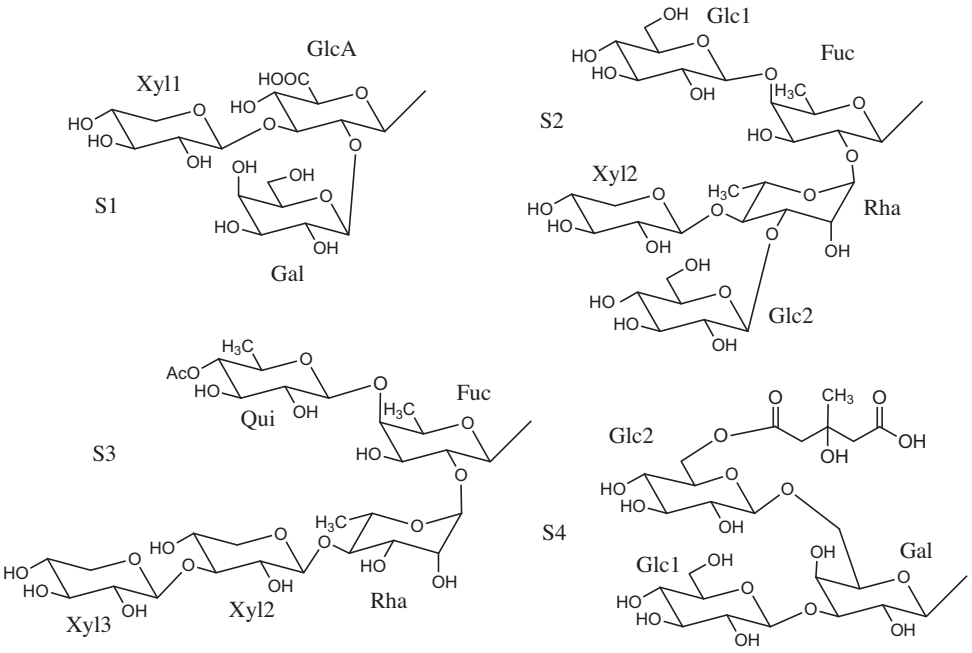

Fig. 1. Saponins from the roots of *G. arrostii* var. *nebulosa* and *G. bicolor*.

were established mainly by spectroscopic methods including 600 MHz NMR experiments and mass spectrometry. Futhermore two known saponins isolated from Ga were identified by comparaison of their spectral data with literature values as 3-*O*-β-D-galactopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→3)]-β-D-glucuronopyranosylgypsogenin 28-*O*-β-D-glucopyranosyl-(1→3)-[β-D-xylopyranosyl-(1→4)]-α-L-rhamnopyranosyl-(1→2)-β-D-fucopyranosyl ester (Nie et al., 2010b) and gypsogenin 28-*O*-[β-D-glucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)]-[β-D-glucopyranosyl-(1→6)]-β-D-galactopyranosyl ester (Elgamal et al., 1995).

Compounds **1**–**4** were isolated as white amorphous powders. The monosaccharides obtained by acid hydrolysis of each compound were identified by comparaison on TLC with authentic samples as glucuronic acid, xylose, galactose, glucose, fucose, rhamnose for **1**, **2**, glucuronic acid, xylose, galactose, fucose, quinovose, rhamnose for **3** and galactose, glucose for **4**. The absolute configurations were determined by GC analysis (Hara et al., 1987) to be D for all the sugars excepted for the rhamnose (L-configuration). The $^3J_{H\text{-}1,H\text{-}2}$ values in the ^{1}H NMR spectrum of the glucuronic acid, xylose, galactose, glucose, fucose, quinovose in their pyranose form (6.2–8.5 Hz) indicated their β anomeric configuration and the large $^1J_{H\text{-}1,C\text{-}1}$ value of the rhamnose (168 Hz) confirmed that the anomeric proton was equatorial (α-pyranoid form).

Compound **1** exhibited in the HR-ESI-MS a quasi-molecular ion peak at *m/z* 1727.7149 $[M+Na]^+$ (calcd. 1727.7152) compatible with the molecular formula $C_{76}H_{120}O_{42}$. Compound **1** showed in ESI-MS spectrum (positive-ion mode) an ion peak at *m/z* 1727 indicating a molecular weight of 1704. The ^{1}H and ^{13}C NMR spectra of **1** displayed resonances due to the triterpene part characteristic of quillaic acid aglycon (Table 1), with six angular methyl groups at δ_H 1.14 (s, H_3-24), 1.00 (s, H_3-25), 0.76 (s, H_3-26), 1.38 (s, H_3-27), 0.86 (s, H_3-29) and 0.95 (s, H_3-30) showing correlations in the HSQC spectrum with their corresponding carbon at δ_C 10.8 (C-24), 16.4 (C-25), 17.9 (C-26), 27.3 (C-27), 33.3 (C-29) and 24.9 (C-30). Futhermore, other characteristic signals were observed

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