

B101 Four new triterpene saponins from *Acanthophyllum glandulosum*G. Gaidi^a, T. Miyamoto^b, M. Ramezani^c and M.A. Lacaille-Dubois^a^a Laboratoire de Pharmacognosie, Unité MIB, J E 2244, Faculté de Pharmacie, Université de Bourgogne, 7, Bd Jeanne d'Arc, BP 87900, 21079 Dijon Cedex, France. ^b Graduate School of Pharmaceutical Sciences, Kyushu University, Fukuoka, Japan. ^c Department of Pharmacognosy and Biotechnology, School of Pharmacy, PO box 91775-1365, Iran.

Acanthophyllum glandulosum Bunge ex Boiss. (Caryophyllaceae) is one of the 6 species of the section *Pleiosperma* endemic to Iran (1). The plant has been used as an expectorant, emetic and detergent. No previous phytochemical investigation has been reported. Here, we describe the isolation and structure elucidation of four new triterpene saponins, glandulosides A-D (**1-4**). The methanolic extract of the roots was purified by column chromatography over Sephadex LH-20 and by successive medium pressure liquid chromatography (MPLC) on normal and reversed phase (C18) Silica gel column yielding four pure saponins. Their structures were elucidated mainly by 600 MHz NMR analysis including 1D and 2D NMR spectroscopy (COSY, TOCSY, NOESY, HSQC and HMBC) (**2**) as 23-O- β -D-galactopyranosyl-gypsogenic acid-28-O- β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-galactopyranosyl-(1 \rightarrow 6)- β -D-galactopyranoside (**1**), 3-O- β -D-galactopyranosyl-(1 \rightarrow 2)- β -D-xylopyranosyl-(1 \rightarrow 3)- β -D-glucuronopyranosyl-gypsogenin-28-O- β -D-xylopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-4-O-acetyl- β -D-fucopyranoside (**2**), 3-O- β -D-galactopyranosyl-(1 \rightarrow 2)- β -D-xylopyranosyl-(1 \rightarrow 3)- β -D-glucuronopyranosyl-gypsogenin-28-O- β -D-xylopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-[4-O-acetyl- β -D-quinovopyranosyl-(1 \rightarrow 4)]- β -D-fucopyranoside (**3**), 3-O- β -D-galactopyranosyl-(1 \rightarrow 2)- β -D-xylopyranosyl-(1 \rightarrow 3)- β -D-glucuronopyranosyl-gypsogenin-28-O- β -D-xylopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-(1 \rightarrow 2)-3,4-di-O-acetyl- β -D-fucopyranoside (**4**).

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B102 Acylated flavonoid glycosides from *Marrubium velutinum*A. Karioti^a, J. Heilmann^b, H. Skaltsa^a and O. Sticher^b^a Department of Pharmacognosy & Chemistry of Natural Products, School of Pharmacy, Panepistimiopolis, Zografou, 15771 Athens, Greece. ^b Department of Applied BioSciences, Institute of Pharmaceutical Sciences, Swiss Federal Institute of Technology (ETH) Zurich, Winterthurerstr. 190, 8057 Zurich, Switzerland.

The genus *Marrubium* L. comprises around 30 species, indigenous in Europe, the Mediterranean area and Asia (1). *Marrubium velutinum* Sibth & Sm. (Lamiaceae) is an endemic herb of central and southern Greece. The air-dried powdered aerial parts of the plant were extracted with petroleum ether, ether, ethyl acetate and methanol. The dried methanol extract was subjected to VLC over silica gel. Further fractionation with repeated CC on silica gel and Sephadex LH-20 led to the isolation of one new acylated flavonoid glucoside, chrysoeriol 7-O-(3'',6''-O-E-di-p-coumaroyl)- β -D-glucopyranoside, together with ten known flavonoids: apigenin 7-O-(3'',6''-O-E-di-p-coumaroyl)- β -D-glucopyranoside, apigenin 7-O-(3''-O-E-p-coumaroyl)- β -D-glucopyranoside, isorhamnetin 3-O-(6''-O-E-p-coumaroyl)- β -D-glucopyranoside, isorhamnetin 7-O-(6''-O-E-p-coumaroyl)- β -D-glucopyranoside, isorhamnetin 3-O- β -D-glucopyranoside, isorhamnetin 3-O- β -D-rutinoside, quercetin 3-O-(6''-acetyl)- β -D-glucopyranoside, isoquercitrin, kaempferol-3-O- β -D-rutinoside and chrysoeriol. The structures of the isolated compounds were established by means of UV, 1D and 2D NMR spectroscopy (¹H, ¹³C/DEPT, COSY, HMQC, HMBC, ROESY), as well as mass spectrometry (HR-MALDI). Earlier flavonoid surveys of *Marrubium* sp. (2-7), revealed a nearly complete dominance of flavones and the presence of only one flavonol (kaempferol) isolated from *M. peregrinum* (7). Therefore the presence of flavonol glycosides at *M. velutinum* appears as a characteristic feature of this plant.

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