

Terpenoid glycosides from the root's barks of *Eriocoelum microspermum* Radlk. ex Engl.

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ARTICLE INFO

Article history:

Received 19 December 2017

Received in revised form

19 March 2018

Accepted 22 April 2018

Keywords:

Eriocoelum microspermum

Sapindaceae

Triterpene saponins

2D NMR

SM

ABSTRACT

Eight undescribed triterpenoid saponins together with a known one, and two undescribed sesquiterpene glycosides were isolated from root's barks of *Eriocoelum microspermum*. Their structures were elucidated by spectroscopic methods including 1D and 2D experiments in combination with mass spectrometry as 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin, 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 3)-[β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin, 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 3)-[β -D-xylopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin, 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin 28-O- β -D-glucopyranosyl ester, 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)- β -D-xylopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranosylhederagenin, 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranosylhederagenin, 3-O- β -D-xylopyranosyl-(1 \rightarrow 4)- α -L-arabinopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranosylhederagenin, 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranosyl-(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin, 1-O- β -D-xylopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-(1 \rightarrow 6)]-[β -D-xylopyranosyl-(1 \rightarrow 3)]-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranosyl-(2E,6E)-farnes-1-ol, 1-O- β -D-glucopyranosyl-(1 \rightarrow 3)-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranosyl-(1 \rightarrow 4)- α -L-rhamnopyranosyl-(1 \rightarrow 6)]-[β -D-xylopyranosyl-(1 \rightarrow 3)]-[α -L-rhamnopyranosyl-(1 \rightarrow 2)]- β -D-glucopyranosyl-(2E,6E)-farnes-1-ol. These results represent a contribution to the chemotaxonomy of the genus *Eriocoelum* highlighting farnesol glycosides as chemotaxonomic markers of the subfamily of Sapindoideae in the family of Sapindaceae.

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1. Introduction

The Sapindaceae family includes more than 2000 species distributed in three subfamilies as Sapindoideae, Dodonaeoideae and Aceroideae (APG III, 2009), whereas a previous classification proposed by Delaude in 1993, reported the division of Sapindaceae

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in two subfamilies Sapindoideae, Dodonaeoideae, thirteen tribes and about 137 genera. These plants are known to contain triterpenoid saponins (Delaude, 1993). *Eriocoelum microspermum* Radlk. ex Engl. (Sapindoideae subfamily) is a medium size tree (30 m) and occurs from Cameroon, Congo and Angola. It is found in humid forest, up to 1400 m altitude. In African traditional medicine, barks were used to treat cough, enteritis and venereal diseases. Previous chemical studies in the Sapindoideae subfamily led to the isolation and characterization of triterpene saponins having hederagenin or oleanolic acid as aglycon with a ⁻³Rha-²Ara-³Agly oligosaccharidic sequence often encountered (Delaude, 1993), and

farnesyl glycosides (Voutquenne-Nazabadioko, 2010). In the present paper, we report the isolation and structure elucidation of eight undescribed triterpene saponins together with a known one and two undescribed sesquiterpene glycosides. Their structures were elucidated by spectroscopic methods including 600 MHz 1D and 2D experiments (^1H , ^{13}C , HSQC, HMBC, COSY, TOCSY, ROESY) in combination with HRESIMS and by comparison of their physical and spectral data with literature values.

2. Results and discussion

The saponin fraction obtained from the aqueous ethanolic extract of the root's barks of *E. microspermum* was fractionated by vacuum-liquid chromatography (VLC) or repeated medium-pressure liquid chromatography (MPLC) on normal- and RP18 silica gel and semi preparative HPLC using RP18 silica gel yielding ten undescribed compounds **1–10** (Fig. 1) and a known one. Their structures were elucidated by spectroscopic methods including 600 MHz 1D and 2D NMR experiments and mass spectrometry. Furthermore, a known saponin was isolated and identified by comparison of its spectral data with literature values as 3-O- α -L-arabinopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-

arabinopyranosylhederagenin which often occurs in the *Sapindaceae* family such as *Smelophyllum capense* (Lavaud et al., 1995), *Lecaniodiscus cupanioides* (Adesegun et al., 2008) or *Lepisanthes rubiginosa* (Adesanya et al., 1999) as example and in other families such as Cucurbitaceae (Kasai et al., 1986a), Araliaceae (Sawada et al., 1993) or Acanthaceae (Rattan et al., 2017).

Compounds **1–10** were isolated as white amorphous powders. The monosaccharides obtained by acid hydrolysis of each compound were identified by comparison on TLC with authentic samples as arabinose and rhamnose for **1**, arabinose, rhamnose and glucose for **2**, **4** and **8**, arabinose, rhamnose and xylose for **3**, **5** and **6** and glucose, xylose and rhamnose for **9** and **10**, and arabinose, rhamnose, xylose and glucose for **7**. The absolute configurations were determined by GC analysis (Hara et al., 1987) to be D- for all the sugars excepted for the rhamnose and arabinose which were found to be in L-configuration (see experimental). The $^3J_{\text{H-1, H-2}}$ coupling constants (7.6–8.0 Hz) in the ^1H NMR spectrum for the glucose and xylose in their pyranose form indicated their β anomeric orientation and the large $^1J_{\text{H-1, C-1}}$ value of the rhamnose (168 Hz) confirmed that the anomeric proton was equatorial in its α -pyranoid form.

Compound **1** exhibited in the HRESIMS a quasi-molecular ion

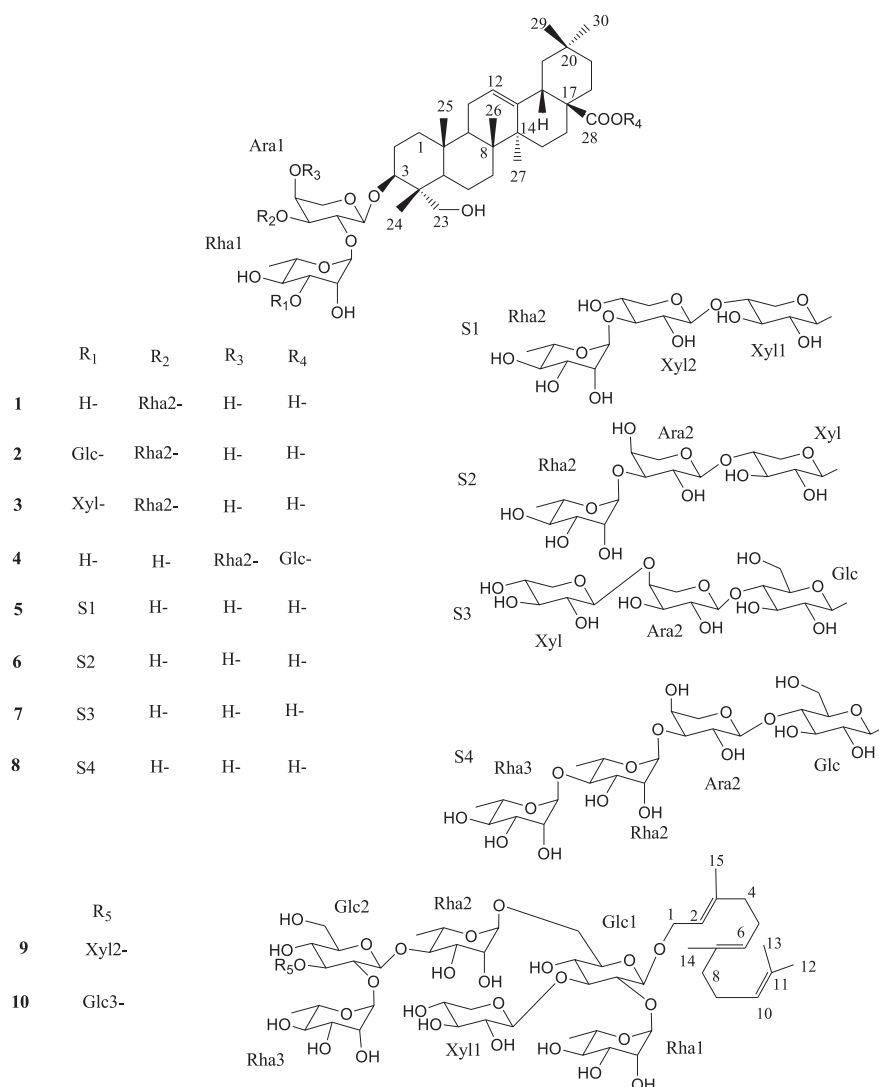


Fig. 1. Structure of compounds **1–10**.

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