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Phytotoxic steroidal saponins from *Agave offoyana* leaves

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ABSTRACT

A bioassay-guided fractionation of *Agave offoyana* leaves led to the isolation of five steroidal saponins (**1**–**5**) along with six known saponins (**6**–**11**). The compounds were identified as (25*R*)-spirost-5-en-2α,3β-diol-12-one 3-*O*-{α-L-rhamnopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-galactopyranoside} (**1**), (25*R*)-spirost-5-en-3β-ol-12-one 3-*O*-{α-L-rhamnopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-galactopyranoside} (**2**), (25*R*)-spirost-5-en-3β-ol-12-one 3-*O*-{β-D-xylopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-galactopyranoside} (**3**), (25*R*)-26-*O*-β-D-glucopyranosylfurost-5-en-3β,22α,26-triol-12-one 3-*O*-{α-L-rhamnopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-galactopyranoside} (**4**) and (25*R*)-26-*O*-β-D-glucopyranosylfurost-5-en-3β,22α,26-triol-12-one 3-*O*-{β-D-xylopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-galactopyranoside} (**5**) by comprehensive spectroscopic analysis, including one- and two-dimensional NMR techniques, mass spectrometry and chemical methods. The phytotoxicity of the isolated compounds on the standard target species *Lactuca sativa* was evaluated.
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1. Introduction

As part of our ongoing search for phytotoxic natural products, the results of further studies into *Agave offoyana* (Agavaceae) are presented here. The bioassay-guided isolation of phytotoxins from *A. offoyana* flowers was reported in our previous article, in which eleven steroidal saponins, including five new examples (Magueyosides A–E), were described (Pérez et al., 2013). The phytotoxicity results for the isolated compounds against lettuce (*Lactuca sativa* L.) were promising.

Despite the positive results obtained in the aforementioned studies and the fact that the saponins content in the flowers was 3.1% of dry weight, the availability of flowers from *A. offoyana* as a raw material for phytotoxins is limited. In the genus *Agave* the flowering stage takes place after several years of growth (6–8 years). The flowering stage happens only once in the lifetime of the plants and they subsequently die (Bousios et al., 2007). The aim of the current investigation was to isolate the phytotoxic constituents from *A. offoyana* leaves (1.9% of dry weight) in a similar bioassay-guided procedure and to carry out a complete structural characterization of the isolated compounds.

2. Results and discussion

2.1. Characterization of compounds

Dried leaves of *A. offoyana* were extracted exhaustively with EtOH/H_2O (7:3). The extract was partitioned in *n*-BuOH/water and the organic phase was subjected to a bioassay-guided fractionation by VLC on RP-18 to give seven fractions. Eleven steroidal saponins **1**–**11** (Fig. 1) were obtained after multiple separation procedures on the active fractions (see Section 2.2). Six of these compounds were previously reported as Agabrittonoside E (**6**) (Macías et al., 2010), Magueyosides A (**7**) and B (**8**) (Pérez et al., 2013), Agabrittonosides D (**9**) and A (**10**) (Macías et al., 2007) and Cantalasaponin-1 (**11**) (Sati and Pant, 1985). The structures

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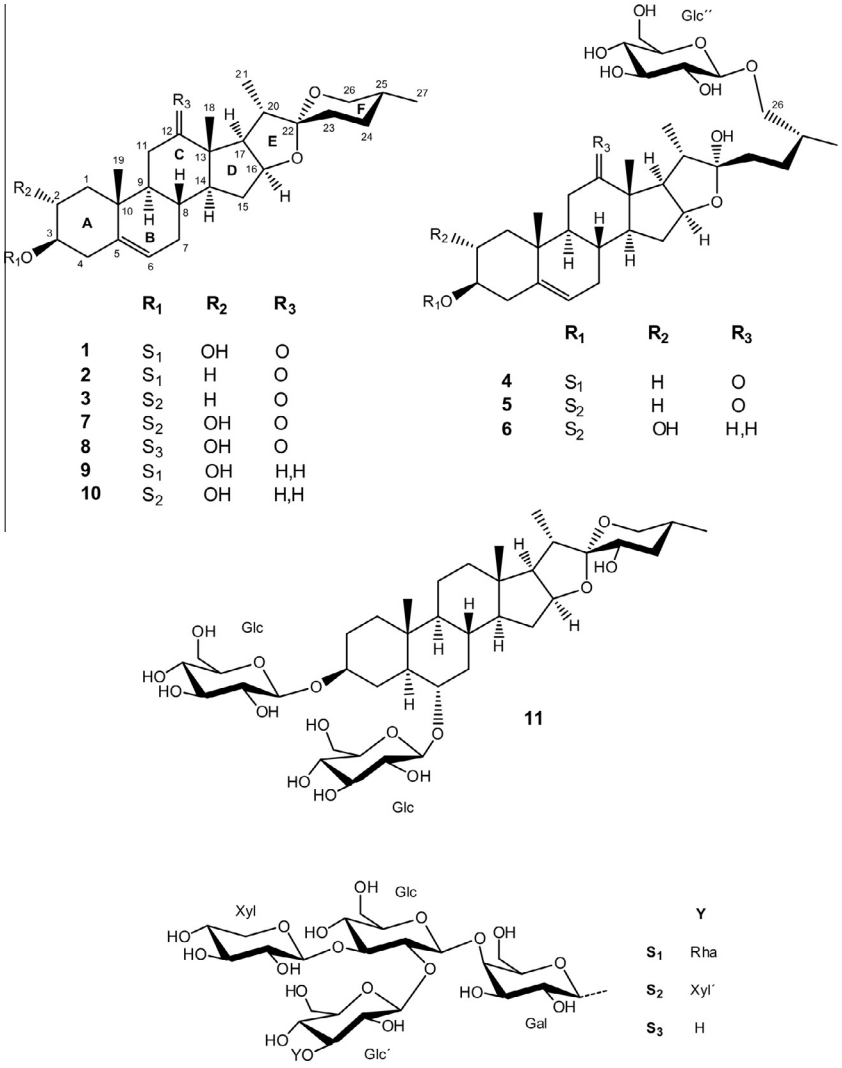

Fig. 1. Chemical structures of saponins **1**–**11**, isolated from *A. offoyana* leaves.

of the compounds were elucidated on the basis of spectroscopic data obtained by ^{1}H, ^{13}C, 2D (HSQC, HMBC, DQF-COSY, TOCSY, ROESY, HSQC-TOCSY), 1D-ROESY (250 ms) and 1D-TOCSY (30, 60, 120 ms) NMR experiments, HRESIMS, ESI-MS/MS and acid hydrolysis. Compounds **6** and **9** were previously characterized as a mixture from *Agave brittoniana* leaves. In the work described here these compounds were isolated in pure form and their HRESI-TOFMS spectra, absolute configuration of sugars and optical rotations were determined.

Compound **1** was obtained as a white amorphous solid and its molecular formula was assigned as $C_{56}H_{88}O_{28}$ based on data from HRESI-TOFMS (positive ion mode; m/z 1231.5345 $[M+Na]^+$, calcd. 1231.5360). ^{1}H and ^{13}C NMR assignments for the aglycone moiety of **1** (Table 1) were in good agreement with those of the aglycone moiety of **7** (Pérez et al., 2013), which suggested that Kammogenin (Marker et al., 1943) was the aglycone of **1**. However, significant differences between compounds **1** and **7** were observed concerning the sugar portion. The ^{1}H NMR spectrum of **1** showed five anomeric signals at δ 4.92, 5.14, 5.24, 5.51 and 6.12 (Table 2) and these showed correlations in the HSQC spectrum with carbons at δ 103.7, 105.3, 104.6, 104.6 and 103.1, respectively. This result indicated a glycosidic chain of five sugar units. Individual sugar units were identified by a combination of ^{1}H–^{1}H COSY, 1D-TOCSY and 1D-ROESY experiments. The latter two spectra were acquired from the selective excitation of each anomeric proton. In this way, signals at δ 5.24 and δ 5.51 revealed typical spin systems of β-glucopyranosyl units (Glc and Glc′) and the signal at δ 5.14 was assigned to a β-xylopyranosyl unit (Xyl). Likewise, a typical spin system for a β-galactopyranosyl unit was detected for the anomeric signal at δ 4.92, which was confirmed by correlations with H-5$_{Gal}$ (δ 4.02, dd, J = 7.7, 6.4 Hz) and H-3$_{Gal}$ (δ 4.14, m) in the 1D ROESY experiment. The 1D TOCSY (120 ms) experiment on the anomeric signal at δ 6.12 showed that magnetization was not properly transferred beyond H-2$_{Rha}$ (δ 4.68, dd, J = 1.7, 3.5 Hz). This finding, together with the presence of a methyl doublet at δ 1.64 (J = 6.2 Hz), is characteristic of a rhamnopyranosyl unit. A further selective TOCSY experiment on this methyl doublet (H-6$_{Rha}$) allowed a sequential assignment of the signals from H-6$_{Rha}$ to H-2$_{Rha}$ and the presence of a rhamnopyranosyl unit was confirmed. The correlations observed in the 1D ROESY experiment between H-1$_{Rha}$ and H-2$_{Rha}$, and the absence of a cross peak with H-3$_{Rha}$ and H-5$_{Rha}$ suggested the α-anomer. Finally, the ^{13}C signal assignments for each sugar unit were made through an exhaustive analysis of the correlations in HSQC and HSQC-TOCSY experiments.

The sequence of sugars chain and the connection with the aglycone were established by means of interglycosidic HMBC/ROESY correlations, which were observed between H-1$_{Rha}$ (δ 6.12) and C-3$_{Glc'}$ (δ 83.9)/H-3$_{Glc'}$ (δ 4.23), H-1$_{Glc'}$ (δ 5.51) and C-2$_{Glc}$ (δ 81.1)/H-2$_{Glc}$ (δ 4.27), H-1$_{Xyl}$ (δ 5.14) and C-3$_{Glc}$ (δ 87.6)/H-3$_{Glc}$ (δ 4.07), H-1$_{Glc}$ (δ 5.24) and C-4$_{Gal}$ (δ 79.2)/H-4$_{Gal}$ (δ 4.60), H-1$_{Gal}$ (δ 4.92)

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