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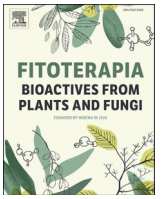
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Research Paper

Oleanane glycosides from a Lebanese edible plant: *Gundelia tournefortii* L. (Asteraceae)

Samir Hobloss [a], Antoine Bruguière [a], David Pertuit [a], Simon Dessertaine [a], Marie-José Penouilh [b], Michel Picquet [b], Christine Belloir [a], Loïc Briand [a], Anne-Claire Mitaine-Offer [a,*]

[a] Centre des Sciences du Goût et de l'Alimentation, CNRS, INRAE, Institut Agro, Université Bourgogne Europe, 9E Bd Jeanne d'Arc, 21000 Dijon Cedex, France
[b] Institut de Chimie Moléculaire de l'Université Bourgogne Europe (UMR 6302), CNRS, Université Bourgogne Europe, 9 Av. Alain Savary, BP 47870, 21078 Dijon Cedex, France

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ABSTRACT

From the leaves and the roots of *Gundelia tournefortii* L. (Asteraceae), an edible plant collected in Lebanon, ten oleanane-type glycosides were extracted, purified by various chromatographic methods, and identified by spectroscopic analysis as eight previously undescribed saponins **1**–**5** and **7**–**9** and two known ones **6** and **10.** Their aglycons possess unusual, oxygenated skeletons in position 29 or 30. Their structures were assigned by spectroscopic analysis mainly 2D NMR (COSY, TOCSY, ROESY, HSQC, HMBC) and mass spectrometry. Some selected saponins were tested for their stimulating activity on the sweet taste receptor.

1. Introduction

As part of our research on edible plants rich in saponins, *Gundelia tournefortii* L. (Asteraceae) was selected for its subtle taste between artichoke and asparagus. In the Middle East, this plant is widely used for various foods: the young shoots are integrated into dishes based on meat, chickpeas or yogurt. Soups and salads are prepared with leaves and stems, while the inflorescences, young stems and leaves are used to prepare the traditional Palestinian dish "A'kub" [1]. In addition, the latex of this plant is used as a base for chewing gum [2]. *G. tournefortii* is also very important in traditional medicine with many uses of the different parts: fresh seeds as diuretic, dried seeds for skin disease [3], root latex to drain the spleen, to treat wounds and snake bites [4] etc… Moreover, a study has been conducted to prove the anti-diabetic effect of this plant. An extract from the aerial part exhibited a stimulatory effect on GLUT4 transporters, acting like insulin [5].

In a botanical point of view, the genus *Gundelia* belongs to the Cichorieae Lam. & DC. Taxon of the Asteraceae family. Its classification has been complex, leading to its designation as one of the rogue genera within the Asteraceae [6]. The species *G. tournefortii* is present in Lebanon, Egypt (northern part of Sinai), Israel, Palestine, Jordan, Syria, Cyprus, and extends to the most southern regions of Turkey, and probably also in Iraq and Iran. It usually blooms from February to June and thrives in varied habitats such as limestone or igneous rocky slopes, steppes, open oak, as weed along roads [7]. This robust perennial plant can reach 20 to 100 cm in height. Its aged stems turn into straw rolls when dry, and all parts of the plant (leaves, stems, roots) contain a milky latex.

The previous study performed in 1984 led to the isolation of seven saponins from the roots, but only two were identified as glycosides of oleanolic acid: 3-*O*-(2-[α-L-arabinopyranosyl-(1 → 3)-β-D-gentiotriosyl-(1 → 6)-β-D-glucopyranosyl]-β-D-xylopyranoside) oleanolic acid, and 3-*O*-(2-[α-L-arabinopyranosyl-(1 → 3)-β-D-gentiobiosyl-(1 → 6)-β-D-glucopyranosyl]-β-D-xylopyranoside) oleanolic acid. The latter presents a classic molluscicide activity [8].

So, the aim of this investigation is to extract, isolate and identify the oleanane-type glycosides from the leaves and the roots of *G. tournefortii* L. (Asteraceae) from Lebanon. The crude extract of the leaves and five purified saponins were tested on the sweet-taste receptor TAS1R2/TAS1R3.

2. Experimental section

2.1. General experimental procedures

Optical rotations were recorded on an AA-OR automatic polarimeter.

* Corresponding author.
E-mail address: anne-claire.offer@u-bourgogne.fr (A.-C. Mitaine-Offer).

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The 1D and 2D NMR experiments (^{1}H, COSY, TOCSY, ROESY, edited ^{1}H—^{13}C HSQC and ^{1}H—^{13}C HMBC) were performed on a Bruker Avance III HD 600 spectrometer equipped with an ATMA BBOF 5 mm Prodigy Cryoprobe with a z-axis gradient coil operating at 600 MHz (^{1}H). Spectra were acquired in 5 mm NMR tubes and all experiments were performed at 298 K and run without spinning to avoid convection. All the samples were prepared in methanol-d_4 (CD_3OD) with 0.1 % Trifluoroacetic acid (TFA). Chemical shifts on the δ scale (ppm) relative to tetramethylsilane were referenced internally with respect to the resonance of residual CH_3OH ($\delta_H = 3.31$ ppm and $\delta_C = 49.00$ ppm). Coupling constants (*J*) were measured in Hz. ESIMS (positive-ion mode) was performed using an Orbitrap Fusion instrument (ThermoScientific) with a resolution of 120,000 and a mass accuracy of 4 ppm for the identification of molecular formulas. The samples were prepared using a resuspension solvent composed of 1 mL methanol/water (70:30) with 0.1 % formic acid (FA). After dissolution, the sample was vortexed and then subjected to microfiltration using a 0.20 μm PTFE filter. Direct injection was carried out at a flow rate of 7 μL/min using a High-Flow needle, and the source and detector parameters were optimized according to the sample. A MARS 6 microwave apparatus (CEM) was used for the extraction. Isolations of the compounds were carried out using column chromatography (CC) with Sephadex LH-20 (550 mm × 20 mm, GE Healthcare Bio-Sciences AB). The vacuum liquid chromatography (VLC) was performed using RP-18 silica gel (75–200 μm, Silicycle). A Gilson M 305 pump (25 SC head pump, M 805 manometric module), a Büchi glass column (203 × 15 mm and 460 × 15 mm) and a Büchi glass precolumn (110 × 15 mm), with silica gel 60 (15–40 μm, Merck) and reverse phase silica RP 18 (75–200 μm, Silicycle), were used for medium pressure liquid chromatography (MPLC). Thin-layer chromatography (TLC, Silicycle) and high-performance thin-layer chromatography (HPTLC, Merck) were carried out on precoated silica gel plates 60 F_{254}, solvent system $CHCl_3$/MeOH/H_2O/CH_3COOH (60:32:7:1). The spray reagent used for saponin identification was vanillin reagent (1 % vanillin in EtOH/H_2SO_4, 50:1). The purification process as well as the profile of crude extracts, have been controlled with TLC. HPTLC and HPLC were used to indicate the purity of the final products. HPLC was performed on a 1260 Agilent instrument, equipped with a degasser, a quaternary pump, an autosampler, a UV detector at 210 nm. Eluent: (A) 0.01 % (*v/v*) aqueous trifluoroacetic acid and (B) acetonitrile, 1 mL/min.

2.2. Plant material

Leaves and roots of *Gundelia tournefortii* were collected in May 2021, from the botanical garden in Mchaa Mrajhine, Lebanon (34.4008771, 32.2088316), and identified by Pr Edy Tabet, Faculty of Agronomy, Lebanese University. A voucher specimen was kept in the herbarium at the laboratory of pharmacognosy, Université Bourgogne Europe, Dijon, under the number 20210519.

2.3. Extraction and isolation

For the leaves, 44 g were dried and powdered before being extracted, using EtOH/H_2O (75:35, 4 × 500 mL) as solvent. The mixture was heated at 50 °C for 30 min using a microwave apparatus. This led to 12 g of crude extract. The isolation started with a reverse phase vacuum liquid chromatography (RP 18, 75–200 μm) using H_2O, H_2O/EtOH (25:75), and EtOH. The fraction eluted with H_2O/EtOH (25:75, 2.67 g) was further separated by CC (Sephadex LH-20, MeOH), yielding four fractions A-D. The fraction B (781.6 mg), rich in saponins, was submitted to successive MPLC on normal phase (silica gel 60, 15–40 μm, $CHCl_3$/MeOH/H_2O 70:30:5 and 60:32:7) and reverse phase silica gel (silica RP 18, 75–200 μm, MeOH/H_2O, 30 % MeOH), yielding compounds **1** (10.4 mg), **3** (17.1 mg), **4** (2.3 mg), **5** (3.0 mg), and **6** (5.3 mg). The fraction C (379.6 mg) was submitted to successive MPLC on normal phase (silica gel 60, 15–40 μm, $CHCl_3$/MeOH/H_2O 70:30:5 and 60:32:7) and reverse phase silica gel (silica RP 18, 75–200 μm, MeOH/H_2O, 35 % MeOH), yielding compounds **2** (10.2 mg). To evaluate their purity, an HPLC (Eluent: (A) 0.01 % (v/v) aqueous trifluoroacetic acid and (B) acetonitrile, 1 mL/min) was performed with a gradient system of 10 % B to 50 % B in 40 min. Each pure compound was injected (10 μL) and analyzed, to give tr = 17.8, 24.7, 24.1, 25.6, 18.2, 31.9 min for **1**–**6**, respectively.

For the roots, 463 g were extracted using the same protocol to obtain 72 g of crude extract. Compounds **1**–**4** and **6,** already found in the leaves, were obtained by the same chromatographic steps, along with four new ones, compounds **7** (1.8 mg)**, 8** (11.9 mg)**, 9** (4.2 mg), and **10** (10.5 mg). For the HPLC (Eluent: (A) 0.01 % (v/v) aqueous trifluoroacetic acid and (B) acetonitrile, 1 mL/min), the gradient system was 30 % B to 80 % B in 30 min, to give tr = 7.4, 8.2, 10.2, 22.3 min for **7**–**10**, respectively.

2.4. Spectroscopic data of the new compounds *1–5, 7–9*

3-*O*-*α*-L-arabinopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-glucopyranosyl ester (**1**).

White amorphous powder; $[\alpha]_D^{20}$ − 54 (*c* 0.055 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 1 and 3); HRESIMS *m/z* 965.4702 $[M + Na]^+$ (calcd. for. $C_{47}H_{74}O_{19}Na$, 965.4722).

3-*O*-*α*-L-arabinopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid (**2**).

White amorphous powder; $[\alpha]_D^{20}$ + 14 (*c* 0.136 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 1 and 3); HRESIMS *m/z* 803.4179 $[M + Na]^+$ (calcd. for. $C_{41}H_{64}O_{14}Na$, 803.4194).

3-*O*-*α*-L-arabinopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl-3*β*-hydroxyolean-12-en-28,29-dioic acid (**3**).

White amorphous powder; $[\alpha]_D^{20}$ − 10 (*c* 0.200 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 1 and 3); HRESIMS *m/z* 817.3972 $[M + Na]^+$ (calcd. For. $C_{41}H_{62}O_{15}Na$, 817.3986).

3-*O*-*β*-D-glucopyranosyl-(1 → 4)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid (**4**).

White amorphous powder; $[\alpha]_D^{25}$ + 15 (*c* 0.090 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 1 and 3); HRESIMS *m/z* 833.4281 $[M + Na]^+$ (calcd. For. $C_{42}H_{66}O_{15}Na$, 833.4299).

3-*O*-*β*-D-glucopyranosyl-(1 → 4)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-glucopyranosyl ester (**5**).

White amorphous powder; $[\alpha]_D^{25}$ + 60 (*c* 0.030 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 2 and 4); HRESIMS *m/z* 995.4805 $[M + Na]^+$ (calcd. For. $C_{48}H_{76}O_{20}Na$, 995.4828).

3-*O*-*β*-D-glucopyranosyl-(1 → 4)-[*β*-D-glucopyranosyl-(1 → 2)]-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid (**7**).

White amorphous powder; $[\alpha]_D^{25}$ + 11 (*c* 0.087 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 2 and 4); HRESIMS *m/z* 995.4805 $[M + Na]^+$ (calcd. for. $C_{48}H_{76}O_{20}Na$, 995.4828).

3-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid (**8**).

White amorphous powder; $[\alpha]_D^{25}$ + 31 (*c* 0.064 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 2 and 4); HRESIMS *m/z* 833.4281 $[M + Na]^+$ (calcd. for. $C_{42}H_{66}O_{15}Na$, 833.4299).

3-*O*-*α*-L-arabinopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl-3*β*,30-dihydroxyolean-12-en-28-oic acid (**9**).

White amorphous powder; $[\alpha]_D^{20}$ + 18 (*c* 0.055 MeOH); ^{1}H NMR and ^{13}C NMR data (600.13 and 150.92 MHz, respectively) (see Tables 2 and 4); HRESIMS *m/z* 803.4179 $[M + Na]^+$ (calcd. for. $C_{41}H_{64}O_{14}Na$, 803.4194).

Table 1
^{1}H and ^{13}C NMR data of the aglycon moieties of compounds **1**–**4** in methanol-d_4 (δ in ppm, J in parentheses in Hz).[a]

	1		**2**		**3**		**4**	
N°	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	39.5	0.97 m, 1.58	38.5	1.02 m, 1.60	39.5	1.01, 1.59	39.5	0.97, 1.58
2	26.8	1.68, 1.96 m	26.8	1.60 m, 2.00	26.8	1.68, 2.00 m	26.7	1.67 m, 1.89
3	90.4	3.17	90.2	3.19 dd (11.7, 4.1)	90.2	3.20	90.5	3.18
4	40.2	–	38.7	–	38.8	–	39.7	–
5	56.8	0.76 d (11.5)	56.8	0.78 d (11.4)	56.8	0.77 d (11.4)	56.8	0.79 d (11.5)
6	19.1	1.37 m, 1.55	19.1	1.39 m, 1.56	19.1	1.40, 1.48 m	19.3	1.42 m, 1.57
7	33.7	1.31, 1.48	33.7	1.29, 1.52 m	33.8	1.30, 1.51	33.8	1.31, 1.52
8	40.7	–	38.7	–	39.9	–	40.2	–
9	48.8	1.57	47.8	1.60	48.8	1.59	48.9	1.58
10	37.9	–	35.7	–	37.0	–	37.1	–
11	24.2	1.87	24.2	1.89	24.2	1.88	24.2	1.86
12	123.6	5.26 br t (3.6)	123.5	5.26 br t (3.3)	123.8	5.28 brt (3.5)	122.6	5.22 br t (3.5)
13	144.5	–	143.6	–	144.8	–	145.7	–
14	42.3	–	41.6	–	42.8	–	42.9	–
15	28.5	1.09, 1.80	28.6	1.10, 1.80	28.6	1.09, 1.78	28.7	1.03, 1.86
16	24.9	1.72 m, 2.05 td (13.7, 3.6)	24.0	1.67, 2.01	24.0	1.60 m, 2.00 td (13.4, 4.1)	24.1	1.60 m, 1.92
17	48.2	–	47.9	–	48.0	–	48.2	–
18	41.6	2.88 dd (13.9, 4.4)	41.8	2.88 dd (14.1, 4.2)	41.9	2.88 dd (13.5, 4.5)	42.1	2.92 dd (14.3, 3.8)
19	41.4	1.10 m, 1.82 t (13.7)	41.2	1.08 m, 1.79	41.1	1.42 m, 2.15 t (13.4)	41.7	1.06 m, 1.77
20	36.4	–	35.3	–	36.4	–	36.4	–
21	29.1	1.17, 1.49	29.1	1.15 m, 1.48	29.7	1.48, 1.86	29.7	1.14 m, 1.46
22	32.9	1.65 m, 1.74 m	32.9	1.59, 1.76	32.7	1.60, 1.76	33.3	1.54, 1.78
23	28.1	1.05 s	28.0	1.06 s	28.0	1.06 s	28.2	1.06 s
24	17.6	0.83 s	17.7	0.84 s	17.6	0.84 s	17.8	0.86 s
25	15.9	0.95 s	15.2	0.95 s	15.5	0.94 s	15.9	0.94 s
26	16.4	0.82 s	16.4	0.82 s	16.4	0.82 s	16.9	0.85 s
27	26.1	1.17 s	26.2	1.17 s	26.1	1.17 s	26.3	1.16 s
28	177.5	–	181.6	–	181.9	–	181.5	–
29	74.1	3.19 br s	74.2	3.18 br s	183.6	–	74.5	3.18 br s
30	19.3	0.92 s	19.3	0.93 s	19.7	1.24 s	19.6	0.95 s

[a] Overlapped signals are reported without designated multiplicity.

Table 2
^{1}H and ^{13}C NMR data of the aglycon moieties of compounds **5**, **7**–**9** in methanol-d_4 (δ in ppm, J in parentheses in Hz).[a]

	5		**7**		**8**		**9**	
N°	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	
1	39.6	0.97 m, 1.58	39.5	0.97 m, 1.61	39.6	0.99 m, 1.62	39.7	0.97, 1.59
2	26.7	1.67, 1.90	26.8	1.71 m, 1.86	27.0	1.71 m, 1.86	26.8	1.69, 1.87
3	90.5	3.16	91.5	3.21	91.6	3.19 dd	90.8	3.17 dd (11.9, 4.6)
4	39.9	–	40.0	–	40.0	–	40.1	–
5	56.8	0.77 d (11.6)	56.7	0.79 d (11.8)	56.7	0.79 d (11.8)	56.8	0.77 d (11.8)
6	19.3	1.40, 1.55	19.1	1.38, 1.53 m	19.1	1.40 m, 1.56	19.0	1.38, 1.56 m
7	33.7	1.31, 1.48	33.7	1.31, 1.51	33.8	1.28, 1.50	33.7	1.30 m, 1.50
8	40.6	–	40.2	–	40.2	–	40.4	–
9	48.8	1.57	48.8	1.59	48.8	1.60	48.8	1.58
10	37.7	–	37.7	–	37.6	–	37.8	–
11	24.2	1.87	24.3	1.90	24.3	1.91	24.4	1.89
12	123.6	5.26 br t (3.5)	123.5	5.25 br t (3.4)	123.5	5.25 br t (3.1)	123.7	5.27 br t (3.1)
13	144.3	–	144.9	–	144.8	–	144.7	–
14	42.2	–	42.6	–	42.6	–	42.7	–
15	28.7	1.10, 1.80	28.7	1.11, 1.78	28.6	1.17, 1.78	28.7	1.10, 1.77
16	23.8	1.73 m, 1.92	23.8	1.60, 2.01 td (14.0, 3.9)	23.8	1.62, 2.02 td (14.0, 3.5)	24.2	1.62, 2.05 td (13.5, 3.8)
17	48.0	–	47.7	–	47.5	–	47.2	–
18	41.6	2.88 dd (14.0, 4.3)	41.6	2.88 dd (14.0, 4.2)	41.8	2.88 dd (14.1, 3.9)	41.9	2.80 dd (14.0, 4.0)
19	41.2	1.10 m, 1.82 t (13.4)	41.0	1.08, 1.79	41.2	1.08 m, 1.80	42.3	1.33, 1.60
20	36.4	–	36.6	–	36.6	–	35.9	–
21	28.9	1.17, 1.49	29.1	1.15, 1.48	29.0	1.17, 1.48	29.5	1.27, 1.48
22	32.1	1.65, 1.74	32.7	1.58, 1.77	32.9	1.61, 1.77	33.2	1.53, 1.70
23	28.3	1.05 s	28.2	1.08 s	28.3	1.08 s	28.1	1.06 s
24	17.4	0.84 s	16.6	0.85 s	16.7	0.86 s	16.4	0.84 s
25	15.8	0.95 s	15.6	0.95 s	15.5	0.95 s	15.8	0.94 s
26	17.5	0.80 s	17.4	0.82 s	17.3	0.82 s	17.5	0.80 s
27	26.1	1.17 s	26.2	1.17 s	26.2	1.17 s	26.2	1.17 s
28	177.6	–	181.4	–	181.4	–	179.2	–
29	74.0	3.19 br s	74.1	3.19 br s	74.2	3.19 br s	28.0	0.89 s
30	19.3	0.92 s	19.1	0.93 s	19.1	0.93 s	66.2	3.42 d (11.2), 3.55

[a] Overlapped signals are reported without designated multiplicity.

Table 3
^{1}H and ^{13}C NMR data of the sugar moieties of compounds **1**–**4** in methanol-d_4 (δ in ppm, J in parentheses in Hz).[a]

	1		**2**		**3**		**4**	
N°	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
GlcA-1	105.1	4.46 d (7.5)	105.1	4.45 d (7.5)	105.1	4.45 d (7.6)	106.2	4.38 d (7.8)
2	83.4	3.44 dd (9.1, 7.5)	83.5	3.45 dd (9.1, 7.5)	83.4	3.44 dd (9.1, 7.6)	74.9	3.30 dd (9.7, 7.8)
3	77.5	3.57 t (9.1)	77.6	3.57 t (9.1)	77.6	3.57 t (9.1)	76.3	3.49 t (9.7)
4	73.4	3.50 t (9.1)	73.4	3.47 t (9.1)	73.3	3.47 t (9.1)	82.6	3.62 t (9.7)
5	76.3	3.57 d (9.1)	76.1	3.53 d (9.1)	76.1	3.53 d (9.1)	76.8	3.75 d (9.7)
6	176.7		176.4		176.3		176.7	
Ara-1	106.2	4.48 d (6.9)	106.3	4.47 d (6.9)	106.3	4.47 d (6.9)		
2	73.4	3.65 dd (8.8, 6.9)	73.5	3.65 dd (9.1, 6.9)	73.3	3.65 dd (8.8, 6.9)		
3	73.8	3.56 dd (8.8, 3.3)	73.8	3.56 dd (9.1, 4.5)	73.8	3.56 dd (8.8, 3.6)		
4	69.3	3.78 m	69.3	3.77 m	69.2	3.78 m		
5	67.0	3.49 dd (12.7, 1.7), 3.86 dd (12.3, 2.8)	67.0	3.49 dd (12.6, 1.8), 3.86 dd (12.6, 3.1)	67.0	3.50 dd (12.5, 1.8), 3.86 dd (12.5, 2.9)		
Glc-1	95.5	5.38 d (8.2)					104.2	4.40 d (7.8)
2	73.7	3.32 dd (9.1, 8.2)					74.8	3.23 dd (9.1; 7.8)
3	78.0	3.41 t (9.1)					77.5	3.35
4	70.8	3.35					70.9	3.30
5	78.4	3.35					77.9	3.30
6	62.1	3.68 dd (12.1, 4.5), 3.82 dd (12.1, 1.5)					62.2	3.65 dd (11.6, 4.5), 3.87 dd (11.6, 1.5)

[a] Overlapped signals are reported without designated multiplicity.

Table 4
^{1}H and ^{13}C NMR data of the sugar moieties of compounds **5**, **7**–**9** in methanol-d_4 (δ in ppm, J in parentheses in Hz).[a]

	5		**7**		**8**		**9**	
N°	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
GlcA-1	106.3	4.37 d (7.9)	105.0	4.56 d (7.7)	105.3	4.51 d (7.8)	105.2	4.51 d (7.8)
2	74.9	3.30 dd (9.1, 7.9)	79.5	3.72 dd (9.2, 7.7)	80.4	3.64 dd (9.0, 7.8)	83.2	3.47 dd (9.1; 7.8)
3	76.2	3.49 t (9.1)	76.2	3.78	77.6	3.59 t (9.0)	77.2	3.59 t (9.1)
4	83.0	3.61 t (9.1)	81.2	3.77	72.8	3.54 t (9.3)	72.9	3.54
5	76.8	3.72 d (9.1)	74.9	3.95 br d (9.0)	76.3	3.78 d (9.3)	76.1	3.74 d (9.4)
6	176.5		172.7		172.4		173.6	
Ara-1							106.3	4.48 d (7.1)
2							73.5	3.65 dd (8.3; 7.1)
3							73.7	3.57
4							69.4	3.80 m
5							67.1	3.50 dd (12.4, 1.2), 3.86 dd (12.4, 2.8)
GlcI-1	104.3	4.41 d (7.8)	104.0	4.73 d (7.8)	104.3	4.68 d (7.8)		
2	74.8	3.21	76.0	3.20	76.1	3.22		
3	77.5	3.36	77.4	3.35 t (9.0)	77.6	3.36 t (9.0)		
4	70.9	3.30	71.6	3.20	71.7	3.21		
5	77.9	3.30	78.0	3.24 m	78.1	3.25 m		
6	62.2	3.68 dd (12.0, 4.5), 3.87 dd (12.0, 1.7)	62.8	3.62 dd (12.0, 6.0), 3.82 dd (12.0, 1.9)	62.7	3.62 dd (11.8, 5.9), 3.83 dd (11.8, 1.9)		
GlcII-1	95.4	5.38 d (8.2)	103.9	4.42 d (7.7)				
2	73.6	3.32	74.5	3.21				
3	78.0	3.40 t (9.3)	77.4	3.35 t (9.0)				
4	70.8	3.35	71.6	3.20				
5	78.5	3.35	77.8	3.31 m				
6	62.1	3.65, 3.82 dd (11.7;1.5)	62.1	3.66 dd 11.7, 5.3), 3.88 dd (11.7, 1.9)				

[a] Overlapped signals are reported without designated multiplicity.

2.5. Acid hydrolysis and absolute configuration determination

An aliquot (150 mg) of a fraction rich saponins was hydrolyzed with 2 N aqueous CF_3COOH (25 mL) for 3 h at 95 °C. After extraction with CH_2Cl_2 (3 × 15 mL), the aqueous layer was evaporated to dryness with H_2O until neutral to give the sugar residue (35 mg). Glucuronic acid, arabinose, and glucose were identified by comparison with authentic samples by TLC using $CH_3COOEt/CH_3COOH/CH_3OH/H_2O$ (65:25:15:15). After purification of these sugars by prep-TLC in the same solvent, the optical rotation of each purified sugar was measured as follows [standard: D-glucuronic acid: $R_f = 0.24$, $[\alpha]_D^{25} + 15$ (c 0.2, H_2O), D-glucose: $R_f = 0.50$, $[\alpha]_D^{25} + 110$ (c 0.2, H_2O), L-arabinose: $R_f = 0.54$, $[\alpha]_D^{25} + 170$ (c 0.2, H_2O)] [9].

2.6. Biological assay

Activation of TAS1R2/TAS1R3 by sucralose, the crude extract of the leaves and compound **1**–**3, 5, 6**.

To assess the ability of compounds to activate the TAS1R2/TAS1R3 sweet taste receptor, we conducted calcium-mobilization assays [10]. Briefly, HEK293T-cells stably expressing the chimeric G protein Gα16gust44 were cultured on 96-well plates at 37 °C; 6.3 % CO_2, 100 %

humidity in DMEM supplemented with 10 % fetal bovine serum. After 24 h, the cells were transiently transfected with the pcDNA6-TAS1R2, pcDNA4-TAS1R3 vectors and pCMV-GCaMP6S (Addgene) plasmid coding protein calcium biosensor, or empty vectors as negative control, using Fugene HD (Promega) according to the manufacturer's protocol. Following another 24 h, the cells were washed with buffer C1 (130 mM NaCl, 5 mM KCl, 10 mM Hepes, 2 mM $CaCl_2$, 5 mM sodium pyruvate, pH 7.4) and placed in a fluorometric imaging plate reader (FlexStation 3, Molecular Devices) for calcium measurements after automatic stimulation by compounds. Chemical compounds, extracted and purified, were initially dissolved at 10 mM in DMSO and then diluted to various concentrations in buffer C1. Since purified compounds were available in limited quantities, the maximum concentration used for cell stimulation was 100 μM, preventing us from reaching the maximal amplitude of the dose-response curve. Data were collected from three independent experiments carried out in duplicate. For analysis, signals from wells receiving the same concentration were averaged, then normalized to background fluorescence, and the fluorescence measurements of corresponding mock-transfected cells were subtracted. EC_{50} values were calculated using four parameters logistic nonlinear model in Sigma Plot software (SigmaPlot version 15 (Grafiti LLC)).

3. Results and discussion

3.1. Structure elucidation of the isolated compounds

From the aqueous ethanolic extract of the leaves of *G. tournefortii*, compounds **1**–**6** were isolated, while compounds **1**–**4** and **6**–**10** were obtained from an aqueous ethanolic extract of the roots. Compounds **6** and **10** are already known, and identified as 3-*O*-β-D-glucopyranosyl-(1 → 4)-[β-D-glucopyranosyl-(1 → 2)]-β-D-glucuronopyranosyl-3β-hydroxyolean-12-en-28-oic acid (**6**) [11] and 3-*O*-β-D-glucuronopyranosyl-3β-hydroxyolean-12-en-28-oic acid (**10**) [12] by comparison of their NMR and mass data with literature (Fig. 1). For the previously undescribed molecules **1**–**5** and **7**–**9**, their complete structural analysis is detailed below.

For compounds **1**–**5** and **7**–**9**, the 2D NMR signals found in the osidic part of the spectra, mainly COSY, TOCSY, HSQC, HMBC, belong to only three different sugars. These monosaccharides were identified as glucuronic acid for **1**–**5** and **7**–**9**, glucose for **1**, **4**, **5**, **7**, **8**, and arabinose for **1**–**3** and **9**. Their absolute configurations were determined to be D for glucuronic acid (GlcA) and glucose (Glc), and L for arabinose (Ara) (see Experimental section). The $^3J_{H\text{-}1,H\text{-}2}$ values in the ^{1}H NMR spectrum of GlcA, Glc, and Ara in their pyranose form (6.9–8.2 Hz), indicated a β anomeric configuration for GlcA and Glc, and an α anomeric configuration for Ara (Fig. 1).

For the further NMR analysis, the aglycon of the saponins will be identified, and then the glycosidic linkage with the genin, and within the oligosaccharidic chains.

Compound **1** was obtained as an amorphous powder with the molecular formula of $C_{47}H_{74}O_{19}$, established by the HRESIMS (positive mode) quasi-molecular ion pic at *m/z* 965.4702 $[M + Na]^+$ (calcd. for $C_{47}H_{74}O_{19}Na$, 965.4722).

The ^{1}H NMR spectrum of the aglycon part displayed classical signals of a oleanene-type skeleton, as six angular methyl groups (3H, s, each) at δ_H 0.82 (H-26), 0.83 (H-24), 0.92 (H-−30), 0.95 (H-25), 1.05 (H-−23) and 1.17 (H-27), one olefinic proton at δ_H 5.26 (1H, br t, 3.6 Hz, H-12), with a secondary alcoholic function at δ_H 3.17 (1H,H-−3), and a primary alcoholic function at δ_H 3.19 ppm (2H, br s, H-29). The CH_2OH group was assigned to position C-29 α-equatorial according to the HMBC cross-peak at δ_H/δ_C 0.92 (3H,H-−30)/74.1 (C-29), and the ROESY effect between δ_H 2.88 (1H, dd, 13.9, 4.4 Hz, H-18 β-axial) and δ_H 0.92 (3H, H-30 β-axial) (Figs. 2 and 3). The configuration of C-3 was determined by the correlation observed in ROESY between δ_H 3.17 (H-3 α-axial) and δ_H 0.76 (1H, d, 11.5 Hz, H-5 α-axial). A 3-*O*-glycosidic linkage can be deduced according to the deshielded HSQC signal of position 3 at δ_C/δ_H 90.4 (C-3)/3.17 ppm (1H, H-3). Moreover, an ester signal at 177.5 ppm (C-28), suggests a bidesmosidic structure [9]. The structure of the aglycone of saponin **1** was therefore recognized as 3β,29-dihydroxyolean-12-en-28-oic acid (mesembryanthemoidigenic acid) [13].

The HSQC spectrum showed three anomeric signals at δ_C/δ_H 105.1/4.46 (1H, d, 7.5 Hz), 106.2/4.48 (1H, d, 6.9 Hz), and 95.5/5.38 (1H, d, 8.2 Hz). The ring protons of the monosaccharide units were assigned mainly by COSY, TOCSY, HSQC and HMBC experiments which allowed the identification of one glucuronopyranosyl (GlcA), one glucopyranosyl (Glc) and one arabinopyranosyl (Ara). The HMBC correlation between δ_H 3.44 (1H, dd, 9.1, 7.5 Hz, GlcA-2) and δ_C 106.2 (Ara-1), and the ROESY cross-peak at δ_H/δ_H 4.48 (1H, Ara-1)/3.44 (1H, GlcA-2), suggest an α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranosyl sequence. The HMBC cross-peak at δ_H/δ_C 4.46 (1H, GlcA-1)/90.4 (C-3) and the ROESY cross-peak at δ_H/δ_H 4.46 (1H, GlcA-1)/3.17 (1H, H-3) proved a 3-*O*-heterosidic linkage between the GlcA and the C-3 of the aglycon (Figs. 2 and 3). The shielded chemical shifts at δ_C 95.5 (Glc-1) and an ester signal at 177.5 (C-28), and the HMBC correlation at δ_H/δ_C 5.38 (1H, Glc-1)/177.5 (C-28), suggest an ester linkage between Glc-1 and the C-28 of the aglycon [14]. Based on those results, the structure of compound **1** was elucidated as 3-*O*-α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranosyl-3β,29-dihydroxyolean-12-en-28-oic acid 28-*O*-β-D-glucopyranosyl ester.

The mass spectrum of compound **2**, an amorphous powder, reveals in HRESIMS (positive mode), a quasi-molecular ion at *m/z* at 803.4179 $[M + Na]^+$ (calcd. 803.4194), in agreement with the molecular formula $C_{41}H_{64}O_{14}Na$. This suggests a loss of 162 uma, probably an hexopyranosyl unit, comparing with molecule **1**.

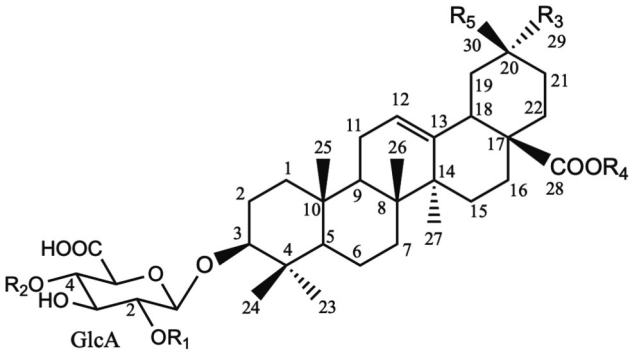
After a comparison between the NMR spectra of compounds **1** and **2**, a common sequence 3-*O*-α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranosyl, and the same aglycon, can be found. The lack of ester linkage at C-28, a signal at 181.6 ppm of a carboxyl function (C-28) [15], and the loss of an hexopyranosyl unit in the mass spectrum, suggest the following structure for **2** as 3-*O*-α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranosyl-3β,29-dihydroxyolean-12-en-28-oic acid.

Compound **3** was obtained as an amorphous powder with the molecular formula of $C_{41}H_{62}O_{15}$, established by the HRESIMS (positive mode) quasi-molecular ion pic at *m/z* 817.3972 $[M + Na]^+$ (calcd. for $C_{41}H_{62}O_{15}Na$, 817.3986).

Signals attributable to six angular methyl groups (3H, s, each) at δ_H 0.82 (H-26), 0.84 (H-24), 0.94 (H-25), 1.06 (H-23), 1.17 (H-27) and 1.24 (H-30), were found in the ^{1}H NMR spectrum part of the aglycon, with one olefinic proton at δ_H 5.28 (1H, br t, 3.5 Hz, H-12), and a secondary alcoholic function at δ_H 3.20 (1H, H-3). A 3-*O*-glycosidic linkage can be deduced by the HMBC correlation between δ_H 4.45 (1H, d, 7.6, GlcA-1) and δ_C 90.2 (C-3), and the ROESY cross-peak at δ_H/δ_H at 4.45 (1H, GlcA-1)/3.20 (1H, H-3). A carboxyl group at δ_C 183.6 ppm was assigned to position C-29 α-equatorial, according to the HMBC cross-peak at δ_H/δ_C 1.24 (3H, H-30)/183.6 (C-29), and the ROESY cross-peak at δ_H/δ_H δ_H 1.24 (3H, H-30 β-axial)/2.88 (1H, dd, 13.5, 4.5 Hz, H-18 β-axial). The ROESY correlation between H-3 α-axial (δ_H 3.20) et H-5 α-axial (δ_H 0.77 ppm) allows the determination of the C-3 configuration.

The structure of the aglycone of saponin **3** was therefore recognized as 3β-hydroxyolean-12-en-28,29-dioic acid (serratagenic acid) [16]. For the osidic part, the same α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranosyl sequence was found, as for compounds **1** and **2**. So, the structure of compound **3** was elucidated as 3-*O*-α-L-arabinopyranosyl-(1 → 2)-β-D-glucuronopyranosyl-3β-hydroxyolean-12-en-28,29-dioic acid.

The mass spectrum of compound **4**, an amorphous powder, in HRESIMS (positive mode) reveals a quasi-molecular ion at *m/z* at 833.4281 $[M + Na]^+$ (calcd. 833.4299), in agreement with the molecular formula $C_{42}H_{66}O_{15}Na$. The NMR signals of the aglycon part are in accordance with a 3β,29-dihydroxyolean-12-en-28-oic acid structure. A 3-*O*-glycosidic linkage can be proved by the HMBC correlation at δ_H/δ_C 4.38 (1H, d, 7.8 Hz, GlcA-1)/90.5 (C-3), and the ROESY cross-peak at δ_H/δ_H 4.38 (1H, GlcA-1)/3.18 (1H, H-3). In the HSQC spectrum, one



	R_1	R_2	R_3	R_4	R_5
1	Ara	H	CH_2OH	Glc	CH_3
2	Ara	H	CH_2OH	H	CH_3
3	Ara	H	COOH	H	CH_3
4	H	Glc	CH_2OH	H	CH_3
5	H	Glc	CH_2OH	Glc	CH_3
6	Glc	Glc	CH_3	H	CH_3
7	Glc	Glc	CH_2OH	H	CH_3
8	Glc	H	CH_2OH	H	CH_3
9	Ara	H	CH_3	H	CH_2OH
10	H	H	CH_3	H	CH_3

Fig. 1. Chemical structure of the isolated compounds **1**–**10**.

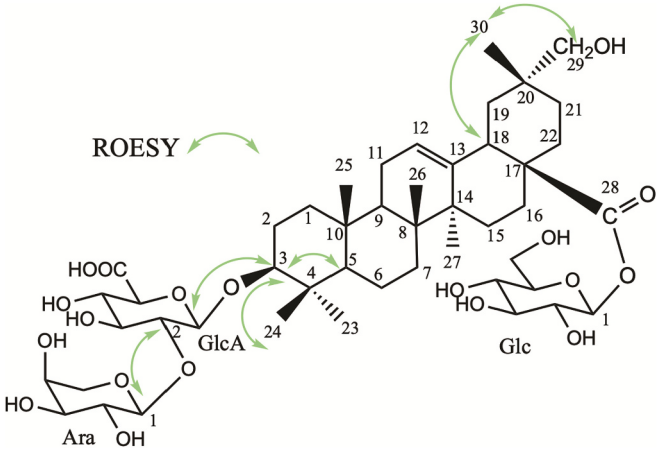


Fig. 2. Key ROESY correlations of compound **1**.

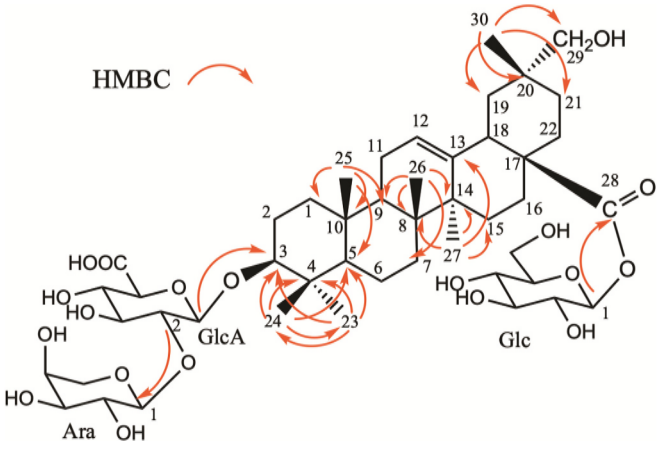


Fig. 3. Key HMBC correlations of compound **1**.

anomeric signal at δ_C/δ_H 104.2/4.40 (1H, d, 7.8 Hz) remains. The ring protons of this monosaccharide unit were assigned mainly by COSY, TOCSY, HSQC and HMBC experiments which allowed the identification of one Glc unit. Moreover, the HMBC correlation between δ_H 3.62 (1H, t, 9.7 Hz, GlcA-4) and δ_C 104.2 (Glc-1), and the ROESY cross-peak at δ_H/δ_H 3.62 (1H, GlcA-4)/4.40 (1H, Glc-1), suggest a *β*-D-glucopyranosyl-(1 → 4)-β-D-glucuronopyranosyl sequence. Based on those results, the structure of compound **4** was elucidated as 3-*O*-*β*-D-glucopyranosyl-(1 → 4)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid.

Compound **5** was obtained as an amorphous powder with the molecular formula of, established by the HRESIMS (positive mode) quasi-molecular ion pic at *m/z* 995.4805 $[M + Na]^+$ (calcd. For $C_{48}H_{76}O_{20}Na$, 995.4828). An extra hexosyl moiety results in 162 uma more than compound **4**, located at the C-28 position. An ester function at δ_C 177.6 (C-28), and an HMBC correlation with δ_H 5.38 (1H, d, 8.2 Hz, Glc II-1), confirm an ester linkage between an additional Glc moiety and the C-28 of the aglycon. Then, the structure of compound **5** was established as 3-*O*-*β*-D-glucopyranosyl-(1 → 4)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-glucopyranosyl ester.

In HRESIMS, compounds **7** and **5** share the same mass, in accordance with the molecular formula of $C_{48}H_{76}O_{20}$. The differences between the two molecules **5** and **7** are located at the aglycon with a signal of a carboxyl function at 181.4 ppm instead of an ester function, and at the position 2 of the GlcA unit: an additional Glc moiety at the GlcA-2 position was deduced by the HMBC correlation at δ_H/δ_C 4.42 (1H, d, 7.7 Hz, Glc II-1)/79.5 (GlcA-2), and the ROESY cross-peak at δ_H/δ_H 4.42 (1H, Glc II-1)/3.72 (1H, dd, 9.2, 7.7 Hz, GlcA-2). This conclusion led to the identification of the saponin **7** as 3-*O*-*β*-D-glucopyranosyl-(1 → 4)-[*β*-D-glucopyranosyl-(1 → 2)]-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid (**7**).

Compound **8**, an amorphous powder, shows in HRESIMS the same mass than compound **4**, with the molecular formula of $C_{42}H_{66}O_{15}$. They share the same genin, but a different linkage of the Glc moiety on the GlcA unit. An HMBC correlation at δ_H/δ_C 4.68 (1H, d, 7.8 Hz, Glc-1)/80.4 (GlcA-2), and a ROESY cross-peak at δ_H/δ_H 4.68 (1H, Glc-1)/3.64 (1H, dd, 9.0, 7.8 Hz, GlcA-2), allow the establishment of the following structure 3-*O*-*β*-D-glucopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl-3*β*,29-dihydroxyolean-12-en-28-oic acid, for compound **8**.

Compound **9** and **2** possess the molecular formula, $C_{41}H_{64}O_{14}$, according to the HRESIMS spectra. After the NMR analysis, the same 3-*O*-*α*-L-arabinopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl sequence can be found but a difference remains in the structure of the aglycon. Its ^1H NMR spectrum part displayed signals of a oleanene-type skeleton, as six angular methyl groups (3H, s, each) at δ_H 0.80 (H-26), 0.84 (H-24), 0.89 (H-29), 0.94 (H-25), 1.06 (H-23) and 1.17 (H-27), a carboxyl group at 179.2 ppm, one olefinic proton at δ_H 5.27 (1H, br t, 3.1 Hz, H-12), with a secondary alcoholic function at δ_H 3.17 (1H, dd, 11.9, 4.6 Hz, H-3), and a primary alcoholic function at δ_H 3.42 (1H, d, 11.2 Hz), 3.55 (1H, overlapped). The CH_2OH group was assigned to the C-30 *β*-axial position according to the HMBC cross-peak at δ_H/δ_C 3.42, 3.55 (2H,*H*-−30)/28.0 (C-29), and the ROESY correlation between δ_H 3.42, 3.55 (2H, H-30 *β*-axial) and δ_H 2.80 (1H, dd, 14.0,4.0 Hz, H-18 *β*-axial). The structure of the aglycone of saponin **9** was therefore recognized as 3*β*,30-dihydroxyolean-12-en-28-oic acid (Queretaroic acid) [17]. Molecule **9** was thus identified as 3-*O*-*α*-L-arabinopyranosyl-(1 → 2)-*β*-D-glucuronopyranosyl-3*β*,30-dihydroxyolean-12-en-28-oic acid.

As the leaves are edible and used in various food, with a subtle sweet taste between artichoke and asparagus, the crude extract, and five isolated saponins (with enough weight), were tested for the activation of the TAS1R2/TAS1R3 receptor. Indeed, saponins can be responsible for the activation of this receptors, as the secondary metabolites of licorice [18]. Even if the sweet taste of the leaves is very light, the hydro-alcoholic extract activates the TAS1R2/TAS1R3 with an EC_{50} value of 4.6 ± 0.4 *μ*g/ml, as the same level of the positive control sucralose (EC_{50}

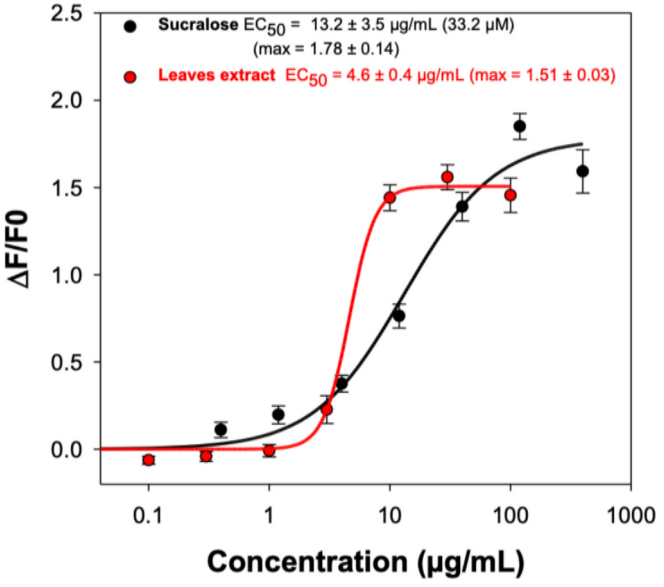


Fig. 4. Human TAS1R2/TAS1R3 dose-response curves obtained with the sweetener sucralose (used as control) and with the leaves crude extract.
The logarithmically scaled x-axis indicates the compounds concentration in µg/ml, and the y-axis shows the variation in fluorescence upon agonist application. Data represent mean ± sem of twelve wells from three independent experiments.

13.2 ± 3.5 μg/ml, Fig. 4). For the pure saponins **1**–**3**, **5**, **6**, surprisingly none of them showed any receptor activity. The sweet taste of the extract might be due to other secondary metabolites than the saponins, and/or to a potentiated effect. Research into these compounds is our next project.

4. Conclusions

From a Lebanese edible plant, *Gundelia tournefortii* L. (Asteraceae), six saponins (**1**–**6**) were isolated from the aqueous ethanolic extract of the leaves, while nine saponins (**1**–**4** and **6**–**10)** were obtained from the roots. Compounds **6** and **10** were already known, and **1**–**5** to **7**–**9** are new oleanolic acid glycosides. These molecules possess various degrees of oxidation at the 29 and 30 positions, with CH_3/CH_2OH/COOH groups. Surprisingly, the saponins present no activation of the TAS1R2/TAS1R3 compared to the crude extract with an EC_{50} value of 4.6 ± 0.4 μg/ml.

Sample availability

Samples of crude extracts are available from the authors.

CRediT authorship contribution statement

Samir Hobloss: Writing – original draft, Investigation. **Antoine Bruguière:** Writing – original draft, Investigation. **David Pertuit:** Writing – original draft. **Simon Dessertaine:** Investigation. **Marie-José Penouilh:** Investigation. **Michel Picquet:** Investigation. **Christine Belloir:** Investigation. **Loïc Briand:** Validation. **Anne-Claire Mitaine-Offer:** Writing – review & editing, Supervision.

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Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fitote.2025.106639.

Data availability

Data is contained within the article or supplementary data.

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