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Further constituents from *Caralluma negevensis*

Ammar Bader[a], Alessandra Braca[b,*], Nunziatina De Tommasi[c], Ivano Morelli[b]

[a]*Faculty of Pharmacy, Al-Zaytoonah University of Jordan, PO Box 130, 11733 Amman, Jordan*
[b]*Dipartimento di Chimica Bioorganica e Biofarmacia, Università degli Studi di Pisa, Via Bonanno 33, I-56126 Pisa, Italy*
[c]*Dipartimento di Scienze Farmaceutiche, Università degli Studi di Salerno, Via Ponte Don Melillo, I-84084 Fisciano (SA), Italy*

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Dedicated to the memory of Professor Serena Catalano

Abstract

Two new megastigmane glycosides (**1** and **2**) and two new flavone glycosides (**3** and **4**) were isolated from the methanol extract of the whole plant of *Caralluma negevensis* Zohary (Asclepiadaceae). The structures of the isolated compounds were characterized as (9*R*)-2β,9-dihydroxymegastigma-4,7-dien-3-one-9-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (**1**), 2β,9-dihydroxy-megastigma-4-en-3-one 9-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (**2**), luteolin 3′-*O*-β-D-glucopyranoside-4′-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside (**3**), and luteolin 3′,4′-di-*O*-β-D-glucopyranoside (**4**). The structures of the isolated compounds were established on the basis of spectral evidence and chemical transformation.

Keywords: *Caralluma negevensis*; Asclepiadaceae; Megastigmane glycosides; Flavone glycosides

1. Introduction

The genus *Caralluma* belongs to the family Asclepiadaceae, which comprises some 200 genera and 2500 species. Plants belonging to this genus are rich in esterified polyhydroxypregnane glycosides, some of which showed antitumor activity and others were postulated as precursors of cardenolides (Deepak et al., 1989, 1997). The genus is also characterized by the presence of flavone glycosides (Ramesh et al., 1999; Rizwani et al., 1990). In the course of our screening for biologically active natural products, we have described 20 new pregnane glycosides and/or their esters from *Caralluma negevensis* Zohary (Braca et al., 2002), a succulent perennial herb occuring wild on the rocky desert of East Saharo-Arabian subregion (Feinbrun-Dothan, 1978). The plant is used by Bedouins to treat chronic lung diseases, such as tubercolosis and cancer. Further studies on the whole plant led to the isolation of two megastigmane glycosides and two flavonol glycosides. The presence of megastigmane glycosides in a plant of the genus *Caralluma* is now reported for the first time.

2. Results and discussion

The 1-butanol fraction of the methanol extract of the whole plant of *C. negevensis* was chromatographed over Sephadex LH-20 followed by DCCC and HPLC to afford four new compounds (**1**–**4**).

Compound **1** was isolated as an oil. Its molecular formula was derived as $C_{25}H_{40}O_{12}$ by ESI-MS, NMR and elemental analysis. The ^{1}H NMR spectrum of **1** showed signals assignable to a vinyl proton at δ 5.94 (*s*) and two mutually coupled vinyl protons at δ 5.78 (*dd*, J = 16.0 and 8.8 Hz) and δ 5.77 (*dd*, J = 16.0 and 6.5 Hz). Proton signals due to three methines (δ 4.39, 4.20, and 2.78), a vinyl methyl (δ 1.96 *d*, J = 1.5 Hz), a secondary methyl (δ 1.32, *d*, J = 6.5 Hz), and two tertiary methyl groups (δ 1.13, 0.94, each *s*) were observed in the aliphatic region. The presence of two sugar residues was suggested by two doublet signals [δ 4.36 (J = 8.0 Hz), and δ 4.74 (J = 1.8 Hz)] due to anomeric protons and a methyl signal [δ_H 1.29 (*d*, J = 6.5 Hz), δ_C 17.9]. The ^{13}C NMR spectrum of **1** showed 25 carbon signals, among

* Corresponding author. Tel.: +39-050-44074; fax: +39-050-43321.
E-mail address: braca@farm.unipi.it (A. Braca).

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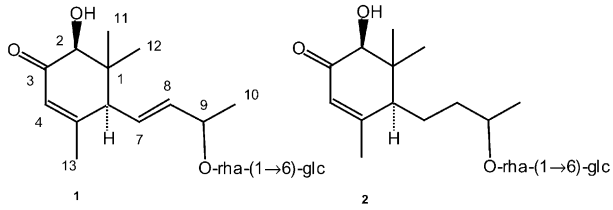

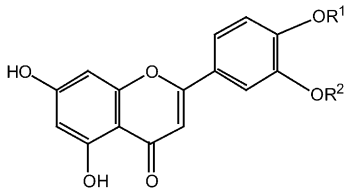

	R^1	R^2
3	Rha-(1→2)-glc	Glc
4	Glc	Glc

which 13 resonances were similar to those corresponding to a megastigmane (α-ionol) skeleton (De Tommasi et al., 1996; Otsuka et al., 1995), with an hydroxy group linked at C-2 (δ 77.3), confirmed by measurement of 2D NMR including DQF–COSY and HSQC spectral analyses. The position of hydroxy group at C-2 was also inferred from the presence of the singlet at δ 4.20, ascribable to a carbinyl proton and from key correlations observed in the HMBC experiment (H-2 and C-1, C-3, and C-12; H-4 and C-2, and C-6; H-6 and C-7, C-8, and C-11; H-8 and C-9). The remaining 12 carbon resonances were assigned to a β-D-glucopyranosyl and an α-L-rhamnopyranosyl moieties by means of 1D-TOCSY, DQF–COSY, and HSQC experiments. Acid hydrolysis of **1**, followed by TLC comparison with standards, yielded D-glucose and L-rhamnose as sugar moieties. The location of the sugar residues in **1** were established by the HMBC experiments. Hence, the anomeric proton signal (δ 4.36) of glucose, which was assigned from the DQF–COSY spectrum, was correlated through a three-bond coupling with C-9 (δ 76.0) of the aglycon. The other anomeric proton of rhamnose at δ 4.74 was also correlated with C-6′ of glucose at δ 68.0. So the disaccharide sugar chain was a rhamnopyranosyl-(1→6)-glucopyranosyl moiety linked at C-9 of the aglycon. In the 1D-ROESY experiment of **1**, correlation peaks between H-2 and H-6 were observed indicating the same α orientation of these protons. The absolute configuration at C-9 of the aglycon was assigned as *R* on the basis of a diagnostic chemical shift of the C-9 signal (76.0 ppm) in the ^{13}C-NMR spectrum (Pabst et al., 1992; Ito et al., 2001). Consequently, the structure of **1** was determined to be (9*R*)-2β,9-dihydroxymegastigma-4,7-dien-3-one 9-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside.

Compound **2** was obtained as an oil, and its ESI-MS showed a $[M+Na]^+$ ion peak at *m*/*z* 557, which was 2 mass units more than **1**. The molecular formula $C_{25}H_{42}O_{12}$ was confirmed by elemental analysis. The ^{1}H and ^{13}C NMR spectra of **2** were similar to those of **1**, both for the aglycon and the sugar moieties, except for the presence of two methylene groups (δ_H 1.62 and 1.60, δ_C 37.6 and 27.4) instead of one double bond. Upon acid hydrolysis, followed by TLC comparison with standards, compound **2** gave D-glucose and L-rhamnose. The DQF–COSY spectrum unambiguously revealed all the proton spin–spin connectivities and the correlations between protons and carbons were fully assigned from the HSQC experiment, allowing us to deduce the position of interglycosidic linkages. The sugar sequence was confirmed by HMBC cross peaks that showed correlations between H-1′–C-9 and H-1″–C-6′. The relative stereostructure of compound **2** was characterized by 1D-ROESY experiment: correlation peaks were observed between the signal at δ 4.18 (H-2) and 2.15 (H-6). The absolute configuration at C-9 of the aglycon was supposed to be *R* referring to the chemical shift of the C-9 signal in the ^{13}C NMR spectrum (75.3 ppm). On the basis of these data, the structure of **2** was assigned as 2β,9-dihydroxymegastigma-4-en-3-one 9-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside.

The molecular formulae $C_{33}H_{40}O_{20}$ for compound **3**, and $C_{27}H_{30}O_{16}$ for compound **4**, were determined by ESI-MS, ^{13}C and DEPT–^{13}C NMR analyses and were supported also by elemental analysis. Their ^{1}H and ^{13}C NMR spectra indicated that glycosides **3** and **4** had an identical aglycon portion but differed only in the saccharide chains. Their ^{1}H NMR spectra showed the presence of a flavone skeleton with two meta-doublet signals at δ 6.23 (J = 1.3 Hz) and 6.52 (J = 1.3 Hz) for compound **3** and δ 6.13 (J = 1.5 Hz) and 6.46 (J = 1.5 Hz) for compound **4**, respectively, one singlet at δ 6.71 and 6.80 ascribable to H-3, and an ABX system of ring B [δ 7.34 (*d*, J = 8.0 Hz, H-5′), 7.70 (*dd*, J = 8.0, 1.7 Hz, H-6′), 7.98 (*d*, J = 1.7 Hz, H-2′) for **3** and δ 7.30 (*d*, J = 8.0 Hz, H-5′), 7.67 (*dd*, J = 8.0, 1.5 Hz, H-6′), 7.93 (*d*, J = 1.5 Hz, H-2′) for **4**, respectively], permitting to identify the aglycon as luteolin (Agrawal, 1989). Their ^{1}H-NMR spectra indicated also signals for three and two sugar residues in compound **3** and **4**, respectively, easily clarified with the help of 1D-TOCSY and DQF–COSY experiments, that led also the assignation of the type of sugar and its anomeric configuration. Acid hydrolysis of both compounds, followed by TLC comparison with standards, yielded two β-D-glucose moieties and one α-L-rhamnose unit for compound **3** and two β-D-glucose residues for compound **4**, respectively. The exact disposition of the monosaccharide units and the position of the interglycosidic linkages in compound **3** and **4** were assigned in the following manner. HSQC permitted assignments of the interglycosidic linkages by comparison of the ^{13}C NMR shifts observed with those of the corresponding methyl pyranosides and taking into account the known effects of glycosidation (Breitmaier

and Voelter, 1987). The absence of any ^{13}C-NMR glycosidation shifts for one glucopyranosyl and the rhamnopyranosyl residues suggested that these sugars were terminal units in compound **3**, while glycosidation shift for C-2 ($\sim +6$ ppm) of the other glucopyranosyl unit indicated that it was substituted at C-2 position. The position of each sugar unit was achieved using HMBC experiment: diagnostic long range correlations were observed between H-1″glc and C-4′, H-1‴rha and C-2″glc, and H-1⁗glc and C-3′, allowing identification of compound **3** as luteolin 3′-*O*-β-D-glucopyranoside-4′-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside. Analogously the absence of any glycosidation shifts for the glucopyranosyl moieties in compound **4** and the HMBC correlation between H-1″glc and C-4′ and H-1‴glc and C-3′, permitted to establish the structure for this compound as luteolin 3′,4′-di-*O*-β-D-glucopyranoside.

3. Experimental

3.1. General

Instrument to obtain physical and spectral data were the same as described by Braca et al. (2002). TLC was performed on precoated Kieselgel 60 F_{254} plates (Merck); compounds were detected by spraying with $Ce(SO_4)_2/H_2SO_4$ solution followed by heating. CC was performed over Sephadex LH-20 (Pharmacia); droplet countercurrent chromatography (DCCC) was performed on an apparatus manufactured by Büchi, equipped with 300 tubes; HPLC separations were conducted on a Shimadzu LC-8A series pumping system equipped with a Waters R401 refractive index detector and with a Waters μ-Bondapak C_{18} column and Shimadzu injector. The other instruments used to obtain physical and spectral data were the same as described by Braca et al. (2002).

3.2. Plant material

The whole plant of *Caralluma negevensis* Zohary was collected in Dabbet Hanoot, Qa' al Naqab, Jordan, in April, 1999 and identified by Professor Sawsan Al Oran, Department of Biology, University of Jordan, Amman, Jordan. A voucher specimen is deposited at the Orto Botanico, Università di Pisa, Pisa, Italy (No. 2000-0051/1).

3.3. Extraction and isolation

The 1-butanol fraction of the methanol extract prepared according the method reported previously (Braca et al., 2002), was chromatographed on Sephadex LH-20 with MeOH as eluent and collecting fractions of 8 ml that were pooled into 20 major fractions. Fraction 6 (760 mg) was submitted to DCCC [*n*-BuOH–Me_2CO–H_2O (33:10:50) descending mode, flow 10 ml/h], to yield two major fractions A (80 mg) and B (70 mg). Fraction A was finally purified by RP-HPLC on a C-18 μ-Bondapak column, (30 cm×7.8 mm, flow rate 2.0 ml/min) with MeOH–H_2O 2:3 as eluent to yield pure compound **1** (5.0 mg, $t_R = 17$ min) and compound **2** (4.8 mg, $t_R = 23$ min). Fractions 12 (93 mg) and 16 (76 mg) from Sephadex LH-20 column were further purified on RP-HPLC on a C-18 μ-Bondapak column, (30 cm×7.8 mm, flow rate 2.0 ml/min) both with MeOH–H_2O 4.5:5.5 to obtain compound **3** (10.5 mg, $t_R = 11$ min) from fraction 12 and compound **4** (7.5 mg, $t_R = 14$ min) from fraction 16, respectively.

3.4. (9R)-2β,9-Dihydroxymegastigma-4,7-dien-3-one 9-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (1)

Oil; $[\alpha]_D^{25} = -18.2^\circ$ (MeOH, *c* 0.1); UV (MeOH) λ_{max} (log ε) 232 sh (4.00) nm; ^{1}H and ^{13}C NMR (600 MHz, CD_3OD): see Table 1; ESI-MS: *m/z* 555 $[M+Na]^+$, 409 $[M+Na-146]^+$, 247 $[M+Na-146-162]^+$; elemental analysis (%): C 56.30, H 7.60, (calc. for $C_{25}H_{40}O_{12}$, C 56.38, H 7.57).

Table 1
^{1}H- and ^{13}C-NMR data of compounds **1** and **2** (CD_3OD, 600 and 150 MHz, respectively)[a,b]

No.		**1**		**2**	
		^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
	1		42.5		43.0
	2	4.20 *s*	77.3	4.18 *s*	77.0
	3		202.3		202.2
	4	5.94 *s*	124.0	5.85 *s*	123.8
	5		164.6		168.5
	6	2.78 *d* (8.8)	58.6	2.15 *dd* (9.0, 1.5)	54.0
	7	5.78 *dd* (16.0, 8.8)	128.4	1.62 *br m*	37.6
	8	5.77 *dd* (16.0, 6.5)	138.3	1.60 *br m*	27.4
	9	4.39 *q* (6.5)	76.0	3.79 *m*	75.3
	10	1.32 *d* (6.5)	21.0	1.18 *d* (6.5)	24.3
	11	0.94 *s*	21.0	0.88 *s*	21.7
	12	1.13 *s*	25.6	1.20 *s*	24.2
	13	1.96 *d* (1.5)	23.4	2.08 *d* (1.5)	24.0
glc	1′	4.36 *d* (8.0)	102.8	4.27 *d* (8.0)	102.3
	2′	3.18 *dd* (9.5, 8.0)	75.0	3.14 *dd* (9.0, 8.0)	75.0
	3′	3.36 *d* (9.5)	78.0	3.34 *d* (9.0)	77.9
	4′	3.28 *d* (9.5)	71.6	3.23 *d* (9.0)	71.4
	5′	3.38 *m*	76.8	3.35 *m*	76.0
	6′a	3.96 *dd* (12.0, 3.5)	68.0	3.94 *dd* (12.0, 3.0)	68.0
	6′b	3.60 *dd* (12.0, 5.0)		3.58 *dd* (12.0, 5.0)	
rha	1″	4.74 *d* (1.8)	102.8	4.73 *d* (1.8)	102.0
	2″	3.85 *dd* (2.5, 1.8)	72.1	3.80 *dd* (2.5, 1.8)	71.4
	3″	3.66 *dd* (9.0, 2.5)	72.3	3.62 *dd* (9.0, 2.5)	72.0
	4″	3.38 *t* (9.0)	73.9	3.35 *t* (9.0)	73.6
	5″	3.67 *m*	69.7	3.63 *m*	69.5
	6″	1.29 *d* (6.5)	17.9	1.26 *d* (6.0)	17.8

[a] Assignments were determined using the DQF–COSY, HSQC, and HMBC experiments.

[b] Multiplicity was determined by DEPT experiments and *J* values are given in parentheses.

3.5. 2β,9-Dihydroxymegastigma-4-en-3-one 9-O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranoside (**2**)

Oil; $[\alpha]_D^{25} = -14.0°$ (MeOH, *c* 0.1); UV (MeOH) λ_{max} (log ε) 235 sh (3.89) nm; ^1H and ^{13}C NMR (600 MHz, CD_3OD): see Table 1; ESI-MS: *m/z* 557 $[M+Na]^+$, 411 $[M+Na-146]^+$, 249 $[M+Na-146-162]^+$; elemental analysis (%): C 56.12, H 7.95, (calc. for $C_{25}H_{42}O_{12}$, C 56.17, H 7.92).

3.6. Luteolin 3′-O-β-glucopyranoside-4′-O-α-L-rhamnopyranosyl-(1→2)-β-D-glucopyranoside (**3**)

Yellow amorphous powder, mp 215–220 °C dec; $[\alpha]_D^{25} = -25.7°$ (MeOH, *c* 0.1); UV (MeOH) λ_{max} (log ε) 267 sh (4.12), 319 (3.85) nm; ^1H and ^{13}C NMR (600 MHz, CD_3OD): see Table 2; ESI-MS: *m/z* 779 $[M+Na]^+$, 633 $[M+Na-146]^+$, 617 $[M+Na-162]^+$, 471 $[M+Na-46-162]^+$; elemental analysis (%): C 52.35, H 5.34, (calc. for $C_{33}H_{40}O_{20}$, C 52.38, H 5.33).

Table 2
^1H and ^{13}C NMR data of compounds **3** and **4** (CD_3OD, 600 and 150 MHz, respectively)[a,b]

	No.	**3**		**4**	
		^1H-NMR	^{13}C-NMR	^1H-NMR	^{13}C-NMR
	2		165.1		165.4
	3	6.71 *s*	105.2	6.80 *s*	105.5
	4		183.8		183.5
	5		163.2		163.0
	6	6.23 *d* (1.3)	100.1	6.13 *d* (1.5)	100.0
	7		166.6		166.0
	8	6.52 *d* (1.3)	95.1	6.46 *d* (1.5)	95.0
	9		159.4		159.6
	10		106.9		106.7
	1′		127.1		126.8
	2′	7.98 *d* (1.7)	118.1	7.93 *d* (1.7)	117.8
	3′		149.2		149.1
	4′		151.4		151.0
	5′	7.34 *d* (8.0)	119.2	7.30 *d* (8.0)	118.9
	6′	7.70 *dd* (8.0, 1.7)	123.3	7.67 *dd* (8.0, 1.7)	123.0
glc	1″	5.34 *d* (7.5)	100.9	5.12 *d* (8.0)	101.5
at C-3′	2″	3.75 *dd* (9.0, 7.5)	80.7	3.66 *dd* (9.0, 8.0)	74.5
	3″	3.63 *d* (9.0)	78.9	3.57 *d* (9.0)	78.5
	4″	3.46 *d* (9.0)	71.4	3.42 *d* (9.0)	71.3
	5″	3.47 *m*	78.1	3.55 *m*	77.9
	6″a	4.06 *dd* (12.5, 3.0)	62.6	3.95 *dd* (12.0, 3.5)	62.4
	6″b	3.86 *dd*(12.5, 5.0)		3.72 *dd* (12.0, 5.0)	
rha	1‴	5.28 *d* (1.8)	102.7		
	2‴	4.04 *dd* (2.0, 1.8)	72.1		
	3‴	3.70 *dd* (9.0, 2.0)	72.1		
	4‴	3.38 *t* (9.0)	74.0		
	5‴	3.87 *m*	70.3		
	6‴	1.25 *d* (6.0)	18.1		
glc	1⁗	5.00 *d* (7.5)	103.8	5.05 *d* (8.0)	103.0
at C-4′	2⁗	3.65 *dd* (9.5, 7.5)	74.8	3.64 *dd* (9.5, 8.0)	74.6
	3⁗	3.54 *d* (9.5)	78.5	3.57 *d* (9.5)	78.2
	4⁗	3.43 *d* (9.5)	71.3	3.40 *d* (9.5)	71.5
	5⁗	3.50 *m*	77.8	3.53 *m*	78.0
	6‴′a	3.97 *dd* (13.0, 3.0)	62.3	3.98 *dd* (12.0, 3.0)	62.5
	6‴′b	3.76 *dd* (13.0, 5.0)		3.79 *dd* (12.0, 5.0)	

[a] Assignments were determined using the DQF–COSY, HSQC, and HMBC experiments.
[b] Multiplicity was determined by DEPT experiments and *J* values are given in parenthesis.

3.7. Luteolin 3′,4′-di-O-β-D-glucopyranoside (**4**)

Yellow amorphous powder, mp 200–205 °C; $[\alpha]_D^{25} = -34.5°$ (MeOH, *c* 0.1); UV (MeOH) λ_{max} (log ε) 263 sh (4.09), 317 (3.94) nm; ^1H and ^{13}C NMR (600 MHz, CD_3OD): see Table 2; ESI-MS: *m/z* 633 $[M+Na]^+$, 471 $[M+Na-162]^+$, 309 $[M+Na-162\times2]^+$; elemental analysis (%): C 53.07, H 4.96, (cal. for $C_{27}H_{30}O_{16}$, C 53.12, H 4.95).

3.8. Acid hydrolysis of **1**–**4**

Each compound was heated with 1 ml of 1 M HCl, 1 ml of dioxane in a sealed tube at 90 °C for 4 h; then 5 ml of water were added and the aglycon was removed by extracting with $CHCl_3$ (3×10 ml). The aqueous layer was neutralized with Ag_2CO_3, filtered and evaporated to dryness. The sugar samples were identified by cellulose TLC (pyridine–AcOEt–AcOH–H_2O 36:36:7:21 as eluent) by comparison with authentic samples.

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