Ursane-Type Triterpene Saponins from *Zygophyllum geslini*

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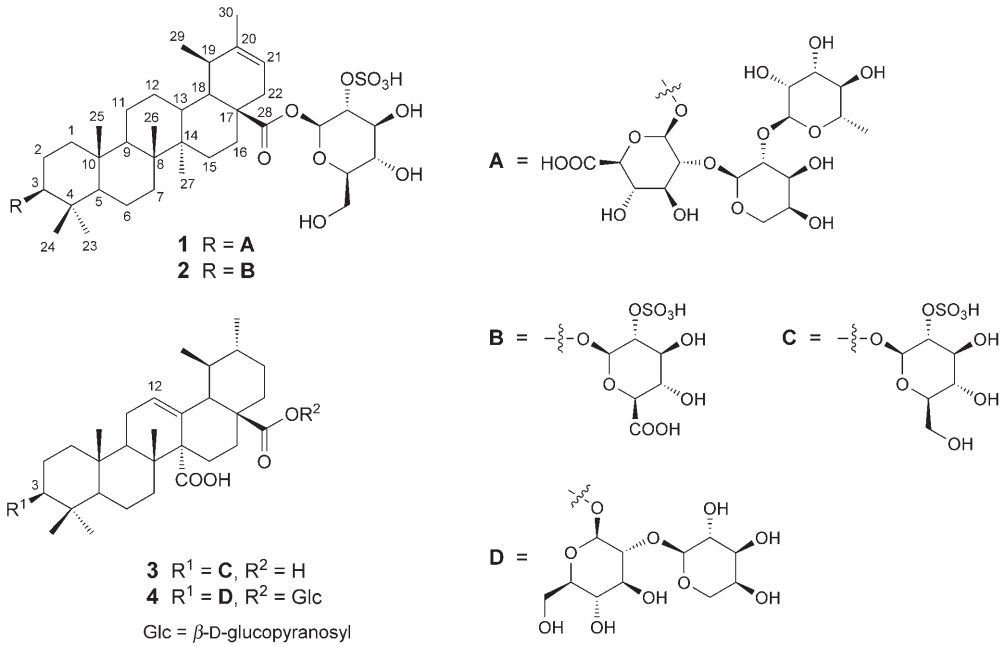
Four new ursane-based triterpene glycosides, compounds **1**–**4**, as well as the known glycosides zygophylosides E, G, and H, and 3-*O*-(*β*-D-quinovopyranosyl)quinovic acid 28-(*O*-*β*-D-glucopyranosyl) ester, were isolated from the BuOH-soluble fraction of the MeOH/H_2O 7:3 extracts of *Zygophyllum geslini* (roots or aerial parts). Their structures were established mainly by 1D- and 2D-NMR techniques, in combination with HR-MS analysis and acid hydrolysis.

Introduction. – During our research on Algerian medicinal plants, *Zygophyllum geslini* Coss. (Zygophyllaceae), traditionally used as antidiabetic [1], was collected in Central Sahara. A cytotoxic triterpene derivative, 3-*O*-[(*E*)-3,4-dihydroxy-cinnamoyl]erythrodiol, was previously isolated from the roots [1], but no triterpene glycoside. In this paper, we describe the isolation and structure elucidation of four new ursane-type triterpene saponins, compounds **1**–**4**, together with four known compounds, zygophylosides E, G, and H [2], and 3-*O*-(*β*-D-quinovopyranosyl)quinovic acid 28-(*O*-*β*-D-glucopyranosyl) ester [3].

Results and Discussion. – Two crude saponin mixtures were obtained from the BuOH-soluble fraction of the MeOH/H_2O 7:3 extracts of the roots and the aerial parts, respectively of *Z. geslini*. They were submitted individually to several purification steps based on preparative chromatography, yielding compounds **1**, **4**, zygophylosides E, G, and H, and 3-*O*-(*β*-D-quinovopyranosyl)quinovic acid 28-(*O*-*β*-D-glucopyranosyl) ester from the roots, and compounds **1**–**3** as well as zygophylosides E and G from the aerial parts, respectively. Their structures were elucidated mainly by NMR spectroscopy, including 1D- and 2D-NMR experiments (^{1}H,^{1}H-COSY, TOCSY, NOESY, HSQC, HMBC), in combination with mass spectrometry (MS).

Compound **1** exhibited in the HR-ESI mass spectrum (positive-ion mode) the $[M+Na]^+$ peak at *m/z* 1175.4932 (calc. 1175.4920), consistent with the molecular formula $C_{53}H_{84}O_{25}S$. Negative-ion FAB-MS showed the $[M-H]^-$ peak at *m/z* 1151, indicating a molecular weight of 1152. Other fragment-ion peaks were observed at *m/z* 909 ($[M-H-162-80]^-$) due to the loss of a sulfo-hexose moiety, and at 873



([M – H – 146 – 132]$^-$) and 697 ([M – H – 146 – 132 – 176]$^-$), suggesting the successive elimination of a 6-deoxyhexose, a pentose, and a hexosuronosyl group, respectively. The structure of the aglycone of **1** was recognized as (3β)-3-hydroxyurs-20(21)-en-28-oic acid by ^{1}H- and ^{13}C-NMR analyses (*Table 1*), especially based on correlations observed in the COSY, NOESY, HSQC and HMBC spectra, and in full agreement with literature data [4]. From these data, the structure of compound **1** was elucidated as (3β)-3-{[6-deoxy-α-L-mannopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 2)-β-D-glucopyranurosonyl]oxy}urs-20-en-28-oic acid 28-(2-*O*-sulfo-β-D-glucopyranosyl) ester.

The ^{1}H-NMR spectrum of **1** displayed six Me *singlet*s at δ(H) 0.61, 0.89, 0.98, 1.07, 1.15, and 1.60, one Me *doublet* at δ(H) 0.97 (J = 6.5 Hz), an olefinic H-atom at δ(H) 5.28 (*dd*, J = 6.7, 1.5 Hz, H–C(21)), and one oxygenated methine at δ(H) 3.25 (*dd*, J = 11.4, 3.8 Hz, H–C(3)). Moreover, the ^{13}C-NMR spectrum showed characteristic signals of an ester group at δ(C) 174.7 (C(28)), and a quaternary olefinic C-atom at δ(C) 142.6 (C(20)). These data indicated an ursane aglycone with a pentacyclic skeleton and a C=C bond at C(20), as well as a carboxylic acid function at C(28), identified as (3β)-3-hydroxyurs-20(21)-en-28-oic acid [4]. HMBC Cross-peaks between δ(H) 5.28 (*dd*, J = 6.7, 1.5 Hz, H–C(21)) and both δ(C) 49.3 (C(17)) and 37.1 (C(22)), and COSY cross-peaks between δ(H) 5.28 (H–C(21)) and δ(H) 1.82, 2.59 (CH_2(22)) revealed the position of the C=C bond. The relative configurations at C(18), C(19), and C(3) were determined from a NOESY experiment, which showed key cross-peaks between H–C(18) at δ(H) 1.20 and H–C(13) at δ(H) 2.59, between H–C(19) at δ(H) 2.26 (*dd*, J = 12.7, 6.5 Hz) and Me(30) at δ(H) 1.60 (*s*), and between H–C(3) at δ(H)

Table 1. *^1H- and ^{13}C-NMR Data of the Aglycone Moieties of* **1**–**4**. At 600/150 MHz, resp., in (D_5)pyridine; δ in ppm, J in Hz. Overlapping signals are reported without signal multiplicities.

Position	**1**		**2**		**3**		**4**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	0.75, 1.44	38.7	0.72, 1.46	38.6	1.15, 1.52	38.3	0.96, 1.44	38.9
2	1.82, 2.32	26.1	1.86, 2.22	26.0	1.86, 2.13	25.7	1.78, 2.14	26.6
3	3.25 (*dd*, J = 11.4, 3.8)	89.4	3.28 (*dd*, J = 11.2, 3.8)	90.2	3.33 (*dd*, J = 11.5, 3.9)	89.5	3.10 (*dd*, J = 11.7, 4.0)	88.7
4		39.1		39.3		39.2		39.1
5	0.56	55.6	0.63	55.7	1.02	54.8	0.80	55.5
6	1.25, 1.32	18.1	1.20, 1.37	18.1	1.14, 1.42	18.1	1.38, n.d.[a])	18.3
7	1.15, 1.55	33.9	n.d.[a])	34.0	n.d.[a])	34.6	1.68, 1.84	36.2
8		41.7		41.8		39.8		39.9
9	1.19	50.4	1.23	50.6	2.76	46.4	2.59	46.9
10		36.5		36.6		36.4		36.7
11	1.07, 1.31	21.3	1.39, n.d.[a])	21.5	1.95, 2.06	22.9	1.18, 1.98	22.9
12	1.02, 1.62	27.4	1.16, 1.74	27.6	6.01 (br. *s*)	127.0	5.90 (br. *s*)	129.0
13	2.59	38.9	2.71	39.0		135.7		133.5
14		40.9		41.0		57.3		56.8
15	1.45, n.d.[a])	29.3	1.55, 2.09	29.3	2.33, 2.59	25.6	2.30, 2.52	25.4
16	1.44, 2.80	32.3	1.52, 2.91	32.5	n.d.[a])	26.5	n.d.[a])	26.2
17		49.3		49.5		49.2		48.8
18	1.20	49.0	1.29	49.2	2.82 (*d*, J = 11.3)	55.0	2.60 (*d*, J = 11.2)	54.5
19	2.26 (*dd*, J = 12.7, 6.5)	36.9	2.40 (*dd*, J = 11.5, 5.9)	37.1	1.75	36.8	1.44	37.1
20		142.6		142.7	1.04	39.1	0.81	38.8
21	5.28 (*dd*, J = 6.7, 1.5)	117.4	5.37 (*dd*, J = 6.5, 1.4)	118.0	1.27, 1.36	30.5	1.25, 1.30	30.4
22	1.82, 2.59	37.1	1.87, 2.68	37.0	1.54, 1.96	37.2	1.60, 1.76	37.2
23	1.15 (*s*)	27.6	1.36 (*s*)	27.8	1.37 (*s*)	27.7	1.03 (*s*)	27.5
24	0.98 (*s*)	16.2	1.10 (*s*)	16.4	1.11 (*s*)	16.7	0.96 (*s*)	16.4
25	0.61 (*s*)	16.0	0.67 (*s*)	16.1	0.80 (*s*)	16.0	0.80 (*s*)	16.3
26	1.07 (*s*)	15.7	1.17 (*s*)	15.9	1.04 (*s*)	18.6	1.13 (*s*)	18.9
27	0.89 (*s*)	14.6	0.99 (*s*)	15.0		178.0		178.4
28		174.7		174.7		180.0		176.7
29	0.97 (*d*, J = 6.5)	23.2	1.07 (*d*, J = 5.9)	23.3	1.29 (*d*, J = 6.2)	18.2	1.11 (*d*, J = 6.0)	17.9
30	1.60 (*s*)	21.6	1.69 (*s*)	21.7	0.85 (*d*, J = 6.3)	21.0	0.70 (*d*, J = 6.2)	20.9

[a]) Not determined.

3.25 (*dd*, J = 11.4, 3.8 Hz) and both H–C(5) at δ(H) 0.56 and Me(23) at δ(H) 1.15 (*s*). These correlations confirmed the β-axial position of H–C(18), and the α-axial positions of H–C(19) and H–C(3). The chemical shifts at δ(C) 89.4 (C(3)) and 174.7 (C(28)) further suggested two glycosidic linkages at C(3) and C(28).

The ^{1}H-NMR spectrum of **1** indicated four anomeric H-atoms at δ(H) 6.03 (*d*, J = 8.1 Hz), 5.66 (br. *s*), 5.51 (*d*, J = 6.0 Hz), and 4.79 (*d*, J = 7.4 Hz), which were HSQC-correlated with four anomeric C-atom signals at δ(C) 92.3, 101.4, 100.7, and 104.6,

respectively. The ring H-atoms of the monosaccharide residues were assigned starting from the readily identifiable anomeric H-atoms by means of COSY, TOCSY, HSQC, and HMBC experiments (*Table 2*). Several sugar moieties were identified, including one α-L-rhamnopyranosyl (Rha), one α-L-arabinopyranosyl (Ara), one β-D-glucopyranosyl (Glc), and one β-D-glucopyranuronosyl (GlcA) unit, in agreement with the results of acid hydrolysis of the crude saponin fraction. The relatively large $^3J(1,2)$ values (6.0–8.1 Hz) for the Glc, GlcA, and Ara residues (*Table 2*) indicated β-anomeric orientation for Glc and GlcA, and α-anomeric orientation for Ara [5]. The multiplicity of the anomeric ^{1}H-NMR signal of Rha (br. *s*) indicated α-anomeric orientation. The monosaccharides obtained by acid hydrolysis of the crude extract were identified as D-glucopyranuronic acid, D-glucose, L-arabinose, and L-rhamnose by TLC and optical-rotation measurements.

An HMBC correlation between δ(H) 6.03 (*d*, $J = 8.1$ Hz, H–C(1) of Glc) and δ(C) 174.7 (C(28) of aglycone) indicated an ester linkage between the aglycone and a Glc moiety. The location of the OSO_3H group in 2-position of Glc was based on the downfield shifts observed in the HSQC spectrum for the Glc H–C(2) and C(2) resonances at δ(H) 4.96 (*t*, $J = 8.4$ Hz) and δ(C) 78.5, respectively. After subtraction of the anomeric signals of the sulfo-glucosyl moiety, the signals of three sugars linked to C(3) of the aglycone remained. HMBC Cross-peaks between H–C(3) of the aglycone at δ(H) 3.25 (*dd*, $J = 11.4$, 3.8 Hz) and GlcA C(1) at δ(C) 104.6, and a reverse correlation between GlcA H–C(1) at δ(H) 4.79 (*d*, $J = 7.4$ Hz) and C(3) at δ(C) 89.4, indicated a glucopyranuronosyl moiety at C(3) of the aglycone. The NOE interaction of GlcA H–C(2) at δ(H) 4.03 (*t*, $J = 8.3$ Hz) with Ara H–C(1) at δ(H) 5.51 (*d*, $J = 6.0$ Hz), and the HMBC connectivities of GlcA H–C(2) with Ara C(1) at δ(C) 100.7, and of Rha H–C(1) at δ(H) 5.66 (br. *s*) with Ara C(2) at δ(C) 75.1, revealed an α-L-Rha-(1 → 2)-α-L-Ara-(1 → 2)-β-D-GlcA oligosaccharide chain at C(3) of the aglycone.

Compound **2** exhibited in the HR-ESI mass spectrum the $[M + Na]^+$ signal at *m/z* 977.3507 (calc. 977.3487), consistent with the molecular formula $C_{42}H_{66}O_{20}S_2$. Negative-ion FAB-MS showed the $[M - H]^-$ peak at *m/z* 953, indicating a molecular weight of 954. The fragment-ion peaks at *m/z* 873 ($[M - H - 80]^-$), 711 ($[M - H - 80 - 162]^-$), and 697 ($[M - H - 80 - 176]^-$) revealed the loss of one sulfo-hexose and one sulfo-hexosuronosyl moiety. 2D-NMR Spectroscopic analyses of **2** led to the establishment of its structure as (3β)-3-[(2-*O*-sulfo-β-D-glucopyranurosonyl)oxy]urs-20-en-28-oic acid 28-(2-*O*-sulfo-β-D-glucopyranosyl] ester.

The ^{1}H- and ^{13}C-NMR signals of **2**, assigned by 2D-NMR analysis, were almost superimposable to those of **1**, except for the sugar part at C(3) of the aglycone (*Tables 1* and *2*). An HMBC correlation between δ(H) 4.91 (*d*, $J = 7.1$ Hz, GlcA H–C(1)) and δ(C) 90.2 (C(3)), and an NOESY cross-peak between GlcA H–C(1) and the aglycone H–C(3) at δ(H) 3.28 (*dd*, $J = 11.2$, 3.8 Hz) confirmed a linkage between the aglycone and a glucopyranurosonyl moiety. In the HSQC spectrum, the location of the sulfate group at C(2) of GlcA was determined by the downfield shift GlcA resonances H–C(2) and C(2) at δ(H) 4.99 (*t*, $J = 8.1$ Hz) and δ(C) 80.0, respectively.

HR-ESI-MS Analysis of **3** showed the $[M + Na]^+$ signal at *m/z* 751.3349 (calc. 751.3339), consistent with the molecular formula $C_{36}H_{56}O_{13}S$. Negative-ion FAB-MS showed the $[M - H]^-$ peak at *m/z* 727, indicating a molecular weight of 728. The fragment-ion peaks at *m/z* 683 ($[M - H - 44]^-$) and at *m/z* 603 ($[M - H - 44 - 80]^-$)

Table 2. *^1H- and ^{13}C-NMR Data of the Sugar Moieties of* **1**–**4**. At 600/150 MHz, resp., in (D_5)pyridine; δ in ppm, J in Hz. Overlapping signals are reported without signal multiplicities.

Atom	**1**		**2**		**3**		**4**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
3-*O*-GlcA:								
H–C(1)	4.79 (*d*, *J* = 7.4)	104.6	4.91 (*d*, *J* = 7.1)	103.6				
H–C(2)	4.03 (*t*, *J* = 8.3)	78.6	4.99 (*t*, *J* = 8.1)	80.0				
H–C(3)	4.15	75.6	4.42 (*t*, *J* = 8.3)	76.8				
H–C(4)	4.14	72.9	4.34	73.3				
H–C(5)	4.24 (*d*, *J* = 8.6)	77.1	4.30	76.0				
COOH		n.d.[a])		n.d.				
Ara:								
H–C(1)	5.51 (*d*, *J* = 6.0)	100.7					5.06 (*d*, *J* = 6.7)	106.1
H–C(2)	4.45	75.1					4.45	73.1
H–C(3)	4.15	71.9					4.12	73.7
H–C(4)	4.17	67.0					4.25	68.7
H_α–C(5)	3.65 (*d*, *J* = 10.7)	63.3					3.66 (*d*, *J* = 10.9)	66.6
H_β–C(5)	4.33 (*dd*, *J* = 10.7, 5.9)						4.26	
Rha:								
H–C(1)	5.66 (br. *s*)	101.4						
H–C(2)	4.47 (br. *s*)	71.5						
H–C(3)	4.42 (*dd*, *J* = 9.5, 3.1)	71.5						
H–C(4)	4.17	73.1						
H–C(5)	4.54 (*dq*, *J* = 9.4, 6.0)	69.5						
Me(6)	1.64 (*d*, *J* = 6.0)	18.1						
Glc:								
H–C(1)					4.80 (*d*, *J* = 7.1)	102.9	4.66 (*d*, *J* = 7.8)	104.6
H–C(2)					4.92 (*t*, *J* = 8.2)	80.6	3.99	83.2
H–C(3)					4.41 (*t*, *J* = 8.8)	77.1	4.19 (*t*, *J* = 9.1)	77.7
H–C(4)					4.12 (*t*, *J* = 9.0)	70.7	4.06 (*t*, *J* = 9.3)	71.7
H–C(5)					3.89	76.7	3.80	77.5
CH_2(6)					4.25 (*dd*, *J* = 11.3, 5.2)	61.7	4.25	62.4
					4.45 (br. *d*, *J* = 11.3)		4.44	
28-*O*-Glc:								
H–C(1)	6.03 (*d*, *J* = 8.1)	92.3	6.18 (*d*, *J* = 8.1)	92.6			6.21 (*d*, *J* = 8.1)	95.4
H–C(2)	4.96 (*t*, *J* = 8.4)	78.5	5.12 (*t*, *J* = 8.4)	78.7			4.15	73.6
H–C(3)	4.26 (*t*, *J* = 8.8)	76.9	4.40 (*t*, *J* = 8.8)	77.2			4.24	78.2
H–C(4)	4.08 (*t*, *J* = 9.4)	70.2	4.23 (*t*, *J* = 9.3)	70.5			4.23	70.8
H–C(5)	3.80	77.8	3.90	78.1			3.98	78.8
CH_2(6)	4.02	61.2	4.15 (*dd*, *J* = 11.9, 4.6)	61.4			4.28	62.0
	4.17		4.29				4.38	

[a]) Not determined.

suggested the sequential loss of CO_2 and SO_3 groups, respectively. The structure of the aglycone of **3** was recognized as (3β)-3-hydroxyurs-12-ene-27,28-dioic acid (= quinovic acid) [2] by ^{1}H- and ^{13}C-NMR analyses (*Table 1*), based on correlations observed in the COSY, NOESY, HSQC, and HMBC spectra, in full agreement with the literature data. The structure of **3** was, thus, elucidated as 3-*O*-(2-*O*-sulfo-β-D-glucopyranosyl)quinovic acid.

The ^{1}H-NMR spectrum of **3** displayed four Me *singlet*s at δ(H) 0.80, 1.04, 1.11, and 1.37, two Me *doublet*s at δ(H) 0.85 (J = 6.3 Hz) and δ(H) 1.29 (J = 6.2 Hz), an olefinic H-atom at δ(H) 6.01 (br. *s*), and one oxygenated methine at δ(H) 3.33 (*dd*, J = 11.5, 3.9 Hz, H–C(3)). Moreover, the ^{13}C-NMR spectrum showed characteristic signals of two carboxy groups, one esterified at δ(C) 180.0 (C(28)), the other as the free acid at 178.0 (C(27)). Further, a quaternary olefinic C-atom was observed at δ(C) 135.7 (C(13)). These data indicated an ursane aglycone with a pentacyclic skeleton and a classical C=C bond at C(12), as well as two COO functions at C(27) and C(28), corresponding to quinovic acid [2]. The relative configurations at C(18), C(19), C(20), and C(3) were determined by a NOESY experiment: cross-peaks between H–C(18) at δ(H) 2.82 (*d*, J = 11.3 Hz) and both Me(29) at δ(H) 1.29 (*d*, J = 6.2 Hz) and H–C(20) at δ(H) 1.04, as well as between H–C(3) at δ(H) 3.33 (*dd*, J = 11.5, 3.9 Hz) and both H–C(5) at δ(H) 1.02 and Me(23) at δ(H) 1.37 (*s*), indicated β-axial positions for H–C(18) and H–C(20), and α-axial positions for H–C(19) and H–C(3), respectively. The downfield shifts for δ(C) 89.5 (C(3)) and δ(C) 180.0 (C(28)) revealed a glycosidic linkage at C(3) and a free COOH group at C(28), respectively.

The ^{1}H-NMR spectrum of **3** showed only one anomeric H-atom signal at δ(H) 4.80 (*d*, J = 7.1 Hz), which correlated in the HSQC spectrum with an anomeric C-atom signal at δ(C) 102.9. This sugar was determined as a Glc moiety with an OSO_3H group in 2-position, as suggested by the Glc H–C(2) and C(2) resonances at δ(H) 4.92 (*t*, J = 8.2 Hz) and δ(C) 80.6, respectively.

In the HR-ESI mass spectrum of **4**, the $[M+Na]^+$ peak was observed at *m/z* 965.4737 (calc. 965.4722), consistent with the molecular formula $C_{47}H_{74}O_{19}$. Negative-ion FAB-MS showed the $[M-H]^-$ peak at *m/z* 941, indicating a molecular weight of 942. 2D-NMR-Spectroscopic analysis of compound **4** led to the establishment of its structure as 3-*O*-[α-L-arabinopyranosyl-(1 $\rightarrow$ 2)-β-D-glucopyranosyl]quinovic acid 28-(β-D-glucopyranosyl) ester.

In the ^{1}H- and ^{13}C-NMR spectra of **4**, the aglycone displayed the same signals as **3**, except for C(28), δ(C) 176.7 revealing esterification. The ^{1}H-NMR spectrum of **4** showed three anomeric H-atom signals at δ(H) 6.21 (*d*, J = 8.1 Hz), 5.06 (*d*, J = 6.7 Hz), and 4.66 (*d*, J = 7.8 Hz), which gave HSQC correlations with three anomeric C-atom signals at δ(C) 95.4, 106.1, and 104.6, respectively. One α-L-Ara group and two β-D-Glc moieties were identified by NMR analysis. An HMBC correlation between δ(H) 6.21 (*d*, J = 8.1 Hz, Glc H–C(1)) and δ(C) 176.7 (C(28)) indicated an ester linkage between the aglycone and a Glc moiety. An HMBC cross-peak between δ(H) 4.66 (*d*, J = 7.8 Hz) and C(3) at δ(C) 88.7, and a NOESY cross-peak between δ(H) 4.66 and H–C(3) at δ(H) 3.10 (*dd*, J = 11.7, 4.0 Hz) indicated that the 3-position of the aglycone carried a second Glc moiety, with HMBC connectivities of Glc H–C(2) at δ(H) 3.99 with Ara C(1) at δ(C) 106.1, and of Ara H–C(1) at δ(H) 5.06 (*d*, J = 6.7 Hz) with Glc C(2) at δ(C) 83.2, revealing an Ara residue at the Glc C(2) position.

The four known compounds were identified as zygophylosides E, G, and H [2], and 3-*O*-(*β*-D-quinovopyranosyl)quinovic acid 28-(*O*-*β*-D-glucopyranosyl) ester [3], on the basis of their NMR and MS data, and by comparison with the literature data.

Notably, all of the eight isolated saponins possess an ursane-type aglycone, most of them carrying sulfate moieties, which is in accordance with related glycosides previously obtained from several species of *Zygophyllum* [4]. These metabolites may represent chemotaxonomic markers of this genus.

Experimental Part

General. Vacuum liquid chromatography (VLC): silica gel *RP-18* (25–40 μm; *Merck*). Medium-pressure liquid chromatography (MPLC): silica gel *60* (15–40 μm; *Merck*), *Gilson M-303* pump, *Büchi* glass column (460 × 25 mm, and 460 × 15 mm), *Büchi* pre-column (110 × 15 mm). TLC and HP-TLC: silica gel *60* F_{254} (*Merck*); solvent systems: $CHCl_3$/MeOH/H_2O 13:7:2, lower phase (*A*), $CHCl_3$/MeOH/H_2O 8:5:1 (*B*); spray reagent: *Komarowsky* reagent, 2% 4-hydroxybenzaldehyde in 50% H_2SO_4/MeOH 1:5. Optical rotations: *AA-OR automatic* polarimeter. 1D- and 2D-NMR Spectra: see [6]; δ in ppm, *J* in Hz. FAB-MS (negative-ion mode; glycerol matrix): *JEOL SX-102* spectrometer; in *m/z*. HR-ESI-MS (positive-ion mode): *Q-TOF 1-Micromass*.

Plant Material. Zygophyllum geslini Coss. was collected in Ouargla, Algeria, in September 2001, and identified by Mr. *Abdelkader Beloued* (*Institut National Agronomique* (*INA*), Alger, Algeria), where a voucher specimen (No. 6063) was deposited.

Extraction and Isolation. The dried, powdered roots of *Zygophyllum geslini* (383 g) were repeatedly extracted at reflux with MeOH/H_2O 7:3 (3 × 4 l) for 1 h each. The extract was concentrated to dryness, and the residue (42.5 g) was dissolved in H_2O (300 ml), and then extracted with H_2O-sat. BuOH (3 × 300 ml). The BuOH layer was concentrated to dryness, and the residue (12.9 g) was solubilized in MeOH (20 ml) and purified by precipitation with Et_2O (3 × 500 ml): 5.9 g of a crude saponin mixture. This residue was fractionated by successive MPLC (SiO_2; $CHCl_3$/MeOH/H_2O 8:5:1, $CHCl_3$/MeOH/H_2O 13:7:2, lower phase) to afford **1** (15 mg), **4** (5 mg), zygophyloside E (11 mg), zygophyloside G (12 mg), zygophyloside H (6 mg), and 3-*O*-(*β*-D-quinovopyranosyl)quinovic acid 28-(*O*-*β*-D-glucopyranosyl) ester (12 mg).

The dried, powdered aerial parts of *Z. geslini* (250 g) were extracted according to the same protocol as reported above for the roots, but the BuOH-soluble residue (19 g) was submitted to VLC (*RP-18*; H_2O/MeOH gradient) to afford five fractions (*Fr. 1–5*). *Fr. 3* (152 mg), eluted with MeOH/H_2O 1:1, was fractionated by MPLC (SiO_2; $CHCl_3$/MeOH/H_2O 13:7:2, lower phase) to afford zygophyloside G (21 mg). *Fr. 4* (107 mg), eluted with MeOH/H_2O 7:3, was purified by MPLC (same system) to afford **1** (7 mg), **2** (6 mg), **3** (7 mg), and zygophyloside E (7 mg).

Acid Hydrolysis. A part (200 mg each) of the Et_2O-precipitated residue from the roots, and of the BuOH-soluble residue from the aerial parts, respectively, was refluxed in 2N aq. CF_3COOH for 2 h. After extraction with $CHCl_3$, the aq. layer was repeatedly evaporated to dryness with MeOH, until neutral. Glucopyranuronic acid, glucose, arabinose, and rhamnose were identified by comparison with authentic samples by TLC (solvent system *B*). After prep. TLC (solvent system *B*) of the sugar mixture, the optical rotation of each purified sugar was measured.

*(3β)-3-{[6-Deoxy-α-*L*-mannopyranosyl-(1 → 2)-α-*L*-arabinopyranosyl-(1 → 2)-β-*D*-glucopyranurosonyl]oxy}urs-20-en-28-oic Acid 28-(2-*O*-Sulfo-β-*D*-glucopyranosyl) Ester* (**1**). Colorless, amorphous powder. TLC (eluent *A*): R_f 0.20. $[\alpha]_D^{25} = +15$ ($c = 0.19$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. FAB-MS (neg.): 1151 ($[M-H]^-$), 909 ($[M-H-162-80]^-$), 873 ($[M-H-146-132]^-$), 697 ($[M-H-146-132-176]^-$). HR-ESI-MS (pos.): 1175.4932 ($[M+Na]^+$, $C_{53}H_{84}NaO_{25}S^+$; calc. 1175.4920).

*(3β)-3-[(2-*O*-Sulfo-β-*D*-glucopyranurosonyl)oxy]urs-20-en-28-oic Acid 28-(2-*O*-Sulfo-β-*D*-glucopyranosyl] Ester* (**2**). Colorless, amorphous powder. TLC (eluent *A*): R_f 0.22. $[\alpha]_D^{25} = +23$ ($c = 0.10$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. FAB-MS (neg.): 873 ($[M-H-80]^-$), 711

([M – H – 80 – 162]$^-$), 697 ([M – H – 80 – 176]$^-$). HR-ESI-MS (pos.): 977.3507 ([M + Na]$^+$, $C_{42}H_{66}NaO_{20}S_2^+$; calc. 977.3487).

*(3β)-3-[(2-*O*-Sulfo-β-*D*-glucopyranosyl)oxy]urs-12-ene-27,28-dioic Acid* (**3**). Colorless, amorphous powder. TLC (eluent *A*): R_f 0.39. $[\alpha]_D^{25} = +15$ ($c = 0.10$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. FAB-MS (neg.): 727 ([M – H]$^-$), 683 ([M – H – 44]$^-$), 603 ([M – H – 44 – 80]$^-$). HR-ESI-MS (pos.): 751.3349 ([M + Na]$^+$, $C_{36}H_{56}NaO_{13}S^+$; calc. 751.3339).

(3β)-3-[(α-L-Arabinopyranosyl-(1→2)-β-D-glucopyranosyl)oxy]urs-12-ene-27,28-dioic Acid 28-(β-D-Glucopyranosyl) Ester (**4**). Colorless, amorphous powder. TLC (eluent *A*): R_f 0.74. $[\alpha]_D^{25} = +20$ ($c = 0.15$, MeOH). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. FAB-MS (neg.): 941 ([M – H]$^-$). HR-ESI-MS (pos.): 965.4737 ([M + Na]$^+$, $C_{47}H_{74}NaO_{19}^+$; calc. 965.4722).

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