New triterpenoid saponin from the stems of *Albizia adianthifolia* (Schumach.) W.Wight

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Abstract

As part of our continuing study of apoptosis-inducing saponins from Cameroonian *Albizia* genus, one new triterpenoid saponin, named adianthifolioside J (**1**), together with the known gummiferaoside E (**2**), were isolated from *Albizia adianthifolia* stems. The structure of the new saponin (**1**), was established on the basis of extensive analysis of 1D and 2D NMR (^{1}H-, ^{13}C-NMR, DEPT, COSY, TOCSY, NOESY, HSQC, HSQC-TOCSY and HMBC) and HRESIMS experiments, and by chemical evidence as 3-*O*-[*β*-D-xylopyranosyl-(1→2)-*β*-D-fucopyranosyl-(1→6)-*β*-D-glucopyranosyl]-21-*O*-{(2E,6S)-2-(hydroxymethyl)-6-methyl-6-*O*-{4-*O*-[(2E,6S)-2,6-dimethyl-6-*O*-(*β*-D-quinovopyranosyl)octa-2,7-dienoyl]-(*β*-D-quinovopyranosyl)octa-2,7-dienoyl]}acacic acid-28-*O*-*β*-D-glucopyranosyl-(1→3)-[5-*O*-acetyl-*α*-L-arabinofuranosyl-(1→4)]-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-glucopyranosyl ester (**1**)**.** The pro-apoptotic activity of the new isolated saponin **1** was evaluated, using Annexin V-FITC binding assay, on the A431 human epidermoid cancer cell. The result showed that adianthifolioside J (**1**) displayed weak pro-apoptotic activity.

Keywords: *Albizia adianthifolia; Mimosaceae; Triterpenoid saponins; NMR; Human epidermoid cancer cell (A431).*

Supplementary material

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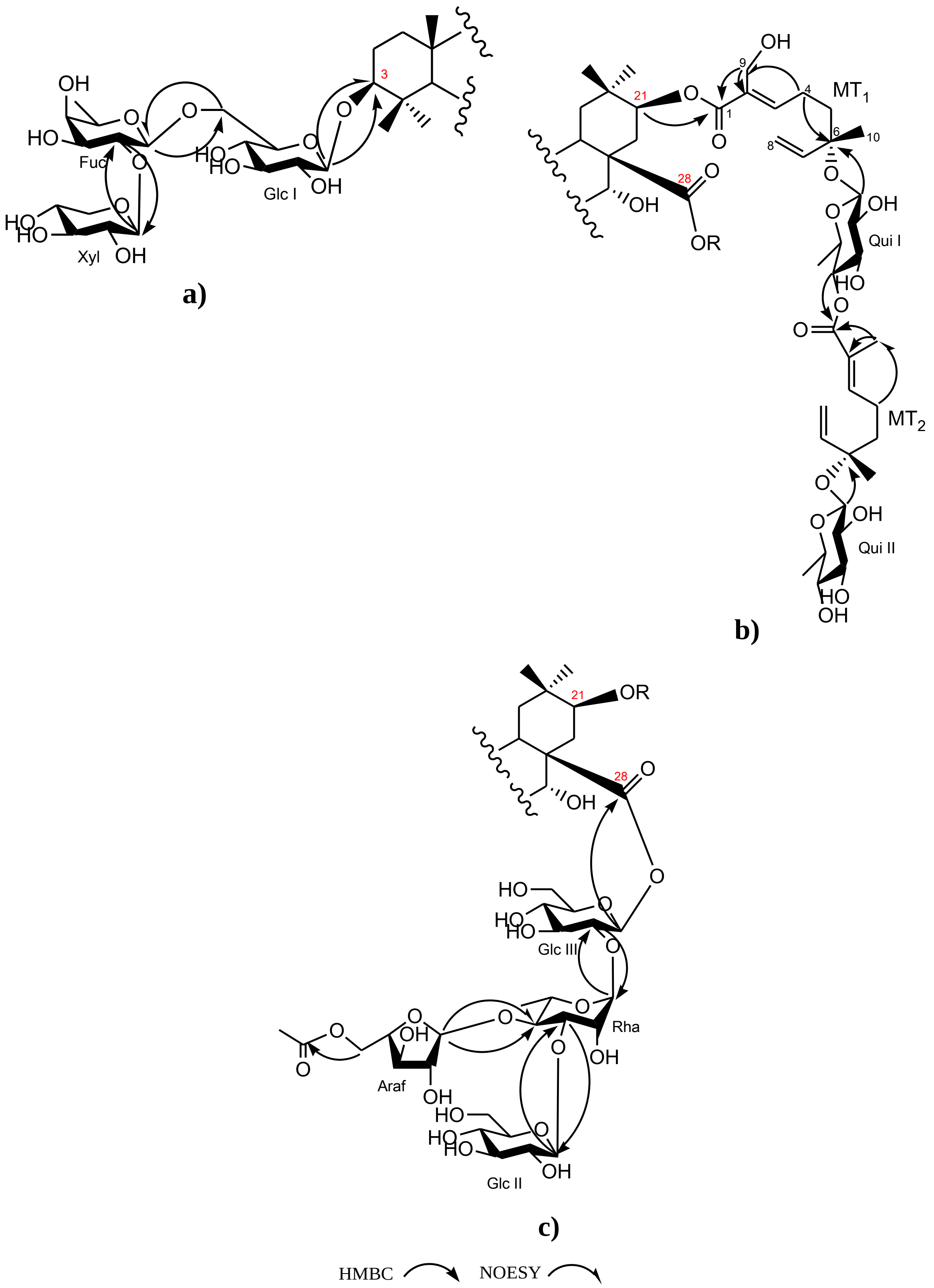

Fig.S1. Key HMBC and NOESY correlations of adianthifolioside J (**1**)

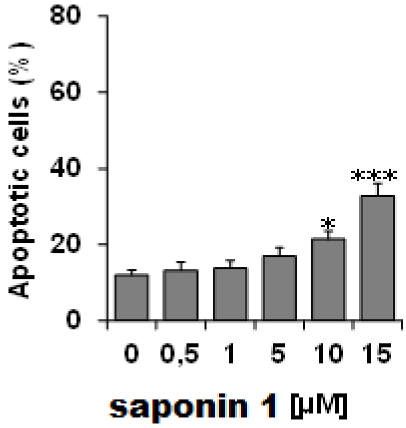

Fig. S2. Effects of saponin **1** on the apoptosis rate.
Cells were exposed to the isolated new saponin (**1**) at the indicated concentrations and incubated for 24 h. Cell apoptosis rate was assessed by flow cytometry using the Annexin V-FITC/ PI staining assay (n = 3). *P < 0.05 and ***P < 0.001 vs. vehicle-treated cells.

Table S1. *^{13}C-NMR (125 MHz) and ^{1}H-NMR (500 MHz) data of the Aglycone part of compounds **1–2** (in pyridine-d_5; δ in ppm)[a].*

DEPT	**1**		**2**	
	δ_C	δ_H (*multiplicity*)	δ_C	δ_H (*multiplicity*)
CH_2 (1)	38.7	1.61 ; 1.19	38.7	1.60 ; 1.19
CH_2 (2)	26.4	2.31; 1.94	26.6	2.29 ; 1.95
CH(3)	88.5	3.52	88.3	3.62
C (4)	39.4	-	39.4	-
CH(5)	55.7	0.99	55.8	0.99
CH_2 (6)	18.5	1.56; 1.70	18.4	1.70 ; 1.48
CH_2 (7)	33.3	1.75; nd	33.4	1.74 ; nd
C (8)	39.9	-	39.9	-
CH(9)	46.9	1.90	46.9	1.93
C (10)	36.8	-	36.8	-
CH_2 (11)	23.7	2.09; 1.53	23.5	2.09 ; 1.52
CH(12)	122.9	5.62 (*brs*)	122.8	5.64 (*brs*)
C (13)	143.0	-	143.1	-
C (14)	41.8	-	41.8	-
CH_2 (15)	35.7	2.29; 2.04	35.7	2.29 ; 2.05
CH(16)	73.6	5.25	73.7	5.24
C (17)	51.4	-	51.4	-
CH(18)	40.6	3.47	40.7	3.46
CH_2 (19)	47.6	2.97; 1.42	47.6	2.97 ; 1.42
C (20)	35.2	-	35.2	-
CH(21)	77.3	6.33	76.9	6.32
CH_2 (22)	36.2	2.74; 2.20	36.2	2.74 ; 2.20
CH_3 (23)	27.9	1.37 (*s*)	27.9	1.30 (*s*)
CH_3 (24)	15.6	0.98 (*s*)	15.7	0.98 (*s*)
CH_3 (25)	17.0	1.06 (*s*)	17.0	1.06 (*s*)
CH_3 (26)	17.0	1.19 (*s*)	17.0	1.18 (*s*)
CH_3 (27)	27.1	1.90 (s)	27.0	1.90 (*s*)
C (28)	174.1	-	174.2	-
CH_3 (29)	29.0	1.06 (*s*)	28.9	1.06 (*s*)
CH_3 (30)	18.9	1.11 (*s*)	18.9	1.11 (*s*)

Assignments based on the HMBC, HSQC, COSY, HSQC-TOCSY, NOESY, and DEPT experiments.
nd, not determined [a)] Overlapped proton NMR signals are reported without designated multiplicity.

Table S2. *^{13}C-NMR (125 MHz) and ^{1}H-NMR (500 MHz) Data of the Sugar Moieties attached at C-3 and C-28 of compounds **1**–**2** (in pyridine-d$_5$; δ in ppm)*[a].

Position	1		2	
	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)
3-O-sugars				
Glc I				
1	104.6	5.08 (*d*, *J*= *8.1*)	104.7	4.90 (*d*, *J* =*7.8*)
2	75.7	4.09	75.3	4.04
3	78.2	4.15	78.2	4.16
4	71.5	3.98	71.9	3.98
5	77.6	4.03	78.0	4.03
6	69.7	4.74; 4.35	69.8	4.74 ; 4.36
Fuc				
1	103.2	5.02 (*d*, *J*=*7.8*)	103.2	4.97 (*d*, *J*=*8.0*)
2	82.1	4.48	82.1	4.44
3	75.0	4.12	75.0	4.14
4	72.0	4.01	71.1	3.76
5	71.4	3.75	70.5	3.69
6	17.0	1.51 (*d*, *J*= *6.5*)	17.0	1.50 (*d*, *J*= *6.4*)
Xyl				
1	107.0	5.00 (*d*, *J*=*7.2*)	106.8	5.08 (*d*, *J*=*7.0*)
2	75.7	4.07	75.7	4.06
3	77.3	4.02	77.4	4.03
4	70.9	4.08	70.5	4.11
5	67.0	4.46; 3.59	67.0	4.46 ; 3.61
28-O-sugars				
Glc II				
1	95.5	6.09 (*d*, *J*=*8.1*)	95.5	6.08 (*d*, *J*=*8.0*)
2	76.6	3.98	76.6	4.03
3	78.2	4.17	78.2	4.14
4	71.6	4.03	71.5	4.10
5	77.3	3.96	77.4	4.05
6	61.6	4.35; 4.23	61.6	4.36 ; 4.23
Rha				
1	101.7	5.83 (*brs*)	101.6	5.92 (*brs*)
2	70.2	5.21	70.2	5.21
3	81.6	4.95	81.8	4.97
4	78.9	4.52	78.9	4.51
5	69.0	4.55	69.0	4.57
6	18.2	1.77 (*d*, *J*=*5.7*)	18.5	1.78 (*d*, *J*=*5.5*)
Glc III				
1	105.6	5.34 (*d*, *J*= *8.0*)	105.5	5.36 (*d*, *J*= *8.0*)
2	75.0	4.00	75.3	4.02
3	77.6	4.16	78.2	4.18
4	71.1	4.07	71.5	4.10
5	78.7	3.96	78.8	3.97
6	62.6	4.50; 4.20	62.5	4.51 ; 4.18
Ara$_f$				
1	110.9	6.24 (*d*, *J*=*6.9*)	110.8	6.29 (brs)
2	84.3	4.96	84.3	5.00
3	78.7	4.48	78.9	4.83
4	81.1	4.74	85.2	4.77
5	64.6	4.69; 4.50	62.3	4.27 ; 4.16
A$_C$	170.4	-		
	20.5	1.92 (*s*)		

Assignments were based on the HMBC, HSQC, COSY, TOCSY, NOESY, and DEPT experiments.
[a)]Overlapped proton NMR signals are reported without designated multiplicity.

Table S3. [13]*C-NMR (125 MHz) and* [1]*H-NMR (500 MHz) Data of the Quinovosyl Moieties attached at C-21 of compounds* ***1*–*3*** *(in pyridine-d_5; δ in ppm)*[a].

Quinovose (Qui)	**1**		**2**	
	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)
Qui I				
1	99.1	4.90 (*d, J =7.8*)	99.1	4.90 (*d, J =7.8*)
2	75.7	3.98	75.3	4.03
3	75.2	4.15	75.2	4.21
4	76.9	5.35	76.9	5.36
5	69.9	3.69	70.9	3.77
6	18.2	1.37 (*d, J =6.0*)	18.7	1.36 (*d, J =6.0*)
Qui II				
1	99.1	4.87 (*d, J =7.8*)	99.1	4.87(*d, J =7.9*)
2	75.3	3.96	75.3	4.03
3	78.2	4.16	75.7	4.21
4	76.7	3.71	76.9	5.37
5	72.4	3.70	72.6	3.76
6	18.7	1.62 (*d, J =5.5*)	18.7	1.63 (*d, J =5.5*)
Qui III				
1			96.7	4.96 (*d, J=8.0*)
2			75.7	4.02
3			75.7	4.23
4			76.7	3.73
5			72.4	3.72
6			18.7	1.60 (*d, J =6.0*)

Assignments based on the HMBC, HSQC, COSY, TOCSY, NOESY, and DEPT experiments.
[a)]Overlapped proton NMR signals are reported without designated multiplicity

Table S4. *^{13}C-NMR (125 MHz) and ^{1}H-NMR (500 MHz) Data of the Monoterpene Moieties Attached at C-21 of compounds **1–2** (in pyridine-d$_5$; δ in ppm)*[a].

Monoterpene (MT)	**1**		**2**	
	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)
MT_1				
1	167.2	-	167.4	-
2	133.6	-	133.6	-
3	143.9	7.05 (*t, J= 7.3*)	145.0	7.06 (*t, J= 7.1*)
4	23.5	2.66; nd	23.5	2.70 ; 2.46
5	40.6	1.84; nd	40.3	1.82 ; 1.75
6	79.5	-	79.3	-
7	143.7	6.23 (*dd, J=11.2; 17.8*)	143.8	6.24 (*dd, J=11.5; 17.7*)
8	114.6	5.44 (*d, J=17.8*); 5.25 (*d, J=11.2*)	114.7	5.44 (*d, J=17.7*); 5.24 (*d, J=11.5*)
9	55.7	4.74 (*brs*)	55.8	4.75 (*brs*)
10	23.7	1.53 (*s*)	23.6	1.56 (*s*)
MT_2				
1	167.5	-	167.3	-
2	127.7	-	127.9	-
3	143.7	7.05 (*t, J= 7.3*)	142.8	7.00 (*t, J= 7.1*)
4	23.5	2.44; nd	23.3	2.70 ; 2.46
5	40.2	1.76; nd	40.6	1.82 ; 1.75
6	79.2	-	79.2	-
7	143.7	6.24 (*dd, J=11.2; 17.8*)	143.9	6.24 (*dd, J=11.5; 17.7*)
8	114.9	5.45 (*d, J=17.8*); 5.24 (*d, J=11.2*)	115.0	5.43 (*d, J=17.7*); 5.26 (*d, J=11.5*)
9	12.5	1.90 (*s*)	12.5	1.90 (*s*)
10	23.5	1.56 (*s*)	23.7	1.53 (*s*)
MT_3				
1			167.0	-
2			127.9	-
3			143.0	7.08 (*t, J= 7.0*)
4			23.2	2.70 ; 2.46
5			40.8	1.82 ; 1.75
6			79.2	-
7			143.6	6.26 (*dd, J=11.0; 17.5*)
8			115.3	5.39 (*d, J=17.5*); 5.31 (*d, J=11.0*);
9			12.5	1.93 (*s*)
10			23.5	1.51 (*s*)

Assignments based on the HMBC, HSQC, COSY, TOCSY, NOESY, and DEPT experiments.
nd, not determined. [a)]Overlapped proton NMR signals are reported without designated multiplicity.

Table S5. HMBC and NOESY correlations of oligosaccharide *moieties attached at C-3, C-28, and C-21 of compounds **1**–**2** (in pyridine-d$_5$; δ in ppm)*

adianthifolioside J (**1**)	***Compound 2***
Oligosaccharide *moiety attached at C-3*	**Oligosaccharide *moiety attached at C-3***
HMBC correlations	HMBC correlations
H-1 Glc I (5.08) – C-3 Agly (88.5)	H-1 Xyl (5.08) – C-2 Fuc (82.1)
H-1 Fuc (5.02) – C-6 Glc I (69.7)	
H-2 Fuc (4.48) – C-1 Xyl (107.0)	
NOESY correlations	NOESY correlations
H-1 Glc I (5.08) – H-3 Agly (3.52)	H-1 Xyl (5.08) – H-2 Fuc (4.44)
H-1 Fuc (5.02) – H-6a Glc I (4.35)	
H-1 Fuc (5.02) – H-6b Glc I (4.74)	
H-1 Xyl (5.00) – H-2 Fuc (4.48)	
Oligosaccharide *moiety attached at C-28*	**Oligosaccharide *moiety attached at C-28***
HMBC correlations	HMBC correlations
H1 Glc II (6.09) – C28 Agly (174.1)	H-1 Glc II (6.08) – C-28 Agly (174.2)
H1 Rha (5.83) – C2 Glc II (76.6)	H-1 Glc III (5.36) – C-3 Rha (81.8)
H2 Glc II (3.98) – C1 Rha (101.7)	H-1 Araf (6.29) – C-4 Rha (78.9)
H1 Glc III (5.34) – C3 Rha (81.6)	
H1 Araf (6.24) – C4 Rha (78.9)	
H4 Rha (4.52) – C1 Araf (110.9)	
H5 Araf (4.50) – C1 Ac (170.4)	
NOESY correlations	NOESY correlations
H1 Rha (5.83) – H2 Glc II (3.98)	H-1 Glc III (5.36) – H-3 Rha (4.97)
H1 Glc III (5.34) – H3 Rha (4.85)	H-1 Araf (6.29) – H-4 Rha (4.51)
H1 Araf (6.24) – H4 Rha (4.52)	
MT-Qui *moiety attached at C-21*	**MT-Qui *moiety attached at C-21***
HMBC correlations	HMBC correlations
H-21 Agly (6.33) – C-1 MT$_1$ (167.2)	H-9 MT I (4.75) – C-1 MT I (167.4)
H-1 Qui I (4.90) – C-6 MT$_1$ (79.5)	H-1 Qui I (4.90) – C-6 MT I (79.3)
H-4 Qui I (5.35) – C-1 MT$_2$ (167.5)	H-9 MT I (4.75) – C-3 MT I (145.0)
H-1 Qui II (4.87) – C-6 MT$_2$ (79.2)	
H-9 MT$_1$ (4.74) – C-1 MT$_1$ (167.2)	H-9 MT II (1.90) – C-1 MT II (167.3)
H-9 MT$_1$ (4.74) – C-2 MT$_1$ (133.6)	H-1 Qui II (4.87) – C-6 MT II (79.2)
	H-9 MT II (1.90) – C-2 MT II (142.8)
H-9 MT$_2$ (1.90) – C-1 MT$_2$ (167.5)	
H-9 MT$_2$ (1.90) – C-2 MT$_2$ (127.7)	H-9 MT III (1.93) – C-1 MT III (167.0)
	H-1 Qui III (4.96) – C-6 MT III (79.2)
	H-9 MT III (1.93) – C-2 MT III (143.0)
NOESY correlations	
H-4a MT$_1$ (2.66) – H_3-9 MT$_1$ (4.74)	
H-4a MT$_2$ (2.44) – H_3-9 MT$_2$ (1.90)	