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Triterpenoid saponins with *N*-acetyl sugar from the bark of *Albizia procera*

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Abstract

Three (**1**,**2**,**4**) and one known (**3**) triterpenoid saponins were isolated from the bark of *Albizia procera*. The saponins were characterized as 3-*O*-[β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-2-acetamido-2-deoxy-β-D-glucopyranosyl] echinocystic acid (**1**), 3-*O*-[α-L-arabinopyranosyl-(1 → 2)-β-D-fucopyranosyl-(1 → 6)-2-acetamido-2-deoxy-β-D-glucopyranosyl] echinocystic acid (**2**) and 3-*O*-[β-D-xylopyranosyl-(1 → 2)-α-L-arabinopyranosyl-(1 → 6)-2-acetamido-2-deoxy-β-D-glucopyranosyl] acacic acid lactone (**4**). Their structures were elucidated by 1D and 2D NMR experiments, FABMS as well as chemical means. Saponins **1** and **3** exhibited cytotoxicity against HEPG2 cell line with IC_{50} 9.13 μg/ml and 10 μg/ml, respectively.

Keywords: *Albizia procera*; Leguminosae; Triterpenoid saponin; Echinocystic acid; Acacic acid lactone

1. Introduction

Albizia procera (Leguminosae) is a tree cultivated in streets and public gardens in Egypt. In folk medicine, the bark is considered useful in pregnancy and stomachache. It is also used as a medicine for water buffalo when given with salt.

As a part of our continuing interest in bioactive saponins from plants grown in Egypt (Miyase et al., 1996; Melek et al., 2002, 2003a,b, 2004a,b), we examined the saponin mixture from the bark of *A. procera* Benth. Previous phytochemical study on saponins from the seeds of this plant led to the isolation of four acylated triterpenoid saponins namely, proceraosides A–D (Yoshikawa et al., 1998). We present in this report the isolation and structure elucidation of four saponins **1**–**4** including three new ones from the bark of *A. procera*.

2. Results and discussion

The dried bark of *A. procera* was extracted twice with methanol followed by once with 50% aqueous methanol. The extracts were combined and the crude saponin mixture from the combined extract was subjected to column chromatography on a porous polymer polystyrene resin (Diaion HP-20) and silica gel followed by HPLC to give four saponins (**1**–**4**) including three new ones (**1**, **2**, **4**). The NMR data of the isolates are shown in Tables 1–3.

The positive ion FAB-mass spectrum of **1** exhibited a quasi-molecular ion peak $[M+Na]^+$ at *m*/*z* 962, corresponding to a molecular formula $C_{48}H_{77}NO_{17}$. The ^1H NMR spectrum of **1** showed signals due to seven tertiary methyl groups at δ 0.87, 0.98, 1.02, 1.06, 1.18, 1.19 and 1.87. Further feature were signals at δ 5.59 (*br t*, $J = 3.0$ Hz) ascribable to a vinylic proton and at δ 3.42 (*dd*, $J = 12.0$, 4.0 Hz) typical for an axial proton attached to a hydroxylate carbon. The ^{13}C NMR spectrum of **1** displayed two signals located at δ 122.5 and 145.1 which confirmed the presence of a double bond and a signal at δ

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Table 1
^{1}H NMR spectral data for compounds **1**–**4** in pyridin-d_5

	1	**2**	**3**	**4**
Aglycone				
3	3.42(*dd*, 12.0, 4.0)	3.46(*dd*, 12.5, 4.5)	3.37(*dd*, 12.0, 5.0)	3.43(*dd*, 11.5, 4.0)
5	0.89	0.93(*d*, 12.0)	0.89	0.98
12	5.59(*br t*, 3.0)	5.58(*br t*, 3.0)	5.61(*br t*, 2.5)	5.30(*br t*, 3.0)
16	5.23(*br s*)	5.23(*br s*)	5.25(*br s*)	4.52(*brs*)
18	3.59	3.59(*dd*, 14.0, 3.0)	3.60(*dd*, 15.0, 3.0)	2.77(*dd*, 17.0, 5.5)
19	1.38	1.37	1.37	1.37
19′	2.80(*t*, 13.0)	2.79(*t*, 13.0)	2.81(*t*, 14.0)	1.82
21	1.38	1.37	1.37	4.23(*d*, 5.0)
21′	2.50(*dt*, 13.0, 4.0)	2.50	2.50	
23	1.19(*s*)	1.22(*s*)	1.19(*s*)	1.21(*s*)
24	0.98(*s*)	1.01(*s*)	0.98(*s*)	0.99(*s*)
25	0.87(*s*)	0.87(*s*)	0.86(*s*)	0.82(*s*)
26	1.02(*s*)	1.03(*s*)	1.03(*s*)	0.80(*s*)
27	1.87(*s*)	1.86(*s*)	1.85(*s*)	1.38(*s*)
29	1.06(*s*)	1.05(*s*)	1.07(*s*)	0.92(*s*)
30	1.18(*s*)	1.19(*s*)	1.18(*s*)	1.07(*s*)
3-O-sugar GlcNHAc				
1	5.03(*d*, 8.0)	5.05(*d*, 8.0)	5.03(*d*, 7.5)	5.05(*d*, 8.0)
2	4.52(*t*, 8.5)	4.56(*t*, 8.5)	4.53(*t*, 9.0)	4.51(*t*, 9.0)
3	4.35(*t*, 8.5)	4.33(*t*, 8.5)	4.33(*t*, 9.0)	4.34(*t*, 9.0)
4	4.11	4.21(*brt*, 8.5)	4.13(*dd*, 9.0, 8.0)	4.11
5	4.03(*m*)	4.03(*m*)	4.02(*m*)	4.02(*m*)
6	4.19(*dd*, 11.0, 4.0)	4.36(*dd*, 11.0, 4.0)	4.22(*dd*, 11.5, 4.0)	4.19(*dd*, 10.0, 4.0)
6′	4.62(*d*, 11.0)	4.70(*d*, 11.0)	4.61(*dd*, 11.5, 2.5)	4.64(*d*, 10.0)
Me(CONH)	2.14(*s*)	2.14(*s*)	2.13(*s*)	2.15(*s*)
NH	8.80(*d*, 9.0)	8.80(*d*, 9.0)	8.79(*d*, 9.0)	8.80(*d*, 9.0)
Ara				
1	5.13(*d*, 5.0)		5.08(*d*, 5.0)	5.14(*d*, 5.0)
2	4.50(*t*, 6.5)		4.52(*t*, 6.0)	4.50(*t*, 6.5)
3	4.37(*dd*, 6.5, 4.0)		4.33(*dd*, 6.0, 3.5)	4.36(*dd*, 6.5, 4.0)
4	4.37(*brs*)		4.33(*brs*)	4.36(*brs*)
5	3.75(*d*, 11.0)		3.73(*dd*, 12.0, 2.0)	3.75(*dd*, 11.5, 2.0)
5′	4.28(*dd*, 11.0, 5.0)		4.30(*dd*, 1 2.0, 4.0)	4.28(*dd*, 11.5, 5.0)
Fuc				
1		4.94(*d*, 7.5)		
2		4.47(*t*, 8.0)		
3		4.12(*dd*, 8.0, 3.5)		
4		3.99(*d*, 3.5)		
5		3.75(*q*, 6.5)		
6		1.48(*d*, 6.5)		
Xyl				
1	4.98(*d*, 7.0)			4.98(*d*, 7.0)
2	4.00(*t*, 8.0)			4.00(*t*, 7.5)
3	4.05(*t*, 8.0)			4.05(*t*, 8.0)
4	4.11			4.11
5	3.58(*dd*, 12.0, 10.0)			3.59(*dd*, 12.0, 10.0)
5′	4.38(*dd*, 12.0, 6.0)			4.38(*dd*, 12.0, 6.0)
Ara				
1		5.22(*d*, 6.0)	5.05(*d*, 5.5)	
2		4.50(*t*, 6.5)	4.47(*dd*, 6.5, 6.0)	
3		4.13(*dd*, 7.0, 3.5)	4.10(*dd*, 7.5, 3.0)	
4		4.24(*brs*)	4.25(*brs*)	
5		3.64(*dd*,11.0, 2.5)	3.67(*dd*, 12.5, 2.0)	
5′		4.48(*dd*,11.0, 3.0)	4.40(*dd*, 12.5, 3.0)	

Values in parantheses are ^{1}H–^{1}H splitting. GlcNHAc, 2-acetamido-2-deoxy-β-D-glucopyranose; Ara, α-L-arabinopyranose; Fuc, β-D-fucopyranose; Xyl, β-D-xylopyranose.

180.0, suggesting the occurrence of COOH group. The spectrum also contained three signals at δ 102.4, 104.9 and 106.3 assigned to anomeric carbons of three sugar units. On the basis of the forgoing data, **1** was concluded to be a triterpene triglycoside with a triterpene acid moiety of oleanene skeleton. The downfield position of the axial