Available online at www.sciencedirect.com
SCIENCE DIRECT®
Phytochemistry 66 (2005) 621–626
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Hopane-type saponins from *Glinus lotoides* Linn

Tanusree Biswas, Moumita Gupta, Basudeb Achari, Bikas C. Pal *

Indian Institute of Chemical Biology, Medicinal Chemistry Division, 4, Raja S.C. Mullick Road, Kolkata 700032, India

Received 15 December 2004; received in revised form 9 February 2005

Abstract

Seven hopane-type saponins were isolated from the methanol extract of *Glinus lotoides*. Six of them were identified as novel compounds and designated as lotoideside A [3-*O*-β-D-xylopyranosyl (1 → 2)-α-L-rhamnopyranosyl-6α-*O*-β-D-xylopyranosyl-22-β-*O*-β-D-glucopyranosyl-16β-hydroxy hopane (**1**)], lotoideside B [3-*O*-β-D-xylopyranosyl (1 → 2)-α-L-rhamnopyranosyl-22-β-*O*-β-D-glucopyranosyl-6α,16β-dihydroxyhopane (**2**)], lotoideside C [3-*O*D-xylopyranosyl-6α-*O*-β-D-xylopyranosyl-16β-*O*-β-D-xylopyranosyl-22β-hydroxyhopane (**3**)], lotoideside D [3-*O*-β-D-xylopyranosyl-16β-*O*-α-L-arabinopyranosyl-6α,22-β-dihydroxyhopane (**4**)], lotoideside E [3-*O*-β-D-xylopyranosyl-6α-*O*-β-D-xylopyranosyl-16 β,22-β-dihydroxyhopane (**5**)], and lotoideside F [3-*O*-β-D-xylopyranosyl-22-β-*O*-β-D-glucopyranosyl-16β-hydroxyhopan-6-one (**6**)]. The known compound succulentoside B (**7**) was also encountered. Their structures were elucidated on the basis of one-and two-dimensional NMR spectroscopic techniques, ESIMS and chemical evidences.

Keywords: *Glinus lotoides*; *Mollugo hirta*; Aizoaceae; Hopane-type saponins; Lotoidesides A–F

1. Introduction

Glinus lotoides Linn. syn *Mollugo hirta* Thunb. (Aizoaceae) is distributed throughout India. It is used as a medicine against diarrhoea and bilious attacks, as a purgative and for curing boils, wounds and pains (Sastri, 2002). Previous work on the plant showed the presence of a number of triterpenoid sapogenins called mollugogenols A–C (Chakrabarti, 1969), mollugogenols E–G, oleanonic acid, a mixture of glycosides of sitosterol and stigmasterol, and mollugocin A (Barua et al., 1976) besides triterpenoid saponins (Hamed et al., 1996; Hamed and El-Emary, 1999). The present communication describes the isolation and characterization of six novel hopane-type saponins (**1**–**6**) besides the known compound succulentoside B (**7**).

2. Results and discussion

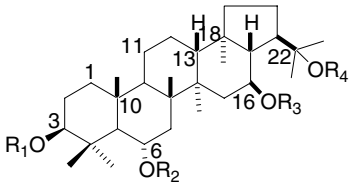
The crude methanolic extract of the whole plant was suspended in H_2O and washed with EtOAc to remove less polar compounds. It was then extracted with *n*-BuOH. The butanol soluble part was repeatedly subjected to normal and reversed-phase silica gel chromatography to give seven saponins. The known compound was identified as succulentoside B (**7**) by comparing its spectral data with those previously reported (Meselhy and Aboutabl, 1997).

The structure elucidation process of the six new saponins had a lot of similarity and therefore a general description is being provided. The isolates showed the expected $[M - H]^-$ ion peak in the negative ion ESIMS (for **1**–**3**) or the $[M + H]^+$ and/or $[M + Na]^+$ ion peak in the positive ion scan (for **4**–**6**). Taken in conjunction with the ^{13}C NMR evidence for the number of carbon atoms, their protonation levels from DEPT spectrum and chemical shift values, the molecular composition could be arrived at. Acid hydrolysis in each case

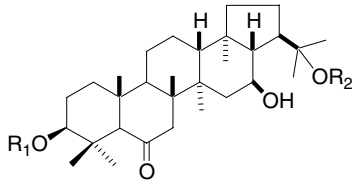
* Corresponding author. Tel.: +91 33 2473 3491; fax: +91 33 2473 5197.
E-mail address: bpal@iicb.res.in (B.C. Pal).

0031-9422/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2005.02.012

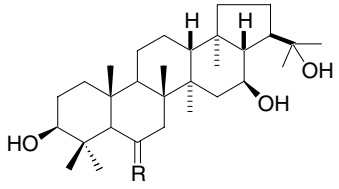
afforded the triterpenoid and the free sugars. Mollugogenol A (**8**) could be identified as the sapogenin for **1**–**5** and mollugogenol E (**9**) for **6** mainly by comparing the NMR data with those reported in the literature (Chakrabarti and Sanyal, 1970; Hamburger et al., 1989; Hamed et al., 1996; Patra et al., 1981). The sugars were identified by TLC comparison with authentic samples and their absolute configurations were determined by the measurement of optical rotation after separation by prep. TLC. That the sapogenins are genuine ones and not artefacts derived through acid mediated rearrangements or other structural changes was confirmed by comparing their ^{13}C NMR values with those of the original saponins.



	R_1	R_2	R_3	R_4
1.	Rha[1,2]-Xyl	Xyl	H	Glc
2.	Rha[1,2]-Xyl	H	H	Glc
3.	Xyl	Xyl	Xyl	H
4.	Xyl	H	Ara	H
5.	Xyl	Xyl	H	H
7.	Xyl	Ara	Xyl	H



	R_1	R_2
6.	Xyl	Glc



8. R = α OH, β H

9. R = O

Although the ^1H NMR spectra of all the compounds were not fully resolved even at 500 MHz, it was not difficult to pick out the anomeric proton signals, which served as convenient starting points for structure determination. The corresponding carbon signals were also easily identified from the HMQC spectrum. The chemical shifts of the anomeric protons of the identified sugars are distinct and well recognized. The observed coupling constants (J_{12}) easily identified the α or β configurations. Starting from the proton signals, thorough analysis of TOCSY, DQF-COSY, HMQC and HMBC spectra helped identify all the proton and carbon signals belonging to a particular sugar unit. The sugars directly attached to the sapogenin core were singled out from observed HMBC correlation of the concerned anomeric proton signal with identified carbon signal of the sapogenin. The inter-sugar linkages were similarly determined by noting the HMBC correlation of the anomeric proton signals with a particular signal of the other sugar.

It is noteworthy that saponins based on hopanes or rearranged hopane skeletons are very few in number. The isolated compounds are an important addition to this group.

3. Experimental

3.1. General

Mps: uncorr. Optical rotations were measured on a JASCO P-1020 polarimeter; IR spectra were taken on a JASCO-FT-IR-Model 410 spectrometer; ^1H NMR, ^{13}C NMR, ^1H–^1H COSY, TOCSY, HMBC and HMQC spectra were recorded using Bruker DRX (at 500 MHz) in DMSO-d_6 or pyridine-d_5. Q-TOF-MS (both positive and negative ion and MS–MS mode) was performed on a Q-TOF-Micromass spectrometer. TLC was carried out on silica gel 60 F_{254} (Merck) plates using $CHCl_3$–MeOH–H_2O (13:7:1) or $CHCl_3$–MeOH–H_2O (28:12:1) as developing solvent and the spots were visualized by spraying with Liebermann–Burchard reagent followed by heating at 120 °C. For HPLC, X-Terra preparative reverse phase C_{18} column (10 μm, 19 × 300 mm) was used [MeOH–H_2O–THF (5:4:1); flow 14 ml/min; RI detector, range 40].

3.2. Plant materials

The plant material was supplied by M/s. United Chemicals Ltd., Kolkata who maintain a voucher specimen at their Herbarium. Dr. N.D. Paria, Department of Botany, University of Calcutta identified the plant materials.

3.3. Extraction and isolation

The powdered air-dried whole plant (1 kg) of *G. lotoides* was extracted at room temperature with MeOH (4 lt × 3) for 7 days. After filtration and removal of solvent

Table 1
^{13}C NMR spectral data for lotoidesides A–F (**1**–**6**) at 125 MHz

	1[a]	**2**[a]	**3**[b]	**4**[b]	**5**[b]	**6**[b]
Aglycone						
1	39.4	39.5	39.2	39.3	39.3	40.0
2	26.4	26.7	26.8	26.8	26.8	26.8
3	89.1	88.9	89.2	89.5	89.5	87.9
4	39.2	39.0	40.8	40.6	40.7	38.6
5	60.7	60.8	60.8	61.8	60.9	65.4
6	80.1	67.2	80.3	66.9	80.0	212.2
7	43.9	44.0	43.7	44.8	44.3	51.9
8	43.0	43.1	43.2	43.3	43.3	48.9
9	49.8	49.7	50.0	50.0	50.0	50.4
10	40.9	40.9	39.3	39.4	39.4	43.6
11	21.3	21.3	21.3	21.4	21.4	21.7
12	24.1	24.1	24.0	24.1	24.1	23.7
13	49.0	49.0	49.2	49.3	49.3	49.2
14	43.8	43.8	44.3	44.4	44.4	44.1
15	43.7	46.0	43.1	44.2	44.8	44.0
16	65.9	65.8	79.9	80.3	66.9	66.1
17	62.1	62.2	59.3	60.9	61.8	62.0
18	45.7	45.7	46.6	46.0	46.0	45.7
19	42.1	42.1	41.9	42.1	42.1	41.9
20	27.5	27.5	28.5	28.2	28.2	27.7
21	50.4	50.4	52.9	52.1	52.1	50.7
22	82.9	82.8	73.3	73.4	73.4	83.2
23	30.6	31.0	31.5	31.5	31.2	27.8
24	16.5	16.8	16.9	17.1	17.1	16.9
25	17.8	17.7	17.5	17.6	17.6	17.3
26	18.8	18.9	18.6	18.7	18.7	16.9
27	18.7	18.7	18.4	18.7	18.7	18.8
28	17.8	17.8	17.4	17.5	17.5	17.4
29	26.6	26.6	31.3	31.3	31.5	26.4
30	24.9	25.1	27.5	27.8	27.8	25.0
Sugar moiety						
Xyl′						
1	105.6	105.8	108.1	108.0	108.0	107.7
2	77.9	77.8	75.8	75.7	75.7	75.6
3	78.5	78.7	78.4	78.6	78.6	78.7
4	70.4	70.8	71.4	71.4	71.4	71.3
5	66.1	66.3	67.5	67.2	67.1	67.3
Xyl″						
1	105.9		106.5		106.8	
2	74.5		75.2		75.2	
3	79.6		79.2		79.2	
4	70.7		71.0		71.2	
5	66.3		67.2		67.0	
Xyl‴						
1			104.8			
2			75.1			
3			78.7			
4			71.2			
5			67.3			
Rha						
1	100.8	100.9				
2	71.3	71.1				
3	71.1	71.3				
4	73.2	72.9				
5	68.8	68.9				
6	18.8	18.7				
Glc						
1	97.5	97.6				98.6
2	74.5	74.6				75.4
3	77.7	77.7				78.8
4	71.1	71.3				71.8
5	77.6	77.5				78.8
6	62.0	62.0				63.0
Ara						
1				106.6		
2				75.1		
3				72.6		
4				69.1		
5				66.1		

[a] DMSO-d_6.
[b] C_5D_5N.

by evaporation in vacuum, a residue (130 g) was obtained. This was suspended in H_2O (500 ml) and washed with EtOAc (500 ml × 2) to remove less polar materials. It was then extracted with *n*-BuOH (500 ml × 3) to separate the more polar materials. Evaporation of the solvent gave the *n*-BuOH soluble residue (52.21 g). A portion (30 g) was chromatographed on silica gel with a $CHCl_3$–MeOH gradient (1:0 → 3:2) to give three fractions.

The $CHCl_3$–MeOH (9:1) eluent (4.71 g) on repeated cc over silica gel yielded the compound lotoideside F (**6**) (110 mg, after crystallization using a mixture of MeOH and EtOAc), lotoideside E (**5**) (60 mg) and lotoideside D (**4**) (43 mg).

The fraction eluted with $CHCl_3$–MeOH (4:1) (4.60 g) on repeated cc over silica gel followed by crystallization using $CHCl_3$ and MeOH yielded 160 mg of colorless needle-like crystals of lotoideside C (**3**) along with 70 mg of succulentoside B (**7**).

The $CHCl_3$–MeOH (7:3 and 3:2) eluents (3.29 g) was further purified by repeated cc over silica gel followed by preparative HPLC, which afforded the compounds lotoideside A (**1**) (42 mg) and lotoideside B (**2**) (40 mg).

*3.4. Lotoideside A (**1**): (3-O-β-D-xylopyranosyl (1 → 2)-α-L-rhamnopyranosyl-6α-O-β-D-xylopyranosyl-22-O-β-D-glucopyranosyl-16β-hydroxy hopane)*

White amorphous solid; $[\alpha]_D^{27.6}$ –7.5 (*c* 3.9, MeOH); molecular formula $C_{52}H_{88}O_{21}$; IR:ν_{max} cm^{-1} (KBr) 3398, 2932, 1640, 1383, 1075, 1043, 480; Q-TOF-MS *m*/*z* 1047 $[M - H]^-$, 915 $[M - H - Xyl]^-$, 901 $[M - H - Rha]^-$, 885 $[M - H - Glc]^-$, 607 $[M - H - Xyl - Rha - Glc]^-$; ^{13}C NMR, ^{1}H NMR and selected HMBC (Tables 1–3).

*3.5. Lotoideside B (**2**): (3-O-β-D-xylopyranosyl (1 → 2)-α-L-rhamnopyranosyl-22-O-β-D-glucopyranosyl-6α,16β-dihydroxyhopane)*

White amorphous solid; $[\alpha]_D^{27.6}$ –10.4 (*c* 1.18, MeOH); molecular formula $C_{47}H_{80}O_{17}$; IR: ν_{max} cm^{-1}

Table 2
^{1}H NMR spectral data for lotoidesides A–F (**1-6**) at 500 MHz (*J* values are in parenthesis)

	1[a]	**2**[a]	**3**[b]	**4**[b]	**5**[b]	**6**[b]
Aglycone						
1	1.54 *m*	1.52 m	1.65 m	1.65 m	1.64 m	1.66 m
	0.86 *m*	0.83 m	1.59 m	0.97[c]	1.02[c]	1.21 m
2	1.73 m	1.69 m	2.21 m	2.19 m	2.19 m	2.13 m
	1.49 m	1.51 m	1.96 m	1.93 m	1.91 m	1.86 m
3	2.89 *dd* (11.5, 4.0)	2.88 dd (11.5, 3.5)	3.39 dd (12.0, 4.0)	3.37 dd (12.0, 4.5)	3.37 dd (11.5, 4.0)	3.30 dd (11.5, 4.0)
5	0.92[c]	0.70 *d* (11.0)	1.30 d (11.0)	1.68 d (13.0)	1.31[c]	2.25 (*s*)
6	3.79 m	3.75 m	4.25 ddd (10.5, 10.5, 3.0)	4.36 m	4.21 m	–
7	1.40 m	1.44 m	2.35 dd (13.0, 3.0)	2.02[c]	2.34 m	2.54 d (11.5) 1.92 d (11.5)
	1.05 m	1.05[c]	1.89 m	1.64 m	1.89 m	
9	1.18[c]	1.10[c]	1.26[c]	1.26 m	1.26 m	1.77 dd (12.5, 2.0)
11	1.47 m	1.47 m	1.49 m	1.52 m	1.48[c]	1.47 m
	1.20 m	1.20[c]	1.46 m	1.48 m	1.48[c]	1.23 m
12	1.32 m	1.46 m	1.31 m	1.37[c]	1.37[c]	1.40 m
	1.30 m	1.33 m	1.15 m	1.37[c]	1.37[c]	1.33 m
13	1.25[c]	1.21[c]	1.32[c]	1.37[c]	1.37[c]	1.25 m
15	1.76 m	1.48 m	2.25 dd (13.5, 3.5)	2.35 dd (12.5, 3.0)	2.01 m	1.65 m
	1.11[c]	1.35 m	1.71 m	1.88 m	1.67[c]	1.39 m
16	3.93 m	3.92 m	4.44 m	4.20 m	4.32[c]	4.22 m
17	1.27 m	1.29 t (11.0)	1.77 t (11.5)	1.30[c]	1.67[c]	1.49[c]
19	1.44 m	1.42 m	1.43 m	1.46[c]	1.47 m	1.41 m
	0.96[c]	0.90[c]	0.95 m	0.97[c]	0.97 m	0.87 m
20	1.74 m	1.72 m	1.74 m	1.75 m	1.73 m	1.64 m
	1.37[c]	1.39 m	1.33[c]	1.39[c]	1.31[c]	1.28 m
21	2.49 m	2.48 m	2.69 q (9.5)	2.74 q (9.5)	2.73 q (9.5)	2.68 q (9.5)
23	1.24 *s*	1.23 s	2.04 s	2.00 s	2.05 s	1.43 s
24	0.91 *s*	0.87 s	1.58 s	1.46 s	1.51 s	1.55 s
25	0.77 s	0.77 s	0.90 s	0.92 s	0.92 s	0.84 s
26	0.95 s	0.95 s	1.05 s	1.11 s	1.10 s	0.93 s
27	0.92 s	0.94 s	1.02 s	1.05 s	1.05 s	1.01 s
28	0.69 s	0.69 s	0.75 s	0.77 s	0.76 s	0.69 s
29	1.10 s	1.11 s	1.25 s	1.30 s	1.29 s	1.36 s
30	1.22 s	1.22 s	1.39 s	1.41 s	1.39 s	1.51 s
Sugar moiety						
Xyl′						
1	4.23 d (6.5)	4.18 d (6.0)	4.88 d (7.0)	4.83 d (7.0)	4.84 d (7.0)	4.77 d (7.5)
2	3.22[c]	3.21 m	4.02 *t* (8.0)	4.00 *t* (8.0)	3.99 *t* (8.0)	3.99 *t* (8.5)
3	3.28[c]	3.25 m	4.15 *t* (8.5)	4.11 m	4.09 m	4.12 *t* (8.5)
4	3.20[c]	2.98 m	4.21 m	4.17 m	4.16 m	4.19 m
5	3.65[c]	3.63 m	4.34 dd (11.0, 5.0)	4.34 m	4.32[c]	4.36 dd (11.0, 5.0)
	3.03[c]	3.01 m	3.73 *t* (10.5)	3.75 *t* (10.5)	3.71 *t* (11.0)	3.74 *t* (10.5)
Xyl″						
1	4.20 d (7.0)		4.87 d (7.0)		4.84 d (7.0)	
2	3.01 m		3.98 t (7.5)		3.95 t (8.0)	
3	3.81[c]		4.18 m		4.06 m	
4	3.25 m		4.07 m		4.07 m	
5	3.61 m		4.42 m		4.12 m	
	2.95 m		3.72 t (10.5)		3.56 m	
Xyl‴						
1			4.68 d (7.0)			
2			3.92 t (7.5)			
3			4.11 m			
4			4.12 m			
5			4.38 m			
			3.79 m			
Rha						
1	5.21 s	5.21 s				
2	3.69 m	2.97 m				
3	3.53 m	3.45 dd (3, 9.0)				
4	3.18 m	3.17 m				

Table 2 (*continued*)

	1[a]	2[a]	3[b]	4[b]	5[b]	6[b]
5	3.92[c]	3.80 m				
6	1.03 s	1.03 s				
Glc						
1	4.41 d (7.5)	4.41 d (7.5)				5.10 d (7.5)
2	2.83 t (8.5)	2.83 t (8.0)				3.96 m
3	3.18 m	3.14 d (11.5)				4.21 m
4	2.97[c]	3.68 m				4.08 t (9.0)
5	3.10 t (8.5)	3.09 m				3.91 m
6	3.64 m	3.55 m				4.46 dd (11.5, 2.0)
	3.37[c]	3.37[c]				4.24 m
Ara						
1				4.83 d (7.0)		
2				4.14 m		
3				4.39 t (8.0)		
4				4.26 m		
5				4.16[c]		
				3.65 m		

[a] DMSO-d_6.
[b] C_5D_5N.
[c] Signal pattern unclear due to overlap.

Table 3
Selected HMBC of lotoidesides A–F (**1–6**)

Selected carbons	Correlated protons in compounds					
	1	**2**	**3**	**4**	**5**	**6**
C-3	Xyl′H-1, 3H-23, 3H-24	Xyl′H-1, 3H-23, 3H-24	Xyl′H-1, 3H-23, 3H-24	Xyl′H-1, 3H-23, 3H-24	Xyl′H-1, 3H-23, 3H-24	Xyl′H-1, 3H-23, 3H-24
C-6	Xyl″H-1, H-5	H-5, H-7	Xyl″H-1, H-5, 2H-7	H-5, H-7	Xyl″H-1, H-5, 2H-7	H-5, 2H-7
C-16	H-17	H-17	Xyl‴H-1, H-15, H-17	AraH-1, 2H-15	2H-15, H-17	H-15, H-17
C-22	GlcH-1, H-17, H-21, 3H-29, 3H-30	GlcH-1, H-17, H-21, 3H-29, 3H-30	H-17, H-21, 3H-29, 3H-30	H-17, H-20, H-21, 3H-29, 3H-30	H-20, H-21, 3H-29, 3H-30	GlcH-1, H-21, 3H-29, 3H-30
Xyl′C-1	Xyl′H-5	Xyl′H-5	H-3, Xyl′H-5	H-3, Xyl′H-5	H-3, Xyl′H-5	H-3, Xyl′H-5
Xyl′C-2	RhaH-1	RhaH-1	–	–	–	–
RhaC-1	Xyl′H-2	Xyl′H-2	–	–	–	–
AraC-1	–	–	–	H-16	–	–

(KBr) 3396, 2940, 1650, 1382, 1043, 627; Q-TOF-MS *m/z* 915 $[M - H]^-$, 753 $[M - H - Glc]^-$; ^{13}C NMR, ^1H NMR and selected HMBC (Tables 1–3).

3.6. Lotoideside C (*3*): (3-O-β-D-xylopyranosyl-6α-O-β-D-xylopyranosyl-16β-O-β-D-xylopyranosyl-22-hydroxyhopane)

White crystalline solid; $[\alpha]_D^{27.6}$ +6.4 (*c* 1.00, pyridine); mp 240 °C; molecular formula $C_{45}H_{76}O_{16}$; IR: ν_{max} cm^{-1} (KBr) 3395, 2934, 1642, 1369, 1159, 1044, 894, 629; Q-TOF-MS *m/z* 871 $[M - H]^-$, 739$[M - H - Xyl]^-$, 607 $[M - H - 2Xyl]^-$, 475 $[M - H - 3Xyl]^-$; ^{13}C NMR, ^1H NMR and selected HMBC (Tables 1–3).

3.7. Lotoideside D (*4*): (3-O-β-D-xylopyranosyl-16β-O-α-L-arabinopyranosyl-6α,22-dihydroxyhopane)

White crystalline solid; mp 222–223 °C; $[\alpha]_D^{27.6}$ +15.5 (*c* 1.42, MeOH); molecular formula $C_{40}H_{68}O_{12}$; IR: ν_{max} cm^{-1} (KBr) 3367, 2941, 1652, 1382, 1159, 1047; Q-TOF-MS *m/z* 763 $[M + Na]^+$, 631 $[M + Na - Ara]^+$; ^{13}C NMR, ^1H NMR and selected HMBC (Tables 1–3).

3.8. Lotoideside E (*5*): (3-O-β-D-xylopyranosyl-6α-O-β-D-xylopyranosyl-16β,22-dihydroxyhopane)

White crystalline solid; mp 225–226 °C; $[\alpha]_D^{27.6}$ +17.5 (*c* 0.73, MeOH); molecular formula $C_{40}H_{68}O_{12}$; IR: ν_{max} cm^{-1} (KBr) 3323, 2937, 1380, 1159, 1045, 974; Q-TOF-MS *m/z* 763 $[M + Na]^+$, 611 $[M + Na - Glc - H_2O]^+$; ^{13}C NMR and ^1H NMR (Tables 1–3).

3.9. Lotoideside F (*6*): (3-O-β-D-xylopyranosyl-22-O-β-D-glucopyranosyl-16-hydroxyhopan-6-one)

White crystalline solid; mp 205–206 °C; $[\alpha]_D^{27.6}$ −22.3 (*c* 1.19, pyridine); molecular formula $C_{41}H_{68}O_{13}$; IR: ν_{max} cm^{-1} (KBr) 3393, 2945, 1703, 1643, 1388, 1155,

1075, 1046; Q-TOF-MS *m/z* 791 $[M + Na]^+$; ^{13}C NMR, ^1H NMR and selected HMBC (Tables 1–3).

3.10. Succulentoside B (7)

White crystalline solid; mp 266–267 °C; IR: ν_{max} cm^{-1} (KBr) 3401, 2941, 1640, 1451, 1387, 1161, 1045; Q-TOF-MS *m/z* 871 $[M - H]^-$. Other spectral data were same as reported (Meselhy and Aboutabl, 1997).

3.11. Acid hydrolysis of saponins

The saponins lotoidesides A–F (each 100 mg) were refluxed with 2 N HCl in dioxane–water (1:1) for 4 h on a water bath. Dioxane was distilled off under reduced pressure and the product after dilution with water was extracted with $CHCl_3$. The $CHCl_3$ soluble part after evaporation was subjected to cc over silica gel to afford the aglycon part. The aqueous layer was neutralized with Ag_2CO_3, then filtered and evaporated. The sugars were identified with authentic samples by TLC in EtOAc–MeOH–H_2O–AcOH (13:4:3:3) [R_f 0.34 (glucose), 0.41 (arabinose), 0.47 (xylose), 0.53 (rhamnose)]. After prep. TLC of the sugar mixture in this solvent system, the optical rotation of each purified sugar was measured. [Glucose $[\alpha]_D^{27.6}$ +51.2 (*c* 0.13, H_2O); arabinose $[\alpha]_D^{27.6}$ +103.8 (*c* 0.10, H_2O); xylose $[\alpha]_D^{27.6}$ +19.5 (*c* 0.20, H_2O); rhamnose $[\alpha]_D^{27.6}$ +7.9 (*c* 0.28, H_2O).]

References

Barua, A.K., Chakravarti, S., Basak, A., Ghosh, A., Chakrabarti, P., 1976. A new triterpene glycoside from *Mollugo hirta*. Phytochemistry 15, 831–832.

Chakrabarti, P., 1969. The structure and stereochemistry of mollugogenol A. Tetrahedron 25, 3301.

Chakrabarti, P., Sanyal, A.K., 1970. The constitution of mollugogenol E – a new sapogenin from *Mollugo hirta*. Indian J. Chem. 8, 1042–1043.

Hamburger, M., Dudan, G., Nair, A.G.R., Jayaprakasam, R., Hostettmann, K., 1989. An antifungal triterpenoid from *Mollugo pentaphylla*. Phytochemistry 28, 1767–1768.

Hamed, A.I., El-Emary, N.A., 1999. Triterpene saponins from *Glinus lotoides* var. *dictamnoides*. Phytochemistry 50, 477–480.

Hamed, A.I., Springuel, I., El-Emary, N.A., Mitome, H., Miyaoka, H., Yamada, Y., 1996. Triterpenoidal saponin glycosides from *Glinus lotoides* var. *dictamnoides*. Phytochemistry 43, 183–188.

Meselhy, M.R., Aboutabl, E.A., 1997. Hopane-type saponins from *Polycarpon succulentum* growing in Egypt. Phytochemistry 44, 925–929.

Patra, A., Mitra, A.K., Chatterjee, T.K., Barua, A.K., 1981. Carbon-13 NMR spectra of some novel migrated hopanes and 21α-H hopanes. Org. Magn. Reson. 17, 148–150.

Sastri, B.N., 2002. The Wealth of India Raw Materials, F–G, vol. IV. CSIR, p. 136.