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TRITERPENOIDAL SAPONIN GLYCOSIDES FROM *GLINUS LOTOIDES* VAR. *DICTAMNOIDES*

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Key Word Index—*Glinus lotoides* var. *dictamnoides*; Molluginaceae; triterpenoidal saponins; glinusides A, B and C.

Abstract—Three triterpenoidal saponins (glinusides A, B and C) were isolated from the *n*-butanol fraction of *Glinus lotoides* var. *dictamnoides*, their structures being determined by means of spectroscopic methods as 3-*O*-*β*-L-arabinopyranosyl-22-*O*-*β*-D-glucopyranosyl(4←1)-*α*-L-rhamnopyranosyl-15*β*-hydroxyhopan-6-one, 3-*O*-*β*-L-arabinopyranosyl-15-*O*-*β*-D-glucopyranosyl-22*β*-hydroxyhopan-6-one and 3-*O*-*β*-D-glucopyranosyl(4←1)-*β*-L-arabinopyranosyl-22*β*-hydroxyhopan-6-one, respectively. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The plant *Glinus lotoides* L. =*G. dictamnoides* Burm. (=*Mollugo glinus* A. Rich) [1] known in Arabic as Hashishet El-aqrab or Moghera [2], is widely distributed in the Allaqi area, south of Aswan [3]. Various species of the genus *Glinus* are used as green vegetables. It is bitter in taste and is used in the indigenous system of medicine as an antiseptic [4], anthelmintic, against diarrhoea, bilious attacks and as a purgative for curing boils, wound and pains. The juice of these plants is taken internally to strengthen weak children [4, 5]. The genus in general is known to produce various saponin compounds and this is important for the chemotaxonomy of the species of this genus.

RESULTS AND DISCUSSION

Successive extraction of a methanolic extract of *G. lotoides* with *n*-butanol led to the isolation of three glycosidic compounds. The first compound (**1**) showed its $[M + 2Na]^+$ ion peak at *m/z* 960 in the FAB mass spectrum, which was consistent with $C_{47}H_{78}O_{17}$. The ^1H NMR spectrum suggested the presence of eight methyl singlets at *δ* 0.73, 0.86, 0.98, 1.04, 1.41, 1.43, 1.56 and 1.79 [6–9]; there was also a signal for one proton at *δ* 3.33 (1H, *dd*, *J* = 3.88, 11.61 Hz, H-3), one broad singlet at *δ* 2.26 for H-5, a signal for one proton at *δ* 2.72 (1H, *dd*, *J* = 9.4 and 9.4 Hz, H-17) and two doublets for two protons at *δ* 2.54 and 1.95 (H-7*α* and *β*), which showed a coupling constant of *J* = 11.73 Hz, suggesting that these protons had a geminal coupling [6–15]. The ^1H NMR spectrum contained signals for three anomeric protons at *δ* 6.51 (1H, *br s*), 5.16 (1H, d, J = 7.8 Hz) and 4.84 (1H, *d*, *J* = 7.33 Hz). A three-proton doublet at *δ* 1.70 (*J* = 6.17 Hz) was typical for the methyl group of a 6-deoxy sugar. The ^{13}C NMR spectrum showed a signal for a ketonic carbon at *δ* 211.6 at C-6, which was confirmed at this position due to the appearance of H-5 as a singlet and H-7 as a doublet with geminal coupling. Acid hydrolysis of this glycoside with 5% HCl–Methanol [16, 17], gave an aglycone (mp 222–224°) and glucose, rhamnose and arabinose. The exact sequence of the sugars was determined by a combined use of ^1H–^1H correlation spectroscopy (COSY), NOESY, 2D heteronuclear multiple quantum coherence (HMQC) and proton detected heteronuclear multiple bond correlation (HMBC), where there were cross peaks between H-1″ (*δ* 5.16) and C-22 (*δ* 82.4), H-1‴ (*δ* 6.51) and C-4″ (*δ* 69.5), and H-1′ (*δ* 4.84) and C-3 (*δ* 87.1). The ^1H and ^{13}C NMR spectra revealed that the aglycone was a triterpenoid with a hopane skeleton [6, 7, 13] and contained three hydroxyl groups (two secondary at C-3, C-15 and one tertiary at C-22). NOESY and HMBC experiments were performed (at 500 MHz) and chemical shifts of the anomeric protons and the coupling constants suggested that the sugar linkage at C-3 was *β*-L-arabinopyranosyl and that at C-22 was *β*-D-glucopyranosyl(4←1)-*α*-L-rhamnopyranosyl.

From the above data we concluded that this compound was a glycoside with a new aglycone, 3*β*,15*β*,22*β*-hydroxyhopan-6-one, which is isolated from a natural source for the first time. Hence, the isolated compound has the structure 3-*O*-*β*-L-arabinopyranosyl-22-*O*-*β*-D-glucopyranosyl(4←1)-*α*-L-

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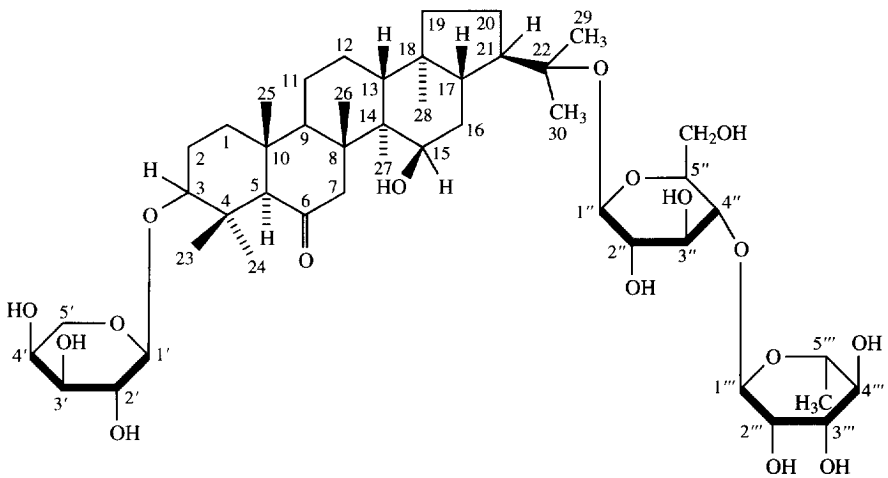
rhamnopyranosyl-15β-hydroxyhopane-6-one (**1**); this compound has been given the name glinuside A.

The second compound (**2**) showed its [M + 2H + 2K] ion peak at *m/z* 847 in the FAB mass spectrum and was consistent with $C_{41}H_{67}O_{13}$. The ^{1}H NMR spectrum suggested the presence of eight singlets for methyl protons at δ 0.75, 0.86, 0.99, 1.07, 1.41, 1.45, 1.57 and 1.59 [6–9]. There was a signal for one proton at 3.30 (1H, *dd*, J = 3.79 and 11.41 Hz, H-3), one broad singlet integrated for one proton at δ 2.27 for H-5, a signal for one proton at δ 2.72 (1H, *dd*, J = 9.37 and 10.11 Hz, H-17) and two signals for two protons at δ 2.62 and 1.99, which showed a coupling constant of 12.16 Hz (H-7α and H-7β), suggesting that these protons had a geminal coupling [6–8, 10–13]. The ^{1}H NMR spectrum showed signals for two anomeric protons at δ 5.16 (1H, *d*, J = 7.72 Hz) and 4.87 (1H, *d*, J = 7.58 Hz), which was confirmed by the ^{13}C NMR spectrum (δ 98.13 and 106.38) [15]. The ^{13}C NMR spectrum showed a signal for a ketonic carbon at δ 211.77 at C-6, which was confirmed at this position due to the appearance of H-5 as a singlet and H-7 as a doublet with geminal coupling. The chemical shifts of C-3 (δ 87.3) and C-15 (δ 84.16) and the coupling constants of the anomeric protons suggest that the sugar linkage was β- on C-3 and β- on C-15. Acid hydrolysis of this compound with 5% HCl–Methanol [16, 17] gave glucose, arabinose and an aglycone (mp 222–224°). Comparison of the ^{1}H and ^{13}C NMR spectra of anomeric protons and carbons with those of the previous compound revealed that arabinose was linked with C-3 and glucose with C-15.

The ^{1}H and ^{13}C NMR spectra revealed that this compound had a triterpenoidal skeleton (hopane skeleton) and, hence, we suggest that it is 3-*O*-β-L-arabinopyranosyl-15β-D-glucopyranosyl-22β-hydroxyhopane-6-one and given it the name glinuside B. This compound is a new saponin isolated for the first time from natural sources and its aglycone was the same as the aglycone of glinuside A.



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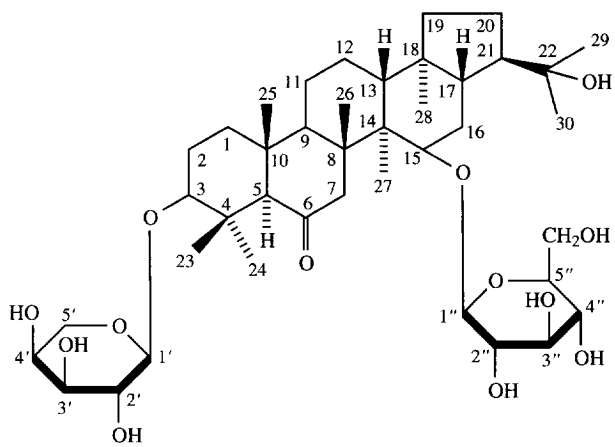

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The third compound (**3**) showed its $[M-H_2O]^+$ ion peak at *m/z* 733 in the FAB mass spectrum and was consistent with $C_{41}H_{67}O_{12}$. The ^1H NMR spectrum suggested the presence of eight methyl singlets at δ 0.74, 0.87, 0.99, 1.06, 1.35, 1.42, 1.57 and 1.62 [7–9, 14]. There was a signal for one proton at δ 3.35 (1H, *dd*, $J = 3.92$ and 11.63 Hz, H-3), one broad singlet integrated for one proton at δ 2.30 for H-5, a signal for one proton at δ 2.73 (1H, *dd*, $J = 9.37$ and 10.11 Hz) for H-17 and two signals for two protons at δ 2.61 and 1.96 having geminal coupling ($J = 11.8$ Hz) for H-7α and β. The ^1H NMR and ^{13}C NMR spectra [15] showed signals for two anomeric protons at δ 5.17 (1H, *d*, $J = 7.7$ Hz) and δ 4.84 (1H, *d*, $J = 7.4$ Hz) and carbon atoms at δ 98.4 and 107.60. The ^{13}C NMR spectrum showed a signal for ketonic carbon at δ 211.99 for C-6, which was confirmed at this position due to the appearance of H-5 as a singlet and the two protons at H-7 as doublets with geminal coupling ($J =$ 11.88 Hz). The ^{13}C NMR spectrum showed also 11 methylene carbons (by DEPT experiment), which included two signals for the sugar moiety and nine signals for the aglycone, which indicated that this compound had no C-15 secondary alcohol group and the sugar was linked at C-3. The ^1H and ^{13}C NMR coupling constants revealed that the sugar was β-linked. The sugar linkages were 3-*O*-β-D-glucopyranosyl(4←1)-β-L-arabinopyranosyl, which was confirmed by chemical shifts for both ^1H and ^{13}C anomeric protons and carbons. The ^1H and ^{13}C NMR spectra of this compound revealed that it had the same skeleton as the previous glycosides (hopane skeleton), except that it had no secondary hydroxyl at C-15 and hence it was a new compound isolated from a natural source for the first time. We assign its structure as 3-*O*-β-D-glucopyranosyl(4←1)-β-L-arabinopyranosyl-22β-hydroxyhopane-6-one (**3**), which is named glinuside C.

EXPERIMENTAL

Mps were taken on a Yamazawa micro-melting point apparatus; optical rotations were measured on a JASCO-360 digital polarimeter; UV spectra were obtained on a Hitachi 200-01 spectrophotometer; IR spectra were taken on a JASCO IR-A-2 spectrophotometer; ^1H and ^{13}C NMR spectra were taken on a Bruker AM-400 (at 400 and 100 MHz, respectively); NOESY, COSY, HMQC and HMBC spectra were taken on a Bruker AM-500 instrument; MS were obtained on a Hitachi RMU-7M spectrometer.

Extraction and isolation of the compounds. The herb of *G. lotoides* L. var. *dictamnoides* was collected in April 1993 from Allaqi area, south of Aswan, Egypt, spread in thin layers and left for drying at room temp. in the shade. The air-dried material (1.6 kg) was powdered and extracted at room temp. with MeOH (95%) by maceration 3×. The MeOH extract was concd under red. pres. to a syrupy consistency (80 g).

Fractionation of the dried extract. The solvent-free extract (80 g) was mixed with 100 ml MeOH, 150 ml H_2O, transferred to a separatory funnel and partitioned between hexane (**A**), $CHCl_3$ (**B**) and *n*-BuOH (**C**). Each fr. was dried over Na_2SO_4 and concd to a syrupy residue.

Column chromatographic fractionation of the n-BuOH *fraction.* Fr. C (5 g) was dissolved in small amount of MeOH and transferred to the top of a Sephadex LH-20 column previously packed by the wet method in MeOH. Elution was with MeOH and two effluent frs (each 500 ml) were collected (C-1 and C-2), screening by TLC showed that C-1 contained 3 saponins and C-2 contained only sugars.

Separation of saponin compounds from C-1 subfraction. Subfr. C-1 (2 g) was subjected to CC on ODS silica gel, eluted with MeOH–H_2O (4:1), which gave subfrs C-1.1, C-1.2 and C-1.3. Subfr. C-1.2 (300 mg) was subjected to flash CC on silica gel, eluted with $CHCl_3$–MeOH–H_2O (7:3:0.3), resulting in sepn of 3 pure saponins.

Acid hydrolysis of the saponins. The saponin (5 mg) was refluxed with 5 ml 5% HCl–MeOH on a steam bath for 6 hr. The product was diluted with H_2O and extracted with $CHCl_3$ in a separatory funnel, and the respective aglycones were sepd. The aq. filtrate was neutralized with $AgCO_3$, filtered and evapd. The resulting syrup was subjected to TLC on silica gel using EtOA–MeOH–HOAc–H_2O (13:3:4:3) as developing solvent against ref. sugars, and the dried chromatograms was sprayed with *p*-anisaldehyde–H_2SO_4 reagent.

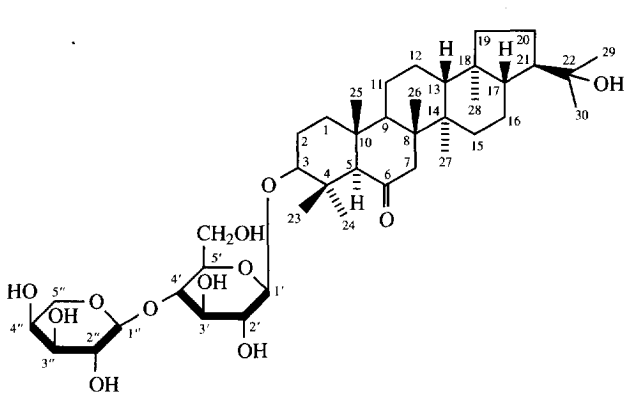

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Table 1. ^{1}H NMR spectral data for the isolated saponin glycosides (400 MHz, pyridine-d_5)

No.	Glinuside A aglycone	Glinuside B aglycone	Glinuside C aglycone
Aglycone moieties			
C-1	2.14, 1.93 (each 1H, *m*)	2.09, 1.93 (each 1H, *m*)	2.18, 1.95 (each 1H, *m*)
C-2	1.65, 1.40 (each 1H, *m*)	1.65, 1.40 (each 1H, *m*)	1.65, 1.40 (each 1H, *m*)
C-3	3.33 (1H, *dd*, $J = 3.9$, 11.6 Hz)	3.30 (1H, *dd*, $J = 4.8$, 11.9 Hz)	3.35 (1H, *dd*, $J = 3.9$, 11.6 Hz)
C-4	—	—	—
C-5	2.26 (1H, *s*)	2.28 (1H, *s*)	2.30 (1*H*, *s*)
C-6	—	—	—
C-7	2.54, 1.95 (each, 1H, *d*, $J = 11.7$ Hz)	2.62, 1.99 (each 1H, *d*, $J = 12.2$ Hz)	2.61, 1.96 (each, 1H, *d*, $J = 11.8$ Hz)
C-8	—	—	—
C-9	1.77 (1H, *m*)	1.77 (1H, *m*)	1.77 (1H, *m*)
C-10	—	—	—
C-11	1.53, 1.29 (each 1H, *m*)	1.53, 1.29 (each 1H, *m*)	1.53, 1.30 (each 1H, *m*)
C-12	1.34, 1.29 (each, 1H, *m*)	1.34, 1.29 (each, 1H, *m*)	1.34, 1.30 (each, 1H, *m*)
C-13	1.53 (1H, *m*)	1.53 (1H, *m*)	1.53 (1H, *m*)
C-14	—	—	—
C-15	4.28 (1H)*	4.29 (1H)*	1.31 (2H, *m*)
C-16	1.67, 1.34 (each, 1H, *m*)	1.67, 1.34 (each, 1H, *m*)	1.31, 1.61 (each, 1H, *m*)
C-17	2.72 (1H, *q*, $J = 9.4$, 9.4 Hz)	2.73 (1H, *q*, $J = 9.3$, 9.3 Hz)	2.73 (1H, *dd*, $J = 93$, 10.1 Hz)
C-18	—	—	—
C-19	1.40, 0.91 (each 1H, *m*)	1.40, 0.91 (each, 1H, *m*)	1.40, 0.92 (each, 1H, *m*)
C-20	1.40, 1.69 (each, 1H, *m*)	1.40, 1.69 (each, 1H, *m*)	1.40, 1.61 (each, 1H, *m*)
C-21	1.65 (1H, *m*)	1.65 (1H, *m*)	1.81 (1H, *m*)
C-22	—	—	–
C-23	0.98 (3H, *s*)	0.99 (3H, *s*)	0.99 (3H, *s*)
C-24	1.04 (3H, *s*)	1.04 (3H, *s*)	1.06 (3H, *s*)
C-25	0.73 (3H, *s*)	0.74 (3H, *s*)	0.74 (3H, *s*)
C-26	0.86 (3H, *s*)	0.86 (3H, *s*)	0.87 (3H, *s*)
C-27	1.79 (3H, *s*)	1.45 (3H, *s*)	1.35 (3H, *s*)
C-28	1.56 (3H, *s*)	1.41 (3H, *s*)	1.41 (3H, *s*)
C-29	1.41 (3H, *s*)	1.57 (3H, *s*)	1.57 (3H, *s*)
C-30	1.43 (3H, *s*)	1.59 (3H, *s*)	1.62 (3H, *s*)
Sugar moieties			
	Arabinose	Arabinose	Arabinose
1′	4.84 (1H, *d*, $J = 7.33$ Hz)	4.78 (1H, *d*, $J = 7.58$ Hz)	4.84 (1H, *d*, $J = 7.4$ Hz)
2′	4.07 (1H)*	4.05 (1H)*	4.16 (1H)*
3′	4.06 (1H)*	4.25 (1H)*	4.27 (1H)*
4′	4.16 (1H)*	4.25 (1H)*	4.27 (1H)*
5′	3.53 (1H, *t*, $J = 10.5$ Hz), 4.22 (1H)*	3.69 (1H, *t*, $J = 9.69$ Hz), 4.24 (1H)*	3.80 (1H, *t*, $J = 10.3$ Hz), 4.27 (1H)*
	Glucose	Glucose	Glucose
1″	5.16 (1H, *d*, $J = 7.8$ Hz)	5.17 (1H, *d*, $J = 7.7$ Hz)	5.17 (1H, *d*, $J = 7.7$ Hz)
2′	3.98 (1H, *d*, $J = 8.5$ Hz)	4.04 (1H, *t*, $J = 8.9$ Hz)	4.03 (1H, *t*, $J = 8.7$ Hz)
3″	4.12 (1H, *d*, $J = 8.5$ Hz)	4.12 (1H, *t*, $J = 8.9$ Hz)	4.19 (1H, *t*, $J = 8.7$ Hz)
4″	4.79 (1H, *m*)	4.24 (1H)*	4.26 (1H)*
5″	3.74 (1H, *m*)	3.99 (1H, *m*)	3.99 (1H, *m*)*
6″	4.50 (1H, *dd*, $J = 2.4$, 11.6 Hz), 4.35 (1H, *dd*, $J = 6.2$, 17.4 Hz)	4.52 (1H, *dd*, $J = 3.3$, 10.6 Hz), 4.24 (1H)*	4.53 (1H, *dd*, $J = 5.1$, 11.6 Hz) 4.41 (1H, *dd*, $J = 5.1$, 11.6 Hz)
	Rhamnose		
1‴	6.51 (1H, *br. s*)		
2‴	4.85 (1H, *dd*, $J = 0.99$, 3.3 Hz)		
3‴	4.67 (1H, *dd*, $J = 3.3$, 9.3 Hz)		
4‴	4.29 (1H)*		
5‴	4.18 (1H, *t*, $J = 9.0$ Hz)		
6‴	1.70 (3H, *d*, $J = 6.17$ Hz)		

Multiplicity was detected by DEPT experiment.
*Overlapping with other signals.

Table 2. ^{13}C NMR data for the isolated saponin glycosides (100 MHz, pyridine-d_5)

No.	Glinuside A aglycone	Glinuside B aglycone	Glinuside C aglycone
Aglycone moieties			
C-1	27.2 (*t*)	27.2 (*t*)	27.5 (*t*)
C-2	26.5 (*t*)	26.5 (*t*)	26.7 (*t*)
C-3	87.1 (*d*)	87.3 (*d*)	87.7 (*d*)
C-4	48.4 (*s*)	48.4 (*s*)	48.7 (*s*)
C-5	65.2 (*d*)	65.2 (*d*)	65.3 (*d*)
C-6	211.6 (*s*)	211.8 (*t*)	211.9 (*s*)
C-7	51.4 (*t*)	51.4 (*t*)	51.7 (*t*)
C-8	43.2 (*s*)	43.2 (*s*)	43.5 (*s*)
C-9	48.8 (*d*)	48.8 (*d*)	48.2 (*d*)
C-10	38.2 (*s*)	38.2 (*s*)	38.5 (*s*)
C-11	21.2 (*t*)	21.2 (*t*)	21.5 (*t*)
C-12	23.2 (*t*)	23.2 (*t*)	23.5 (*t*)
C-13	49.9 (*d*)	49.9 (*t*)	50.2 (*d*)
C-14	45.3 (*s*)	45.3 (*s*)	45.6 (*s*)
C-15	78.4 (*d*)	84.2 (*d*)	29.9 (*t*)
C-16	39.7 (*t*)	39.4 (*t*)	39.8 (*t*)
C-17	50.3 (*d*)	50.2 (*d*)	50.5 (*d*)
C-18	43.7 (*s*)	43.7 (*s*)	44.0 (*s*)
C-19	41.5 (*t*)	41.5 (*t*)	41.7 (*t*)
C-20	43.6 (*t*)	43.6 (*t*)	43.9 (*t*)
C-21	65.7 (*d*)	65.0 (*d*)	65.9 (*d*)
C-22	82.4 (*s*)	82.8 (*s*)	83.0 (*s*)
C-23	17.0 (*q*)	17.0 (*q*)	17.1 (*q*)
C-24	17.0 (*q*)	17.0 (*q*)	17.3 (*q*)
C-25	16.8 (*q*)	16.8 (*q*)	16.8 (*q*)
C-26	16.4 (*q*)	16.4 (*q*)	16.7 (*q*)
C-27	24.6 (*q*)	24.6 (*q*)	25.0 (*q*)
C-28	18.4 (*q*)	18.4 (*q*)	18.6 (*q*)
C-29	25.9 (*q*)	25.9 (*q*)	26.2 (*q*)
C-30	27.3 (*q*)	27.3 (*q*)	27.6 (*q*)
Sugar moieties			
	Arabinose	Arabinose	Arabinose
1′	105.6 (*d*)	106.4 (*d*)	107.6 (*d*)
2′	73.8 (*d*)	75.0 (*d*)	75.5 (*d*)
3′	78.4 (*d*)	78.3 (*d*)	78.7 (*d*)
4′	71.2 (*d*)	71.3 (*d*)	71.2 (*d*)
5′	66.7 (*t*)	66.0 (*t*)	66.1 (*t*)
	Glucose	Glucose	Glucose
1″	98.2 (*d*)	98.1 (*d*)	98.4 (*d*)
2″	79.2 (*d*)	73.5 (*d*)	73.3 (*d*)
3″	75.0 (*d*)	78.3 (*d*)	78.6 (*d*)
4″	69.5 (*d*)	69.4 (*d*)	71.8 (*d*)
5″	78.4 (*d*)	78.3 (*d*)	78.6 (*d*)
6″	62.7 (*t*)	62.5 (*t*)	63.0 (*t*)
	Rhamnose		
1‴	101.6 (*d*)		
2‴	72.2 (*d*)		
3‴	71.5 (*d*)		
4‴	77.5 (*d*)		
5‴	72.3 (*d*)		
6‴	18.4 (*d*)		

Glinuside A (**1**). Powder, mp 256–260°; $[\alpha]_D$ −15.85 (MeOH, $c = 0.33$); IR ν_{max}^{KBr} cm^{-1}: 3240, 1715. Negative FAB-MS *m/z* (rel. int.): 960 $[M + 2Na]^+$ (25) ($C_{47}H_{79}O_{17}$), 732 $[M - Rham - H_2O - OH]^+$ (30), 627 $[M - Rha - Ara - H_2O]^+$ (20), 586 $[M - Glu - Rha - H_2O]^+$ (30), 311 $[M - Glu - Rha - Ara]^+$ (40); ^1H NMR (400 MHz, pyridine-d_5) and ^{13}C NMR (100 MHz, pyridine-d_5): Tables 1 and 2.

Glinuside B (**2**). Powder, mp 235–238°; $[\alpha]_D$ −9.41 (MeOH, $c = 0.34$); IR ν_{max}^{KBr} cm^{-1}: 3240, 1715. FAB-MS *m/z* (rel. int.): 847 $[M + 2H + 2K]^+$ (100) ($C_{41}H_{67}O_{13}$), 765 $[M - 2H]^+$ (20), 473 $[M - Glu-Ara]^+$ (25), 417 $[M - Me_2 - COH + Glu - Ara[+3H]^+$ (25), other important peaks observed were at *m/z* 315, 227, 153. ^1H NMR (400 MHz, pyridine-d_5) and ^{13}C NMR (100 MHz, pyridine-d_5): Tables 1 and 2.

Glinuside C (**3**). Powder, mp 177–181°; $[\alpha]_D$ −4.0 (MeOH, $c = 0.01$); IR ν_{max}^{KBr} cm^{-1}: 3235, 1715; FAB-MS *m/z* 733 $[M - H_2O]^+$ (50) ($C_{41}H_{67}O_{12}$), 604 $[M - Ara - Me]^+$ (40), 562 $[M - Ara - (Me)_2COH + 2H]^+$ (37); other peaks at *m/z* 389, 301, 255, 176. ^1H NMR (400 MHz, pyridine-d_5) and ^{13}C NMR (100 MHz, pyridine-d_5): Tables 1 and 2.

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