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Further saponins from *Taverniera aegyptiaca*

Zedan Z. Ibraheim*, Hashem A. Hassanean, Daoud W. Bishay

Pharmacognosy Department, Faculty of Pharmacy, Assiut University, Assiut, Egypt

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Abstract

From the saponin fraction of the total methanolic extract of the dried root and stem barks of *Taverniera aegyptiaca* Boiss, six new triterpenoidal saponins of oleanane type were isolated and identified as 28-methyl serratagenate-3-β-*O*-β-xylopyranosyl (1→2)-β-glucopyranoside (**2**), 28-methyl serratagenate 3-β-*O*-α-rhamnopyranosyl (1→2)-β-glucopyranoside (**3**), 3β-*O*-α-rhamnopyranosyl (1→2) β-glucopyranosyl-olean-11,13(18)-dien-1β, 3β, 22β-triol (**4**), 3β-*O*-β-glucopyranosyl (1→2)-β-glucuronopyranosylolean-11,13(18)-dien-1β,3β,22β-triol (**5**), 3β-*O*-β-xylopyranosyl(1→2)-β-glucuronopyranosylolean-11,13(18)-dien-1β,3β,22β-triol (**6**), 3β-*O*-α-rhamnopyranosyl (1→2)-β-glucuronopyranosylolean-11,13(18)-dien-1β, 3β, 22β-triol (**7**) together with the known oleanolic acid 3-β-*O*-β-glucoside (**1**). The identification of the isolated compounds was done on the basis of chemical and spectral evidences.

Keywords: *Taverniera aegyptiaca*; Fabaceae; Stem and root barks; Saponins

1. Introduction

Taverniera aegyptiaca Boiss (Fabaceae) is a branched shrub common to the Red Sea coastal region of Egypt (Tackholm, 1974). In previous reports, seven oleanane based saponins were identified from the polar methanolic extract of the bark of this plant (Hassanean and Mohamed, 1998; Hassanean, 1998). In continuation to our study on this plant we describe here the isolation and identification of six new saponins based on two aglycones 28-methyl serratagenate and 1β, 3β, 22β-trihydroxyolean 11,13(18) diene beside the known oleanolic acid 3-β-*O*-β-glucoside from the plant collected at 2001. TLC screening of the saponin fractions of the plant collected at 1994 and 2001 showed nearly similar constituents, so no need to repeat the isolation of compounds previously isolated (Hassanean and Mohamed, 1998; Hassanean, 1998).

2. Results and discussion

The dried methanolic extract of the root and stem barks of *T. aegyptiaca* Boiss was suspended in distilled water and partitioned with CH_2Cl_2. The aqueous layer was chromatographed on Diaion HP-20 and the fraction eluted with 50% methanol was repeatedly chromatographed on columns of silica gel, reversed phase RP-18 and finally on MPLC to afford seven glycosides.

Separate acid hydrolysis of each of the compounds **2** and **3** afforded the same aglycone giving signals in the ^{13}C NMR spectrum which corresponded to 28-methyl serratagenate **8** previously reported from the plant (Hassanean and Mohamed, 1998) (Table 1), further confirmation was carried out by direct comparison (mmp, co-chromatography and other spectral data), besides glucose and xylose from **2** and glucose and rhamnose from **3** (TLC and PC).

Compound **2** showed a molecular formula deduced as $C_{42}H_{66}O_{14}$ [negative FABMS and DEPT ^{13}C NMR spectra (Tables 1 and 2)]. The negative FAB-MS of **2** revealed a pseudomolecular ion at m/z 793 $[M-H]^-$ indicating the presence of pentosyl and hexosyl units attached to the aglycone, further peaks at m/z 661, 499 and 291 $[(M-H)-502]^-$ corresponding to the subsequent loss of the two sugars (xylose and glucose, identified after acid hydrolysis) from the $[M-H]^-$ and to the D/E ring fragment after retro Diels–Alder cleavage of ring-C, respectively (Budzikiewicz et al., 1963) indicating that the glycosylation was present in the lower part of the aglycone. The ^1H NMR of **2** displayed two anomeric

* Corresponding author.

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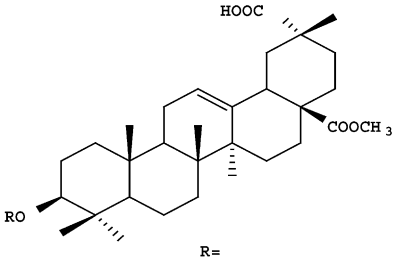
proton signals at δ_H 4.56 (1H, *d*, $J=7.6$ Hz) and 5.10 (1H, *d*, $J=7.5$ Hz), while the ^{13}C NMR further confirmed this conclusion by showing two anomeric carbon signals at δ_C 106.66 and 102.43 confirming the β-xylopyranosyl and β-glucopyranosyl moieties in **2**.

Comparison of the ^{13}C NMR data of **2** with respective data of its aglycone **8** showed a downfield shift of C-3 of **2** (+ 9.9 ppm) indicating glycosylation at C-3. Furthermore, the downfield shift of the C-2 of glucose moiety (+ 7.12 ppm) and the upfield shift of C-1 and C-3 (−2.3 and −1.7 ppm, respectively) indicated a terminal xylopyranosyl structure linked to C-2 of glucopyranosyl

Table 1
^{13}C NMR spectral data of aglycone moities of **1**–**7** and aglycones **8**, **9** in C_5D_5N

C. No.	1	2	3	8	4	5a	6a	7a	9
1	38.56	39.10	39.11	39.11	76.77	76.77	76.81	76.83	76.73
2	25.98	26.24	26.21	28.04	35.15	35.15	35.21	35.25	37.55
3	89.32	89.12	89.10	79.22	89.06	89.04	89.11	89.14	79.64
4	39.54	39.58	39.57	39.28	38.91	38.93	38.91	39.03	39.33
5	55.67	55.45	55.45	55.43	51.86	51.86	51.88	51.86	51.86
6	18.55	18.75	18.73	18.83	18.27	18.28	18.26	18.28	18.28
7	33.08	32.27	32.25	32.23	32.14	32.14	32.16	32.16	32.24
8	39.81	39.82	39.78	39.68	40.70	40.72	40.68	40.65	40.62
9	47.88	47.75	47.72	47.55	54.41	54.41	54.44	54.61	54.61
10	36.87	37.14	37.15	37.24	41.21	41.24	41.22	41.21	41.04
11	23.54	23.83	23.83	23.79	126.21	126.25	126.26	126.15	125.05
12	122.93	123.74	123.74	123.44	131.13	131.12	131.14	131.15	131.42
13	144.08	144.21	144.22	144.12	135.85	135.86	135.87	135.88	135.88
14	42.09	42.17	42.17	42.14	42.31	42.34	42.29	42.29	42.29
15	28.17	28.25	28.27	28.32	32.25	32.26	32.24	32.24	32.24
16	23.66	23.71	23.72	23.78	24.65	24.65	24.66	24.65	24.65
17	46.78	46.55	46.52	46.53	42.93	42.93	42.91	42.93	42.93
18	41.55	42.13	42.17	42.33	135.78	135.78	135.78	135.68	135.68
19	46.18	40.43	40.51	40.63	38.91	38.92	38.92	38.91	38.91
20	30.78	42.54	42.60	42.64	33.23	33.22	33.23	33.22	33.52
21	33.97	28.76	28.79	28.89	44.45	44.46	44.45	44.44	44.44
22	32.56	33.58	33.61	33.62	75.69	75.65	75.69	75.67	75.59
23	28.07	28.63	28.62	28.66	27.76	27.77	28.78	28.67	28.27
24	16.84	16.57	16.56	16.54	15.61	15.62	15.61	15.62	15.62
25	15.45	15.54	15.53	15.51	14.89	14.87	14.97	14.98	14.97
26	17.36	17.27	17.29	17.28	17.10	17.11	17.10	16.96	16.96
27	26.11	26.09	26.11	26.04	18.31	18.33	18.28	18.31	18.28
28	183.64	178.15[a]	178.11[a]	178.05[a]	20.32	20.34	20.33	20.36	20.42
29	33.11	178.86[a]	178.88[a]	179.56[a]	25.02	25.01	24.99	25.03	25.01
30	23.43	19.06	19.02	19.12	32.50	32.54	32.52	32.51	32.44
OCH_3	–	51.58	51.68	51.68	–	–	–	–	–

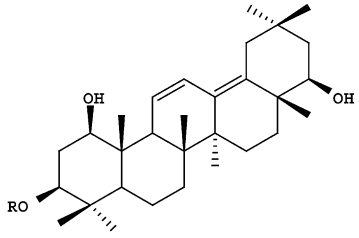
[a] These values may be interchangeable in each column.



(2) Xylose(1→2) glucose

(3) Rhamnose(1→2) glucose

(8) H



R

(4) Rhamnose(1→2) glucose

(5) Glucose(1→2) methylglucuronate

(6) Xylose(1→2) methylglucuronate

(7) Rhamnose(1→2) methylglucuronate

(9) H

Table 2
^{13}C NMR of the sugar moities of compounds **1**–**7** in C_5D_5N

C. No	1	2	3	4	5a	6a	7a
	Glucose	Glucose	Glucose	Glucose	GlcA[a]	GlcA[a]	GlcA[a]
1′	104.75	102.43	102.33	102.36	105.14	105.33	105.25
2′	75.01	82.13	82.16	82.22	78.17a	78.18a	78.20
3′	78.01	76.34a	76.30	76.40	76.58b	76.55b	76.61a
4′	71.68	71.55b	71.52	71.62	73.33	73.31	73.30
5′	78.22	78.34c	78.33	78.43	76.80b	76.81b	76.82a
6′	62.83	62.77	62.75	62.82	170.42	170.41	170.44
OCH_3	–	–	–	–	52.12*	52.14*	52.11*
		Xylose	Rhamnose	Rhamnose	Glucose	Xylose	Rhamnose
1″		106.66	102.23	101.98	105.64	106.64	102.25
2″		76.55a	72.33a	72.41a	75.21	76.57b	72.20b
3″		78.04c	72.81a	72.78a	78.11a	78.06a	72.78b
4″		71.24b	74.51	74.48	71.70	71.18	74.53
5″		67.31	69.44	69.36	78.21a	67.33	69.41
6″		–	18.90	18.91	62.64	–	18.91

[a] GlcA = β-methylglucuronate where the methyl group was introduced by CH_2N_2. a–c = Assignments may be interchangeable within each column.

inner moiety (Kasai et al., 1979, 1987; Bradbury and Jenkins, 1984). Consequently, the structure of **2** was deduced as 28-methyl serratagenate-3-β-*O*-β-xylopyranosyl (1→2)-β-glucopyranoside.

Compound **3** showed a molecular formula calculated as $C_{43}H_{68}O_{14}$ from the negative FAB-MS which showed pseudomolecular ion at *m/z* 807 $[M-H]^-$ and the ^{13}C NMR (off resonance decoupled and DEPT spectra). The negative FAB-MS showed two further peaks at *m/z* 661 [(M−H)-rhamnose]$^-$ and 499 [(M−H)-rhamnose-glucose]$^-$ and the peak at *m/z* 291 [(M−H)$^-$516]$^-$ for the D/E ring fragment as mentioned in **2**. The ^1H NMR of **3** showed an α-anomeric proton signal at δ_H 5.54 (1H, *d*, *J* = 2 Hz) together with an additional doublet methyl at δ_H 1.23 (3H, *d*, *J* = 6.3 Hz) associated with the α-rhamnose moiety and a β-anomeric proton at δ_H 4.56 (1H, *d*, *J* = 7.5 Hz) for β-sugar. Comparison of ^{13}C NMR of **2** and **3** (Tables 1 and 2) indicated glycosylation at C-3 and that, the α-rhamnosyl moiety was linked to C-2 of the β-glucose. In a similar manner the structure of **3** was deduced as 28-methyl serratagenate-3-β-*O*-α-rhamnopyranosyl (1→2) β-glucopyranoside.

Acid hydrolysis of **4** afforded rhamnose and glucose beside the aglycone **9** identified as 1β, 3β, 22β-trihydroxyolean-11, 13(18) diene previously reported from the same plant (Hassanean, 1998) by direct comparison (mmp, co-chromatography and spectral data).

The negative FAB-MS of **4** revealed a pseudo-molecular anion at *m/z* 763 $[M-H]^-$ and a further peaks at *m/z* 617 and *m/z* 455 assigned for respective losses of rhamnose and rhamnose plus glucose from the *m/z* 763 peak (see Experimental). Further confirmation was achieved from ^1H and ^{13}C NMR data of **4** (experimental and Tables 1 and 2, respectively) which showed two olefinic signals at δ_H 6.77 (1H, *d*, *J* = 10.2 Hz) and 6.36 (1H, *dd*, *J* = 10.2 and 3.0 Hz) assigned for the protons H-12 and H-11 of the aglycone part, respectively. The signals at δ_H 5.51 (1H, *d*, *J* = 2.1 Hz) together with the signal at δ_H 1.12 (3H, *d*, *J* = 6.3 Hz) and δ_C 101.9 respectively assigned for terminal α- rhamnopyranosyl moiety, the signals at δ_H 4.51 (1H, *d*, *J* = 7.8 Hz) and δ_C 102.36 were assigned for β-glucopyranosyl moiety and the signals at δ_C 126.21, 131.13, 135.78 and 135.85 (Table 1) are indicative of olean-$\Delta^{11,13(18)}$ system in **4** (Ishii et al., 1980; Mahato and Kundu, 1994). In ^{13}C NMR, the downfield of C-2 (+7.2 ppm) and the upfield shift of C-1 and C-3 (−2.3 and −1.6 ppm respectively) of glucose moiety comparing with **1** indicated that α-rhamnose is attached to C-2 of β-glucose (Bradbury and Jenkins, 1984).

Comparing The ^{13}C NMR data of **4** with respective aglycone **9** showed a downfield shift of C-3 (+9.4 ppm) indicating glycosylation at C-3 of **4** (Table 1). Hence the structure of **4** was established therefore as 3β-*O*-α-rhamnopyranosyl (1→2) β-glucopyranosylolean-11,13(18)-dien-1β, 3β, 22β-triol (**4**).

Fraction 6 (eluted with $CHCl_3$–MeOH 6:4) contains many inseparable spots on normal and reversed phase TLC, so derivatization with diazomethane is a must. Compounds **5**–**7** were isolated as methyl esters (**5a**–**7a**) after diazomethane treatment (see Experimental) and further extensive fractionation over MPLC using RP-18 column.

Acid hydrolysis of compounds **5a**–**7a** afforded also the same aglycone **9** identified as 1β, 3β, 22β-trihydroxyolean-11, 13 (18) diene previously reported from the same plant (Hassanean, 1998) by direct comparison (mmp and co-chromatography and spectral data). Besides, the glycosides **5a**–**7a** afforded the sugar moieties glucose and methylglucuronate from **5a**, xylose and methylglucuronate from **6a** and rhamnose and methylglucuronate from **7a** (TLC and PC).

The molecular formula $C_{43}H_{68}O_{14}$ of **5a** was deduced from FAB-MS and DEPT ^{13}C NMR spectra. The negative FAB-MS of **5a** afforded a pseudomolecular ion at *m/z* 807 $[M-H]^-$ and other fragments at *m/z* 645 and 455 for subsequent loss assigned for a glucosyl and glucosyl plus methyl-glucuronyl moieties respectively. The ^1H NMR of **5a** displayed signals for two β-anomeric sugar proton signals at δ_H 4.56 (1H, *d*, *J* = 7.5 Hz) and δ 4.88 (1H, *d*, *J* = 7.8 Hz), while the ^{13}C NMR revealed two anomeric carbons at δ_C 105.14 and 105.64 besides a carbomethoxy signals for β-methylglucuronopyranosyl moiety at δ_C 52.12 and δ 170.42 (Table 2). The downfield shift of C-2 of β-glucuronyl moiety (+3.1 ppm) and the upfield shift observed in C-1 and C-3 (−2.0 and −1.5 ppm respectively) in comparison with unlinked β-glucuronic acid indicated linkage of the β-glucose moiety at C-2 of β-methylglucuronate (Mohamed et al., 1999; Tan et al., 1999). Similar shifts have been observed in compounds **6a** and **7a** (Table 2).

The downfield shift of C-3 of **5a** in comparison with its respective aglycone **9** (+ 9.4 ppm) indicated clearly glycosylation at C-3. Again similar shifts have been observed at C-3 of both **6a** and **7a** (Table 1). Consequently the structure of **5** was deduced as 3β-*O*-β-glucopyranosyl (1→2)-β-glucuronopyranosylolean-11,13(18)-dien-1β, 3β, 22β-triol (**5**).

Comparison of the ^1H NMR, ^{13}C NMR, FAB-MS and hydrolytic products of **6a** and **7a** with those of **5a** (Tables 1 and 2 and Experimental) lead to the conclusion that **6** has the structure 3β-*O*-β-xylopyranosyl(1→2)-β-glucuronopyranosylolean-11,13(18)-dien-1β, 3β, 22β-triol (**6**), while **7** has the structure 3β-*O*-α-rhamnopyranosyl (1→2)-β-glucuronopyranosylolean-11,13(18)-dien-1β, 3β, 22β-triol.

Compound **1** was identified as the well known oleanolic acid-3β-*O*-β- glucoside by comparison of its ^{13}C NMR spectral data of the original compound, its acetate and its hydrolysate product with those previously reported (Rukunga and Waterman, 2001; Mahato and Kundo, 1994).

It is pertinent to mention that, many saponins with a saikogenin moiety related to this present in compounds **4**–**7** have a broad range of biological activities (Abe et al., 1980; Luo et al. 1993; Benito et al., 1998; Zong et al., 1998; Kyo et al., 1999). Further follow up of these products is in progress now.

3. Experimental

Mps: uncorr.; ^{1}H and ^{13}C NMR (TMS as internal standard): 400 and 100 MHz, respectively were recorded on a Jeol JNM α-400 spectrometer. FAB MS were taken on a Jeol JMS-SX 102 spectrometer by direct inlet method at an ionizating voltage of 70 eV. MPLC; CIG column system (22 mm. i.d. × 30 cm, Kusano Scientific Co.) was used for final purification. CC: Kieselgel 60 (70–230 mesh, Merck) and Diaion HP-20 AG (75–150 μ, Mitsubishi). TLC was carried out on silica gel 60 precoated sheets, F-254 and RP-18 precoated plates, F-254s (Merck). The solvent systems used with silica gel sheets as follows: for aglycones, using $CHCl_3$–MeOH (49:1), for glycosides **2**–**7** using $CHCl_3$–MeOH–H_2O (70:27: 3) and $CHCl_3$–MeOH-H_2O (65:30: 6.5) and for RP-18 precoated sheets using MeOH–H_2O (3:7). For sugar hydrolysate on precoated silica gel sheets using acetonitrile-H_2O (85:15) and for PC using *n*-butanol–acetone–formic acid–water (60:17:8:15).

3.1. Plant material

The root and stem barks of *T. aegyptiaca* Boiss were collected from a region 75 Km South to EL-Kosair city along the road between EL-Kosair and Marsa Alam Cities in October 2001. A voucher sample was identified by Prof. A. Fayed, Professor of Taxonomy, College of Science, Assiut University and kept in the Herbarium section of Dept. of Pharmacognosy, Faculty of Pharmacy, Assiut University, Assiut, Egypt.

3.2. Extraction and isolation of saponins (*1*–*7*)

The air-dried powdered root and stem barks (500 g) were extracted with methanol three times by maceration at room temp. After removal of the solvent under reduced pressure, the syrupy extract was diluted with distilled water and extracted with CH_2Cl_2, the aqueous fraction was chromatographed over Diaion HP-20 column and eluted with distilled H_2O, MeOH–H_2O (1:1) and finally with methanol. 15 g of the saponin fraction (total 55 g) eluted with MeOH–H_2O (1:1) were further chromatographed on silica gel column using $CHCl_3$–MeOH gradiently to give six fractions. Fractions 1 and 2 are not used in this work since they contain mainly some of the previously isolated compounds and their isolation again is not our aim. Fraction 3 (320 mg) eluted with $CHCl_3$–MeOH (85:15) upon repeated silica gel CC under the same condition afforded **1** as amorphous powder (110 mg), fraction 4 (430 mg) eluted with $CHCl_3$–MeOH (72:28) was subjected to RP-18 prepacked column using 30% MeOH to afford compounds **2** (150 mg) and **3** (90 mg). Fraction 5 (100 mg) eluted with $CHCl_3$–MeOH (65:35) was subjected to RP-18 prepacked column using 30% MeOH to afford **4** (70 mg). Fraction 6 (0.6 g) eluted with $CHCl_3$–MeOH (60:40) contain many inseparable spots on silica gel and RP-18 sheets using different solvent systems, so it was first diazomethane methylated (dissolved in methanol and treated with etherial CH_2N_2) followed by extensive chromatography using MPLC and RP-18 pre-packed column and MeOH–H_2O (3:7) as solvent system to afford compounds **5**–**7** in their methyl ester form [**5a** (40 mg), **6a** (70 mg) and **7a** (150 mg)] as amorphous powders.

3.3. Acid hydrolysis of glycosides *2*–*7*

Each glycoside (10 mg) was refluxed with 3% H_2SO_4 for about 3 h. After completion; the reaction mixture in each case was shaken with ether. The ether soluble fraction afforded aglycone **8** for compounds **2** and **3** and aglycone **9** for compounds **4**–**7**. After neutralization with $BaSO_4$ and usual work up (Mohamed et al., 1999), the mother liquor of **2** afforded xylose and glucose, **3** afforded rhamnose and glucose, **4** afforded rhamnose and glucose, **5** afforded glucose and methylglucuronate, **6** afforded xylose and methylglucuronate, and **7** afforded rhamnose and methylglucuronate identified by TLC on precoated silica gel sheets (acetonitrile–H_2O 85 : 15) and PC (*n*-butanol–acetone–formic acid–water 60:17:8:15).

3.3.1. Compound *1*

Oleanolic acid 3-β-*O*-β-glucoside, white powder (110 mg); its spectral data are similar to those reported (Mahato and Kundo 1994; Rukunga and Waterman, 2001).

3.3.2. Compound *2*

White amorphous powder (MeOH), negative FAB-MS, *m/z* 793 $[(M-H)]^-$, 661 $[(M-H)$-pentose$]^-$, 499 $[(M-H)$-pentose-hexose$]^-$ and *m/z* 291 $[(M-H)-502]^-$. ^{1}H NMR (C_5D_5N) δ 5.42, (1H, *br. d*, *J* = 2.2 Hz, H-12), 5.10 (1H, *d*, *J* = 7.5 Hz), 4.56 (1H, *d*, *J* = 7.6 Hz), ^{13}C NMR (C_5D_5N, Tables 1 and 2).

3.3.3. Compound *3*

White amorphous powder (MeOH), negative FAB-MS, m/z 807 $[(M-H)]^-$, 661 $[(M-H)$-methyl pentose$]^-$, 499 $[(M-H)$-methyl pentose-hexose$]^-$ and *m/z* 291 $[(M-H)$-516$]^-$. ^{1}H NMR (C_5D_5N) δ 5.54 (1H, *d*, *J* = 2.0 Hz, H-1 rhamnose), 5.40 (1H, *d*, *J* = 2.2 Hz, H-12), 4.56 (1H, *d*, *J* = 7.5 Hz, H-1 glucose) and 1.23 (3 H, *d*, *J* = 6.3 Hz, CH_3-rhamnose), ^{13}C NMR (C_5D_5N, Tables 1 and 2).

3.3.4. Compound **4**

Amorphous powder (MeOH), negative FAB-MS, *m/z* 763 $[M-H]^-$, 617 [(M−H)-methyl pentose]$^-$ and 455 [(M−H)-methyl pentose-hexose]$^-$. ^{1}H NMR (C_5D_5N), δ 6.77 (1H, *d*, $J=10.2$ Hz, H-12), 6.36 (1H, *dd*, $J=10.2$ and 3.0 Hz, H-11), 5.51 (1H, *d*, $J=2.1$ Hz, H-1 rhamnose), 4.51 (1H, *d*, $J=7.8$ Hz, H-1 Glu), 1.12 (3H, *d*, $J=6.3$ Hz, CH_3-rhamnose). ^{13}C NMR (C_5D_5N, Tables 1 and 2).

3.3.5. Compound **5a**

Amorphous powder (MeOH), negative FAB-MS 807, *m/z* $[M-H]^-$, 645 [(M−H)- hexose]$^-$, 455 [(M−H)-hexose-GlcA]$^-$. ^{1}H NMR (C_5D_5N) δ 6.71 (1H, *d*, *br. d.*, $J=10.2$ Hz, H-12), 6.32 (1H, *dd*, $J=10.2$ and 3.0 Hz, H-11), 4.88 (1H, *d*, $J=7.8$ Hz) and 4.56 (1H, *d*, $J=7.5$ Hz). ^{13}C NMR (C_5D_5N, Tables 1 and 2).

3.3.6. Compound **6a**

Amorphous powder (MeOH), negative FAB-MS, *m/z* 777 $[M-H]^-$, 645 [(M−H)- pentose]$^-$, 455 [(M−H)-pentose-GlcA]$^-$. ^{1}H NMR (C_5D_5N) δ 6.72 (1H, *d*, $J=10.2$ Hz, H-12), 6.30 (1H, *dd,* $J=10.2$ and 3.0 Hz, H-11), 4.85 (1H, *d*, $J=7.8$ Hz) and 4.58 (1H, *d*, $J=7.6$ Hz) . ^{13}C NMR (C_5D_5N, Tables 1 and 2).

3.3.7. Compound **7a**

Amorphous powder (MeOH), negative FAB-MS, *m/z* 791 $[M-H]^-$, 645 [M−H-methyl pentose]$^-$, 455 [M−H-methyl pentose- GlcA]$^-$. ^{1}H NMR (C_5D_5N) δ 6.73 (1H, *br. d.*, $J=10.2$ Hz, H-12), 6.34 (1H, *dd*, $J=10.2$ and 3.0 Hz, H-11), 5.36 (1H, *d*, $J=2.1$ Hz, H-1 rhamnose), 4.88 (1H, *d*, $J=7.8$ Hz, H-1 GluA) and 1.20 (3H, *d*, $J=6.7$ Hz, CH_3 rhamnose). ^{13}C NMR (C_5D_5N, Tables 1 and 2).

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