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TRITERPENOIDS AND GLYCOSIDES FROM *GEUM JAPONICUM*

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Key Word Index—*Geum japonicum*; Rosaceae; triterpenoids; glycosides; 2α-hydroxyursolic acid; 2α-hydroxyoleanolic acid; 2α,19α-dihydroxyursolic acid; glucosides of 2-isopropyl-5-methylhydroquinone; niga-ichigoside F1; suavissimoside F1; ^{1}H NMR; ^{13}C NMR.

Abstract—Two new glucosides and two known ester glucosides have been isolated from *Geum japonicum*. The two new glucosides were isolated by formation of their acetates and were identified as glucosides of 2-isopropyl-5-methylhydroquinone by chemical and spectral studies. The two known ester glucosides were identified as niga-ichigoside F1 and suavissimoside F1 by direct comparison with authentic samples. 2α,19α-Dihydroxyursolic acid and the known glycoside, gein, were also isolated from the same plant, in addition to a mixture of 2α-hydroxyursolic acid and 2α-hydroxyoleanolic acid.

INTRODUCTION

Geum japonicum Thunberg is a perennial herb and the flowering plant has been used in Japan as a diuretic. An eugenol glycoside, gein [1], has been isolated from the plant and the presence of tannins has been reported [2]. This paper deals with the isolation and characterization of three kinds of triterpene acid and four kinds of glycoside in addition to gein.

RESULTS AND DISCUSSION

The methanolic extract of the plant was subjected to solvent fractionation and repeated column chromatography to give a mixture of triterpene acids (**1**–**3**), a mixture of phenolic glycosides (**5** and **6**), the known triterpene ester glycosides niga-ichigoside F1 and suavissimoside F1, and gein (**7**).

Triterpene acids

The mixture of triterpene acids (**1**–**3**) was methylated and the resulting methyl esters were separated by column chromatography into the methyl ester of **1** and a mixture of the methyl esters of **2** and **3**. The mass spectral data (*m/z* 486, 262 and 223) of the mixture of two esters suggested the presence of the methyl esters of hydroxyoleanolic acid (**2**) and hydroxyursolic acid (**3**). The ^{1}H NMR spectrum of this mixture showed two ester methyl signals at δ3.59 and 3.61 and two doublet signals at δ2.94 and 3.02 (each J = 10 Hz) due to H-3α indicating that it was indeed a mixture of methyl 2α-hydroxyoleanolate and methyl 2α-hydroxyursolate [3]. The mass spectra (*m/z* 502, 278, 260, 223, 219, 205 and 201) of the methyl ester of **1** suggested methyl 2α,19α-dihydroxyursolate (tormentic acid methyl ester) [4]. The ^{1}H NMR spectra of the methyl ester and its diacetate indicated that the ester was identical to methyl 2α,19α-dihydroxyursolate [5]. Therefore, the mixture of triterpene acids was made up of 2α-hydroxyoleanolic acid (**2**), 2α-hydroxyursolic acid (**3**) and 2α,19α-dihydroxyursolic acid (**1**).

Phenolic glycosides

The spectral data of the mixture of phenolic glycosides indicated the presence of a benzene derivative which had the following four groups on a benzene nucleus: hydroxy, glucosyloxy, methyl and isopropyl. However, the ^{1}H NMR aromatic proton signals of the mixture and its acetate showed that it contained a major and a closely related minor compound. The mixture was acetylated and separated by HPLC into two acetates. Since the hydrolysis of the mixture of glycosides with β-glucosidase yielded glucose and only one aglycone, the structural difference between the two acetates was considered to be only in the location of the glucose residue. The aglycone was identified as 2-isopropyl-5-methylhydroquinone (thymohydroquinone) [6] by direct comparison with an authentic sample. The ^{13}C NMR spectral data of the major acetate (**4**) suggested that the acetoxy group must be located *ortho* to the isopropyl group because one of the isopropyl methyl groups showed a considerable downfield shift (from δ23.6 or 23.7 to 26.3) upon acetylation of the phenolic hydroxy group, whereas the aromatic methyl carbon signal (δ16.1) showed almost no change (0.1 ppm). Therefore, the structure of the major acetate was deduced as 2-isopropyl-4-glucosyloxy-5-methylphenyl acetate (**4**). The ^{1}H NMR spectrum of the minor acetate showed an anomeric proton signal at δ5.08 as a doublet (J = 7.3 Hz), indicating β-configuration. Accordingly, the major and minor glucosides can be represented by structures **5** and **6**, respectively. The other phenolic glycoside was identified as gein (**7**) [7, 8] by its chemical and spectral data in addition to its mp and optical rotation.

Triterpene ester glucosides

The first glucoside (niga-ichigoside F1) had an MW of 666 (FDMS) and its ^{13}C NMR spectrum (Table 1) suggested an ester glucoside because the anomeric carbon signal was observed at considerably high field (δ95.6) [9]. On acidic and basic hydrolyses, it gave glucose and an aglycone, respectively. The spectral data of the aglycone

Table 1. ^{13}C NMR spectral data of triterpene ester glucosides (pyridine-d_5, TMS as internal standard)

C	Niga-ichigoside F1		Suavissimoside F1
	Glucoside	Aglycone	
1*t*	47.7	47.8	48.2
2*d*	68.8	68.9	68.7
3*d*	78.4	78.5	79.0
4*s*	43.5	43.5	54.4
5*d*	48.5	48.3	52.2
6*t*	18.8	18.8	21.5
7*t*	33.1	33.2	33.3
8*s*	40.6	40.5	40.7
9*d*	48.0	48.3	48.6
10*s*	38.4*	38.1	38.6‡
11*t*	24.2	24.2	24.2
12*d*	128.3	128.0	128.1
13*s*	139.1	140.0	139.1
14*s*	42.1	42.2†	42.1
15*t*	29.1	29.3	29.1
16*t*	26.0	26.4	26.1
17*s*	49.6	48.3	49.6
18*d*	54.3	54.6	54.7
19*s*	72.6	72.8	72.7
20*d*	42.1	42.3†	42.1
21*t*	26.7	26.9	26.7
22*t*	37.6*	38.1	37.6‡
23	66.8*t*	67.0*t*	179.9*s*
24*q*	14.2	14.1	13.3
25*q*	17.4	17.4	17.4
26*q*	17.4	17.4	17.4
27*q*	24.5	24.7	24.5
28*s*	176.9	180.5	176.9
29*q*	27.0	27.1	27.0
30*q*	16.6	16.7	16.6
1′*d*	95.6		95.7
2′*d*	73.8		74.0
3′*d*	80.8		78.8
4′*d*	71.2		71.4
5′*d*	78.7		80.9
6′*t*	62.3		62.5

*, †, ‡Signals are interchangeable.

and its triacetate showed that the aglycone was 2α,3β,19α,23-tetrahydroxyurs-12-en-28-oic acid (19α-hydroxyasiatic acid) (**8**) [10]. The ^1H NMR spectrum of the heptaacetate of the glucoside showed an anomeric proton signal as a doublet (δ 5.50, J = 8.1 Hz), indicating β-linkage with the aglycone. Consequently, the structure of the glucoside was concluded to be 2α,3β,19α,23-tetrahydroxyurs-12-en-28-oic acid 28-*O*-β-D-glucopyranoside, which was identical to niga-ichigoside F1, recently isolated from *Rubus microphyllus* and two other *Rubus* species [11] and *R. suavissimus* [12]. It is noteworthy that the 28-*O*-α-D-glucopyranoside of the same aglycone has been isolated from *Quercus ilex* [13] and from *Anchusa officinalis* [14]. The second glucoside (suavissimoside F1), mp 260–265°, showed *m/z* 680 (FDMS) and the ^1H NMR spectrum of its dimethyl ester was quite similar to that of the first glucoside, except for the ester methyl signals. Its ^{13}C NMR spectrum (Table 1) was also similar to that of the first glucoside, but showed one more carbonyl carbon signal at δ 179.9 instead of the primary alcoholic carbon signal. On reduction with lithium aluminium hydride, the aglycone dimethyl ester gave a pentanol, the acetate of which was identified with the acetate of the pentanol, similarly obtained from the aglycone of the first glucoside. Therefore, the structure of the aglycone was deduced as 2α,3β,19α-trihydroxyurs-12-en-23,28-dioic acid (**9**). Accordingly, the second glucoside was considered to be 2α,3β,19α-trihydroxyurs-12-en-23,28-dioic acid 28-*O*-β-D-glucopyranoside and identified by direct comparison with suavissimoside F1, which was recently isolated [12] from *R. suavissimus*.

EXPERIMENTAL

Mps: uncorr.; TLC: Kieselgel GF-254 (Merck) with the following solvent systems: (a) $CHCl_3$–MeOH (19:1 to 4:1); (b) *n*-hexane–EtOAc (9:1 to 3:2); and (c) $CHCl_3$–MeOH–H_2O (7:3:1).

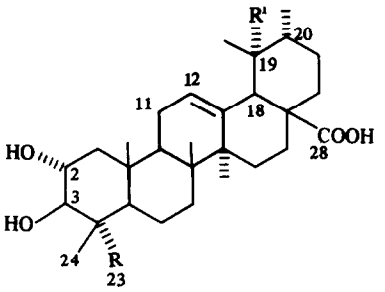
Extraction and isolation. The plant material was collected in Nagasaki Prefecture in September 1982. After 4 days air-drying, the cut material (6.2 kg) was extracted with MeOH to give a MeOH extract (600 g), which was suspended in H_2O and extracted with *n*-hexane, EtOAc and *n*-BuOH successively. The weights (g) of the extracts were: *n*-hexane, 52; EtOAc, 30; *n*-BuOH, 85; H_2O, 270; and insol., 40. The *n*-BuOH extract was then fractionated on an Amberlite XAD-2 column eluted with H_2O, H_2O–MeOH (1:1) and MeOH successively. The latter two eluants were combined and again fractionated on a Sephadex LH-20 column, eluting with MeOH and Me_2CO. The main fraction was chromatographed with Toyopearl HW-40 (70% MeOH) followed by repeated silica gel CC ($CHCl_3$–MeOH) to give a mixture (80 mg) of triterpene acids (**1**–**3**), a mixture (32 mg) of phenolic glucosides (**5** and **6**), niga-ichigoside F1 (740 mg), suavissimoside F1 (350 mg) and gein (**7**, 160 mg).

The triterpene acids were methylated with CH_2N_2 and purified with repeated silica gel CC (*n*-hexane–EtOAc) to give the following compounds.

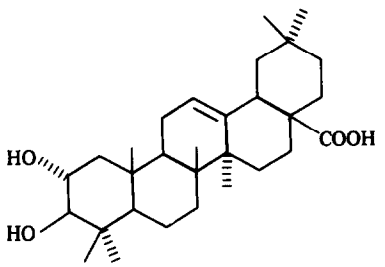
Methyl 2α-hydroxyursolate plus methyl 2α-hydroxyoleanolate. Yield 20 mg, colourless needles from MeOH, mp 223–223.5°; MS *m/z*: 486 $[M]^+$, 468, 450, 262 and 223; ^1H NMR ($CDCl_3$): δ 2.94, 3.02 (each 1H, *d*, J = 10 Hz, H-3), 3.59, 3.61 (each 3H, *s*, COOMe), 3.70 (1H, *m*, H-2) and 5.24 (1H, *m*, H-12). *Diacetate.* Colourless needles from *n*-hexane–EtOAc, mp 117–121°. MS *m/z*: 570 $[M]^+$, 510, 450, 262 and 223; ^1H NMR ($CDCl_3$): δ 1.97, 2.03 (each 3H, *s*, OAc), 3.60, 3.62 (each 3H, *s*, COOMe), 4.73 (1H, *d*, J = 10 Hz, H-3), 5.02 (1H, *m*, H-2) and 5.25 (1H, *m*, H-12).

Methyl 2α,19α-dihydroxyursolate. White powder from MeOH, mp 145–150°, $[\alpha]_D^{15}$ +34.0° (*c* 0.2; $CHCl_3$). MS *m/z*: 502 $[M]^+$, 484, 466, 278, 260, 223, 219, 205 and 201; ^1H NMR ($CDCl_3$): δ 0.68–1.26 (7 × Me), 2.59 (1H, *s*, 18-βH), 2.99 (1H, *d*, J = 11 Hz, H-3), 3.60 (3H, *s*, COOMe), 3.74 (1H, *m*, H-2) and 5.36 (1H, *m*, H-12). *Diacetate.* White powder from MeOH, mp 158–163°. MS *m/z*: 586 $[M]^+$, 568, 526, 484, 466 and 454; ^1H NMR ($CDCl_3$): δ 1.98, 2.06 (each 3H, *s*, 2OAc), 2.60 (1H, *s*, 18-βH), 3.60 (3H, *s*, COOMe), 4.74 (1H, *d*, J = 10.2 Hz, H-3), 5.02 (1H, *m*, H-2) and 5.34 (1H, *m*, H-12).

The mixture of phenolic glycosides (**5** *and* **6**). Colourless needles (EtOAc), mp 103–107°, $[\alpha]_D^{24}$ −15.8° (*c* 0.26, MeOH). MS *m/z*: 328 $[M]^+$, 259, 185 and 165; ^1H NMR (CD_3OD): δ 1.15 (6H, *d*, J = 7 Hz, –CH<u>Me</u>$_2$), 2.13 (3H, *s*, aromatic Me), 3.2–3.8 (sugar protons), 6.53, 6.62, 6.92 and 6.95 (each 1H, *s*, aromatic H); ^{13}C NMR (CD_3OD): δ 151.7 (*s*), 149.0 (*s*), 138.2 (*s*), 123.2 (*s*),



	R	R^1
1	Me	OH
3	Me	H
8	CH_2OH	OH
9	COOH	OH



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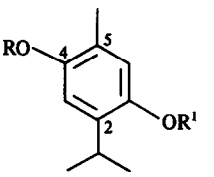
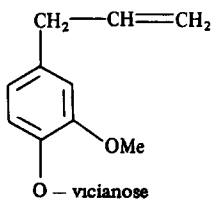


4 R = β–D–glucopyranoside
R^1 = Ac

5 R = β–D–glucopyranoside
R^1 = H

6 R = H
R^1 = β–D–glucopyranoside



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120.3 (*d*), 113.1 (*d*), 104.3 (*d*, anomeric), 78.2 (*d*, C-3′), 77.9 (*d*, C-5′), 75.1 (*d*, C-2′), 71.5 (*d*, C-4′), 62.7 (*t*, C-6′), 27.0 (*d*), 23.6 (*q*), 23.7 (*q*) and 16.1 (*q*). Signals due to minor component: 150.5 (*s*), 117.9 (*d*), 116.1 (*d*), 27.8 (*d*) and 23.1 (*q*). *Pentaacetates.* Colourless needles (MeOH), mp 138–143°. MS *m/z*: 538 $[M]^+$. The acetate was purified by HPLC (Finepak SIL column, 4.6 mm × 250 mm, at a flow rate of 2.6 ml $CHCl_3$/min) to give a major component and a minor component. *Major acetate.* ^1H NMR ($CDCl_3$): δ1.13, 1.14 (each 3H, *d*, J = 6.8 Hz, –CH<u>Me</u>$_2$), 2.05 (9H, *s*, 3OAc), 2.08, 2.12 (each 3H, *s*, OAc), 2.31 (3H, *s*, aromatic Me), 3.19 (1H, *sext.*, J = 6.8 Hz, C<u>H</u>Me_2), 4.20 (2H, *m*, H-6′), 4.96–5.36 (4H, *m*, sugar protons), 5.08 (1H, *d*, J = 7.3 Hz, anomeric), 6.83 and 6.86 (each 1H, *s*, aromatic H); ^{13}C NMR ($CDCl_3$): δ170.4, 170.1, 169.4 (2C), 169.0 (each *s*, CO), 151.6, 145.0, 137.4, 128.0 (each *s*), 119.7, 118.0, 99.6, 72.9, 72.0, 71.2, 68.5 (each *d*), 62.2 (*t*), 29.7 (*d*), 26.3 (*q*), 22.9 (*q*), 22.7 (*q*, 2C), 20.6 (*q*, 3C) and 16.2 (*q*). *Minor acetate.* ^1H NMR ($CDCl_3$): δ1.13, 1.14 (each 3H, *d*, J = 7.0 Hz), 2.04, 2.05, 2.07, 2.08, 2.12, (5 OAc), 2.31 (Me), 3.19 (1H, *sext.*, J = 7.0 Hz), 4.20, 4.96–5.36 (5H, *m*), 6.77 and 6.93 (each 1H, *s*).

Hydrolysis of the mixture of **5** *and* **6**. A sample (10 mg) was dissolved in phthalate buffer, pH 4.5, and kept at 37° with β-glucosidase (5 mg) for 5 hr and then extracted with $CHCl_3$. The aq. layer was treated with Sephadex LH-20 (H_2O) and subjected to Abicel TLC with the following solvents: (a) Me_2CO–HOAc–H_2O (3:1:1), R_f 0.40 and (b) pyridine–EtOAc–HOAc–H_2O–*n*-BuOH (36:36:7:21:3), R_f 0.50. In both systems, the sample had the same R_f values as glucose. The $CHCl_3$ layer was purified by silica gel CC (*n*-hexane–EtOAc, 4:1) to give colourless needles of 2-isopropyl-5-methylhydroquinone, mp 136–138°. MS *m/z*: 166 $[M]^+$; ^{13}C NMR (CD_3OD): δ149.3, 148.0, 134.3, 123.0 (each *s*), 118.5, 113.7, 27.8 (each *d*), 23.2 (*q*, 2C) and 15.9 (*q*). These data were the same as those of an authentic sample of thymohydroquinone.

Niga-ichigoside F1. Colourless needles (aq. MeOH), mp 230–232°, no mp depression on admixture with niga-ichigoside F1 [11]. The identity was also confirmed by co-TLC and comparison of ^1H NMR spectra. $[\alpha]_D^{11}$ +12.1° (*c* 1.0; MeOH); FDMS *m/z*: 689 $[M+Na]^+$ and 527 $[aglycone+Na]^+$; IR ν_{max}^{KBr} cm^{-1}: 3500–3000 (OH) and 1720 (ester); ^1H NMR (CD_3OD): δ0.70–1.34 (6 Me), 2.52 (1H, *s*, 18-βH), 3.0–3.8 (H-2, H-3 and sugar protons) and 5.32 (1H, *m*, H-12); ^{13}C NMR: see Table 1. *Heptaacetate.* Colourless needles (MeOH), mp 170–172°. EIMS *m/z*: 962 $[M]^+$, 902 $[M-HOAc]^+$, 842 and 331 (acetyl glucose); ^1H NMR ($CDCl_3$): δ0.72–1.24 (6 Me), 1.98,

2.06, 2.08 (each 3H, *s*, OAc), 2.01, 2.03 (each 6H, *s*, 4 OAc), 2.52 (1H, *s*, 18-βH), 3.54, 3.58 (each 1H, *d*, J = 12 Hz, H-23), 3.7–4.4 (3H, *m*, H-2, H-3 and H-5'), 5.0–5.3 (4H, *m*, sugar protons), 5.38 (1H, *m*, H-12) and 5.50 (1H, *d*, J = 8.1 Hz, anomeric H).

Hydrolysis of niga-ichigoside F1. (a) 50 mg was hydrolysed with 3% H_2SO_4 (4 ml) on a steam bath for 4 hr. After being neutralized with $Ba(OH)_2$, the filtrate was subjected to Abicel TLC to detect glucose in the same way as described above. (b) 102 mg was dissolved in 1 M KOH (50 ml) and kept for 2 hr on a steam bath. The mixture was extracted with EtOAc and the organic phase was washed with H_2O and evapd to yield a solid, which was recrystallized from aq. MeOH to give colourless crystals (78 mg), mp 286–288°, $[\alpha]_D^{20}$ +27.9° (*c* 0.54; MeOH); IR ν_{max}^{nujol} cm^{-1}: 3500–3000 (OH) and 1685 (COOH). EIMS *m/z*: 504 $[M]^+$, 486, 273, 264, 259, 219, 205 and 201; ^1H NMR (CD_3OD): δ0.70–1.19 (6 Me), 2.49 (1H, *s*, 18-βH), 3.1–4.2 (4H, *m*, H-2, H-3 and H-23), 5.28 (1H, *m*, H-12); ^{13}C NMR (pyridine-d_5): see Table 1.

Triacetate of the aglycone of niga-ichigoside F1. Colourless needles, mp 213–214° (MeOH). EIMS *m/z*: 630 $[M]^+$; ^1H NMR ($CDCl_3$): δ0.74–1.26 (6 Me), 1.99, 2.03, 2.10 (each 3H, *s*, OAc), 2.55 (1H, *s*, 18-βH), 3.58, 3.86 (each 1H, *d*, J = 12 Hz, H-23), 5.04 (2H, *m*, H-2 and H-3) and 5.35 (1H, *m*, H-12).

Suavissimoside F1. Colourless needles from aq. MeOH, mp 260–265° (dec.), no mp depression on admixture with suavissimoside F1 [12]. The identity was also confirmed by co-TLC and comparison of ^1H NMR spectra. $[\alpha]_D^{25}$ +21.8° (*c* 0.5; MeOH). FDMS *m/z*: 703 $[M+Na]^+$, 541 $[aglycone+Na]^+$; IR ν_{max}^{KBr} cm^{-1}: 3500–3000 (OH), 1720 (ester) and 1685 (COOH); ^1H NMR (CD_3OD): δ0.76–1.20 (6 Me), 2.51 (1H, *s*, 18-βH), 3.0–3.8 (H-2, H-3 and sugar protons) and 5.30 (1H, *m*, H-12); ^{13}C NMR (pyridine-d_5): see Table 1. *Hexaacetate.* Colourless needles (MeOH), mp 263–265° (dec). EIMS *m/z*: 946 $[M]^+$, 886 $[M-HOAc]^+$ and 331 (acetyl glucose); ^1H NMR ($CDCl_3$): δ0.70–1.26 (6 Me), 1.98, 1.99, 2.01, 2.02, 2.04, 2.06 (6 OAc), 2.51 (1H, *s*, 18-βH), 3.6–4.4 (sugar protons, H-2', H-3', H-4' and H-6'), 4.9–5.3 (3H, *m*, H-2, H-3 and H-5'), 5.35 (1H, *m*, H-12) and 5.51 (1H, *d*, J = 7.2 Hz, H-1').

Hydrolysis of suavissimoside F1. 50 mg was dissolved in 1 M KOH (5 ml) was kept for 2 hr on a steam bath under N_2. After neutralization with 2 M HCl, the reaction mixture was extracted with *n*-BuOH. The BuOH extract (44 mg) was methylated with CH_2N_2 and purified by silica gel CC ($CHCl_3$–MeOH, 19:1) to form a white crystalline powder (26 mg) from $CHCl_3$ (aglycone dimethyl ester); EIMS *m/z*: 546 $[M]^+$; ^1H NMR ($CDCl_3$): δ0.66–1.27 (6 Me), 2.43 (1H, *d*, J = 10 Hz, H-3), 2.63 (1H, *s*, 18-βH), 3.59, 3.73 (each 3H, *s*, COOMe), 3.78 (1H, *m*, 2-H) and 5.32 (1H, *m*, 12-H).

Diacetate of the aglycone dimethyl ester. Colourless powder (EtOAc), mp 133–137° EIMS *m/z*: 630 $[M]^+$; ^1H NMR ($CDCl_3$): δ0.67–1.26 (6 Me), 1.98 (6H, *s*, 2 OAc), 2.59 (1H, *s*, 18-βH), 3.59, 3.68 (each 3H, *s*, COOMe), 5.01 (1H, *d*, J = 3 Hz, 3-αH), 5.30 (1H, *m*, 2-H) and 5.33 (1H, *m*, 12-H).

Reduction of the aglycone dimethyl ester with $LiAlH_4$. The dimethyl ester (23 mg) was dissolved in THF (7 ml) and reduced with $LiAlH_4$ in an oil bath of 80° for 4 hr. MeOH was added and the filtrate with washings was evapd to dryness. The residue was purified by silica gel CC ($CHCl_3$–MeOH, 9:1) to give colourless needles (10 mg) (urs-12-ene-2,3,19,23,28-pentaol), mp 180–182°. EIMS *m/z*: 490 $[M]^+$.

Tetraacetate of the pentaol. Colourless needles (MeOH), mp 189–190°, EIMS *m/z*: 658 $[M]^+$, 640, 598, 538 and 478; ^1H NMR ($CDCl_3$): δ0.90–1.28 (6 Me), 1.98, 2.03, 2.04, 2.09 (each 3H, *s*, OAc), 3.50 (2H, *s*, H-28), 3.64 (1H, *s*, 18-βH), 3.76, 4.01 (each 1H, *d*, J = 11.4 Hz, H-23), 5.07 (1H, *d*, J = 11.5 Hz, H-3), 5.12 (1H, *m*, H-2) and 5.25 (1H, *m*, H-12).

Gein (7). Colourless needles (aq. MeOH), mp 186–187° (reported [1]: 183°), $[\alpha]_D^{20}$ −48.1° (*c* 0.71; MeOH) (reported [1]: −52.8° (H_2O)). FDMS *m/z*: 481 $[M+Na]^+$, ^1H NMR ($CDCl_3$): δ3.4–4.14 (sugar protons), 3.84 (3H, *s*, OMe), 4.28 (1H, *d*, J = 6.7 Hz, anomeric H), 4.8–5.0 (2H, *m*, CH=C$\underline{H}_2$), 5.10 (1H, *d*, J = 4.4 Hz, H-1''), 5.92 (1H, *m*, CH_2–C$\underline{H}$=CH_2), 6.75 (1H, *dd*, J = 2 and 8 Hz, H-6), 6.81 (1H, *d*, J = 2 Hz, H-2) and 7.10 (1H, *d*, J = 8 Hz, H-5); ^{13}C NMR (pyridine-d_5): δ150.2 (*s*), 146.3 (*s*), 138.2 (*d*), 134.5 (*s*), 121.6 (*d*), 117.7 (*d*), 115.5 (*t*), 113.8 (*d*), 104.9 (*d*), 102.8 (*d*), 78.2 (*d*), 77.3 (*d*), 74.7 (*d*), 74.1 (*d*), 72.3 (*d*), 71.4 (*d*), 69.1 (*d*), 69.0 (*t*), 66.2 (*t*), 56.1 (*q*) and 39.9 (*t*).

Hydrolysis of 7. 7 (20 mg) was dissolved in 3% H_2SO_4 and kept on a steam bath for 4 hr. After usual work-up, glucose and arabinose were detected by TLC on Abicel plates.

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