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TWO IRIDOID GLYCOSIDES FROM *REHMANNIA GLUTINOSA**

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Key Word Index—*Rehmannia glutinosa* var. *hueichingensis*; Scrophulariaceae; iridoid glycosides; iridoid arabinoside; iridoid rutinoside; jioglutosides.

Abstract—Two new iridoid glycosides named jioglutosides A and B, together with 11 known iridoid glycosides, have been isolated from the fresh roots of *Rehmannia glutinosa* var. *hueichingensis*. On the basis of chemical and spectral analyses, the structures of jioglutosides A and B have been elucidated.

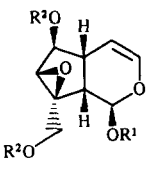
INTRODUCTION

In the course of our investigations on Rehmanniae radix, we reported the isolation of immunosuppressive phenenethylalcohol glycosides (jionosides) and non-glycosidic iridoids (jioglutins, jioglutolide etc) from the steamed roots of *Rehmannia glutinosa* Libosch. var. *hueichingensis* (Chao et Schih)Hsiao (Scrophulariaceae) [1–3], and iridoid glycosides (6-*O*-acylated ajugols) from the dried roots of *R. glutinosa* Libosch. var. *purpurea* Makino [4]. We have now examined the fresh roots of *R. glutinosa* var. *hueichingensis*. As a result, two new iridoid glycosides, jioglutosides A (**1**) and B (**2**), were isolated along with 11 known iridoid glycosides. This paper describes the structural elucidation of two new iridoid glycosides from the fresh roots of this plant.

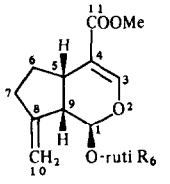
RESULTS AND DISCUSSION

The methanol extract of the fresh roots was fractionated by CC and prep. HPLC to give two new iridoid glycosides (**1** and **2**), together with 11 known iridoid glycosides: catalpol (**3**) [5], geniposide (**4**) [6], 8-epiloganic acid [4], rehmannioside D [7], ajugol (= leonuride) [4], ajugoside (**5**) [8] and five 6-*O*-acylated ajugols [4].

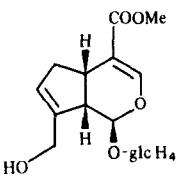
Jioglutoside A (**1**) was obtained as a white amorphous powder, FDMS *m/z*: 332 $[M]^+$, $[\alpha]_D$ −158.8° (MeOH), and gave a brown coloration with hydrochloric acid. Acetylation of **1** afforded the pentaacetate (**1a**), whose high resolution FABMS confirmed the molecular formula, $C_{24}H_{30}O_{14}$. Compound **1** was presumed to be an iridoid glycoside from its ^1H and ^{13}C NMR data (Tables 1 and 2). The ^1H NMR spectrum of **1** exhibited the olefinic proton signals at δ5.07 (*dd*, *J* = 6.0, 4.5 Hz) and 6.34 (*dd*, *J* = 6.0, 1.9 Hz), easily assigned to H-4 and H-3, respectively, indicative of the presence in **1** of the enol-ether group characteristic of C_9-iridoids [9]. The ^1H and ^{13}C signals due to the aglycone moiety of **1** closely resembled those of catalpol (**3**). On the other hand, the signals arising from the glycone differed from that of **3**. The ^{13}C NMR spectrum of **1** showed five signals due to the sugar moiety, whose chemical shifts were consistent with those for methyl arabinofuranoside described in the literature [10]. GC analysis on the TMSi ether of the hydrolysate of **1** demonstrated the presence of arabinofuranose in **1**. The absolute structure (D, L) of the arabinofuranose was established by the method reported by Oshima *et al* [11]. A reductive amination of the acid hydrolysate of **1** with $NaBH_3CN$ and L-(−)-α-methylbenzylamine [L-(−)-MBA], and subsequent acetylation, gave 1-(*N*-acetyl-α-MBA)-1-deoxy-L-arabitol acetate, which was identified with an authentic sample by HPLC. Lastly, the anomeric carbon of L-arabinofuranose in **1** was shown to be α, because the coupling constant of the anomeric proton signal at δ5.44 (*d*, *J* = 1.1 Hz) of **1** was consistent with that (*J* = 1.5 Hz) of methyl α-L-arabinofuranoside prepared from L-arabinose, while the *J* value of β-anomer was 4.2 Hz. On the basis of the evidence mentioned above, jioglutoside A (**1**) was established as catalpolgenin 1-*O*-α-L-arabinofuranoside.



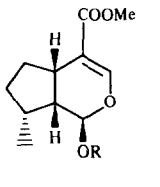
1 R^1 = ara H_3 R^2 = H
1a R^1 = ara Ac_3 R^2 = Ac
3 R^1 = glc H_4 R^2 = H



2 R = H
2a R = Ac



4



2b R = ruti H_6
2c R = glc H_4

*Part 4 in the series 'Chemical and Biological Studies on Rehmanniae Radix'. For part 3 see ref. [4].

Table 1. ^{1}H NMR spectral data for glycosides **1**, **2**, **2b** and **3** and their acetates (**1a** and **2a**) at 500 MHz*

H	1	1a	2	2a	2b†	3
1	4.83 *d* (9.7)	4.81 *d* (9.5)	5.29 *d* (5.3)	5.31 *d* (4.0)	5.31 *d* (5.9)	5.03 *dd* (9.8, 0.4)
3	6.34 *dd* (6.0, 1.9)	6.32 *dd* (6.0, 1.9)	7.46 *d* (1.2)	7.39 *d* (1.0)	7.43 *br s*	6.34 *ddd* (6.0, 1.9, 0.4)
4	5.07 *dd* (6.0, 4.5)	4.95 *dd* (6.0, 4.4)	—	—	—	5.06 *ddd* (6.0, 4.5, 0.5)
5	2.25 *dddd* (8.2, 7.7, 4.5, 1.9)	2.59 *dddd* (8.2, 7.6, 4.4, 1.9)	3.01 *br q* (*ca* 7.0)	2.99 *m*	2.90 *m*	2.27 *dddd* (8.2, 7.6, 4.5, 1.9)
6	3.87 *dd* (8.2, 1.2)	4.84 *dd* (8.2, 1.2)	1.69 *m* 2.06 *m*	1.81 *m* 2.05 *m*	1.69 *m* 2.08 *m*	3.90 *dd* (8.2, 1.2)
7	3.39 *d* (1.2)	3.73 *d* (1.2)	2.34 (2H) *m*	2.30 (2H) *m*	2.20 (2H) *m*	3.44 *br d* (1.2)
8	—	—	—	—	1.35 *m*	—
9	2.53 *dd* (9.7, 7.7)	2.65 *dd* (9.5, 7.6)	2.77 *t*-like	2.84 *m*	1.83 *m*	2.53 *br dd* (9.8, 7.6)
10	3.57 *d* (13.2) 4.18 *d* (13.2)	4.43 *d* (13.0) 4.56 *d* (13.0)	5.11 (2H) *br dq* (*ca* 7.3, 2.1)	5.06 *br s* 5.08 *br s*	1.11 *d* (6.6)	3.78 *d* (13.1) 4.13 *d* (13.1)
COOMe		—	3.67 *s*	3.70 *s*	3.69 *s*	—
Sugar moiety						
	ara	*ara*	*glc*	*glc*	*glc*	*glc*
1	5.44 *d* (1.1)	5.63 *s*	4.65 *d* (7.9)	4.88 *d* (8.1)	4.68 *d* (7.6)	4.76 *d* (7.9)
2	4.08 *dd* (2.3, 1.1)	5.24 *dd* (1.8, 0.8)	3.20 *dd* (9.1, 7.9)	4.99 *dd* (9.7, 8.1)	3.19 *dd* (9.1, 7.6)	3.25 *dd* (9.3, 7.9)
3	3.95 *dd* (3.8, 2.3)	5.07 *dd* (4.3, 1.8)	3.36 *t* (*ca* 9.0)	5.23 *t* (*ca* 9.5)	3.1–3.5 *m*	3.39 *dd* (9.3, 8.5)
4	4.11 *dt* (5.5, 3.9)	4.48 *dt* (5.7, 4.0)	3.29 *dd* (9.7, 9.0)	5.06 *t* (*ca* 9.9)	3.1–3.5 *m*	3.26 *dd* (9.8, 8.5)
5	3.65 *dd* (11.6, 5.5) 3.71 *dd* (11.6, 4.1)	4.21 *dd* (11.9, 5.7) 4.42 *dd* (11.9, 3.8)	3.43 *ddd* (9.7, 6.2, 1.9)	3.76 *ddd* (9.8, 6.5, 2.9)	3.1–3.5 *m*	3.31 *m*‡
6	—	—	3.63 *dd* (11.3, 6.2) 3.97 *dd* (11.3, 1.9)	3.67 *dd* (11.8, 6.5) 3.72 *dd* (11.8, 2.9)	3.6–3.8 *m* 3.98 *dd* (*ca* 11.0, 2.0)	3.63 *dd* (11.9, 6.4) 3.90 *dd* (11.9, 2.1)
rham						
1			4.73 *d* (1.7)	4.78 *d* (1.4)	4.73 *br s*	
2			3.81 *dd* (3.4, 1.7)	5.23 *dd* (3.5, 1.4)	3.80 *dd* (3.4, 1.7)	
3			3.65 *dd* (9.5, 3.4)	5.27 *dd* (10.0, 3.5)	3.6–3.8 *m*	
4			3.36 *t* (9.5)	4.98 *t* (9.7)	3.1–3.5 *m*	
5			3.64 *dq* (9.5, 6.3)	3.87 *dq* (9.7, 6.3)	3.6–3.8 *m*	
6			1.25 *d* (6.3)	1.22 *d* (6.3)	1.25 *d* (6.3)	
OAc		2.07, 2.10, 2.12, 2.13, 2.14		1.93, 1.99, 2.00, 2.04, 2.06, 2.13		

ara = α-L-Arabinofuranose; *glc* = β-D-glucopyranose; *rham* = α-L-rhamnopyranose.
Assignments for **1**–**3** were confirmed by H–H COSY experiments.
*Measured in CD_3OD for glycosides and in $CDCl_3$ for acetates. Coupling constants(Hz) are given in parentheses.
†Measured at 200 MHz.
‡Overlapped in solvent signals.

Table 2. ^{13}C NMR spectral data for glycosides at 125 MHz

C	1		2*	2b	2c†	3*	*Me-ara**
	CD_3OD	D_2O	CD_3OD	D_2O	D_2O	CD_3OD	D_2O
1	95.8 *d*	95.4	96.8 *d*	97.1 *d*	96.3 *d*	95.4 *d*	
3	141.7 *d*	140.8	153.7 *d*	152.6 *d*	152.6 *d*	141.8 *d*	
4	104.1 *d*	103.7	111.2 *s*	113.5 *s*	113.8 *s*	104.1 *d*	
5	39.0 *d*	37.6	35.7 *d*	33.2 *d*	32.6 *d*	39.2 *d*	
6	79.7 *d*	76.5	31.9 *t*	31.6[a] *t*	31.6[a] *t*	79.6 *d*	
7	62.2 *d*	62.3	31.9 *t*	32.8[a] *t*	33.1[a] *t*	62.6 *d*	
8	66.1 *s*	66.0	149.9 *s*	36.4 *d*	36.1 *d*	66.3 *s*	
9	43.4 *d*	42.1	46.1 *d*	43.4 *d*	43.4 *d*	43.7 *d*	
10	63.5 *t*	60.6	110.3 *t*	16.4 *q*	16.3 *q*	63.0 *t*	
11	—	—	169.2 *s*	171.1 *s*	171.2 *s*	—	
COOMe	—	—	51.7 *q*	52.6 *q*	52.6 *q*	—	
Sugar moiety							
	ara	*ara*	*glc*	*glc*	*glc*	*glc*	
1	106.4 *d*	105.2	100.1 *d*	99.5 *d*	99.3 *d*	99.8 *d*	108.8 *d*
2	82.5 *d*	81.4	74.6 *d*	73.5 *d*	73.5 *d*	74.9 *d*	81.3 *d*
3	78.5 *d*	78.0	77.8 *d*	76.5 *d*	76.6 *d*	77.8 *d*	77.0 *d*
4	88.7 *d*	85.9	71.5 *d*	70.4 *d*	70.4 *d*	71.8 *d*	84.3 *d*
5	62.0 *t*	61.7	76.9 *d*	75.8 *d*	77.1 *d*	78.6 *d*	61.7 *t*
6	—	—	68.0 *t*	67.7 *t*	61.5 *t*	61.6 *t*	—
			rham	*rham*		OMe	55.3 *q*
1			102.1 *d*	101.4 *d*			
2			72.1[a] *d*	70.9[b] *d*			
3			72.3[a] *d*	71.1[b] *d*			
4			73.8 *d*	72.8 *d*			
5			69.7 *d*	69.6 *d*			
6			18.0 *q*	17.5 *q*			

Me-ara = Methyl α-L-arabinofuranoside; *ara* = α-L-arabinofuranose; *glc* = β-D-glucopyranose; *rham* = α-L-rhamnopyranose.

Assignments were established by C–H COSY experiments. Multiplicity was confirmed by off-resonance or DEPT spectra.

* Measured at 50 MHz.

† Data taken from ref. [12].

[a,b] Interchangeable in each column.

Jioglutoside B (**2**) was isolated as a white amorphous powder, $[\alpha]_D -50.1°$ (MeOH), and gave the crystalline hexaacetate (**2a**), mp 164–165°, $C_{35}H_{46}O_{19}$, upon acetylation. Its UV (λ_{max}: 237 nm), IR [ν_{max} cm^{-1}: 1696 (C=O), 1634 (C=C)] and ^1H NMR [δ7.46 (*d*, *J* = 1.2 Hz, H-3) and 3.67 (*s*, COOMe)] data revealed the presence of an enol-ether group conjugated with COOMe. Furthermore, the ^1H NMR spectrum of **2** exhibited two anomeric proton signals at δ4.65 (*d*, *J* = 7.9 Hz) and 4.73 (*d*, *J* = 1.7 Hz), respectively. Hence **2** seemed to be a disaccharide of a C_{10}-iridoid. Moreover, the presence of an extra olefinic proton signal at δ5.11 (2H, *m*) pointed to the occurrence of an exo methylene in **2**. The ^{13}C spectral data [δ110.3 (*t*) and 149.9 (*s*)], as well as biosynthetic considerations, showed that the exo methylene could be placed at C-8. Hydrogenation of **2** catalysed with platinum dioxide gave the dihydro derivative **2b** as a white amorphous powder, FDMS *m/z*: 521 $[M+H]^+$. The ^{13}C chemical shifts for the aglycone moiety of **2b** were in good agreement with those of 8-epideoxyloganin (**2c**) reported by Damtoft *et al.* [12]. With regard to the sugar moiety, hydrolysis of **2** with 10% HCl gave rhamnose and glucose. The ^{13}C NMR spectrum of **2** showed that the C-6 methylene of glucose appeared at lower field, δ68.0 (*t*), due to 'glycosylation shifts' [13]. This indicates that the sugar of **2** is α-L-rhamnopyranosyl-(1 → 6)-D-glucopyranose, i.e. rutinose [14]. The linkage between rutinose and the aglycone moiety was confirmed to be in the β-form from the *J* value (7.9 Hz) of anomeric proton signal of glucose. Thus, the structure of jioglutoside B was elucidated as **2**.

From the fresh roots of *R. glutinosa* var. *hueichingensis*, we have isolated 13 iridoid glycosides. Two of them, jioglutosides A (**1**) and B (**2**), are new compounds and are the first examples of iridoid glycosides having an arabinofuranose or rutinose moiety. Moreover, it is for the first time that geniposide (**4**) and ajugoside (**5**) have been isolated from *R. glutinosa*. From the chemotaxonomic viewpoint, it is interesting that geniposide, well known as the major component in the fruits of *Gardenia jasminoides* Ellis (Rubiaceae) [6], has been found in *Rehmannia* plant.

EXPERIMENTAL

Mps: uncorr. ^1H and ^{13}C NMR spectra were measured with TMS or TSPA [3-(trimethylsilyl) propionic acid Na salt, in case of D_2O] as the int. standard. 2D COSY spectra were recorded under standard conditions. Prep. HPLC was run on a Shimadzu LC-6A unit with a CIG Si-10 column (30 cm × 15 mm i.d.).

Acetylation was conducted with Ac_2O, pyridine and a catalytic amount of 4-dimethyl aminopyridine.

Plant material. Fresh roots of *R. glutinosa* var. *hueichingensis* were cultivated at Izu Experimental Farm, Tsumura & Co. (Shizuoka Prefecture), and were collected in January 1987. Plant material was identified by Dr M. Okada of this Laboratory.

Extraction and isolation. The fresh roots (40 kg) of *R. glutinosa* var. *hueichingensis* were sliced and then extracted with MeOH (200 l × 2). The MeOH extract, after concn to *ca* 10 l, was defatted with *n*-hexane and applied to a Diaion HP-20 column which was eluted with H_2O (fr. 1) and then MeOH (fr. 2). Fr. 1 was subjected to a charcoal column, eluted with H_2O, to remove sugars. Subsequent elution with MeOH gave a glycosidic fraction, which was partitioned between H_2O and *n*-BuOH. The aq. layer was subjected to CC on MCI gel CHP20P and subsequent μ Bondapak C_{18} (eluting with an increasing amount of MeOH in H_2O) to give catalpol (**3**, 8.7 g), ajugol (5.0 g), rehmannioside D (3.0 g) and 8-epiloganic acid (0.2 g). The *n*-BuOH layer (37 g) was repeatedly subjected to silica gel CC and prep. HPLC (eluting with an increasing amount of MeOH in $CHCl_3$) to give jioglutoside A (**1**, 50 mg).

Fr. 2, after washing with $CHCl_3$, was passed through Sephadex LH-20 column for removal of phenolic compounds, and was repeatedly subjected to silica gel CC (eluted with $CHCl_3$–MeOH, 5:1), and to prep. HPLC (eluted with EtOAc–MeOH–H_2O, 40:2:1 and then with $CHCl_3$–MeOH, 9:1), to afford jioglutoside B (**2**, 67 mg), geniposide (**4**, 112 mg), ajugoside (**5**, 183 mg), 6-*O*-vanilloylajugol (44 mg), 6-*O*-*p*-coumaroylajugol (30 mg), 6-*O*-*E*-feruloylajugol (190 mg), 6-*O*-*Z*-feruloylajugol (10 mg) and 6-*O*-(4″-*O*-α-L-rhamnopyranosyl) vanilloylajugol (57 mg).

Known compounds except for ajugoside (**5**) and rehmannioside D were identified by direct comparison with authentic samples [4–6]. Rehmannioside D was identified by comparison of physico-chemical and spectral data with those described in the literature [7]. Ajugoside: see below.

Jioglutoside A (**1**). White amorphous powder, $[\alpha]_D^{20}$ −158.8° (MeOH; *c* 1.65). IR ν_{max}^{KBr} cm^{-1}: 3380 (OH), 1654 (C=C). ^{1}H NMR (CD_3OD): see Table 1. ^{13}C NMR (CD_3OD, D_2O): see Table 2. ^{13}C NMR (125 MHz, pyridine-d_5): δ 38.9 (*d*, C-5), 42.9 (*d*, C-9), 61.7 (*t*, C-10), 62.1 (*t*, C-7), 63.2 (*t*, ara C-5), 66.0 (*s*, C-8), 78.5 (*d*, ara C-3), 79.1 (*d*, C-6), 82.2 (*d*, ara C-2), 89.6 (*d*, ara C-4), 95.4 (*d*, C-1), 104.3 (*d*, C-4), 106.4 (*d*, ara C-1), 140.9 (*d*, C-3). FDMS *m/z*: 332 [M]$^+$.

Jioglutoside A pentaacetate (**1a**). White amorphous powder, $[\alpha]_D^{26}$ −117.6° ($CHCl_3$; *c* 1.00). ^{1}H NMR (500 MHz, $CDCl_3$): see Table 1. ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.6 (2C, *q*, OAc × 2), 20.7, 20.8, 20.9 (each *q*, OAc × 3), 34.8 (*d*, C-5), 42.4 (*d*, C-9), 58.6 (*d*, C-7), 60.8 (*t*, C-10), 62.6 (*s*, C-8), 63.3 (*t*, ara C-5), 76.9 (*d*, ara C-3), 79.6 (*d*, C-6), 80.9 (*d*, ara C-2), 82.5 (*d*, ara C-4), 93.9 (*d*, C-1), 101.8 (*d*, ara C-1), 102.5 (*d*, C-4), 141.2 (*d*, C-3), 169.4, 170.2, 170.4, 170.6, 171.2 (each *s*, C=O × 5). High resolution FABMS *m/z*: 543.1691 [M + H]$^+$ (calc. for $C_{24}H_{31}O_{14}$: 543.1713).

Identification of α-L-*arabinofuranose.* (*i*) *Preparation of methyl arabinosides.* A soln of L-arabinopyranose (1 g) in 2.5% HCl–MeOH (150 ml) was heated at 50° for 30 min. The reaction mixture was neutralized with Amberlite IRC 50 (OH^- form) resins and was subjected to prep. HPLC with EtOAc–MeOH (9:1) as eluent to give methyl α-L-arabinofuranoside (0.5 g), methyl β-L-arabinofuranoside (0.2 g) and methyl β-L-arabinopyranoside (0.1 g) [15]. *Methyl* α-L-*arabinofuranoside.* White amorphous powder, $[\alpha]_D^{25}$ −128.7° (MeOH; *c* 0.86). ^{1}H NMR (200 MHz, CD_3OD): δ 3.36 (3H, *s*, OMe), 3.62 (1H, *dd*, *J* = 11.9, 5.3 Hz, H-5), 3.75 (1H, *dd*, *J* = 11.9, 3.3 Hz, H-5), 3.82 (1H, *dd*, *J* = 6.1, 3.5, 3.3 Hz, H-3), 3.91 (1H, *ddd*, *J* = 6.1, 5.3, 3.3 Hz, H-4), 3.94 (1H, *dd*, *J* = 3.5, 1.5 Hz, H-2), 4.75 (1H, *d*, *J* = 1.5 Hz, H-1). ^{13}C NMR (50 MHz, D_2O): see Table 2. $^1J_{C1-H1}$ = 170.0 Hz. *Methyl* β-L-*arabinofuranoside.* White amorphous powder, $[\alpha]_D^{25}$ +109.8° (MeOH; *c* 1.11). ^{1}H NMR (200 MHz, CD_3OD): δ 3.41 (3H, *s*, OMe), 3.54 (1H, *dd*, *J* = 11.6, 6.8 Hz, H-5), 3.68 (1H, *dd*, *J* = 11.6, 3.4 Hz, H-5), 3.76 (1H, *dt*, *J* = *ca* 7.0, 3.4 Hz, H-4), 3.90 (1H, *t*-like, *J* = *ca* 7.2 Hz, H-3), 3.96 (1H, *dd*, *J* = 7.6, 4.2 Hz, H-2), 4.74 (1H, *d*, *J* = 4.2 Hz, H-1). ^{13}C NMR (50 MHz, D_2O): δ 55.4 (*q*, OMe), 63.5 (*t*, C-5), 75.0 (*d*, C-3), 76.8 (*d*, C-2), 82.5 (*d*, C-4), 102.5 (*d*, C-1). $^1J_{C1-H1}$ = 176.0 Hz. *Methyl* β-L-*arabinopyranoside.* White amorphous powder. ^{13}C NMR (50 MHz, D_2O): δ 55.6 (*q*, OMe), 62.9 (*t*, C-5), 68.6 (*d*, C-2), 69.2 (*d*, C-3), 69.3 (*d*, C-4), 100.3 (*d*, C-1); $^1J_{C1-H1}$ = 169.8 Hz. These methyl arabinosides were identified by comparison of these data with those described in the literature [10].

(*ii*) *Hydrolysis of* **1**. Compound **1** (3 mg) was hydrolysed as described in (i) to give methyl α-arabinofuranoside, which was detected by TLC [EtOAc–MeOH (4:1), R_f 0.50]. Furthermore, the presence of methyl α-arabinofuranoside was demonstrated as a TMSi ether by GC [column: 3% SE-30 (2 m × 4 mm i.d.), column temp.: 130°, inj. temp.: 200°, carrier: He at 50 ml/min, detection: FID, R_t 9.4 min].

(*iii*) *Determination of absolute structure* (D, L) *of arabinose in* **1**. A soln of **1** (5 mg) in 10% HCl aq. (50 μl) was heated at 50° for 1 hr, neutralized with 10% NaOH aq., and then added 100 μl of a soln prepared from L-(−)-MBA (50 μl) and $NaBH_3CN$ (20 mg) in MeOH (1 ml). The mixture was kept at room temp. overnight, acidified to pH 3–4 with HOAc, and evapd to dryness. The residue was acetylated with Ac_2O and pyridine (each 0.4 ml) at 100° for 1 hr. The reaction mixture was then diluted with water (5 ml) and extracted with $CHCl_3$. The $CHCl_3$ extract was subjected to HPLC [column: TSK-SIL 60 (30 cm × 4.6 mm i.d.), mobile phase: 5% EtOH in *n*-hexane, flow: 1.3 ml/min, detection: UV 230 nm], which demonstrated the presence of 1-[*N*-acetyl-L-(−)-α-MBA]-1-deoxy-L-arabitol acetate (R_t 23.3 min) [11]. Standard samples of 1-[*N*-acetyl-L-(−)-MBA]-1-deoxy-L-arabitol acetate (R_t 23.3 min) and 1-[*N*-acetyl-L-(−)-MBA]-1-deoxy-D-arabitol acetate (R_t 20.0 min) were prepared from commercially available L- and D-arabinose, respectively, by the same method as described above in case of **1**.

Jioglutoside B (**2**). White amorphous powder, $[\alpha]_D^{24}$ −50.1 (MeOH; *c* 1.11). UV λ_{max}^{EtOH} nm (ε): 237 (8780). IR ν_{max}^{KBr} cm^{-1}: 3416 (OH), 1696 (C=O), 1634 (C=C). ^{1}H NMR (CD_3OD): see Table 1. ^{13}C NMR (CD_3OD): see Table 2. FDMS *m/z*: 519 [M + H]$^+$.

Jioglutoside B hexaacetate (**2a**). Colourless needles, mp 164–165°. $[\alpha]_D^{26}$ −45.8° ($CHCl_3$; *c* 0.65). UV λ_{max}^{EtOH} nm (ε): 232 (8230). IR ν_{max}^{KBr} cm^{-1}: 1758 (acetyl C=O), 1714 (C=O), 1638 (C=C). ^{1}H NMR (500 MHz, $CDCl_3$): see Table 1. ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.5 (*q*, rham C-6), 20.3, 20.6, 20.7 (2C), 20.8, 20.9 (each *q*, OAc × 6), 30.0, 30.9 (each *t*, C-6, 7), 33.6 (*d*, C-5), 45.0 (*d*, C-9), 51.1 (*q*, COOMe), 66.7 (*d*, rham C-5), 67.2 (*t*, glc H-6), 68.9 (*d*, glc C-4), 69.3, 69.7 (each *d*, rham C-2, 3), 70.8 (*d*, rham C-4), 71.0 (*d*, glc C-2), 72.5 (*d*, glc C-5), 73.5 (*d*, glc C-3), 95.1 (*d*, C-1), 95.9 (*d*, glc C-1), 98.2 (*d*, rham C-1), 109.2 (*t*, C-10), 110.9 (*s*, C-4), 148.4 (*s*, C-8), 151.4 (*d*, C-3), 167.2 (*s*, C-11), 169.1, 169.5, 169.9, 170.0 (2C), 170.2 (each *s*, C=O × 6). EIMS *m/z*: 770 [M]$^+$, 710, 561, 317, 273. (Found: C, 54.34; H, 6.03. $C_{35}H_{46}O_{19}$ requires: C, 54.54; H, 6.02%).

Acid hydrolysis of **2**. A soln of **2** (*ca* 3 mg) in 10% HCl aq. (1 ml) was heated at 80° for 1 hr. The reaction mixture was concd under a stream of N_2 to give a residue, in which rhamnose (R_f 0.70) and glucose (R_f 0.42) were detected by TLC (cellulose, *n*-BuOH–pyridine–H_2O, 6:4:3).

Hydrogenation of **2**. Compound **2** (19 mg) was hydrogenated with H_2–PtO_2 in EtOH at room temp. to give the dihydro derivative **2b** (17 mg) as a white amorphous powder, $[\alpha]_D^{25}$ −63.9° (MeOH; *c* 0.75). UV λ_{max}^{EtOH} nm (ε): 237 (9300). IR

ν_{max}^{KBr} cm^{-1}: 3424 (OH), 1703 (C=O), 1637 (C=C). ^1H NMR (CD_3OD): see Table 1. ^{13}C NMR (D_2O): see Table 2. FDMS *m/z*: 521 $[M+H]^+$.

Catalpol (**3**). Colourless needles, mp 210–211°. $[\alpha]_D^{20}$ −102.2° (MeOH; *c* 0.85). ^1H NMR (CD_3OD): see Table 1. ^{13}C NMR (CD_3OD): see Table 2. FDMS *m/z*: 362 $[M]^+$, 385 $[M+Na]^+$. (Found: C, 49.81; H, 6.09. Calc. for $C_{15}H_{22}O_{10}$: C, 49.72; H, 6.12%) [5].

Geniposide (**4**). Colourless granules, mp 164–165°. $[\alpha]_D^{25}$ +16.2° (EtOH; *c* 0.75). UV λ_{max}^{EtOH} nm (ε): 239 (9770). IR ν_{max}^{KBr} cm^{-1}: 3532 (OH), 1714 (C=O), 1640 (C=C). ^1H NMR (500 MHz, D_2O): δ2.14 (1H, *ddt*, *J* = 16.6, 4.7, 2.3 Hz, H-6), 2.83 (1H, *br dd*, *J* = 16.6, 8.1 Hz, H-6), 2.86 (1H, *br t*, *J* = *ca* 7 Hz, H-9), 3.23 (1H, *dq*, *J* = 8.1, 1.1 Hz, H-5), 3.35 (1H, *dd*, *J* = 9.4, 8.0 Hz, glc H-2), 3.42 (1H, *dd*, *J* = 9.7, 8.4 Hz, glc H-4), 3.46 (1H, *ddd*, *J* = 9.7, 5.4, 1.9 Hz, glc H-5), 3.52 (1H, *dd*, *J* = 9.4, 8.4 Hz, glc H-3), 3.73 (1H, *dd*, *J* = 12.4, 5.4 Hz, glc H-6), 3.76 (3H, *s*, COOMe), 3.90 (1H, *dd*, *J* = 12.4, 1.9 Hz, glc H-6), 4.25 (1H, *br dd*, *J* = 14.2, 1.9 Hz, H-10), 4.32 (1H, *br d*, *J* = 14.2 Hz, H-10), 4.83 (1H, *d*, *J* = 8.0 Hz, glc H-1), 5.29 (1H, *d*, *J* = 6.8 Hz, H-1), 5.87 (1H, *br s*, H-7), 7.57 (1H, *d*, *J* = 1.1 Hz, H-3). ^{13}C NMR (125 MHz, D_2O): δ37.1 (*d*, C-5), 40.9 (*t*, C-6), 48.6 (*d*, C-9), 54.7 (*q*, COOMe), 62.6 (*t*, C-10), 63.4 (*t*, glc C-6), 72.3 (*d*, glc C-4), 75.6 (*d*, glc C-2), 78.5 (*d*, glc C-3), 79.1 (*d*, glc C-5), 100.0 (*d*, C-1), 101.7 (*d*, glc C-1), 114.5 (*s*, C-4), 131.9 (*d*, C-7), 144.1 (*s*, C-8), 155.4 (*d*, C-3), 173.0 (*s*, C-11). FDMS *m/z*: 388 $[M]^+$ [6].

Ajugoside (**5**). White amorphous powder, $[\alpha]_D^{26}$ −102.9° (MeOH; *c* 0.40). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1710 (C=O), 1658 (C=C). ^1H NMR (200 MHz, CD_3OD): δ1.53 (3H, *s*, H-10), 2.00 (3H, *s*, OAc), 2.07 (1H, *dd*, *J* = 14.5, 4.3 Hz, H-7), 2.20 (1H, *dd*, *J* = 14.5, 1.3 Hz, H-7), 2.85 (2H, *m*, H-5 and 9), 3.2–3.5 (4H, *m*, glc H-2, 3, 4 and 5), 3.67 (1H, *m*, glc H-6), 3.89 (1H, *dd*, *J* = 12.3, 2.0 Hz, glc H-6), 4.01 (1H, *m*, H-6), 4.65 (1H, *d*, *J* = 6.5 Hz, glc H-1), 4.71 (1H, *ddd*, *J* = 6.2, 2.0, 1.5 Hz, H-4), 5.85 (1H, *d*, *J* = 1.8 Hz, H-1), 6.21 (1H, *dd*, *J* = 6.2, 2.0 Hz, H-3). ^{13}C NMR (50 MHz, CD_3OD): δ22.3 (*q*, OAc), 22.8 (*q*, C-10), 41.7 (*d*, C-5), 48.7 (*d*, C-9), 63.0 (*t*, glc C-6), 71.7 (*d*, glc C-4), 74.8 (*d*, glc C-2), 76.9 (*d*, glc C-3), 78.0 (*d*, glc C-5), 90.1 (*s*, C-8), 94.6 (*d*, C-1), 100.0 (*d*, glc C-1), 104.2 (*d*, C-4), 141.5 (*d*, C-3), 173.2 (*s*, C=O). FABMS *m/z*: 429 $[M+K]^+$, 413 $[M+Na]^+$ [8].

Ajugoside pentaacetate (**5a**). Colourless needles, mp 175–176°. $[\alpha]_D^{25}$ −148.8° ($CHCl_3$; *c* 0.28). IR ν_{max}^{KBr} cm^{-1}: 1752 (C=O), 1658 (C=C). ^1H NMR (200 MHz, $CDCl_3$): δ1.54 (3H, *s*, H-10), 1.97, 1.99, 2.00, 2.01, 2.03, 2.11 (each 3H, *s*, OAc × 6), 2.12 (1H, *dd*, *J* = 15.4, 4.6 Hz, H-7), 2.31 (1H, *br d*, *J* = 15.4 Hz, H-7), 2.77 (1H, *d*, *J* = 8.3 Hz, H-9), 2.88 (1H, *d*, *J* = 8.3 Hz, H-5), 3.77 (1H, *ddd*, *J* = 9.8, 4.4, 2.4 Hz, glc H-5), 4.12 (1H, *dd*, *J* = 12.5, 2.4 Hz, glc H-6), 4.39 (1H, *dd*, *J* = 12.5, 4.9 Hz, glc H-6), 4.72 (1H, *d*, *J* = 6.4 Hz, H-4), 4.89 (1H, *m*, H-6), 5.01 (1H, *t*, *J* = 9.3 Hz, glc H-4), 5.10 (1H, *t*, *J* = 9.5 Hz, glc H-2), 5.24 (1H, *t*, *J* = 9.3 Hz, H-3), 5.82 (1H, *d*, *J* = 1.5 Hz, H-1), 6.17 (1H, *dd*, *J* = 6.4, 2.2 Hz, H-3). Compound **5a** was identical with ajugol hexaacetate prepared from ajugol [4, 5].

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