Saponins from Leaves of *Acanthopanax senticosus* HARMS., Ciwujia. II. Structures of Ciwujianosides A_1, A_2, A_3, A_4 and D_3

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Further investigation of the chemical constituents of the leaves of *Acanthopanax senticosus* HARMS. resulted in the isolation of five new triterpenoid saponins, named ciwujianosides A_1 (1), A_2 (2), A_3 (3), D_3 (4) and A_4 (5). The structures of these saponins were elucidated as follows: 1, 3-*O*-β-glucopyranosyl-(1→2)-α-arabinopyranosyloleanolic acid 28-*O*-α-rhamnopyranosyl-(1→4)-β-glucopyranosyl-(1→6)-β-glucopyranosyl ester; 2, 3-*O*-β-glucopyranosyl-(1→2)-α-arabinopyranosyl-30-norolean-12,20(29)-dien-28-oic acid 28-*O*-α-rhamnopyranosyl-(1→4)-β-glucopyranosyl-(1→6)-β-glucopyranosyl ester; 3, 3-*O*-α-rhamnopyranosyl-(1→2)-α-arabinopyranosylmesembryanthemoidigenic acid 28-*O*-α-rhamnopyranosyl-(1→4)-β-glucopyranosyl-(1→6)-β-glucopyranosyl ester; 4, 3-*O*-α-arabinopyranosylmesembryanthemoidigenic acid 28-*O*-α-rhamnopyranosyl-(1→4)-6-*O*-acetyl-β-glucopyranosyl-(1→6)-β-glucopyranosyl ester; 5, 3-*O*-β-glucopyranosyl-(1→2)-α-arabinopyranosylmesembryanthemoidigenic acid 28-*O*-α-rhamnopyranosyl-(1→4)-6-*O*-acetyl-β-glucopyranosyl-(1→6)-β-glucopyranosyl ester.

Keywords *Acanthopanax senticosus*; Araliaceae; saponin; Chinese folk medicine; ciwujianoside; oleanolic acid glycoside; noroleanolic acid glycoside; mesembryanthemoidigenic acid glycoside; ciwujia

In the preceding paper,[1] we reported the isolation and structure determination of eight new saponins, named ciwujianosides, B, C_1, C_2, D_2 and E (noroleanolic acid saponins), and ciwujianosides C_3, C_4 and D_1 (oleanolic acid saponins), from leaves of *Acanthopanax senticosus* (RUPR. *et* MAXIM.) HARMS. (Araliaceae). Further investigation of the leaves led to the isolation of five additional new saponins, named ciwujianosides A_1 (**1**), A_2 (**2**), A_3 (**3**), D_3 (**4**) and A_4 (**5**). This paper deals with the structure determination of these saponins.

The methanolic extract of the dried leaves of *A. senticosus* was chromatographed as described in the preceding paper[1] and finally purified by high-performance liquid chromatography (HPLC) to give **1**—**5**.

Inspection of the ^{1}H- and ^{13}C-nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra (Table I) indicated that saponin **1** is the 3,28-bisdesmoside of oleanolic acid (**6**) having five monosaccharide units. On acid hydrolysis, **1** afforded oleanolic acid, arabinose, glucose and rhamnose.[2] On selective cleavage of the ester–glycoside linkage with anhydrous LiI and 2,6-lutidine in anhydrous methanol,[3] **1** gave a prosapogenin **7** and a methyl oligoglycoside **8**. Compound **7** was identified as saponin P_E isolated from *Akebia quinata* by comparison of spectral and physical data with reported values.[4] The product **8** was identified as an anomeric mixture of methyl α-rhamnopyranosyl-(1→4)-β-glucopyranosyl-(1→6)-(α and β)-glucopyranoside by comparison of its ^{13}C-NMR data with those of an authentic sample.[1] From these results coupled with the inspection of the ^{13}C-NMR signals due to the ester-glycosyl moiety,[5] the structure of **1** was established as shown in Chart 1.

In the ^{13}C-NMR spectrum of **2** (Table I), the signals due to the aglycone moiety were in good agreement with those of previously reported ciwujianosides B and C_1,[1] indicating that **2** is a 3,28-bisdesmoside of 30-norolean-12,20(29)-dien-28-oic acid (**9**). On acid hydrolysis, **2** gave arabinose, glucose and rhamnose, while a genuine aglycone could not be obtained owing to the acid-catalyzed modification. On selective cleavage of the ester–glycoside linkage (*vide supra*), **2** also afforded **8** as a methyl oligoglycoside, and a pro-

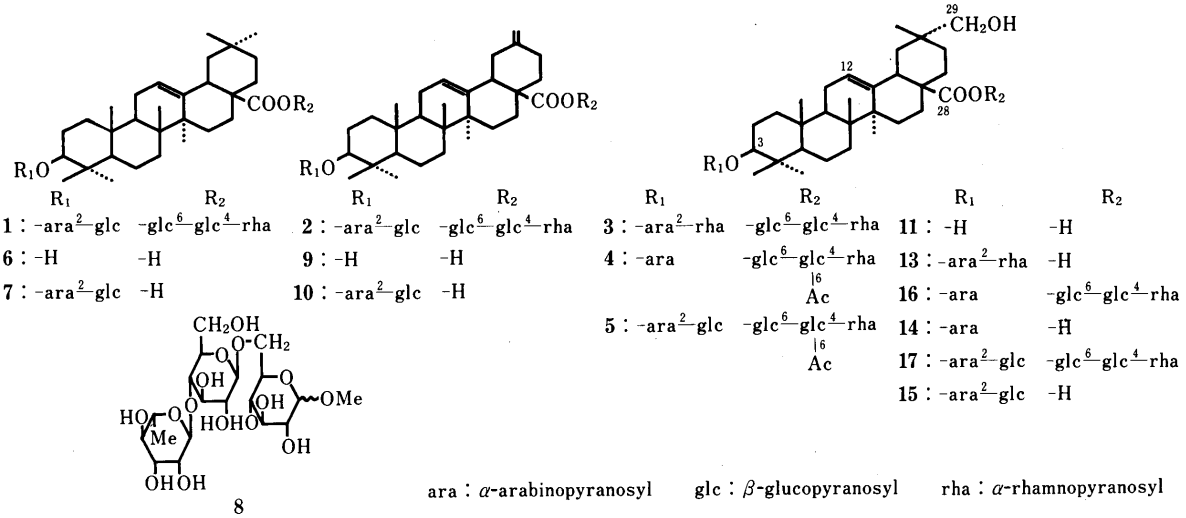

Chart 1

TABLE I. ^{13}C-NMR Chemical Shifts of Aglycone Moieties in C_5D_5N

	1	2	10	4	14	3	13	5	15	11	12[a]	9	6
C-1	38.7	38.7	38.9	38.8	38.7	38.9	38.8	38.8	38.6	38.9	39.0	38.9	38.9
C-2	26.4	26.4	26.5	26.5	26.6	26.5	26.4	26.1	26.3	28.1	26.4	28.3	28.2[b]
C-3	88.9	88.8	88.8	88.7	88.6	88.8	88.8	88.8	88.8	78.1	86.2	78.1	78.0
C-4	39.5[b]	39.4[b]	39.6[b]	39.5[b]	39.5[b]	39.5[b]	39.5[b]	39.5[b]	39.5[b]	39.4[b]	53.7	39.3[b]	39.4[c]
C-5	55.8	55.7	55.8	55.9	55.8	55.9	55.9	55.9	55.7	55.9	51.9	55.8	55.8
C-6	18.5	18.3	18.5	18.4	18.5	18.5	18.6	18.5	18.5	18.8	21.6	18.4	18.8
C-7	33.1	32.8	33.1	33.0	33.1	33.1	33.2	33.2	33.1	33.3	32.9	33.2	33.3
C-8	39.8[b]	39.7[b]	39.9[b]	39.9[b]	39.7[b]	39.9[b]	39.7[b]	39.9[b]	39.6[b]	39.8[b]	40.3	39.7[b]	39.8[c]
C-9	48.0	47.9	48.1	48.0	48.0	48.1	48.0	48.0	47.9	48.2	48.2	48.0[c]	48.1
C-10	37.0	36.8	37.0	37.0	37.0	37.0	37.0	37.0	36.9	37.4	36.6	37.3	37.4
C-11	23.7	23.5	23.7	23.7	23.8	23.8	23.8	23.8	23.7	23.8	23.6	23.7	23.8
C-12	122.5	122.5	122.9	122.8	122.5	122.8	122.9	122.9	122.5	122.5	—	123.0	122.5
C-13	144.1	143.3	144.1	144.2	144.9	144.3	144.9	144.3	144.9	144.9	144.4	144.1	144.8
C-14	42.1	41.6	42.1	42.1	42.1	42.1	42.2	42.1	42.1	42.2	42.2	42.0	42.0
C-15	28.1	28.1	28.3	28.2	28.2	28.1	28.1	28.2	28.1	28.4	28.4	28.0	28.3[b]
C-16	23.7	23.5	23.7	23.7	23.7	23.8	23.8	23.8	23.7	23.8	23.6	23.7	23.8
C-17	47.1	47.2	47.2	47.4	47.1	47.5	47.1	47.5	47.1	47.2	47.4	47.0	46.7
C-18	42.1	47.2	48.1	41.0	41.3	41.1[c]	41.4	41.1	41.3	41.4	41.2	47.9[c]	42.0
C-19	47.1	41.7	42.1	41.0	41.3	41.4[c]	41.4	41.4	41.3	41.4	41.2	42.0	46.7
C-20	30.7	148.1	148.3	36.4	36.6	36.4	36.6	36.4	36.5	36.6	36.2	149.0	31.0
C-21	34.2	29.8	30.0	28.8	29.0	29.0	29.1	29.0	29.1	29.1	29.0	30.4	34.3
C-22	33.1	37.5	38.4	32.1	32.6	32.1	32.7	32.1	32.6	32.7	32.1	38.3	33.3
C-23	28.1	28.1	28.3	28.2	28.2	28.1	28.1	28.2	28.1	28.8	186.5	28.8	28.7[b]
C-24	16.9	16.5	16.7	16.9	16.9	17.0	17.0	16.7	16.7	16.5	13.2	16.5	16.5
C-25	15.7	15.5	15.6	15.6	15.4	15.6	15.5	15.6	15.4	15.5	16.0	15.5	15.5
C-26	17.4	17.3	17.4	17.4	17.4	17.5	17.4	17.5	17.3	17.4	17.4	17.3	17.5
C-27	26.1	25.9	26.3	26.1	26.1	26.0	26.1	26.1	26.1	26.2	26.4	26.1	26.2
C-28	176.5	175.6	179.8	176.5	180.2	176.5	180.3	176.5	180.2	180.2	176.5	179.3	180.2
C-29	33.1	107.0	107.1	73.7	73.8	73.9	73.8	73.7	73.4	73.9	73.8	107.0	33.3
C-30	23.7			19.7	19.7	19.7	19.8	19.7	19.7	19.8	19.6		23.8

a) Data from reference.[6] *b, c*) Assignments in any column may be reversed.

sapogenin **10**. The carbon signals due to the sugar moiety of **10** were found to be almost superimposable on those of **7**. These observations led to the formulation of **2** as shown in Chart 1.

The ^{13}C-NMR spectra of **3**, **4** and **5** indicated that these saponins were composed of the same sapogenin (Table I). On enzymatic hydrolysis with crude hesperidinase,[6] **3** yielded an aglycone **11**. Comparison of the ^{13}C-NMR spectrum (Table I) of **11** with those of **6** and dianoside C (**12**, 29-hydroxyhederagenin glycoside), isolated from *Dianthus superbus* var. *longicalycinus*,[7] revealed that **11** was 29-hydroxyoleanolic acid, *i.e.* mesembryanthemoidigenic acid. This compound has already been isolated from the hydrolysate of the crude saponin fraction of *Rhipsalis mesembryanthemoides*, and the identification of **11** was confirmed by comparison of physical data with the reported values.[8]

On acid hydrolysis, **3** gave arabinose, glucose and rhamnose. Selective cleavage of the ester–glycoside linkage (*vide supra*) of **3** yielded **13** and **8**. The carbon signals due to the sugar moiety of **13** were almost superimposable over those of ciwujianoside E reported in the preceding paper,[1] leading to the formulation of **13** as a 3-*O*-α-rhamnopyranosyl-(1→2)-α-arabinopyranoside of **11**. From these data, the structure of **3** was established to be as shown in Chart 1.

Acid hydrolysis of **4** and **5** gave arabinose, glucose and rhamnose. On selective cleavage of the ester–glycoside linkage (*vide supra*), these saponins afforded the corresponding prosapogenins (**14** from **4** and **15** from **5**) and **8**. Based on analysis of the ^{1}H- and ^{13}C-NMR spectra, **14** was assigned as a 3-*O*-α-arabinopyranoside of **11**. The structure of **15** was formulated as a 3-*O*-β-glucopyranosyl-(1→2)-α-arabinopyranoside of **11** by comparison of the sugar carbon signals with those of **7** and **10** (prosapogenins of **1** and **2**, respectively). The ^{1}H- and ^{13}C-NMR data (Table II) of **4** and **5** showed the presence of an acetyl group. Mild alkaline saponification of **4** and **5** afforded the deacetylated compounds **16** and **17** without cleavage of the ester–glycoside linkage, respectively. Comparison of the ^{13}C-NMR data of **4** and **5** with those of the corresponding deacetyl products (Table II) demonstrated that in both the saponins, the acetyl group is located at the C-6 hydroxyl group of the central glucosyl unit of the C-28-glycosyl moiety. On the basis of these results, **4** and **5** can be assigned as shown in Chart 1.

Experimental

General Procedures Optical rotations were measured with a Union PM-101 automatic digital polarimeter. Infrared (IR) spectra were taken on a Shimadzu IR-408 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL FX-100 spectrometer in C_5D_5N solution using tetramethylsilane (TMS) as an internal standard. For gas liquid chromatography (GLC), a Shimadzu GC-6A was used. For column chromatography, Kieselgel 60 (70—230 mesh, Merck), LiChroprep RP-8 (40—63 μm, Merck) and Diaion HP-20 (Mitsubishi Chem. Ind. Co., Ltd.) were used. All solvent systems for chromatography were homogeneous.

Acid hydrolysis of saponins and identification of the resulting monosaccharides: see a previous paper.[2]

Separation of Saponin Refer to the preceding paper[1]; fr. A and fr. D were chromatographed on a reversed-phase column (LiChroprep RP-8) and then purified by HPLC (column, TSK-Gel ODS-120T, 21 mm × 30 cm; solvent, 50% MeOH; flow rate, 6 ml/min, detection, RI) to give **1** (0.005%), **2** (0.005%), **3** (0.008%) and **5** (0.006%) from fr. A, and **4**

TABLE II. ^{13}C-NMR Chemical Shifts of Sugar Moieties in C_5D_5N

		1	2	10	3	13	4	16	14	5	17	15
3-*O*-Sugar moieties												
ara	1	104.7	104.6	104.8	104.9	104.8	107.4	107.4	107.4	104.7	104.8	104.7
	2	80.6	80.5	80.9	75.9	75.7	72.8[a]	72.7	72.8	80.9	80.9	80.8
	3	72.5	72.4[b]	72.5	73.9	74.0	74.6	74.5	74.6	72.6[a]	72.5[a]	72.5
	4	68.1	68.1	68.1	69.8	69.9	69.4	69.1	69.4	68.3	68.3	68.2
	5	64.7	64.7	64.7	64.5	64.5	66.7	66.1	66.6	64.7	64.8	64.5
glc	1	105.7	105.5	105.8						105.9	105.9	105.8
	2	76.3	76.1	76.1						76.3	76.4	76.2
	3	78.3[a]	78.3[a]	78.2						78.1[b]	78.2[b]	78.1
	4	71.5	71.4	71.4						71.5	71.6	71.5
	5	78.3[a]	78.2[a]	78.2						78.1[b]	78.2[b]	78.1
	6	62.5	62.5	62.5						62.6	62.6	62.5
rha	1				101.7	101.8						
	2				72.5	72.4						
	3				72.5	72.4						
	4				73.9	74.0						
	5				68.6	68.6						
	6				18.5	18.6						
28-*O*-Sugar moieties												
glc inner	1	95.5	95.5		95.6		95.5	95.7		95.6	95.6	
	2	74.0	73.7		73.9		73.7	73.9		73.7	73.9	
	3	78.3[a]	78.2[a]		78.2		78.6	78.7		78.7[b]	78.6[b]	
	4	70.7	70.5		70.8		70.8[b]	71.3		70.6	70.8	
	5	78.3[a]	77.9		78.2		77.9	78.0		78.1[b]	78.2[b]	
	6	69.4	70.1		69.8		69.4	70.4		69.5	69.4	
glc outer	1	104.7	104.6		104.9		104.7	104.8		104.7	104.8	
	2	75.1	75.0		75.3		75.0	75.3		75.0	75.3	
	3	76.9	76.8		76.5		76.3	76.6		76.3	76.4	
	4	78.5[a]	78.2[a]		78.7		79.1	78.9		79.1	78.6[b]	
	5	76.9	76.8		77.2		73.7	77.1		73.7	77.2	
	6	61.3	61.2		61.2		63.6	61.6		63.7	61.4	
rha terminal	1	102.6	102.4		102.7		102.8	102.7		102.8	102.7	
	2	72.5	72.3[b]		72.5		72.6[a]	72.7		72.6[a]	72.7[a]	
	3	72.5	72.3[b]		72.5		72.3[a]	72.7		72.3[a]	72.5[a]	
	4	74.0	73.7		73.9		73.7	73.9		73.7	73.9	
	5	70.4	70.1		70.3		70.6[b]	71.3		70.3	70.3	
	6	18.5	18.3		18.5		18.4	18.4		18.5	18.5	
$CH_3\underline{C}O$							170.6			170.6		
$\underline{C}H_3CO$							20.6			20.6		

a, b) Assignments in any column may be reversed.

(0.01%) from fr. D, respectively.

1: A white powder, $[\alpha]_D^{25}$ −9.7° (*c*=0.72, MeOH). *Anal.* Calcd for $C_{59}H_{96}O_{26}\cdot 3H_2O$: C, 55.56; H, 8.06. Found: C, 55.24; H, 7.98. ^{1}H-NMR δ: 0.94 (9H, s), 1.02 (3H, s), 1.24 (3H, s), 1.64 (3H, d, *J*=6 Hz, Me of rhamnoside), 5.44 (1H, br s, 12-H), 5.72 (1H, s; anomeric proton of rhamnoside), 4.78 (1H, d, *J*=7 Hz, anomeric proton), 4.96 (2H, d, *J*=7 Hz, anomeric protons), 6.16 (1H, d, *J*=7 Hz, anomeric proton). On mineral acid hydrolysis, **1** yielded **6**, glucose, arabinose and rhamnose.

Selective Cleavage of the Ester–Glycoside Linkage[3] of 1 A solution of **1** (120 mg), anhydrous LiI (50 mg) and 2,6-lutidine (4 ml) in anhydrous MeOH (2 ml) was refluxed for 16 h. The reaction mixture was deionized with Amberlite MB-3 resin and concentrated to dryness. The residue was chromatographed on silica gel ($CHCl_3$–MeOH, 6:1) to give **7** (20 mg) and **8** (15 mg), the latter of which was identified by comparison of the ^{13}C-NMR spectrum with that of an authentic sample.[3] **7**: A white powder, $[\alpha]_D^{25}$ +25.1° (*c*=0.55, MeOH). ^{1}H-NMR δ: 0.84 (3H, s), 0.98 (9H, s), 1.26 (9H, s), 5.48 (1H, br s, 12-H), 4.96, 5.16 (each 1H, d, *J*=7 Hz, anomeric protons).

2: A white powder, $[\alpha]_D^{25}$ +10.7° (*c*=0.66, MeOH). *Anal.* Calcd for $C_{58}H_{92}O_{26}\cdot 3H_2O$: C, 55.31; H, 7.84. Found: C, 55.32; H, 7.92. ^{1}H-NMR δ: 0.82 (3H, s), 0.96 (3H, s), 1.17 (6H, s), 1.60 (3H, d, *J*=7 Hz, Me of rhamnoside), 4.88 (2H, d, *J*=7 Hz, anomeric protons), 4.98 (1H, d, *J*=7 Hz, anomeric proton), 5.42 (1H, br s, 12-H) and 5.60 (1H, s, anomeric proton of rhamnoside), 6.02 (1H, d, *J*=7 Hz, anomeric proton). On acid hydrolysis, **2** gave glucose, arabinose and rhamnose.

Selective cleavage of ester–glycoside linkage of **2** (110 mg) by the aforementioned procedure afforded **10** (17 mg) and **8** (12 mg). **10**: A white powder, $[\alpha]_D^{25}$ +50.3° (*c*=0.34, MeOH). *Anal.* Calcd for $C_{40}H_{62}O_{12}\cdot 3H_2O$: C, 60.89; H, 8.69. Found: C, 61.79; H, 8.45. ^{1}H-NMR δ: 0.84, 0.96, 1.00, 1.21, 1.24 (each 3H, s), 4.77 (2H, s, 29-H_2), 4.96, 5.20 (each 1H, d, *J*=7 Hz, anomeric protons) and 5.44 (1H, br s, 12-H).

3: A white powder, $[\alpha]_D^{18}$ −21.8° (*c*=0.55, MeOH). *Anal.* Calcd for $C_{59}H_{96}O_{26}\cdot 3H_2O$: C, 55.56; H, 8.06. Found: C, 55.39; H, 7.90. ^{1}H-NMR δ: 0.89 (3H, s), 1.08 (12H, s), 1.26 (3H, s), 1.62, 1.72 (each 3H, d, *J*=6 Hz, Me of rhamnosides), 5.48 (1H, br s, 12-H), 5.88, 6.16 (each 1H, s, anomeric protons of rhamnosides), 4.96, 5.02, 6.24 (each 1H, d, *J*=7 Hz, anomeric protons). On acid hydrolysis, **3** yielded glucose, arabinose and rhamnose. On selective cleavage of the ester–glycoside linkage as described above, **3** (150 mg) afforded **13** (25 mg) and **8** (13 mg). **13**: A white powder, $[\alpha]_D^{25}$ +9.7° (*c*=0.31, MeOH). *Anal.* Calcd for $C_{41}H_{66}O_{12}\cdot 2H_2O$: C, 62.21; H, 8.98. Found: C, 62.18; H, 8.80. ^{1}H-NMR δ: 0.84, 1.01, 1.07, 1.16, 1.23, 1.32 (each 1H, s), 1.62 (3H, d, *J*=6 Hz, Me of rhamnoside), 4.92 (1H, d, *J*=7 Hz, anomeric proton of arabinoside), 5.49 (1H, br s, 12-H), 6.16 (1H, s, anomeric proton of rhamnoside).

Enzymatic Hydrolysis[5] of 3 A solution of **4** (100 mg) and crude hesperidinase (400 mg, Tanabe Pharm. Co., Ltd., Osaka, Japan) in H_2O (25 ml) was incubated at 37 °C for 7 d. The reaction mixture was diluted with water and then extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated to dryness and then subjected to chromatography on silica gel [C_6H_6–acetone (4:1)] to give **11** (9 mg). **11**: A white powder, $[\alpha]_D^{20}$ +66.7° (*c*=0.42, MeOH). ^{1}H-NMR δ: 0.96, 0.99, 1.02, 1.28 (each 3H, s), 1.24 (6H, s, CH_2OH), 5.52 (1H, br s, 12-H).

4: A white powder, $[\alpha]_D^{25}$ +18.3° (*c*=0.49, MeOH). *Anal.* Calcd for $C_{55}H_{88}O_{23}\cdot 2H_2O$: C, 57.28; H, 8.04. Found: C, 57.30; H, 8.37. ^{1}H-NMR δ: 0.87 (3H, s), 0.94 (3H, s), 1.08 (6H, s), 1.25 (6H, s), 1.66 (3H, d, *J*=6 Hz, Me of rhamnoside), 1.92 (3H, s, CH_3COO), 4.78, 4.99, 6.23 (each 1H, d,

$J=7$ Hz, anomeric protons), 5.42 (1H, br s, 12-H), 5.52 (1H, s, anomeric proton of rhamnoside). On acid hydrolysis, **4** gave glucose, rhamnose and arabinose. On selective cleavage of the ester–glycoside linkage as described above, **4** (100 mg) afforded **14** (16 mg) and **8** (10 mg). **14**: A white powder, $[\alpha]_D^{25}$ +22.0° ($c=0.50$, MeOH). *Anal.* Calcd for $C_{35}H_{56}O_8 \cdot 3H_2O$: C, 63.80; H, 9.49. Found: C, 63.74; H, 9.58. ^{1}H-NMR δ: 0.88 (3H, s), 0.94 (3H, s), 0.98 (3H, s), 1.17 (6H, s), 1.27 (3H, s), 4.74 (1H, d, $J=6$ Hz, anomeric proton of arabinoside), 5.49 (1H, br s, 12-H).

5: A white powder, $[\alpha]_D^{25}$ −7.4° ($c=0.54$, MeOH). *Anal.* Calcd for $C_{61}H_{98}O_{28} \cdot 2H_2O$: C, 55.69; H, 7.82. Found: C, 55.74; H, 7.53. ^{1}H-NMR δ: 0.88 (6H, s), 1.09 (6H, s), 1.20 (3H, s), 1.24 (3H, s), 1.68 (3H, d, $J=6$ Hz, Me of rhamnoside), 1.94 (3H, s, CH_3COO), 5.01, 5.20, 5.50, 6.24 (each 1H, d, $J=7$ Hz, anomeric protons), 5.52 (1H, br s, 12-H). On selective cleavage of the ester–glycoside linkage as described above, **5** gave **15** (21 mg) and **8** (12 mg). **15**: A white powder, $[\alpha]_D^{20}$ +13.3° ($c=0.57$, MeOH). *Anal.* Calcd for $C_{41}H_{66}O_{13} \cdot 3H_2O$: C, 59.98; H, 8.84. Found: C, 59.91; H, 8.62. ^{1}H-NMR δ: 0.84 (3H, s), 1.04 (6H, s), 1.22 (6H, s), 1.28 (3H, s), 4.98, 5.21 (each 1H, d, $J=7$ Hz, anomeric protons), 5.52 (1H, br s, 12-H).

Deacetylation of 4 and 5 A solution of **4** (40 mg) in 0.05 N aqueous KOH (2 ml) was allowed to stand at 4 °C for 24 h. The reaction mixture was neutralized with Amberlite MB-3 resin. Then, the mixture was extracted with BuOH and the BuOH layer was concentrated to dryness to give **16** (23 mg): a white powder, $[\alpha]_D^{25}$ +22.2° ($c=0.36$, MeOH).

Deacetylation of **5** (30 mg) gave **17** (20 mg): a white powder, $[\alpha]_D^{25}$ −3.9° ($c=0.51$, MeOH).

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