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TRITERPENOID SAPONINS FROM THE BARK OF *NOTHOPANAX DAVIDII*

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Key Word Index—*Nothopanax davidii*; Chinese folk medicine; Yiyeliang Wanosides IX, X and XI; Serratagenic acid; triterpenoid Saponin.

Abstract— Three new triterpenoid saponins were isolated from the alcoholic extract of the bark of *Nothopanax davidii*. Their structures have been determined on the basis of spectral and chemical data as 3-*O*-α-(4′-*O*-acetyl)-L-arabinopyranosyl-3β-hydroxyolean-12-ene-28,29-dioic acid-28-*O*-[α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl (1 → 6)-β-D-glucopyranosyl]ester, named yiyeliangwanoside IX; 3-*O*-α-(2′-*O*-acetyl)-L-arabinopyranosyl-3β-hydroxyolean-12-ene-28,29-dioic acid-28-*O*-[α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl] ester, named yiyeliangwanoside X; and 3-*O*-β-D-xylopyranosyl-3β-hydroxyolean-12-ene-28,29-dioic acid-28-*O*-[α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl]ester, named yiyeliangwanoside XI.

INTRODUCTION

Nothopanax davidii (Franch) Harms, a well-known chinese folk medicine 'Liang Wang Cha' is a tall tree which grows in south-west China. The bark is used to remedy rheumatoid arthritis, fractures and strains. In preceding papers [1–4], we reported the isolation and structural elucidation of eight new triterpenoid saponins from the alcoholic extract of the bark of *N. davidii*. As a continuation of studies on this plant, we present here the spectral and chemical evidence for three new triterpenoid saponins, designated as yiyeliangwanoside IX (**1**), X (**2**) and XI (**3**).

RESULTS AND DISCUSSION

Dried and pulverized bark of *N. davidii* was extracted with 70% ethanol. The purified extract obtained by means of column chromatography with highly porous polymer (see Experimental) was subjected to column chromatography to give **1**–**3**, which responded to the Liebermann–Burchard test [5]. The IR spectra of **1**–**3** showed ester group absorptions (**1**:1720, 1710 cm^{-1}; **2**:1740, 1710 cm^{-1}; **3**:1710 cm^{-1}) together with strong hydroxyl and olefinic absorptions.

Acid hydrolysis of **1**–**3** afforded the same aglycone **4**, which was identified as 3β-hydroxyolean-12-ene-28,29-dioic acid(serratagenic acid) [6] by comparison with an authentic sample (mp, ^1H and ^{13}C NMR spectral data).

On acid hydrolysis, both **1** and **2** gave L-arabinose, L-rhamnose and D-glucose; **3** gave D-xylose, L-rhamnose and D-glucose, which were identified by HPTLC [7] and PC. The ^{13}C NMR spectra indicated the presence of four sugar residues in **1**–**3** by their anomeric carbon signals (**1**:δ95.7, 102.7, 104.8 and 107.2; **2**:δ96.0, 102.9, 104.8 and 105.0; **3**:δ95.7, 102.7, 104.9 and 107.6). The signals at δ95.7, 96.0 and 95.7 suggested that **1**–**3** have a glycosidic ester linkage [8] at either the 28 or 29-COOH, which was supported by slight shifts of the signals of one of two carboxyl groups [9] (Table 1). The simultaneous presence of a 3-*O*-glycosidic linkage was easily seen by the attendant downfield shifts of C-3 [10]. Thus **1**–**3** are bidesmosidic saponins.

On alkaline hydrolysis, both **1** and **2** yielded **5**, and **3** yielded **6**, which were, respectively, formulated as the 3-*O*-α-L-arabinopyranoside and 3-*O*-β-D-xylopyranoside of **4** based on their acid hydrolysis, ^1H, ^{13}C NMR and FAB mass spectral data.

The positive FAB mass spectra of **1** and **2** yielded the same molecular ions at *m/z* 1169 $[M + K]^+$, indicating their molecular weights of 1130; The FD mass spectrum of **3** revealed a molecular ion at *m/z* 1112 $[M + Na + H]^+$, indicating a molecular weight of 1088. On the other hand, the EI mass spectra of the peracetates of **1** and **2** displayed the same fragment ions at *m/z* 561 $[(Glc\text{-}Rha)Ac_6]^+$, 273 $[(Rha)Ac_3$, terminal rhamnose$]^+$, 259 $[(Ara)Ac_3$, terminal arabinose$]^+$; and the peracetate of **3** similarly displayed fragment ions at *m/z* 561 $[(Glc\text{-}Rha)Ac_6]^+$, 273 $[(Rha)Ac_3$, terminal rhamnose$]^+$, 259 $[(Xyl)Ac_3$, terminal xylose$]^+$. Therefore, the sequence of oligosaccharide chains of **1**–**3** is rhamnose-glucose-glucose-aglycone.

It was determined that one acetyl group was attached to the sugar moieties of both **1** and **2** by FAB mass

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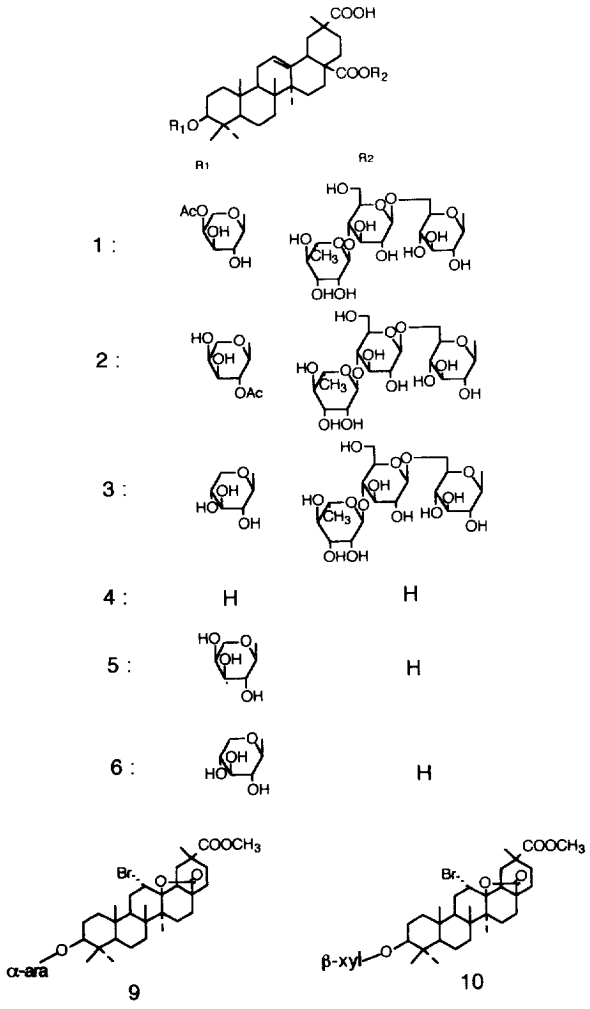

Table 1. ^{13}C NMR chemical shifts of aglycone moieties (125 MHz, in C_5D_5N)

C	1	2	3	4	5	6
1	38.8	38.9	38.8	38.9	38.8	38.8
2	26.6	26.9	26.7	28.0	26.7	26.6
3	89.0	89.3	88.6	78.1	88.6	88.7
4	39.5	39.8	39.6	39.4	39.6	39.5
5	55.9	56.0	55.9	55.8	55.9	55.9
6	18.5	18.8	18.5	18.8	18.5	18.5
7	33.1	33.4	33.1	33.2	33.2	33.2
8	40.0	40.2	39.9	39.7	39.8	39.8
9	48.1	48.3	48.0	48.0	48.0	48.0
10	37.1	37.3	37.1	37.4	37.1	37.1
11	23.8	23.8	23.8	23.8	23.9	23.9
12	123.0	124.0	123.1	122.2	123.3	123.2
13	143.6	144.0	143.6	144.3	144.3	144.3
14	42.3	42.7	42.3	42.5	42.6	42.6
15	28.2	28.5	28.2	28.3	28.3	28.3
16	23.6	24.2	23.5	23.8	23.9	23.9
17	47.0	47.3	47.0	46.9	46.6	46.6
18	40.8	40.2	40.8	41.1	41.1	41.1
19	40.8	41.1	40.8	41.1	41.1	41.1
20	42.2	42.5	42.2	42.2	42.6	42.6
21	29.1	29.4	29.1	29.4	29.3	29.3
22	31.7	31.9	31.7	32.4	32.4	32.4
23	28.2	28.3	28.2	28.3	28.2	28.2
24	16.9	17.2	17.0	16.6	17.0	16.9
25	15.6	15.9	15.6	15.5	15.5	15.5
26	17.5	17.8	17.5	17.4	17.4	17.4
27	26.0	26.3	26.0	26.1	26.1	26.1
28	176.2	177.0	176.3	180.0	179.9	179.8
29	180.5	181.9	180.9	181.1	180.2	180.5
30	19.9	20.2	19.9	20.0	20.0	20.0

spectra, ^{1}H and ^{13}C NMR. On examination of ^{1}H, ^{13}C NMR, ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY spectra of **1** and **2**, it was found that H-4 of arabinose shifted downfield to δ5.55 (*m*), C-4 of arabinose shifted downfield to δ72.2, whereas C-3 and C-5 shifted upfield for **1** (compared with these of **5**, Table 2), H-2 of arabinose shifted downfield to δ5.70, C-2 of arabinose downfield to δ73.9, whereas C-1 and C-3 of arabinose shifted upfield for **2** (compared with these of **5**, Table 2). Thus, the acetyl group was linked to C-4 of arabinose for **1** and C-2 of arabinose for **2**.

In the oligosaccharide chains of **1**–**3**, glycosylation shifts were all at C-4 and C-6 of two glucoses (shifted downfield to δ78.7 and 69.5 for **1**; δ78.9 and 69.0 for **2**; δ78.7 and 69.4 for **3**; respectively) by analysis of their ^{13}C NMR, ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY spectra. The correlation between rhamnose H-1 and outer glucose C-4 was observed in COLOC experiments of **1** and **3**. The correlations between H-1 of rhamnose and H-4 of outer glucose, H-1 of outer glucose and H-6, H-6′ of inner glucose were shown in the NOESY spectrum of **2**. So, it was concluded that rhamnose was linked to C-4 of outer glucose, and outer glucose was attached to C-6 of inner glucose in the oligosaccharide chains of **1**–**3**.

The location of a glycosyl linkage at the 28-COOH was revealed as follows. Formation of the characteristic bromolactone has been used as chemical evidence of the presence of a free carboxyl group at C-17 of olean-12-ene triterpenes [11]. On treatment with dioazomethane, **1** afforded a monomethyl ester, **7**. On selective hydrolysis of the ester linkage with alkali, **7** yielded a monodesmoside **8**. Formation of a bromolatone, **9**, from **8** was observed on treatment of **8** with bromine in the presence of sodium acetate. It follows that **1** should be formulated as the 28-glycosyl ester of 3-*O*-α-arabinopyranosyl-serratagenic acid. Location of the oligosaccharide chains of **2** and **3** at 28-COOH was supported by the formation of the bromolactone as in the case of **1**. When subjected to the same procedure, **2** also afforded **9**, and **3** gave **10**.

In the ^{1}H NMR spectra, the anomeric proton signals for **1** at δ4.73 (1H, *d*, J = 6.0 Hz), 4.93 (1H, *d*, J = 7.8 Hz), 5.79 (1H, *s*), 6.22 (1H, *d*, J = 8.0 Hz), for **2** at δ4.70 (1H, *d*, J = 7.4 Hz), 5.00 (1H, *d*, J = 7.8 Hz), 5.80 (1H, *s*), 6.20 (1H, *d*, J = 8.0 Hz), for **3** at δ4.79 (1H, *d*, J = 7.5 Hz), 4.92 (1H, *d*, J = 7.6 Hz), 5.80 (1H, *s*), 6.21 (1H, *d*, J = 8.1 Hz) led to the assignments of the anomeric configurations of glucose and xylose units as β, and rhamnose and arabinose units as α; these assignments were supported by their carbon signals (Table 2).

Table 2. ^{13}C NMR chemical shifts of sugar moieties (125 MHz, in C_5D_5N)

	1	2	3	5	6
28-*O*-sugar					
Glc-1	95.7	96.0	95.7		
Glc-2	73.9	73.8	73.9		
inner					
Glc-3	78.7	77.9	78.7		
Glc-4	71.1	72.5	70.9		
Glc-5	77.9	77.0	77.1		
Glc-6	69.5	69.0	69.4		
Glc-1	104.8	104.8	104.9		
Glc-2	75.2	73.6	75.5		
outer					
Glc-3	76.5	77.6	77.9		
Glc-4	78.7	78.9	78.7		
Glc-5	77.1	76.1	77.1		
Glc-6	61.2	61.0	61.3		
Rha-1	102.7	102.9	102.7		
Rha-2	72.4	72.5	72.5		
Rha-3	72.7	72.4	72.7		
Rha-4	73.6	73.9	74.0		
Rha-5	70.3	70.1	70.3		
Rha-6	18.4	18.3	18.5		
3-*O*-Sugar					
Xyl-1			107.6		107.5
Xyl-2			73.8		74.0
Xyl-3			78.7		78.5
Xyl-4			71.2		71.2
Xyl-5			67.0		67.0
Ara-1	107.2	105.0(−2.2)		107.2	
Ara-2	73.1	73.9(+1.0)		72.9	
Ara-3	72.2(−2.3)	72.0(−2.5)		74.5	
Ara-4	72.4(+2.1)	69.0		69.3	
Ara-5	65.7(−0.8)	66.9		66.5	
MeCO	170.7	171.0			
Me	21.0	21.8			

Based on the above results, **1**–**3** were established as 3-*O*-α-(4′-*O*-acetyl)-L-arabinopyranosyl-, 3-*O*-α-(2′-*O*-acetyl)-L-arabinopyranosyl- and 3-*O*-β-D-xylopyranosyl-3β-hydroxyolean-12-ene-28,29-dioic acid-28-*O*-[α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl (1-6)-β-D-glucopyranosyl] ester, respectively.

EXPERIMENTAL

General procedures. NMR spectra were taken on a Bruker AM-500 (^1H NMR at 500 MHz and ^{13}C NMR at 125 MHz) spectrometer in C_5D_5N with tetramethylsilane (TMS) as int. standard.

MS were recorded on JEOL JMS-DX 300 and JMS-DX 300 mass spectrometers.

The IR were recorded on a Perkin-Elmer 683 IR spectrometer. Mps were determined on a mmp apparatus and were uncorr. Optical rotations were measured with Perkin Elmer 241 automatic digital polarimeter. The plant was identified by Prof. Jia-Lin Wu, Sichuan School of Chinese Traditional Medicine. A voucher specimen is deposited in Institute of Materia Medica, Chinese Academy of Medical Sciences.

Extraction and isolation of saponins. The dried bark (11 kg) of *N. davidii* was collected in the Sichuan province of China in the autumn of 1990. The bark was pulverized and extracted with 70% EtOH (25 l × 4, 2 hr for each extraction) at 80°. The extracts were combined and concd *in vacuo* to give a brown residue (2.5 kg). The residue (0.5 kg) was subjected to CC on highly porous polymer with H_2O, 80% EtOH and EtOH, successively. The EtOH eluate (80%, 28 g) was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (75:25:10, 70:30:10 and 65:35:10) to give 5 frs (I ~ V).

Fr. III (1.0 g) was chromatographed on silica gel ($CHCl_3$–MeOH–EtOAc–H_2O 2:2:4:1) and reversed-phase MPLC (eluted with MeOH–H_2O 60:40) to give **1** (100 mg).

The chromatography of fr. IV on silica gel (eluted with $CHCl_3$–MeOH–H_2O 7:3:1) and reversed-phase MPLC (eluted with MeOH–H_2O 57:40) gave **2** (160 mg).

Fr. V was chromatographed on silica gel ($CHCl_3$–MeOH–H_2O 65:35:10) and reversed-phase MPLC (eluted with MeOH–H_2O 57:44) to afford **3** (80 mg).

Characterization of **1**. A powder, mp 228–230° (dec.). $[\alpha]_D^{12}$ −9.43 (MeOH; *c* 5.3 × 10^{-2}). Analyt. calcd for $C_{55}H_{86}O_{24} \cdot 5/2H_2O$: C 56.36, H 7.77, found C 56.18, H 7.54. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2925 (C–H), 1720 (C=O, ester), 1710 (C=O, ester), 1700 (O=C–OH), 1640 (C=C). ^1H NMR (C_5D_5N): δ0.88, 0.94, 1.11, 1.24, 1.26, 1.45 (each 3H, *s*, Me), 1.68 (3H, *d*, *J* = 6.1 Hz, H-6 of α-rha), 2.0 (3H, *s*, O=CMe), 4.73 (1H, *d*, *J* = 6.0 Hz, H-1 of α-ara), 4.93 (1H, *d*, *J* = 7.8 Hz, H-1 of β-glc), 5.48 (1H, *m*, H-12), 5.79 (1H, *s*, H-1 of α-rha), 6.20 (1H, *d*, *J* = 8.0 Hz, H-1 of β-glc). ^{13}C NMR: Tables 1 and 2. FAB-MS *m/z*: 1169 [M + K], 1123 [M − HAc − 2H + K]$^+$, 977 [M − HAc-Rha − 2H + K]$^+$, 653 [M − HAc − Rha − Glc − Glc − 2H + K]$^+$. Liebermann–Burchard reaction reddish purple.

Characterization of **2**. A powder, mp 210–212° (dec.). $[\alpha]_D^{20}$ −3.9 (MeOH; *c* 0.1). Analyt. calcd for $C_{55}H_{86}O_{24} \cdot 5/2H_2O$: C 56.36, H 7.77, found C 56.03, H 7.47. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2925 (C–H), 1740 (C=O, ester), 1710 (C=O, ester), 1700 (O=C–OH), 1640 (C=C). ^1H NMR (C_5D_5N): δ0.83, 0.88, 1.05, 1.08, 1.22, 1.44 (each 3H, *s*, Me), 1.69 (3H, *d*, *J* = 6.1 Hz, H-6 of α-rha), 2.10 (3H, *s*, O=C–Me), 4.70 (1H, *d*, *J* = 7.4 Hz, H-1 of α-ara), 5.00 (1H, *d*, *J* = 7.8 Hz, H-1 of β-glc), 5.44 (1H, *m*, H-12), 5.84 (1H, *s*, H-1 of α-rha), 6.25 (1H, *d*, *J* = 8.0 Hz, H-1 of β-glc). ^{13}C NMR: Tables 1 and 2. FAB-MS *m/z*: 1169 [M + K]$^+$. Liebermann–Burchard reaction reddish purple.

Characterization of **3**. A powder, mp 219–224° (dec.). $[\alpha]_D^{12}$ −21.62 (MeOH; *c* 9.3 × 10^{-2}). Analyt. clacd for $C_{53}H_{84}O_{23} \cdot 7H_2O$: C 52.56, H 8.09, found C 52.56, H 7.25. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1710 (C=O, ester), 1700 (O=C–OH), 1630 (C=C). ^1H NMR (C_5D_5N): δ0.85, 1.02, 1.11, 1.22, 1.24, 1.43 (each 3H, *s*, Me), 1.67 (3H, *d*, *J* = 6.2 Hz, H-6 of α-rha), 4.79 (1H, *d*, *J* = 7.5 Hz, H-1 of β-xyl), 4.92 (1H, *d*, *J* = 7.6 Hz, H-1 of β-glc), 5.45 (1H, *m*, H-12), 5.80 (1H, *s*, H-1 of α-rha), 6.21 (1H, *d*, *J* = 8.1 Hz, H-1

of β-glc). ^{13}C NMR: Tables 1 and 2. FD-MS *m/z*: 1112 $[M + H + Na]^+$. Liebermann–Burchard reaction reddish purple.

Acid hydrolysis of **1–3**. A soln of sample (20 mg) and 7% HCl–EtOH (1:1) was refluxed for 4 hr. The mixt. was diluted with H_2O and extracted with Et_2O. The Et_2O layer was evapd to dryness. The residue was recrystallized in MeOH to afford **4** (6 mg), needles, mp 300.5–301 [6], $[\alpha]_D^{20}$ + 23.0 (MeOH; *c* 0.15). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1701 (O=C–OH), 1643 (C=C). ^{1}H NMR (C_5D_5N): δ0.91, 1.00, 1.03, 1.26, 1.29, 1.55 (each 3H, *s*, Me), 5.54 (1H, *m*, H-12). ^{13}C NMR: Table 1. EI-MS *m/z*: 486 $[M]^+$, 469 $[M - H_2O + H]^+$, 268, 233, 189. Liebermann–Burchard reaction reddish purple.

Identification of sugars. The aq. layer was neutralized with 1 N NaOH, concd, and subjected to HPTLC analysis on Kieselgel 60 F254 (Merck) [using $CHCl_3$–MeOH–H_2O (30:12:4) 9 ml and HOAc 1 ml] and PC [using *n*-BuOH–HOAc–H_2O (4:1:5); phenol–H_2O (4:1); *n*-BuOH–C_5H_5N–benzene–H_2O (5:3:1:3)], which showed Glc, Rha and Ara in **1** and **2**; Glc, Rha and Xyl in **3**.

Alkaline hydrolysis of **1–3**. A mixt. of sample (25 mg) and 2% KOH in 70% EtOH (7 ml) was refluxed for 6 hr. After being slowly neutralized with 0.1 N HCl, the reaction mixt. was extracted with *n*-BuOH satd with H_2O. The *n*-BuOH soln was concd *in vacuo*. The residue showing a spot on TLC ($CHCl_3$–MeOH–H_2O 80:10:1) was recrystallized to give **5** in **1** and **2**; **6** in **3**.

Compound **5**, powder, mp 250–252° (dec.). $[\alpha]_D^{20}$ − 8.9 (MeOH; *c* 0.10). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2915 (C–H), 1700 (O=C–OH), 1645 (C=C). ^{1}H NMR (C_5D_5N): δ 0.86, 0.93, 0.99, 1.24, 1.29, 1.57 (each 3H, *s*, Me), 4.74 (1H, *d*, *J* = 6.9 Hz, H-1 of α-ara), 5.52 (1H, *m*, H-12). ^{13}C NMR: Tables 1 and 2. FAB-MS *m/z*: 657 $[M + K]^+$, Liebermann–Burchard reaction reddish purple.

Compound **6**, powder, mp 265–267° (dec). $[\alpha]_D^{20}$ + 23.8 (MeOH *c* 0.1). Analyt. calcd for $C_{35}H_{54}O_9 \cdot 3/2H_2O$: C 65.32, H 8.89, found C 65.69, H 8.64. IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 2950 (C–H), 1700 (O=C–OH), 1640 (C=C). ^{1}H NMR (C_5D_5N): δ0.84, 0.97, 0.99, 1.28, 1.29, 1.57 (each 3H, *s*, Me), 4.80 (1H, *d*, *J* = 7.5 Hz, H-1 of β-xyl), 5.53 (1H, *m*, H-12). ^{13}C NMR: Tables 1 and 2. FAB-MS *m/z*: 657 $[M + K]^+$. Liebermann–Burchard reaction reddish purple.

Acetylation of **1–3**. A soln of sample (10 mg) in a mixt. of Ac_2O (0.4 ml) and pyridine (0.4 ml) was allowed to stand at room temp., and the mixt. was worked-up as usual to give the peracetate of **1** (6 mg, **2** gave the same peracetate as that of **1**), a powder (EtOH), 157–158° (dec.), EI-MS *m/z*: 561 $[(glc\text{-}rha)Ac_6]^+$, 273 $[(rha)Ac_3]^+$, 259 $[(ara)Ac_3]^+$; peracetate of **3** (7 mg), a powder (EtOH), mp 153–154° (dec.); EI-MS *m/z*: 561 $[(glc\text{-}rha)Ac_6]^+$, 273 $[(rha)Ac_3]^+$, 259 $[(xyl)Ac_3]^+$.

Formation of the bromolactone [6]. Compound **1** (21 mg) was methylated with CH_2N_2 in MeOH, and the product **7** was dissolved in 1 N NaOH (9 ml) and heated at 80° for 2 hr. After cooling, the reaction mixt. was neutralized with 2 N H_2SO_4 and passed through RA highly porous polymer (Seventh Chemical and Industrial Factory of Beijing) eluting with H_2O and MeOH. The MeOH soln was concd to give **8**. AcOH (6 ml) containing Br_2 (0.3 ml) was added to a soln of **8** and AcONa (30 mg) in 90% AcOH (3 ml) and the mixt. was stirred at room temp. for 15 hr under a N_2 stream. The reaction mixt. was poured into an aq. soln with $NaHSO_3$ and extracted with $CHCl_3$. The $CHCl_3$ layer was evapd to dryness and the residue was purified by silica gel CC ($CHCl_3$–MeOH–H_2O, 80:10:1) to give **9** (6 mg) as a powder, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1768 (five-membered ring lactone), 1724 (COOMe), ^{1}H NMR (C_5D_5N): δ0.82, 1.00, 1.20, 1.25, 1.28, 1.48 (each 3H, *s*, Me), 3.64 (3H, *s*, H-29), 4.26 (1H, *m*, H-12). When subjected to the same procedure, **2** also afforded **9** (6.5 mg) and **3** gave **10** (7 mg), a powder, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1765 (five-membered ring lactone), 1720 (COOMe); ^{1}H NMR (C_5D_5N): δ0.82, 1.00, 1.21, 1.24, 1.28, 1.47 (each 3H, *s*, Me), 3.61 (3H, *s*, H-29), 4.23 (1H, *m*, H-12).

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