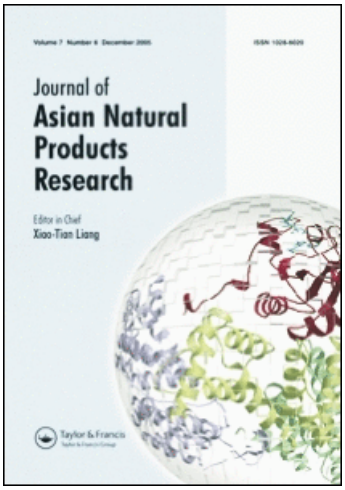

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FOUR NEW TRITERPENE SAPONINS FROM THE SEEDS OF *AESCULUS CHINENSIS*

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Two pairs of new geometrically isomeric triterpenoid saponins were isolated from the seeds of *Aesculus chinensis* and characterized as 28-acetyl-21-tigloylprotoaescigenin 3-*O*-[β-D-xylopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] [β-D-glucopyranosiduronic acid (isoescin IIa, **1**) and 28-acetyl-21-angeloylprotoaescigenin 3-*O*-[β-D-xylopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid (isoescin IIb, **2**); 28-acetyl-21-tigloylbarringtogenol C 3-*O*-[β-D-galactopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid (isoescin IIIa, **3**) and 28-acetyl-21-angeloylbarringtogenol C 3-*O*-[β-D-galactopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid (isoescin IIIb, **4**). Their structures were established on the basis of spectroscopic and chemical evidence.

Keywords: *Aesculus chinensis*; Triterpenoid glycosides; Isoescins IIa, IIb, IIIa, and IIIb

INTRODUCTION

The *Aesculus* genus (Family Hippocastanaceae) consists of about thirty species distributed in Asia, Europe and America. Of these plants, *Aesculus hippocastanum* L. has been a subject of research for many years. Its seeds are prolific in acylated triterpenoid saponins—escins, which exhibit extraordinary anti-inflammatory activity and have been used for the treatment of peripheral chronic venous insufficiency or as ingredients in cosmetics. Recently, Yoshikawa *et al.* [1–3] reported the isolation of several new compounds from the seeds of *A. hippocastanum* L. and their anti-inflammatory and hypoglycemic activities, as well as inhibitory effects on ethanol absorption. During our search for a substitute in China, we were interested to investigate the seeds of *A. chinensis* Bge., a plant indigenous in China. The dried ripe seeds are used as a remedy for abdominal ailments by local people [4], and a series of structurally analogous triterpenoid saponins have been isolated and identified [5,6]. In addition, we have reported moderate anti-HIV-1 protease activities of escins Ia and Ib [5]. Here we describe the isolation and structural determination of four new triterpenoid saponins, named as isoescins IIa (**1**), IIb (**2**), IIIa (**3**) and IIIb (**4**).

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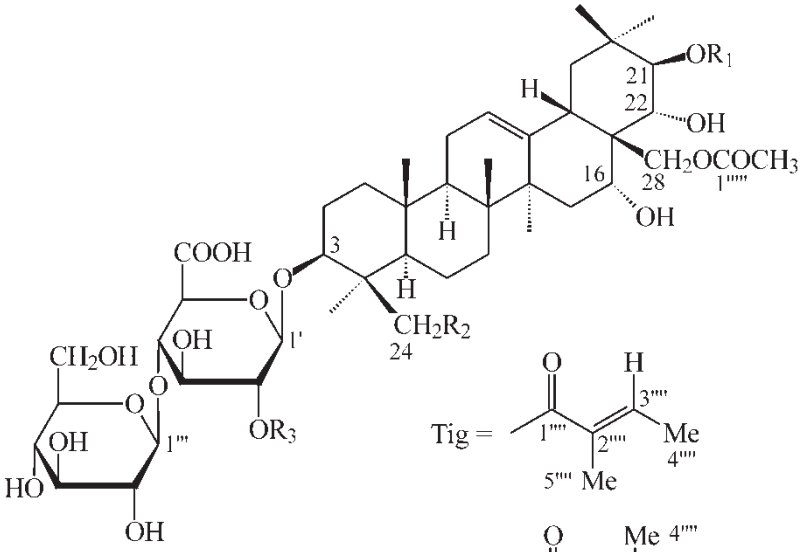
RESULTS AND DISCUSSION

A crude saponin was obtained from the 70% ethanolic extract of the seeds of *A. chinensis*, as described previously [5], and the fraction eluted from a Diaion-101 column with 70% EtOH was subjected to repeated HPLC to afford the four new saponins **1**–**4**.

Compound **1** was isolated as a white amorphous powder. The molecular formula of **1** was assigned as $C_{54}H_{84}O_{23}$ on the basis of quasi-molecular ion peaks at *m/z* 1099.5323 $[M - H]^-$ (calcd for $C_{54}H_{83}O_{23}$, 1099.5325) and *m/z* 1123 $[M + Na]^+$ in the negative-ion high-resolution secondary ion mass (HR-SI-MS) and matrix-assisted laser desorption ionization time-of-flight-mass (MALDI-TOF-MS) spectra, respectively. The IR spectrum of **1** exhibited absorption bands at 1713 and 1604 cm^{-1} assignable to carbonyl groups including an α,β-unsaturated ester, along with bands at 3416 and 1075 cm^{-1} that are characteristic for the oligoglycosidic structure. After acid hydrolysis of **1**, glucuronic acid, xylose, glucose and 28-acetyl-21-tigloylprotoaescigenin were detected by TLC and PPC and compared with authentic samples. The ^{13}C NMR spectrum of **1** showed 54 carbon signals, of which those at δ 123.0 (d) and 142.6 (s) were assigned to olefinic carbons by the DEPT spectrum and comparison with ^{13}C NMR data of escin IVa [7]. In addition, four hydroxyl-bearing methines [δ 90.5 (C-3), 67.5 (C-16), 81.5 (C-21) and 71.2 (C-22)] and two hydroxymethyls [δ 62.8 (C-24) and 66.3 (C-28)] were ascribed to the aglycon moiety after inspection of the 2D-NMR spectra. Furthermore, the ^1H NMR spectrum showed an olefinic signal at δ 5.44 (br s, H-12), which is characteristic in the Δ^{12}-oleanane skeleton. Furthermore, the ^1H NMR spectrum showed six *tert*-methyls (δ 0.65, 0.88, 1.04, 1.27 × 2, and 1.78). These NMR spectral features were in accord with a protoaescigenin skeleton. Also, signals characteristic to a tigloyl group [^1H NMR: δ 1.55 (H_3-4‴), 1.88 (H_3-5‴), and 6.97 (H-3‴); ^{13}C NMR: δ 168.5 (C-1‴), 129.7 (C-2‴), 136.3 (C-3‴), 14.0 (C-4‴) and 12.3 (C-5‴)] and an acetyl group [^1H NMR: δ 1.97 (H_3-2⁗); ^{13}C NMR: δ 170.7 (C-1⁗) and 20.7 (C-2⁗)] were observed. The locations of a tigloyl group at C-21 and an acetyl group at C-28 were determined by the HMBC experiment and further confirmed by comparison with the reported data [3]. In addition, the presence of a trisaccharide moiety was suggested by observation of proton signals at δ 5.50 (d, $J = 7.0$ Hz, H-1″), 5.19 (d, $J = 7.5$ Hz, H-1‴), and 4.76 (d, $J = 7.5$ Hz, H-1′), as well as carbon signals at δ 104.5 (C-1′ and C-1″) and 104.7 (C-1‴). The HMBC correlations observed for signals of C-3/H-1′, C-2′ (δ 79.5)/H-1″ and C-4′ (δ 83.2)/H-1″ confirmed the sugar sequence of 3-*O*-[β-D-xylopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid. The structure of **1** was consequently determined to be 28-acetyl-21-tigloylprotoaescigenin 3-*O*-[β-D-xylopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid, and named as isoescin IIa (Fig. 1).

Compound **2** was isolated as a white amorphous powder. In the MALDI-TOF-MS spectrum, a quasi-molecular ion peak was assigned at *m/z* 1123 $[M + Na]^+$ and the molecular formula of **2** was determined as $C_{54}H_{84}O_{23}$ by negative-ion HR-SI-MS [*m/z* 1099.5322 $[M - H]^-$ (calcd for 1099.5325), identical with that of **1**]. The IR spectrum also showed absorption bands ascribable to an α,β-unsaturated ester. After acid hydrolysis of **2**, glucuronic acid, xylose, glucose and 28-acetyl-21-angeloylprotoaescigenin were detected by TLC and PPC and were compared with authentic samples. The ^1H and ^{13}C NMR spectra of **2** showed close resemblance to those of **1**, implying the same protoaescigenin skeleton, as well as the trisaccharide moiety. In addition, ^1H and ^{13}C NMR signals due to an acetyl group were also observed. However, the ^1H and ^{13}C NMR data [^1H NMR: δ 5.87 (H-3⁗), 1.94 (H_3-5⁗) and 2.01 (H_3-4⁗)]; ^{13}C NMR: δ 168.5 (C-1⁗), 129.4 (C-2⁗), 136.1 (C-3⁗), 15.8 (C-4⁗) and 20.9 (C-5⁗)] indicated the replacement of a tigloyl group by an angeloyl group in the molecule. The HMBC experiment verified the identical acylation and sugar linkage patterns. Consequently, **2** was determined to be 28-acetyl-21-angeloylprotoaescigenin



	R_1	R_2	R_3
1	Tig	OH	Xyl
2	Ang	OH	Xyl
3	Tig	H	Gal
4	Ang	H	Gal

Gal = β - D - galactopyranosyl
Xyl = β - D - xylopyranosyl

FIGURE 1 Structures of compounds **1**–**4**.

3-*O*-[β-D-xylopyranosyl (1 → 2)] [β-D-glucopyranosyl(1 → 4)] β-D-glucopyranosiduronic acid, and named as isoescin IIb (Fig. 1).

Compound **3**, a white amorphous powder, was assigned the molecular formula $C_{55}H_{86}O_{23}$ by negative-ion high-resolution SI-MS (*m/z* 1113.5479 $[M - H]^-$, calcd 1113.5482). The IR spectrum of **3** also showed absorption bands ascribable to an α,β-unsaturated ester. After acid hydrolysis of **3**, glucuronic acid, glucose and galactose were detected by PPC. In the ^1H and ^{13}C NMR spectra, signals due to the tigloyl [^1H NMR: δ 7.00 (H-3‴), 1.83 (H_3-5‴), and 1.57 (H_3-4‴); ^{13}C NMR: δ 168.4 (C-1‴), 129.8 (C-2‴), 136.2 (C-3‴), 14.1 (C-4‴) and 12.4 (C-5‴)] and an acetyl group [^1H NMR: δ 2.00 (H_3-2''''); ^{13}C NMR: δ 170.7 (C-1'''') and 20.7 (C-2'''')] were observed. However, the presence of seven additional *tert*-methyls in the ^1H NMR spectrum [δ 0.82 (H_3-25), 0.97 (H_3-26), 1.03 (H_3-27), 1.10 (H_3-29), 1.17 (H_3-23), 1.31 (H_3-30), and 1.82 (H_3-27)] suggested a different aglycon moiety to that of **1**. Careful interpretation of the HMQC and HMBC spectra led us to conclude that the aglycon is barringtogenol C, *i.e.* olean-12-ene-3β,16α,21β,22α,28-pentaol. Next, the tigloyl and acetyl groups were confirmed to be attached to C-21 and C-28, respectively, by analysis of the HMBC spectra and comparison with the spectral data of similar compounds [3]. The presence of a trisaccharide moiety was inferred by the observation of anomeric protons at δ 4.75 (d, $J = 7.5$ Hz, H-1′), 5.30 (d, $J = 7.5$ Hz, H-1‴), and 5.31 (d, $J = 6.5$ Hz, H-1″), as well as the respective anomeric carbons at δ 104.8 (C-1′), 105.1 (C-1″) and 104.4 (C-1‴). The sugar chain of 3-*O*-[β-D-galactopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid was established by the HMBC experiment and also by comparison of the NMR data with those of escin IIIa [1]. Consequently, the structure of **3** was determined to be 28-acetyl-21-tigloylbarringtogenol C 3-*O*-[β-D-galactopyranosyl

(1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid, named as isoescin IIIa (Fig. 1).

Compound **4** was isolated as a white amorphous powder. In the MALDI-TOF-MS spectrum, a quasi-molecular ion peak was assigned at *m/z* 1137 $[M + Na]^+$. Based on the HR-SI-MS spectrum, the molecular formula was determined to be $C_{55}H_{86}O_{23}$, identical with that of **3**. On acid hydrolysis of **4**, glucuronic acid, galactose and glucose were detected by TLC and PPC. The ^1H and ^{13}C NMR spectra of **4** showed high analogy with those of **3**. Besides, like compound **2**, characteristic ^1H and ^{13}C NMR signals due to an angeloyl group instead of a tigloyl group were observed for **4**. The HMBC spectrum further confirmed the same linkage patterns for the angeloyl group, the acetyl group and the trisaccharide moiety. Consequently, the structure of **4** was determined to be 28-acetyl-21-angeloylbarringtogenol C 3-*O*-[β-D-galactopyranosyl (1 → 2)] [β-D-glucopyranosyl (1 → 4)] β-D-glucopyranosiduronic acid, named as isoescin IIIb (Fig. 1).

EXPERIMENTAL

General Experimental Procedures

IR spectra were recorded on a Perkin-Elmer 983 spectrometer with KBr pellets. 1D and 2D NMR experiments were performed on a Varian INOVA-500 spectrometer at 500 MHz for ^1H and 125 MHz for ^{13}C, including COSY, HMQC, HMBC and NOESY. Chemical shifts are given in δ relative to TMS as an internal standard. MALDI-TOF-MS: BIFLEX III (Bruker). HR-SI-MS: APEX II FT-ICR-MS (Bruker Daltonics). For preparative HPLC (pump: P2000; detector: UV 3000 and software: PC1000. Thermo Separation Products, USA) purification, an ODS [10 μ, C_{18}, 250 × 21.2 mm, Phenomenex, USA] column was used. For HPLC analysis, an ODS [LUNA 5 μ, C_{18}, 250 × 4.60 mm, Phenomenex, USA] was used.

Plant Material

The seeds of *Aesculum chinensis* Bge. were collected at Lueyang County, Shaanxi Province, China, in September 1997. Voucher specimens are deposited at the State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences of Peking University.

Extraction and Isolation

The seeds of *Aesculum chinensis* were extracted as described previously [5]. Further chromatography of the 70% EtOH fraction by repeated prep. HPLC [MeCN–0.5% HOAc aq. (7:3 and 6:4, v/v)] yielded isoescins IIa (**1**, 75 mg), IIb (**2**, 101 mg), IIIa (**3**, 72 mg) and IIIb (**4**, 89 mg).

Acid Hydrolysis of 1–4

4M HCl (1 ml) was added to the EtOH solution (1.5 ml) of the saponin (**1**–**4**, 10 mg, respectively) and refluxed for 2 h. The reaction mixture was then neutralized with saturated aqueous $NaHCO_3$ and extracted with EtOAc (10 ml × 3) to give an EtOAc layer and an H_2O layer. The water layer was evaporated to dryness *in vacuo* and subjected to paper chromatography [*n*-BuOH–EtOH–H_2O–con.NH_3/H_2O, 45:5:49:1] for examination of sugars (glucuronic acid $R_f = 0.06$, galactose $R_f = 0.16$, glucose $R_f = 0.19$, and xylose $R_f = 0.23$).

Isoescin IIa (1)

A white amorphous power; $C_{54}H_{84}O_{23}$, $[\alpha]_D^{23}$ −26.6 (*c* 1.15, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3416, 2960, 1604, 1411, 1382, 1261, 1159, 1075, 1042, 800, 615; MALDI-TOF-MS *m/z* 1123 $[M + Na]^+$; HR-SI-MS (negative-ion model): *m/z* 1099.5323 $[M - H]^-$ (calcd for $C_{54}H_{83}O_{23}$, 1099.5325); ^{1}H NMR (500 MHz, pyridine-d_5) δ 0.65 (3H, s, Me-25), 0.76 (1H, d-like, H-5), 0.79 (1H, m, Ha-1), 0.88 (3H, s, Me-26), 1.04 (3H, s, Me-29), 1.17 (1H, m, Ha-7), 1.19 (1H, m, Hb-7), 1.27 (3H, s, Me-23), 1.27 (3H, s, Me-30), 1.34 (1H, m, Ha-19), 1.44 (2H, m, Ha,b-6), 1.55 (3H, d, $J = 7.0$ Hz, Me-4‴′), 1.60 (1H, m, H-9), 1.78 (3H, s, Me-27), 1.80 (3H, s, Me-5‴′), 1.97 (3H, s, Me−CO−), 2.80 (1H, t, $J = 12.0$ Hz, H-18), 3.05 (1H, dd-like, Hb-19), 3.28 (1H, d-like, Ha-24), 3.40 (1H, dd-like, H-3α), 4.47 (1H, d, $J = 9.0$ Hz, H-22β), 4.70 (1H, m, H-16β), 4.76 (1H, d, $J = 7.5$ Hz, H-1′), 5.19 (1H, d, $J = 7.5$ Hz, H-1‴), 5.44 (1H, br s, H-12), 5.50 (1H, d, $J = 7.0$ Hz, H-1″), 6.38 (1H, d, $J = 9.0$ Hz, H-21α), 6.97 (1H, dq-like, H-3‴′); ^{13}C NMR (125 MHz, pyridine-d_5) spectral data are shown in Table I.

Isoescin IIb (2)

A white amorphous power, $C_{54}H_{84}O_{23}$; $[\alpha]_D^{23}$ −28.6 (*c* 1.05, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3413, 2926, 1710, 1604, 1381, 1240, 1161, 1042, 616; MALDI-TOF-MS *m/z* 1123 $[M + Na]^+$, 829 $[M + Na - glc(162) - xyl(132)]^+$; HR-SI-MS (negative-ion model): *m/z* 1099.5322 $[M - H]^-$ (calcd for $C_{54}H_{83}O_{23}$, 1099.5325); ^{1}H NMR (500 MHz, pyridine-d_5) δ 0.70 (3H, s, Me-25), 0.81 (1H, d, $J = 12.0$ Hz, H-5), 0.82 (1H, m, Ha-1), 0.91(3H, s, Me-26), 1.08 (3H, s, Me-29), 1.27 (3H, s, Me-23), 1.27 (3H, s, Me-30), 1.62 (1H, m, H-9), 1.80 (3H, s, Me-27), 1.94 (3H, s, Me-5‴′), 1.95 (3H, s, Me−CO−), 2.01 (3H, d, $J = 7.5$ Hz, Me-4‴′), 2.82 (1H, t-like, H-18), 3.07 (1H, dd-like, Hb-19), 3.33 (1H, d-like, Ha-24), 3.45 (1H, dd-like, H-3α), 4.44 (1H, d, $J = 10.0$ Hz, H-22β), 4.71 (1H, br s, H-16), 4.80 (1H, d, $J = 7.5$ Hz, H-1′), 5.12 (1H, d, $J = 7.5$ Hz, H-1‴), 5.42 (1H, d, $J = 7.0$ Hz, H-1″), 5.43 (1H, br s, H-12), 5.87 (1H, dq-like, H-3‴′), 6.46 (1H, d, $J = 10.0$ Hz, H-21α); ^{13}C NMR (125 MHz, pyridine-d_5) spectral data are shown in Table I.

Isoescin IIIa (3)

A white amorphous power, $C_{55}H_{86}O_{23}$; $[\alpha]_D^{23}$ +15.7 (*c* 1.15, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3409, 2926, 1598, 1382, 1269, 1158, 1076, 1042, 621; MALDI-TOF-MS *m/z* 1137 $[M + Na]^+$, 814 $[M + Na - glc(162) - gal(162) + H]^+$; HR-SI-MS (negative-ion model): *m/z* 1113.5479 $[M - H]^-$ (calcd for $C_{55}H_{85}O_{23}$, 1113.5482); ^{1}H NMR (500 MHz, pyridine-d_5) δ 0.82 (3H, s, Me-25), 0.91(1H, d-like, H-5), 0.97 (3H, s, Me-26), 1.03 (3H, s, Me-24), 1.10 (3H, s, Me-29), 1.17 (3H, s, Me-23), 1.31 (3H, s, Me-30), 1.39 (1H, d-like, Ha-19), 1.57 (3H, d, $J = 6.5$ Hz, Me-4‴′), 1.64 (1H, d, $J = 16.5$ Hz, H-9), 1.64 (1H, m, Ha-15), 1.82 (3H, s, Me-27), 1.83 (3H, s, Me-5‴′), 1.88 (1H, m, Hb-15), 2.00 (3H, s, *Me*−CO−), 2.86 (1H, t, $J = 10.5$ Hz, H-18), 3.10(1H, dd-like, Hb-19), 3.11 (1H, dd-like, H-3α), 4.25 (2H, d-like, Ha, b-28), 4.51 (1H, d, $J = 9.5$ Hz, H-22β), 4.73 (1H, br s, H-16β), 4.75 (1H, d, $J = 7.5$ Hz, H-1′), 5.30 (1H, d, $J = 7.5$ Hz, H-1‴), 5.31 (1H, d, $J = 6.5$ Hz, H-1″), 5.48 (1H, br s, H-12), 6.45 (1H, d, $J = 9.5$ Hz, H-21α), 7.00 (1H, dq-like, H-3‴′); ^{13}C NMR (125 MHz, pyridine-d_5) spectral data are shown in Table I.

Isoescin IIIb (4)

A white amorphous power, $C_{55}H_{86}O_{23}$; $[\alpha]_D^{23}$ +3.0 (*c* 1.00, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3406, 2926, 1711, 1600, 1381, 1240, 1161, 1074, 1041, 600; MALDI-TOF-MS *m/z* 1137

TABLE I ^{13}C NMR spectral data for isoescins IIa (**1**), IIb (**2**), IIIa (**3**) and IIIb (**4**) (δ)*

C	**1**	**2**	**3**	**4**
1	38.7	38.7	38.7	38.7
2	26.3	26.4	26.4	26.4
3	90.5	90.5	89.4	89.3
4	44.1	44.1	39.4	39.4
5	56.2	56.2	55.6	55.6
6	18.5	18.6	18.3	18.3
7	33.2	33.2	33.0	33.0
8	39.8	39.8	40.0	39.9
9	46.6	46.6	46.9	46.9
10	36.4	36.4	36.7	36.6
11	24.0	24.0	23.9	23.8
12	123.0	123.0	123.3	123.0
13	142.6	142.6	142.7	142.7
14	41.7	41.7	41.7	41.7
15	34.5	34.5	34.6	34.6
16	67.5	67.5	67.6	67.6
17	47.0	47.0	47.0	47.0
18	40.5	40.5	40.5	40.5
19	47.2	47.2	47.2	47.2
20	36.2	36.0	36.3	36.0
21	81.5	81.1	79.7	79.7
22	71.2	71.2	71.7	71.7
23	22.5	22.6	28.0	27.9
24	62.8	62.8	16.7	16.7
25	15.4	15.4	15.6	15.6
26	16.8	16.8	17.0	16.9
27	27.3	27.3	27.4	27.4
28	66.3	66.3	66.4	66.4
29	29.7	29.7	29.7	29.7
30	20.0	20.1	20.1	20.2
3-*O*-β-D-Glucuronopyranosyl moiety				
1′	104.5	104.5	104.8	104.8
2′	79.5	78.9	82.9	82.3
3′	76.6	76.5	76.3	76.8
4′	83.2	83.3	81.5	81.1
5	75.5	75.5	75.0	74.9
6′	175.1	175.5	175.5	173.3
2′-*O*-β-D-Xylopyranosyl or galactopyranosyl moiety				
1″	104.5	104.5	105.1	105.2
2″	75.5	75.5	74.9	74.9
3″	78.8	78.8	75.0	74.9
4″	70.7	70.7	71.1	71.0
5″	66.9	66.9	76.8	76.8
6″			62.1	62.0
4′-*O*-β-D-Glucopyranosyl moiety				
1‴	104.7	104.5	104.4	104.5
2‴	74.9	74.8	74.9	74.9
3‴	78.3	78.3	78.1	78.1
4‴	71.1	71.0	71.3	71.3
5‴	77.5	77.5	78.1	77.8
6‴	62.0	62.0	62.8	62.8
Tigloyl or angeloyl group				
1″	168.5	168.5	168.4	168.5
2″	129.7	129.4	129.8	129.4
3″	136.3	136.1	136.2	135.7
4″	14.0	15.8	14.1	15.8
5″	12.3	20.9	12.4	20.9
Acetyl group				
1⁗	170.7	170.6	170.7	170.6
2⁗	20.7	20.6	20.7	20.6

* Measured in pyridine-d_5.

$[M + Na]^+$, 814 $[M + Na - glc\ (162) - gal(162) + H]^+$; HR-SI-MS (negative-ion model): *m/z* 1113.5479 $[M - H]^-$ (calcd for $C_{55}H_{85}O_{23}$, 1113.5468); ^1H NMR (500 MHz, pyridine-d_5) δ 0.80 (3H, s, Me-25), 0.91 (1H, d, $J = 12.0$ Hz, H-5), 0.96 (3H, s, Me-26), 1.03 (3H, s, Me-24), 1.09 (3H, s, Me-29), 1.16 (3H, s, Me-23), 1.22 (1H, d, $J = 13.5$ Hz, Ha-19), 1.28 (3H, s, Me-30), 1.62 (1H, m, Ha-15), 1.64 (1H, d, $J = 12.5$ Hz, H-9), 1.81 (3H, s, Me-27), 1.88 (1H, m, Hb-15), 1.94 (3H, s, Me–CO–), 1.96 (3H, s, Me-5$''''$), 2.02 (3H, d, $J = 6.5$ Hz, Me-4$''''$), 2.83 (1H, t, $J = 10.5$ Hz, H-18), 3.08 (1H, dd-like, Hb-19), 3.13 (1H, dd-like, H-3α), 4.23 (2H, d-like, Ha, b-28), 4.51 (1H, d, $J = 9.5$ Hz, H-22β), 4.72 (1H, br s, H-16β), 4.79 (1H, d, $J = 7.5$ Hz, H-1$'$), 5.32 (1H, d, $J = 7.5$ Hz, H-1$'''$), 5.33 (1H, d, $J = 6.5$ Hz, H-1$''$), 5.43 (1H, br s, H-12), 5.87 (1H, dq-like, H-3$''''$), 6.48 (1H, d, $J = 9.5$ Hz, H-21α). ^{13}C NMR (125 MHz, pyridine-d_5) spectral data are shown in Table I.

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