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Phenylethanoid and aliphatic alcohol glycosides from *Acanthus ilicifolius*

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Abstract

A phenylethanoid glycoside (ilicifolioside A) and an aliphatic alcohol glycoside (ilicifolioside B), have been isolated from the aerial parts of *Acanthus ilicifolius*, together with eight known compounds. Their structures were determined from spectroscopic analyses.

Keywords: *Acanthus ilicifolius*; Acanthaceae; Phenylethanoid glycoside; Aliphatic alcohol glycoside; Ilicifoliosides A and B

1. Introduction

Acanthus ilicifolius L. (Acanthaceae) is widely distributed in southeastern Asia and is traditionally used in Chinese medicine as anti-inflammatory and anti-hepatitis agents. In preliminary investigations of this plant, a triterpenoidal saponin (Minocha and Tiwari, 1981), 2-benzoxazolinone (Kapil and Sharma, 1994), acanthicifoline (Cordell, 1999), seven lignan glucosides, two phenylethanoid glycosides (Kanchanapoom et al., 2001a) and five benzoxazinoid glucosides (Kanchanapoom et al., 2001b) were isolated. In the present study, six phenylethanoid glycosides (**1**–**6**), one aliphatic alcohol glycoside (**7**) and three other compounds (**8**–**10**) were isolated from the aerial parts of the plant. Their structures were determined from analysis of spectral data.

2. Results and discussion

The ethanolic extract of the aerial parts of *A. ilicifolius* was subjected to extraction and solvent partitioning as described in the Experimental. The resulting *n*-butanol extract was applied to column chromatography using silica gel, octadecylsilyl silica gel, Sephadex LH-20 gel and C18 HPLC-ODS to yield compounds **1**–**10**, of which eight were previously known. The eight known compounds were identified by comparison of their spectral data with literature values: campneoside I (**1**) (Imakura et al., 1985), acteoside (**3**) (Miyase et al., 1982), phenylethyl-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranoside (**4**) (Ono et al., 1999), cistanoside E (**5**) and cistanoside F (**6**) (Kobayashi et al., 1985), (+)-lyoniresinol 3a-*O*-β-D-glucopyranoside (**8**) (Achenbach et al., 1992), (2*R*)-2-*O*-β-D-glucopyranosyl-2*H*-1,4-benzoxazin-3(4*H*)-one (**9**) (Kanchanapoom et al., 2001b) and adenosine (**10**) (Otsuka et al.,1989). Two new compounds, named ilicifoliosides A (**2**) and B (**7**), were elucidated based on chemical and spectroscopic evidence. Among the six phenylethanoid glycosides isolated, compounds **1**, **2** and **6** each consisted of a pair of epimers (see below) (Fig. 1).

The molecular formula of compound **2** was determined as $C_{31}H_{40}O_{16}$ by HR-ESI mass spectrometry. The ^1H and ^{13}C NMR spectral data were similar to those of campneoside I (**1**). The ^1H NMR spectrum showed the presence of two overlapping secondary methyl groups of rhamnose [δ 1.08 (6H, *d*, $J = 6.0$ Hz)],

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two methyl groups coupled with methylene [δ 1.16, 1.18 (3H each, *t*, $J=6.8$ Hz)], two β-D-glucose-anomeric protons [δ 4.37, 4.42 (1H each, *d*, $J=8.0$ Hz)], two α-L-rhamnose-anomeric protons [δ 5.18, 5.21 (1H each, *d*, $J=1.7$ Hz)], one pair of overlapped *trans* olefinic protons as AB type signals [δ 6.25, 7.57 (2H each, *d*, $J=16.0$ Hz)], two pairs of overlapped ABX system protons at δ 6.75 (2H, *d*, $J=8.0$ Hz), 6.94 (2H, *dd*, $J=8.0$, 2.0 Hz), and 7.04 (2H, *d*, $J=2.0$ Hz), two pairs of partially overlapped ABX system protons at δ 6.73 (1H, *d*, $J=8.0$ Hz), 6.68 (1H, *dd*, $J=8.0$, 2.0 Hz), 6.78 (1H, *d*, $J=2.0$ Hz), and δ 6.73 (1H, *d*, $J=8.0$ Hz), 6.65 (1H, *dd*, $J=8.0$, 2.0 Hz), 6.76 (1H, *d*, $J=2.0$ Hz). The above spectroscopic data, together with two adjacent peaks in HPLC suggested that **2** might be a pair of epimers of phenylethanoid disaccharide glycoside, though further preparative isolation of these two epimers failed. Comparison of ^{13}C NMR spectral data with those of campneoside I (Table 1) revealed the upfield shift of β-carbon of aglycone (−2.2 ppm) and an ethoxyl group, indicating that instead of a methoxyl group, **2** has an ethoxyl group attached to β-carbon of the aglycone. Furthermore, the ^{1}H–^{1}H COSY spectrum demonstrated the existence of the ethoxyl group and revealed correlations between the β-H and α-H of the aglycone. The HMBC experiment also displayed a correlation between oxygenated methylene protons [δ 3.42 (m)] of the ethoxyl group and the β-carbon (δ 81.68/82.54) of the aglycone (Fig. 2). Consequently, **2** was assigned as β-ethoxy-β-(3′,4′-dihydroxyphenyl)-ethyl-*O*-α-L-rhamnopyranosyl-(1→3)-4-*O*-caffeoyl-β-D-glucopyranoside, named ilicifolioside A.

Through a series of chemical reactions with methylation, oxidation and reduction, campneoside I (**1**) was established to exist as pair of epimers at the β-carbon of the aglycone (*R*,*S*-β-OMe) (Imakuwa et al., 1985). Similarly, I the ^{1}H NMR and ^{13}C NMR spectral data of **2** (Table 1) showed two kinds of chemical shifts for each

Table 1
^{1}H NMR and ^{13}C NMR spectral data of 1, 2 and 3 (400 MHz for ^{1}H and 100 MHz for ^{13}C, methanol-d_4)

No.	**1** (campneoside I)		**2**		**3**	
Aglycone	^{1}H δ [mult., *J* (Hz)]	^{13}C δ_C	^{1}H δ [mult., *J* (Hz)]	^{13}C δ_C	^{1}H δ [mult., *J* (Hz)]	^{13}C δ_C
1		130.91/131.32		131.51/131.91		131.52
2	6.82, 6.80 (1H each, *d*, 2.0)	115.26/115.40	6.78, 6.76 (1H each, *d*, 2.0)	114.97/115.14	6.68 (1H, *d*, 2.0)	116.35
3		146.82/146.86		146.42/146.49		146.13
4		146.73/146.80		146.25/146.33		144.67
5	6.79 (2H, d, 2.0)	116.51/116.57	6.73 (2H, *d*, 2.0)	116.27/116.33	6.66 (1H, *d*, 8.0)	117.15
6	6.71, 6.69 (1H each, *dd*, 8.0, 2.0)	120.14/120.25	6.68, 6.65 (1H each, *dd*, 8.0, 2.0)	119.79/119.92	6.54 (1H, *dd*, 8.0, 2.0)	121.29
α(8)	3.93, 3.84, 3.80, 3.59 (1H each, *m*)	74.87/75.29	3.98, 3.82, 3.70, 3.62 (1H each, *m*)	74.62/75.15	4.05, 3.62 (1H each, *m*)	72.09
β(7)	4.39 (2H, *m*)	83.88/84.71	4.45 (2H, *m*)	81.68/82.54	2.76 (2H, *m*)	36.56
OCH_3	3.38, 3.29 (3H each, *s*)	56.96/57.05				
Ethoxyl						
OCH_2			3.42 (4H, *m*)	65.09/65.16		
CH_3			1.18, 1.16 (3H each, *t*, 6.8)	15.51/15.55		
Caffeoyl						
1		127.88		127.67		127.69
2	7.09 (2H, *d*, 2.0)	115.46	7.04 (2H, *d*, 2.0)	115.29	7.05 (1H, *d*, 1.8)	115.29
3		147.13		146.80		146.83
4		150.14		149.77		149.78
5	6.81 (2H, *d*, 8.0)	116.78	6.75 (2H, *d*, 8.0)	116.57	6.76 (1H, *d*, 8.2)	116.55
6	6.99 (2H, *dd*, 8.0, 2.0)	123.48	6.94 (2H, *dd*, 8.0, 2.0)	123.28	6.94 (1H, *dd*, 8.2, 1.8)	123.23
α(8)	6.31 (2H, *d*, 16)	114.90	6.25 (2H, *d*, 16)	114.71	6.25 (1H, *d*, 16)	114.75
β(7)	7.63 (2H, *d*, 16)	148.28/148.30	7.57 (2H, *d*, 16)	148.05	7.57 (1H, *d*, 16)	148.02
CO		168.52		168.30/168.33		168.31
Glc						
1	4.46, 4.43 (1H each, *d*, 8.0)	104.30/104.77	4.37, 4.42 (1H each, *d*, 8.0)	104.00/104.64	4.35 (1H, *d*, 8.0)	104.21
2		76.43/76.63		76.11/76.35		76.22
3	3.75, 3.74 (1H each, *t*, 9.6)	81.66/81.74	3.82, 3.80 (1H each, *t*, 9.6)	81.42/81.50	3.80 (1H, *t*, 9.6)	81.66
4	4.96 (2H, *t*, 9.6)	70.76/70.80	4.91 (2H, *t*, 9.6)	70.49/70.59	4.91 (1H, *t*, 9.6)	70.62
5		76.35/76.39		76.02/76.05		76.03
6		62.55/62.67		62.37		62.39
Rha						
1	5.25, 5.23 (1H each, *d*, 1.5)	103.21/103.26	5.18, 5.21 (1H each, *d*, 1.7)	102.93/102.98	5.18 (1H, *d*, 1.1)	103.02
2		72.64		72.36		72.37
3		72.34		72.07		72.25
4		74.07		73.81		73.83
5		70.70		70.41		70.42
6	1.14, 1.13 (3H each, *d*, 6.0)	18.76	1.08 (6H, *d*, 6.0)	18.48	1.08 (3H, *d*, 6.0)	18.47

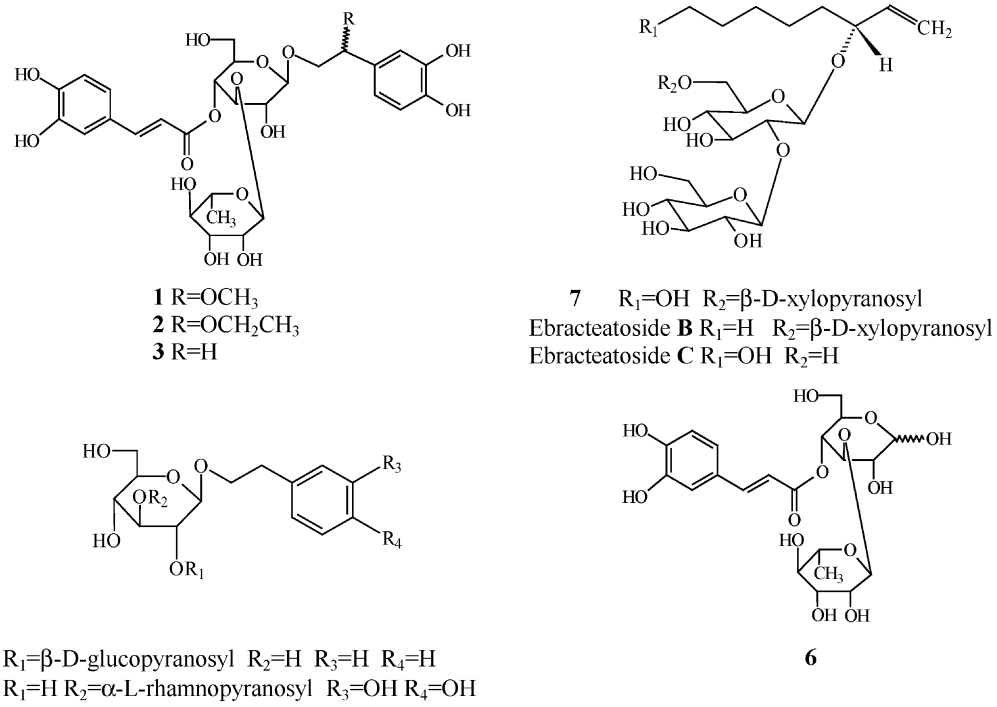

Fig. 1. Structures of compounds **1**–**7**, ebracteatoside B and C.

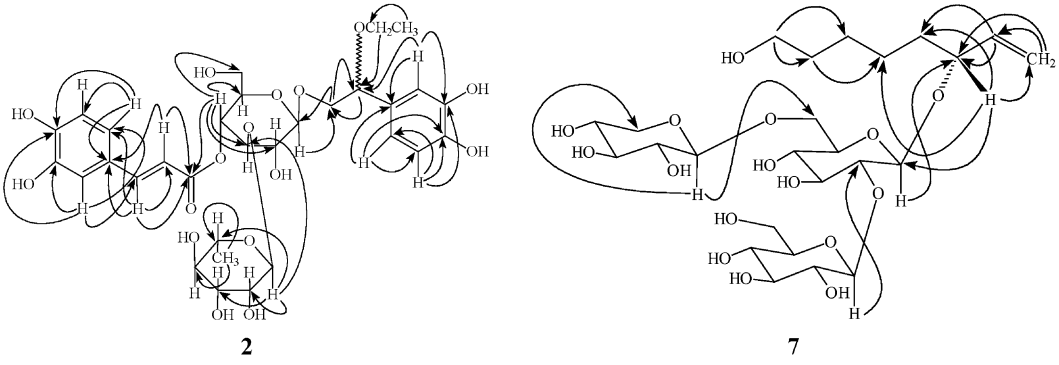

Fig. 2. The HMBC correlations of **2** and **7**.

proton (such as H-1 in the glucose and rhamnose moiety, β-ethoxy in the aglycone) and each carbon (such as C-1 – C-5 of the glucose moiety, C-1 – C-6, α-C, β-C and β-ethoxy of the aglycone in the vicinity of the asymmetric β-C), though **2** only gave one spot on TLC. These findings indicated that **2** existed as epimers at the β-C of the aglycone (*R*, *S*-β-OEt) like campneoside I (**1**). Through subsequent HPLC analysis of plant extracts, where EtoH was not used in any of the isolation steps, **2** was proven not to be an artifact of extraction and separation, but a naturally occurring compound present in *A. ilicifolius* (see Experimental). In addition, on reduction with sodium borohydride, **6** was shown to exist as a pair of anomeric epimers at C-1 of the glucose (α/β) moiety (Kobayashi et al., 1985). These results led us to conclude that compounds **1**, **2** and **6** each consisted of a pair of epimers.

The molecular formula of compound **7** was determined as $C_{25}H_{44}O_{16}$ by HR-ESI mass spectrometric analysis. The ^{1}H NMR and ^{13}C NMR (Table 2) spectra showed the presence of three sugar moieties [δ 4.31, 4.61, 4.42 (1H each, *d*, $J = 7.8$ Hz) for ^{1}H NMR and δ 101.8,105.0, 105.3 for ^{13}C NMR], which were identified to be a terminal β-D-glucopyranose, a terminal β-D-xylopyranose, connected to a core β-D-glucopyranose unit. Additionally, eight carbon signals were assignable for the aglycone. Acid hydrolysis of **7** gave (3*R*)-1-octene-3,8-diol, D-glucose and D-xylose, which were identified by TLC and comparison of the optical rotation with authentic samples. DEPT experiment indicated the presence of six methylenes (δ 25.7, 26.9, 33.6, 35.8, 62.9 and 116.8) and two methines (δ 83.5, 140.6) in the aglycone moiety. Comparison of these ^{13}C NMR spectral data with those of ebracteatoside C (Table 2)

Table 2
^{13}C NMR spectral data of compounds ebracteatoside B, C and 7 (100 MHz, methanol-d_4)

Carbon no.	Ebracteatoside B	Carbon no.	Ebracteatoside C	7
Aglycone		Aglycone		
1	116.9	8	116.6	116.8
2	140.5	7	140.8	140.6
3	83.8	6	83.6	83.5
4	35.7	5	35.7	35.8
5	25.5	4	25.7	25.7
6	32.9	3	33.6	33.6
7	23.6	2	26.9	26.9
8	14.5	1	62.9	62.9
Glc-1′	101.7	Glc-1′	101.7	101.8
2′	82.3	2′	82.6	82.5
3′	77.5[a]	3′	77.7[a]	77.6[a]
4′	71.0	4′	71.3	71.2
5′	77.5[a]	5′	78.0[a]	77.5[a]
6′	69.3	6′	62.8	69.4
Glc-1″	104.8	Glc-1″	105.0	105.0
2″	75.9	2″	76.1	76.1
3″	77.8[a]	3″	77.7[a]	77.9[a]
4″	71.4	4″	71.5	71.4
5″	78.0[a]	5″	78.2[a]	78.2[a]
6″	62.7	6″	62.6	62.9
Xyl-1‴	105.1	Xyl-1‴		105.3
2‴	74.7	2‴		74.8
3‴	77.5[a]	3‴		77.7[a]
4‴	71.4	4‴		71.6
5‴	66.7	5‴		66.8

[a] Assignments may be interchanged in each column.

revealed that **7** had the same aglycone as ebracteatoside C (Kanchanapoom et al., 2001c). Furthermore, the chemical shifts of three sugar moieties of **7** were the same as those of ebracteatoside B (Table 2) (Kanchanapoom et al., 2001c). Thus, the structure of compound **7** was assigned as (6*R*)-7-octene-1,6-diol-6-*O*-β-D - xylopyranosyl - (1‴→6′) - *O* - [β - D - glucopyranosyl - (1″→2′)]-*O*-β-D-glucopyranoside, named ilicifolioside B. The absolute configuration at C-6 was suggested to be in the *R*-form by comparing the optical rotation value of aglycone ($[\alpha]_D^{25}$ −22.5°) with that of (3*R*)-3-benzoyloxy-1-octene-8-ol ($[\alpha]_D^{25}$ −18.2°) (Martin et al., 1992). HMBC experiments also confirmed the above structure from the correlations of protons to corresponding carbons as shown in Fig. 2.

3. Experimental

3.1. General

NMR spectra were recorded in methanol-d_4 using a Bruker ARX-400 spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) with tetramethylsilane as internal standard. The ESI-HRMS were measured on a Bruker APEX II spectrometer in either the positive or negative ion mode. Optical rotations were measured with an AA-10R digital polarimeter. Prep HPLC was carried out on ODS columns (250×10 mm i.d.,YMC) with a Waters 996 photodiode array detector. For CC, silica gel (200–300 mesh) (Qingdao Mar. Chem. Ind. Co. Ltd.), octadecylsilyl silica gel (80–100 μm) (Unicorn), Sephadex LH-20 gel (Pharmacia) and highly porous copolymer of styrene and divinylbenzene (Tianjing Chem. Ind. Co. Ltd.) were used. The solvent systems were: (I) $CHCl_3$–MeOH–H_2O (9:1:0.1) (II) $CHCl_3$–MeOH–H_2O (5:1:0.1) (III) $CHCl_3$–MeOH–H_2O (3:1:0.1), (IV) $CHCl_3$–MeOH–H_2O (7:3:0.2), (V) $CHCl_3$–MeOH–H_2O (6:4:0.3), (VI) $CHCl_3$–MeOH–H_2O (6:4:0.6), (VII) $CHCl_3$–MeOH–H_2O (6:4:1), (VIII) 70% MeOH (IX) 50% MeOH, (X) 30% MeOH, (XI) 20% MeOH. The spray reagent used for TLC visualization was 5% H_2SO_4 and 5% phosphomolybdic acid in 95% ethanol.

3.2. Plant material

A. ilicifolius L. was collected in July 2001 from Sanya of Hainan Province, southern China. The identification of the plant was performed by Prof. Yongshui Lin, Laboratory of Marine Biology, South China Sea Institute of Oceanology, Chinese Academy of Sciences. A voucher sample is kept in the Herbarium of South China Sea Institute of Oceanology (GKLMMM-001).

3.3. Extraction and isolation

The dried aerial part (10.0 kg) of *A. ilicifolius* was extracted with hot 95% and 50% EtOH three times, respectively. After removal of the solvent by evaporation, the residue (1.3 kg) was suspended in water and defatted with petroleum ether. The aqueous layer was further extracted with ethyl acetate and *n*-butanol successively. The *n*-butanol extract (120 g) was subjected to CC of a highly porous copolymer of styrene and divinylbenzene and eluted with H_2O, 30% EtOH, 60% EtOH and 95% EtOH, successively. The fractions eluted with different concentrations of ethanol were combined (70 g) and subjected to silica gel cc (systems I–VII) to afford ten fractions. Fraction 6 (8.3 g) was further separated on Unicorn-ODS (system VIII) and Pharmacia-Sephadex LH-20 (system VIII) columns to afford compounds **8** (190 mg), **9** (50 mg), and **10** (20 mg). Fraction 7 (9.8 g) was subjected to ODS column (system IX) and Sephadex LH-20 (system IX) to give four fractions. Fraction 7-2 (2.6 g) and fraction 7-3 (1.3 g) were subjected to prep. HPLC-ODS chromatography (system X) to provide compounds **1** (86 mg), **2** (222 mg), and **4** (30 mg). Fraction 8 (7.2 g) was subjected to ODS column (system IX) and Sephadex LH-20 (system IX) to give five fractions. Fraction 8-3 (2.2 g) and fraction

8-5 (1.6 g) were subjected to prep. HPLC-ODS chromatography (system XI) to afford compounds **3** (520 mg), **5** (60 mg), **6** (418 mg), and **7**(80 mg).

3.4. HPLC analysis of **2** in the water extract of plant of *Acanthus ilicifolius*

The dried aerial part (50 g) of *A. ilicifolius* was extracted with hot water (60 °C) three times. After concentration the water extract was further extracted with chloroform and *n*-butanol successively. Then after removal of the solvent by evaporation the *n*-butanol extract was used for HPLC analysis.

HPLC analysis was performed with Waters Delta PAK C_{18} column (150×3.9 mm I.D.) at a column temp of 25 °C. The mobile phase composed of MeOH–water (containing 0.1% phosphoric acid) (28:72 v/v) was eluted at a flow rate of 1 ml/min. Eluates were monitored by a 996 photodiode array detector at detection wavelength of 330 nm.

HPLC analysis of the crude plant extract revealed a peak with the same retention time (17.6 min) as compound **2** (17.4 min), which indicated that compound **2** was a naturally occurring compound and not an artifact formed during extraction and separation.

3.5. Acid hydrolysis of ilicifolioside B (7)

Ilicifolioside B (40 mg) was treated with a 1:1 mixture of 2 M HCl and 1, 4-dioxane (6 ml) at 100 °C for 3 h. The reaction mixture was neutralized by addition of Ag_2CO_3 and filtered. The filtrate was concentrated and the residue suspended in water (10 ml) was extracted with diethyl ether (20 ml, twice). Then the extract concentrated to dryness afforded the aglycone of **7**, whose optical rotation value ($[\alpha]_D^{25}$ −22.5°) was identical with that of (3*R*)-3-benzoyloxy- 1-octene-8-ol ($[\alpha]_D^{25}$ −18.2°) (Martin et al., 1992). The aqueous layer containing monosaccharides was concentrated and applied to a silica gel column (system III) to afford D-glucose (9 mg, R_f 0.15, $[\alpha]_D^{25}$ +50°) and D-xylose (5 mg, R_f 0.30, $[\alpha]_D^{25}$ +20°), comparing with authentic samples.

3.6. Ilicifolioside A (2)

Amorphous powder, $[\alpha]_D^{25}$ −72° (MeOH, *c* 0.8); ^{1}H NMR and ^{13}C NMR (methanol-d_4): Table 1; HR-ESI-MS, *m*/*z*: 691.2205 $[M+Na]^+$ ($C_{31}H_{40}O_{16}Na$ requires 691.2209).

3.7. Ilicifolioside B (7)

Amorphous powder, $[\alpha]_D^{25}$ −51° (MeOH, *c* 0.6); ^{1}H NMR (methanol-d_4) δ: 5.87(1H, *ddd*, *J* = 17.2, 10.4, 7.6 Hz, H-7), 5.24 (1H, *brd*, *J* = 17.2 Hz, H-8), 5.14 (1H, *brd*, *J* = 10.4 Hz, H-8), 4.61 (1H, d, *J* = 7.8 Hz, H-1″ Xyl), 4.42 (1H, *d*, *J* = 7.8Hz, H-1′ Glc), 4.31 (1H, *d*, *J* = 7.8 Hz, H-1″ Glc), 4.15 (1H, *dd*, *J* = 12.8, 6.2 Hz, H-6), 3.53 (2H, *t*, *J* = 6.2 Hz, H-1), 1.73 (1H, *m*, H-5), 1.56 (1H, *m*, H-5), 1.53 (2H, *m*, H-3), 1.35–1.44 (4H, *m*, H-2, 4); ^{13}C NMR (methanol-d_4): Table 2; HR-ESI-MS, *m*/*z*: 623.2518 $[M+Na]^+$ ($C_{25}H_{44}O_{16}Na$ requires 623.2522).

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