New Oleanane-type glycosides and secoiridoid glucoside from *Aptandra zenkeri*

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New Oleanane-type glycosides and secoiridoid glucosides from Aptandra zenkeri

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New oleanane-type glycosides and secoiridoids glucosides from *Aptandra zenkeri*

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Abstract

Four new saponins, camelliagenin A and B derivatives, and three new secoiridoid glucosides were isolated from the stem bark of *Aptandra zenkeri* Engl. (Aptandraceae). Their structures were determined based on a combination of 1D- and 2D-NMR experiments techniques and HR-ESI-MS analysis. This is the first report on saponins in genus *Aptandra*.

Keywords:

Aptandra zenkeri Engl.; Aptandraceae; triterpenoid saponins; secoiridoid glucosides.

For Peer Review Only

1. Introduction

The genus *Aptandra* belonging to the Aptandraceae family, is formed by four species, found in south America regions except *Aptandra zenkeri* Engl. present in Africa region (Nickrent et al. 2010). *Aptandra zenkeri* Engl. is a shrub, up to 15 m tall with reddish bark. The fruit are ellipsoid ovoid drupe, subtended by much enlarged, up to 10 cm wide, pink calix. As a folk medicine, this species has usually been used to treat hepatitis and coughing (Aubreville 1959; Burkill 1997; Louis et al. 1948; Neuwinger 2000; Villiers, 1973; List et Horhammer 1972). However, there has been no chemical or biological study reported on this plant. Only phytosterols and tocopherols were mentioned in *Aptandra sprucea* (Wiat et al. 2001). As a part of a continuing study for the discovery of medicinal Ivory Coast species, seven compounds, including four saponins, camelliagenin A and B derivatives, and three secoiridoid glucosides derivatives of kingiside, were isolated from the stem bark of *A. zenkeri*. This paper deals with their isolation and structure elucidation of these compounds.

2. Results and Discussion

The aqueous methanol extract obtained from the stem bark of *A. zenkeri* was concentrated under reduced pressure and then dissolved in water and extracted successively with CHCl_3 and *n*-BuOH. The *n*-BuOH was fractionated by vacuum-liquid chromatography (VLC) and purified by medium-pressure liquid chromatography on RP-18 and semi-preparative HPLC to yield four undescribed triterpenoid glycosides (**1-4**) (Figure 1) and three secoiridoid glucosides (**5-7**) (Figure 2). Their structures were established by a detailed analysis of their spectral data mainly by 500 MHz 2D NMR experiments and mass spectrometry. TLC analysis and NMR analysis of COSY, TOCSY, NOESY and HSQC spectra, allowed the full identification of the sugar units as β -D-glucopyranosiduronic acid (glcA), β -D-xylopyranose (xyl), β -D-glucopyranose (glc), and β -D-galactopyranose (gal).

Compound **1** was separated as a white, amorphous powder. The molecular formula $\text{C}_{58}\text{H}_{90}\text{O}_{26}$ was deduced from the HR-ESI-MS $[\text{M} + \text{Na}]^+$ ion at m/z 1225.5627 (calcd 1255.5618) (Figure S1). The ^1H NMR spectrum of **1** (Figure S2) indicated the presence of six singlet methyl groups at δ 0.93, 0.98, 1.05, 1.07, 1.19, 1.52 (each 3H, s, H₃-29, H₃-26, H₃-25, H₃-30, H₃-24, H₃-27), a methylene and three methines bearing an oxygen function at δ_{H} 3.08, 3.28 (each 1H, d, $J=11.0$ Hz, H-28), 3.91 (1H, dd, $J=11.3, 4.5$ Hz, H-3), 4.13 (1H, brs, H-16), 5.45 (1H, dd, $J=12.1, 5.6$ Hz, H-22), an olefinic proton at δ 5.37 (1H, t, $J=3.6$ Hz, H-

12), and an aldehyde signal at δ_{H} 9.48 (1H, s, H-23), which were characteristic of a polyhydroxyolean-12-ene triterpene derivative. In the HMBC spectrum (Figure S6), the cross-peaks observed between H-24 and δ 84.7 (C-3) and δ 209.3 (C-23) placed a secondary OH at C-3 and an aldehyde group at C-4. The location of the aldehyde group at C-23 was deduced from the chemical shift of C-24 at δ_{C} 9.5 characteristic of an axial position, and by comparison of the ^{13}C NMR spectrum (Figure S3) with that of camelliagenin B (Miyose et al. 2012). In the HMBC spectrum, correlations between H-28 and δ_{C} 69.5 (C-16) and 72.4 (C-22) allowed the location of the two secondary OH at C-16 and C-22 and of a primary OH at C-28. Full assignments of the proton and carbon resonances of the aglycone were achieved by analysis of the COSY, HSQC and HMBC spectra (Table S1). The relative configuration of the aglycone of **1** was established from its ROESY spectrum. In the ROESY spectrum (Figure S7), correlations between H-3 and δ 1.38 (H-5) confirmed the α -axial orientation of the two protons. Similarly, the cross-peaks between the protons of the methyl angular groups H-25 and H-24 on one hand and H-26 on the other, confirmed the β -axial orientation of these three methyl groups. The cross peaks between H-22 and H-30, H-22 and H-18 (δ 2.56), as well as those between H-16 and H-28, suggested that H-22 and H-16 are both β -oriented, which means that 22-OH and 16-OH group are both α -orientations. The H-3 correlated with H-23 at δ 9.91, indicating that the glycosidic chain group at C-3 is β -configured. The triterpene skeleton of **1** was identified as camelliagenin B (3 β ,16 α ,22 α ,28-tetrahydroxy,23-aldehyde-olean-12-ene) (Table S1) (Miyose et al. 2012). In addition, the signals of angeloyl (ang) group at δ_{H} 1.92 (3H, s, ang-5), 1.99 (3H, d, $J=7.2$ Hz, ang-4), and 6.09 (1H, q, $J=7.2$ Hz, ang-3) were observed. The downfield chemical shift of H-22 (δ 5.45) of **1** and its correlation with C-1 (δ 168.3) of angeloyl moiety in the HMBC experiment, established that angeloyl esterified C-22 of the aglycone. The aglycone of **1** was thus 22-*O*-angeloyl-camelliagenin B. Furthermore, the presence of four sugar moieties in **1** was evidenced by the ^1H -NMR spectrum which displayed four anomeric protons at δ 4.47, 4.64, 4.95, and 5.00, giving correlations with four anomeric carbons at δ 103.3, 104.7, 101.7, and 100.6, respectively in the HSQC spectrum (Figure S5). A glucuronic acid was identified starting from the anomeric proton at δ_{H} 4.47 (d, $J=7.3$ Hz), and characterized by a five spin system possessing large coupling constants ($J=7.3$ Hz) and by a carbonyl (C-6) resonating at δ_{C} 172.1 coupled with H-5 (δ 3.82, d, $J=9.6$ Hz) of the same sugar in the HMBC. The ^{13}C -NMR signals of the glucuronic acid of **1** were fully determined in the HSQC experiments and revealed it to be substituted at positions C-2 (δ 76.7) and C-3 (δ 82.4) as summarized in Table S2. A β -D-galactopyranose (gal) whose anomeric proton resonated at δ 4.95 was characterized

by the large coupling constants $J_{H-2,H-1}$ and $J_{H-2,H-3}$ (≥ 8.1 Hz) and the small coupling constant between H-3 and H-4 ($J_{H-3,H-4} = 3.3$ Hz) as summarized in Table S2 (Agrawal 1992). The third sugar, with an anomeric proton resonating at δ 5.00 (d, $J=6.9$ Hz), was a pentose identified as β -D-xylopyranose (xyl) and was found to be substituted in the C-2 position (δ 82.6) (Table S2). The last sugar unit was identified as terminal β -D-glucopyranose (glc), starting from its anomeric proton signal at δ 4.64 (d, $J=7.1$ Hz). The rOe interactions observed in the ROESY spectrum between H-1, H-3 and H-5 of each sugar unit confirmed the α -axial orientation of these protons and the β -anomeric configuration. Complete assignments of the proton and carbon resonances of each sugar (Table S2) were achieved by analysis of COSY (Figure S4), TOCSY (Figure S8), and HSQC (Figure S5) experiments. The position of the sugar components was determined on the basis of the HMBC experiment (Figure S6), which showed long-range correlations between the following proton and carbon pairs: glcA-H-1 and δ 84.7 (C-3 of the aglycone), indicating that the glycosidic chain was located at C-3 of the aglycone, gal-H-1 and δ 76.7 (glcA-C-2), xyl-H-1 and δ 82.4 (glcA-C-3), and glc-H-1 and δ 82.6 (xyl-C-2). Thus, the structure of **1** was elucidated to be 3-*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-xylopyranosyl-(1 $\rightarrow$ 3)-[β -D-galactopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin B.

Compound **2** was separated as a white, amorphous powder. The HR-ESI-MS peak at m/z 1195.5522 [$M + Na$]⁺ (Figure S9) indicated the molecular formula of **2** to be C₅₇H₈₈O₂₅ (calcd 1195.5522), suggesting one methylene bearing an oxygen (-CH₂OH) less than that of **1**. The ¹H- and ¹³C-NMR data of **2** were superimposable on those of **1** except for the sugar moiety (Tables S1 and S2). These data suggested that **2** is a 22-angeloyl-camelliagenin B derivative as **1**, which was further confirmed by COSY, HSQC, HMBC and ROESY experiments on **2** (Figures S12, S13, S14 and S15 respectively). The 1D- and 2D-NMR data of **2** confirmed the presence, as in **1**, of one β -D-glucopyranosiduronic acid (glcA), one β -D-galactopyranose (gal), and one β -D-xylopyranose (xyl) (Table S2). Further analysis indicated that the glucose sugar unit at C-2 of the xylose moiety in **1** was replaced by a β -D-xylopyranose (xyl') in **2** (Table S2). In addition, the xyl' was assigned to C-2 of xyl from the HMBC correlation between the xyl'-H-1 (δ 4.53, d, $J=7.6$ Hz) and xyl-C-2 (δ 83.7).

In a similar fashion, the linkage of gal at C-2 of glcA, of xyl at C-3 of glcA, and of glcA at C-3 of the aglycone were indicated by the correlations between xyl-H-1 (δ 4.92, d, $J=7.4$ Hz) and glcA-C-2 (δ 76.4), gal-H-1 (δ 4.99, d, $J=7.3$ Hz) and glcA-C-3 (δ 82.5), and glcA-H-1 (δ 4.45, d, $J=7.4$ Hz) and C-3 of the aglycone (δ 84.9), respectively. Consequently, the structure

of **2** was concluded to be 3-*O*- β -D-xylopyranosyl-(1 $\rightarrow$ 2)- β -D-xylopyranosyl-(1 $\rightarrow$ 3)-[β -D-galactopyranosyl)-(1 $\rightarrow$ 2)]- β -D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin B

Compound **3**, separated as a white, amorphous powder, was assigned a molecular formula of C₅₈H₉₂O₂₅ according to the HR-ESI-MS peak at *m/z* 1211.5834 [M+Na]⁺ (calc 1211.5825) (Figure S16). The 2D NMR analysis showed that compounds **1** and **3** differed only in the aglycone part at C-23 position (Table S1). The aldehyde function signal (δ_{H} 9.48; δ_{C} 209.3) in **1** was replaced by an angular methyl group at δ_{H} 1.12/ δ_{C} 27.0 (CH₃-23) in **3**. This was confirmed by a HMBC correlation between δ_{H} 0.91 (s) (H₃-24)/ δ_{C} 27.0 (C-23), and the reverse one, between δ_{H} 1.12 (s) (H₃-23)/ δ_{C} 15.6 (C-24) (Figure S21). The triterpene skeleton of **3** was thus determined as the known camelliagenin A (3 β ,16 α ,22 α ,28-tetrahydroxy-olean-12-ene) (Table S1) (Myose et al. 2012). The downfield chemical shift of H-22 (δ 5.46) of **3** and its correlation with C-1 (δ 168.3) of angeloyl moiety in the HMBC experiment, established that angeloyl esterified the hydroxyl at C-22 of the aglycone. The sequence and the attachment of the tetrasaccharide chain in **3** were confirmed as in **1** by an HMBC experiment (Figure S21). Thus, the structure of **3** was elucidated as 3-*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 2)- β -D-xylopyranosyl-(1 $\rightarrow$ 3)-[β -D-galactopyranosyl)-(1 $\rightarrow$ 2)]- β -D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin A.

Compound **4** exhibited in the HR-ESI-MS (positive-ion mode) a pseudo-molecular ion peak at *m/z* 1181.5732 [M+Na]⁺ (calcd 1181.5720) (Figure S24) consistent with a molecular formula of C₅₇H₉₀O₂₄Na. The NMR signals of compound **4** sugar portion were superimposable to those of **2** (Table S2). The structural analysis also revealed that the NMR signals of the aglycone part of **4** were superimposable to those of **3** (Table S1). Full assignments of the proton and carbon resonances of the aglycone and the sugar parts were achieved by analysis of the COSY, HSQC and HMBC spectra (Table S1). The sequence and the attachment of the tetrasaccharide chain in **4** were confirmed as in **2** and **3** by an HMBC experiment (Figure S29). Thus, the structure of **4** was elucidated as 3-*O*- β -D-xylopyranosyl-(1 $\rightarrow$ 2)- β -D-xylopyranosyl-(1 $\rightarrow$ 3)-[β -D-galactopyranosyl)-(1 $\rightarrow$ 2)]- β -D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin A.

Compound **5**, obtained as colorless amorphous powder, possessed the molecular formula C₁₉H₂₆O₁₂ as deduced from its HR-ESI-MS at *m/z* 469.1313 ([M + Na]⁺ calcd for C₁₉H₂₆O₁₂Na 469.1322) and 487.1418 ([M + H₂O + Na]⁺ calcd for C₁₉H₂₈O₁₃Na 487.1428) (Figure S32). The ¹H NMR spectrum (Figure S33) revealed signals attributed to a trisubstituted olefinic proton at δ_{H} 7.50 (s, H-3), an acetal proton at δ_{H} 5.80 (d, *J*=6.8, H-1), an

oxymethine at δ_{H} 5.21 (dq, $J=6.6, 4.6$ Hz, H-8), an oxymethyl signal at δ_{H} 3.70 (s, H₃-12), two methines at δ_{H} 3.35 (H-5) and 2.24 (H-9), a methylene at δ_{H} 2.55 and 2.65 (H₂-6), and a secondary methyl at δ_{H} 1.00 (H₃-10), together with a β -anomeric proton at δ_{H} 4.73 (d, $J=7.9$ Hz, H-1') and an acetyl group δ_{H} 2.03 (H₃-2"). The ^{13}C NMR spectrum (Figure S34) exhibited signals for a carboxyl carbon at δ_{C} 174.4 (C-7), an ester carbon at δ_{C} 167.3 (C-11), a methoxy carbon at δ_{C} 50.3 (C-12), a trisubstituted double bond at δ_{C} 152.7 (C-3), 109.4 (C-4), and an acetal carbon at δ_{C} 95.5 (C-1), along with signals for a glycoside moiety and an acetyl group (δ_{C} 170.9, C-1"; 20.0, C-2"). These data suggested **5** to be an esterified secoiridoid-type monoterpene glycoside (Tan and Kong 1997; Garcia et al. 1990). The COSY and HSQC experiments (Figures S35 and S36 respectively) allowed assignment of the protons and carbons of a β -D-glucose unit (glc) starting from the anomeric proton (Table S3). The β -D-glucose unit possessed two deshielded protons H₂-6' (δ_{H} 3.68 and 3.92), which have HMBC correlations with the carbonyl carbon at δ_{C} 170.9, confirming the acetylated position of glucose. In the COSY experiment (Figure S35), correlations were observed between H-9/H-1, H-5 and H-8, H-5/H-6, and H-8/H-10. In the HMBC experiment (Figure S37), long-range correlations were observed between the following protons and carbons (H-1 and C-1', C-3, C-5, C-8, C-9, C-10; H-3 and C-4, C-5, C-11; H-5 and C-3, C-6, C-7, C-1; H-8 and C-1, C-5, C-7, C-10; H-12/C-11). The above evidence indicated **5** as a derivative of kingiside (Damtoft et al. 1993). The α position of the methyl group (C-10) at C-8 was deduced from the chemical shift value of C-10 signal which appeared at δ_{C} 17.9 (17.7 for kingiside against 21.7 for 8-epikingiside) (Damtoft et al. 1993; Xu et al. 2008). The relative configuration of the other stereogenic centers C-1, C-5, and C-9 was established by analyzing coupling constant values, NOESY experiments and comparison with literature data (Damtoft et al. 1993; Garcia et al. 1990; Tan and Kong 1997). Thus, compound **5** was identified as 6'-O-acetyl-kingiside.

The positive HR-ESI-MS of compounds **6** and **7** (Figures S38 and S45 respectively) showed the same pseudomolecular ion peak $[\text{M} + \text{H}_2\text{O} + \text{Na}]^+$ at m/z 527.1733, in accordance with the molecular formula of $\text{C}_{22}\text{H}_{32}\text{O}_{13}$ (calcd for $\text{C}_{22}\text{H}_{32}\text{O}_{13}\text{Na}$ 527.1741). The spectral data of **6** and **7** obtained from NMR experiments (Table S3) were similar to those of **5** except for the acyl groups, suggesting that **6** and **7** were kingiside derivatives. The characteristic NMR signals of a tigloyl group at δ_{H} 6.91 (dq, $J = 6.6, 1.2$ Hz, H-3"), δ_{C} 13.0 (C-4") and 10.8 (C-5") were observed and further assigned by a combination of HSQC (Figures S42 and S49) and HMBC (Figures S43 and S50) experiments (Alabdul Magid et al. 2012). The downfield chemical shift of H₂-6' of glc (δ_{H} 3.67 and 3.92) of **6** and their correlations with C-1" (δ_{C} 167.4) of tigloyl in

the HMBC experiment, established that tigloyl esterified C-6' of the β -D-glucose unit. Thus, compound **6** was concluded to be 6'-O-tigloyl-kingside.

Information from 1D and 2D NMR spectra of **7** indicated the presence of signals due to an angeloyl group at δ_{H} 6.14 (1H, dq, $J = 7.2, 1.4$ Hz, H-3''), 2.01 (3H, dd, $J = 7.2, 1.4$ Hz, H-4''), 1.92 (3H, d, $J = 1.4$ Hz, H-5'') and at δ_{C} 167.3 (C-1'), 127.9 (C-2''), 138.3 (C-3''), 14.7 (C-4'') and 19.5 (C-5''). These data were in agreement with the corresponding ones reported for angeloyl moiety (Zong et al. 2015). Thus, compound **7** was elucidated as 6'-O-angeloyl-kingside. This is the first report of triterpenoid saponins and iridoid glucosides from *Aptandra* genus and *Aptandraceae* family.

3. Experimental procedures

3.1. General experimental procedures

Optical rotations were measured on a Perkin Elmer model 341 polarimeter (589 nm, 20 °C). NMR data were performed in CD₃OD on Bruker Avance 500. HRESIMS data were gained using a Micromass Q-TOF high-resolution mass spectrometer. Mass spectra were recorded in the positive-ion mode in the range m/z 100–2000, with a mass resolution of 20000 and an acceleration voltage of 0.7 kV. CC was carried out on HP-20 resin (Sigma Aldrich). Flash chromatography was conducted on a Grace Reveleris system equipped with dual UV and ELSD detection using Grace® cartridges (Silica gel or RP-C₁₈). HPLC separations were performed on a Dionex apparatus equipped with an ASI-100 autosampler, an Ultimate 3000 pump, a STH 585 column oven, a diode array detector UVD 340S and a Chromeleon software. A prepacked RP-C₁₈ column (Phenomenex 250 x 15 mm, Luna 5 μ) was used for semi-preparative HPLC. The eluting mobile phase consisted of H₂O with TFA (0.0025%) and CH₃CN with a flow rate of 5 mL/min and the chromatogram was monitored at 205 and 210 nm. TLC were carried out using silica gel 60 F₂₅₄ pre-coated aluminium plates (0.2 mm, Merck). Spots were visualized through developing agent (CHCl₃:MeOH:H₂O, 14:6:1) and chromogenic agent (50% aq. H₂SO₄) subsequent heating.

3.2. Plant material

The stem bark of *Aptandra zenkeri* Eng. were collected at Adiopodoumé, in August 2016. Its authenticated by National center of floristic of FHB University of Cocody (Ivory Coast). A voucher specimen has been deposited in herbarium of this center (Ake assi 6542).

3.3. Extraction and isolation

Dried and powdered stem bark (800 g) were macerated for 3h with 15 l of 80% aqueous MeOH and further refluxed for 3 h. After cooling, the solution was filtered and concentrated under reduced pressure to give a crude extract (150 g). The MeOH extract was then suspended in H₂O (2 l) and successively partitioned with CHCl₃ (3 × 1 l), and *n*-BuOH (3 × 1 l). The aqueous residues was subjected to a Diaion HP-20 open column and eluted with a 100% H₂O and 100% MeOH to provide methanol and aqueous fraction. The *n*-BuOH extract (33 g) was fractionated by silica gel-*vacuum* liquid chromatography (VLC) (235 g, 10 cm × 6 cm) using a step-gradient solvent system CHCl₃-MeOH-H₂O from 10:0:0, 9:1:0, 8:2:0, 7:3:0.5 to 6:4:0 to obtain 6 fractions, each 1.5 l [A-F]. A portion of fraction C (3 g) was purified by a flash chromatography over RP18, eluted by a gradient system of CH₃CN-H₂O (10% to 50%), in 40 min to afford 40 sub-fractions (C₁-C₄₀). Fractions C₂₂ (131 mg) was purified by semi-prep. HPLC using a gradient from 10- 45% MeCN during 20 min, to yield compounds **5** (*R_t* 8.3; 11 mg), **6** (*R_t* 16.2; 2 mg), and **7** (*R_t* 17.2; 16 mg). A portion of fraction E (1 g) was purified by flash chromatography over RP18, eluted by a gradient system of CH₃CN-H₂O (20% to 60%), in 40 min to afford 40 sub-fractions (E₁-E₄₀). Fractions E₂₅ (58 mg) was purified by semi-prep. HPLC using an isocratic elution 45% MeCN during 20 min, to yield compounds **1** (*R_t* 11.5 ; 13 mg), **2** (*R_t* 12.4; 11 mg), **3** (*R_t* 14.8 ; 5 mg), and **4** (*R_t* 16.0 ; 6 mg).

3.4. Compound 1 : 3-*O*-β-*D*-glucopyranosyl-(1→2)-β-*D*-xylopyranosyl-(1→3)-[β-*D*-galactopyranosyl)-(1→2)]-β-*D*-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin B.

White, amorphous powder ; $[\alpha]_D^{20} +8$ (*c* 1, CH₃OH); HRESIMS (positive-ion mode) *m/z* 1225.5627 [M + Na]⁺ (C₅₈H₉₀O₂₆Na ; calcd for 1225.5618); ¹H NMR (CD₃OD, 500 MHz) δ: 1.05 (1H, td, *J* = 12.3, 4.5 Hz), 1.74 (1H, dt, *J* = 12.3, 3.2 Hz) (H-1), 1.81 (1H, m), 1.98 (1H, m) (H-2), 3.91 (1H, dd, *J* = 11.3, 4.5 Hz, H-3), 1.38 (1H, m, H-5), 0.94 (1H, m), 1.58 (1H, m) (H-6), 1.28 (1H, m), 1.65 (1H, td, *J* = 13.0, 4.5 Hz) (H-7), 1.83 (1H, m, H-9), 1.97 (2H, m, H-11), 5.37 (1H, t, *J* = 3.6 Hz, H-12), 1.33 (1H, m), 1.74 (1H, brd, *J* = 14.3 Hz) (H-15), 4.13 (1H, brs, H-16), 2.56 (1H, dd, *J* = 14.0, 3.5 Hz, H-18), 1.09 (1H, m), 2.49 (1H, t, *J* = 14.0 Hz, H-19), 1.54 (1H, m), 2.29 (1H, t, *J* = 11.9 Hz) (H-21), 5.45 (1H, dd, *J* = 12.1, 5.6 Hz, H-22), 9.48 (1H, s, H-23), 1.19 (3H, s, H-24), 1.05 (3H, s, H-25), 0.98 (3H, s, H-26), 1.52 (3H, s, H-27), 3.08 (1H, d, *J* = 11 Hz), 3.28 (1H, d, *J* = 11Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.09 (1H, q, *J* = 7.2 Hz, H-3''), 1.99 (3H, d, *J* = 7.2 Hz, H-4''), 1.92 (3H, s, H-5''); ¹³C NMR (CD₃OD, 500 MHz) δ: 37.9 (C-1), 24.3 (C-2), 84.7 (C-3), 54.8 (C-4), 47.8 (C-5), 19.8 (C-6), 31.8 (C-7), 39.9 (C-8), 46.5 (C-9), 35.6 (C-10), 23.2 (C-11), 122.8 (C-12), 142.6

(C-13), 41.1 (C-14), 33.8 (C-15), 69.5 (C-16), 43.9 (C-17), 40.4 (C-18), 46.6 (C-19), 31.1 (C-20), 40.7 (C-21), 72.4 (C-22), 209.3 (C-23), 9.5 (C-24), 15.0 (C-25), 15.9 (C-26), 26.4 (C-27), 63.4 (C-28), 32.2 (C-29), 23.9 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.7 (C-3''), 14.5 (C-4''), 19.5 (C-5''); ¹H- and ¹³C NMR data for sugar moieties (see Table S2).

3.5. Compound 2: 3-O-β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl)-(1→2)]-β-D-glucuronopyranosyl-22-O-angeloyl-camelliagenin B.

White, amorphous powder ; [α]_D²⁰ +6 (c 0.81, CH₃OH); HRESIMS (positive-ion mode) *m/z* 1195.5522 [M + Na]⁺ (C₅₇H₈₈O₂₅Na; calcd for 1195.5512); ¹H NMR (CD₃OD, 500 MHz) δ : 1.06 (1H, m), 1.74 (1H, dt, *J* = 14.0, 3.5 Hz) (H-1), 1.80 (1H, m), 1.98 (1H, m) (H-2), 3.89 (1H, dd, *J* = 11.5, 4.5 Hz, H-3), 1.38 (1H, brd, *J* = 12.3 Hz, H-5), 0.55 (1H, m), 1.58 (1H, m) (H-6), 1.28 (1H, dt, *J* = 13.1, 3.5 Hz), 1.64 (1H, td, *J* = 13.1, 4.6 Hz) (H-7), 1.81 (1H, m, H-9), 1.97 (2H, m, H-11), 5.37 (1H, t, *J* = 3.6 Hz, H-12), 1.33 (1H, brd, *J* = 14.0 Hz), 1.73 (1H, td, *J* = 14.0, 3.5 Hz) (H-15), 4.13 (1H, brs, H-16), 2.55 (1H, dd, *J* = 14.3, 3.5 Hz, H-18), 1.08 (1H, m), 2.49 (1H, t, *J* = 14.3 Hz, H-19), 1.55 (1H, m), 2.29 (1H, t, *J* = 11.9 Hz) (H-21), 5.46 (1H, dd, *J* = 12.1, 5.5 Hz, H-22), 9.48 (1H, s, H-23), 1.19 (3H, s, H-24), 1.05 (3H, s, H-25), 0.98 (3H, s, H-26), 1.52 (3H, s, H-27), 3.08 (1H, d, *J* = 11.0 Hz), 3.28 (1H, d, *J* = 11.0 Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.08 (1H, q, *J* = 7.3 Hz, H-3''), 1.99 (3H, d, *J* = 7.3 Hz, H-4''), 1.92 (3H, s, H-5''); ¹³C NMR (CD₃OD, 500 MHz) δ : 37.9 (C-1), 24.3 (C-2), 84.9 (C-3), 54.9 (C-4), 47.8 (C-5), 19.8 (C-6), 31.8 (C-7), 39.9 (C-8), 46.5 (C-9), 35.6 (C-10), 23.2 (C-11), 122.8 (C-12), 142.6 (C-13), 41.1 (C-14), 33.8 (C-15), 69.5 (C-16), 43.9 (C-17), 40.4 (C-18), 46.6 (C-19), 31.1 (C-20), 40.7 (C-21), 72.4 (C-22), 209.3 (C-23), 9.4 (C-24), 15.0 (C-25), 15.9 (C-26), 26.4 (C-27), 63.4 (C-28), 32.2 (C-29), 23.8 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.7 (C-3''), 14.5 (C-4''), 19.5 (C-5''); ¹H- and ¹³C NMR data for sugar moieties (see Table S2).

3.6. Compound 3: 3-O-β-D-glucopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl)-(1→2)]-β-D-glucuronopyranosyl-22-O-angeloyl-camelliagenin A.

White, amorphous powder ; [α]_D²⁰ -5 (c 0.12, CH₃OH); HRESIMS (positive-ion mode) *m/z* 1211.5834 [M + Na]⁺ (C₅₈H₉₂O₂₅Na; calcd for 1211.5825); ¹H NMR (CD₃OD, 500 MHz) δ : 1.01 (1H, m), 1.65 (1H, dt, *J* = 12.2, 3.5 Hz) (H-1), 1.74 (1H, m), 1.94 (1H, m) (H-2), 3.22 (1H, dd, *J* = 11.8, 4.0 Hz, H-3), 0.81 (1H, brd, *J* = 11.7 Hz, H-5), 1.44 (1H, m), 1.61 (1H, m) (H-6), 1.37 (1H, m), 1.64 (1H, m) (H-7), 1.69 (1H, m, H-9), 1.94 (2H, m, H-11), 5.36 (1H, t, *J* = 3.3 Hz, H-12), 1.33 (1H, brd, *J* = 13.0 Hz), 1.78 (1H, dd, *J* = 13.0, 4.2 Hz) (H-15), 4.13

(1H, brs, H-16), 2.55 (1H, dd, $J = 12.7, 3.4$ Hz, H-18), 1.06 (1H, m), 2.49 (1H, t, $J = 13.1$ Hz, H-19), 1.58 (1H, m), 2.29 (1H, t, $J = 12.9$ Hz) (H-21), 5.46 (1H, dd, $J = 12.1, 5.7$ Hz, H-22), 1.12 (3H, s, H-23), 0.91 (3H, s, H-24), 1.01 (3H, s, H-25), 0.97 (3H, s, H-26), 1.50 (3H, s, H-27), 3.08 (1H, d, $J = 11.0$ Hz), 3.29 (1H, d, $J = 11.0$ Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.09 (1H, q, $J = 7.4$ Hz, H-3''), 1.99 (3H, d, $J = 7.4$ Hz, H-4''), 1.92 (3H, s, H-5''); ^{13}C NMR (CD_3OD , 500 MHz) δ : 38.6 (C-1), 25.7 (C-2), 90.4 (C-3), 39.0 (C-4), 55.7 (C-5), 17.9 (C-6), 32.6 (C-7), 39.6 (C-8), 46.6 (C-9), 36.4 (C-10), 23.3 (C-11), 123.1 (C-12), 142.6 (C-13), 41.1 (C-14), 33.9 (C-15), 69.6 (C-16), 43.9 (C-17), 40.7 (C-18), 47.1 (C-19), 31.1 (C-20), 40.7 (C-21), 72.5 (C-22), 27.0 (C-23), 15.6 (C-24), 14.8 (C-25), 15.9 (C-26), 26.3 (C-27), 63.4 (C-28), 32.2 (C-29), 23.9 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.6 (C-3''), 14.5 (C-4''), 19.5 (C-5''); ^1H - and ^{13}C NMR data for sugar moieties (see Table S2).

3.7. Compound 4 : 3-*O*- β -D-xylopyranosyl-(1 $\rightarrow$ 2)- β -D-xylopyranosyl-(1 $\rightarrow$ 3)-[β -D-galactopyranosyl-(1 $\rightarrow$ 2)]- β -D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin A.

White, amorphous powder; $[\alpha]_{\text{D}}^{20} -3$ (c 0.26, CH_3OH); HRESIMS (positive-ion mode) m/z 1181.5732 $[\text{M} + \text{Na}]^+$ ($\text{C}_{57}\text{H}_{90}\text{O}_{24}\text{Na}$; calcd for 1181.5720); ^1H NMR (CD_3OD , 500 MHz) δ : 1.05 (1H, m), 1.65 (1H, dt, $J = 13.5, 3.5$ Hz) (H-1), 1.77 (1H, m), 1.95 (1H, m) (H-2), 3.21 (1H, dd, $J = 11.2, 4.0$ Hz, H-3), 0.81 (1H, brd, $J = 11.4$ Hz, H-5), 1.45 (1H, m), 1.58 (1H, m) (H-6), 1.37 (1H, m), 1.64 (1H, m) (H-7), 1.69 (1H, m, H-9), 1.94 (2H, m, H-11), 5.36 (1H, t, $J = 3.6$ Hz, H-12), 1.33 (1H, brd, $J = 13.7$ Hz), 1.78 (1H, dd, $J = 13.7, 4.0$ Hz) (H-15), 4.13 (1H, brs, H-16), 2.56 (1H, dd, $J = 12.5, 3.6$ Hz, H-18), 1.06 (1H, m), 2.48 (1H, t, $J = 14.1$ Hz, H-19), 1.59 (1H, m), 2.29 (1H, t, $J = 12.2$ Hz) (H-21), 5.46 (1H, dd, $J = 12.2, 5.7$ Hz, H-22), 1.11 (3H, s, H-23), 0.91 (3H, s, H-24), 1.01 (3H, s, H-25), 0.97 (3H, s, H-26), 1.50 (3H, s, H-27), 3.07 (1H, d, $J = 11.1$ Hz), 3.29 (1H, d, $J = 11.1$ Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.08 (1H, q, $J = 7.4$ Hz, H-3''), 1.99 (3H, d, $J = 7.4$ Hz, H-4''), 1.92 (3H, s, H-5''); ^{13}C NMR (CD_3OD , 500 MHz) δ : 38.6 (C-1), 25.6 (C-2), 90.7 (C-3), 39.1 (C-4), 55.7 (C-5), 17.9 (C-6), 32.6 (C-7), 39.6 (C-8), 46.6 (C-9), 36.4 (C-10), 23.2 (C-11), 123.2 (C-12), 142.5 (C-13), 41.1 (C-14), 33.9 (C-15), 69.6 (C-16), 43.9 (C-17), 40.4 (C-18), 47.1 (C-19), 31.1 (C-20), 40.7 (C-21), 72.5 (C-22), 27.0 (C-23), 15.5 (C-24), 14.8 (C-25), 15.9 (C-26), 26.3 (C-27), 63.4 (C-28), 32.2 (C-29), 23.9 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.7 (C-3''), 14.5 (C-4''), 19.5 (C-5''); ^1H - and ^{13}C NMR data for sugar moieties (see Table S2).

3.8. Compound 5: 6'-*O*-acetyl-kingiside.

Colorless, amorphous powder ; $[\alpha]^{20}_D$ -101 (*c* 1, CH₃OH); HRESIMS (positive-ion mode): *m/z* 469.1313 [M + Na]⁺ (C₁₉H₂₆O₁₂Na ; calcd for 469.1322) and *m/z* 487.1418 [M + H₂O + Na]⁺ C₁₉H₂₈O₁₃Na ; calcd for 487.1428); ¹H NMR (CD₃OD, 500 MHz) δ : 5.80 (1H, d, *J* = 6.8 Hz, H-1), 7.50 (1H, s, H-3), 3.35 (1H, m, H-5), 2.55 (1H, dd, *J* = 15.9, 7.0 Hz), 2.65 (1H, dd, *J* = 15.9, 6.1 Hz) (H-6), 5.21 (1H, dq, *J* = 6.6, 4.6 Hz, H-8), 2.24 (1H, dt, *J* = 6.8, 5.0 Hz, H-9), 1.00 (3H, d, *J* = 6.6 Hz, H-10), 3.0 (3H, s, 12-OCH₃), 4.73 (1H, d, *J* = 7.9 Hz, H-1'), 3.23 (1H, dd, *J* = 9.2, 7.9 Hz, H-2'), 3.40 (1H, t, *J* = 9.5 Hz, H-3'), 3.30 (1H, t, *J* = 9.7 Hz, H-4'), 3.33 (1H, m, H-5'), 3.68 (1H, dd, *J* = 11.8, 4.5 Hz), 3.92 (1H, dd, *J* = 11.8, 2.0 Hz) (H-6'), 2.03 (3H, s, H-2''); ¹³C NMR (CD₃OD, 125 MHz) δ : 95.5 (C-1), 152.7 (C-3), 109.4 (C-4), 28.6 (C-5), 34.5 (C-6), 174.4 (C-7), 69.2 (C-8), 42.8 (C-9), 17.9 (C-10), 167.3 (C-11), 50.3 (C-12-OCH₃), 99.0 (C-1'), 73.4 (C-2'), 76.9 (C-3'), 70.2 (C-4'), 77.1 (C-5'), 61.5 (C-6'), 170.9 (C-1''), 20.0 (C-2'').

3.9. Compound 6: 6'-O-tigloyl-kingside.

Colorless, amorphous powder ; $[\alpha]^{20}_D$ -78 (*c* 1, CH₃OH); HRESIMS (positive-ion mode) *m/z* 527.1733 [M + Na]⁺ (C₂₂H₃₂O₁₃Na ; calcd for 527.1741); ¹H NMR (CD₃OD, 500 MHz) δ : 5.85 (1H, d, *J* = 6.7 Hz, H-1), 7.49 (1H, s, H-3), 3.38 (1H, m, H-5), 2.52 (1H, dd, *J* = 15.9, 6.9 Hz), 2.63 (1H, dd, *J* = 15.9, 6.7 Hz) (H-6), 5.27 (1H, dq, *J* = 6.5, 4.5 Hz, H-8), 2.30 (1H, dt, *J* = 6.8, 4.5 Hz, H-9), 1.42 (3H, d, *J* = 6.5 Hz, H-10), 3.70 (3H, s, 12-OCH₃), 4.74 (1H, d, *J* = 7.9 Hz, H-1'), 3.20 (1H, dd, *J* = 9.1, 7.9 Hz, H-2'), 3.38 (1H, t, *J* = 9.5 Hz, H-3'), 3.27 (1H, t, *J* = 9.7 Hz, H-4'), 3.35 (1H, m, H-5'), 3.67 (1H, dd, *J* = 11.9, 4.9 Hz), 3.92 (1H, dd, *J* = 11.9, 2.1 Hz) (H-6'), 6.91 (1H, dq, *J* = 6.6, 1.2 Hz, H-3''), 1.42 (3H, dd, *J* = 6.6, 1.2 Hz, H-4''), 1.84 (3H, d, *J* = 1.2 Hz, H-5'') ; ¹³C NMR (CD₃OD, 125 MHz) δ : 95.2 (C-1), 152.7 (C-3), 109.4 (C-4), 28.7 (C-5), 34.5 (C-6), 174.5 (C-7), 69.0 (C-8), 42.9 (C-9), 17.9 (C-10), 167.2 (C-11), 50.3 (C-12-OCH₃), 98.7 (C-1'), 73.3 (C-2'), 77.0 (C-3'), 70.1 (C-4'), 76.5 (C-5'), 61.4 (C-6'), 167.4 (C-1''), 128.5 (C-2''), 137.8 (C-3''), 13.0 (C-4''), 10.8 (C-5'').

3.10. Compound 7: 6'-O-angeloyl-kingside.

Colorless, amorphous powder ; $[\alpha]^{20}_D$ -90 (*c* 0.26, CH₃OH); HRESIMS (positive-ion mode) *m/z* 527.1733 [M + Na]⁺ (C₂₂H₃₂O₁₃Na ; calcd for 527.1741) ¹H NMR (CD₃OD, 500 MHz) δ : 5.85 (1H, d, *J* = 6.4 Hz, H-1), 7.48 (1H, s, H-3), 3.40 (1H, m, H-5), 2.54 (1H, dd, *J* = 15.9, 6.9 Hz), 2.60 (1H, dd, *J* = 15.9, 6.4 Hz) (H-6), 5.32 (1H, dq, *J* = 6.9, 4.5 Hz, H-8), 2.30 (1H, dt, *J* = 6.9, 4.9 Hz, H-9), 1.44 (3H, d, *J* = 6.5 Hz, H-10), 3.70 (3H, s, 12-OCH₃), 4.75 (1H, d, *J* = 7.9 Hz, H-1'), 3.22 (1H, dd, *J* = 9.3, 7.9 Hz, H-2'), 3.38 (1H, t, *J* = 9.5 Hz, H-3'), 3.28 (1H, t,

$J = 9.7$ Hz, H-4'), 3.33 (1H, m, H-5'), 3.67 (1H, dd, $J = 11.9, 5.9$ Hz), 3.90 (1H, dd, $J = 11.9, 2.1$ Hz) (H-6'), 6.14 (1H, dq, $J = 7.2, 1.4$ Hz, H-3''), 2.01 (3H, dd, $J = 7.2, 1.4$ Hz, H-4''), 1.92 (3H, d, $J = 1.4$ Hz, H-5'') ; ^{13}C NMR (CD_3OD , 125 MHz) δ : 95.2 (C-1), 152.7 (C-3), 109.3 (C-4), 28.4 (C-5), 34.4 (C-6), 174.4 (C-7), 68.4 (C-8), 42.8 (C-9), 18.0 (C-10), 167.1 (C-11), 50.9 (C-12- OCH_3), 99.0 (C-1'), 73.4 (C-2'), 76.9 (C-3'), 70.2 (C-4'), 77.1 (C-5'), 61.5 (C-6'), 167.3 (C-1''), 127.9 (C-2''), 138.3 (C-3''), 14.7 (C-4''), 19.5 (C-5'').

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Disclosure statement

The authors have declared no conflict of interest.

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Appendix A. Supplementary Material

Supplementary data associated with this article can be found in the online version.

Figure 1. The structures of triterpenoid glycosides (1-4) isolated from the stem bark of *Aptandra zenkeri* Engl.

Figure 2. The structures of secoiridoid glucosides (5-7) isolated from the stem bark of *Aptandra zenkeri* Engl.

SUPPLEMENTARY MATERIAL

New oleanane-type glycosides and secoiridoids glucosides from *Aptandra zenkeri*

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Abstract: Four new saponins, camelliagenin A and B derivatives, and three new secoiridoid glucosides were isolated from the stem bark of *Aptandra zenkeri* Engl. (Aptandraceae). Their structures were determined based on a combination of 1D- and 2D-NMR experiments techniques and HR-ESI-MS analysis. This is the first report on saponins in genus *Aptandra*.

Keywords: *Aptandra zenkeri* Engl.; Aptandraceae; triterpenoid saponins; secoiridoid glucosides

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Table S1. ^1H (500 MHz) and ^{13}C (125 MHz) data of the aglycone moieties of compounds **1** - **4**(CD₃OD)

	1		2		3		4	
	δ_{H} (m, J Hz)	δ_{C}	δ_{H} (m, J Hz)	δ_{C}	δ_{H} (m, J Hz)	δ_{C}	δ_{H} (m, J Hz)	δ_{C}
1	1.05, td (12.3, 4.5)	37.9	1.06, m	37.9	1.01, m	38.6	1.05, m	38.6
	1.74, dt (12.3, 3.2)		1.74, dt (14.0, 3.5)		1.65, dt (12.2, 3.5)		1.65, dt (13.5, 3.5)	
2	1.81, m	24.3	1.80, m	24.3	1.74, m	25.7	1.77, m	25.6
	1.98, m		1.98, m		1.94, m		1.95, m	
3	3.91, dd (11.3, 4.5)	84.7	3.89, dd (11.5, 4.5)	84.9	3.22, dd (11.8, 4.0)	90.4	3.21, dd (11.2, 4.0)	90.7
4		54.8		54.9		39.0		39.1
5	1.38, m	47.8	1.38, brd (12.3)	47.8	0.81, brd (11.7)	55.7	0.81, brd (11.4)	55.7
6	0.94, m	19.8	0.55, m	19.8	1.44, m	17.9	1.45, m	17.9
	1.58, m		1.58, m		1.61, m		1.58, m	
7	1.28, m	31.8	1.28, dt (13.1, 3.5)	31.8	1.37, m	32.6	1.37, m	32.6
	1.65, td (13.0, 4.5)		1.64, td (13.1, 4.6)		1.64, m		1.64, m	
8		39.9		39.9		39.6		39.6
9	1.83, m	46.5	1.81, m	46.5	1.69, m	46.6	1.69, m	46.6
10		35.6		35.6		36.4		36.4
11	1.97, m	23.2	1.97, m	23.2	1.94, m	23.3	1.94, m	23.2
12	5.37, t (3.6)	122.8	5.37, t (3.6)	122.8	5.36, t (3.3)	123.1	5.36, t (3.6)	123.2
13		142.6		142.6		142.6		142.5
14		41.1		41.1		41.1		41.1
15	1.33, m	33.8	1.33, brd (14.0)	33.8	1.33, brd (13.0)	33.9	1.33, brd (13.7)	33.9
	1.74, brd (14.3)		1.73, td (14.0, 3.5)		1.78, dd (13.0, 4.2)		1.78, dd (13.7, 4.0)	
16	4.13, brs	69.5	4.13, brs	69.5	4.13, brs	69.6	4.13, brs	69.6
17		43.9		43.9		43.9		43.9
18	2.56, dd (14.0, 3.5)	40.4	2.55, dd (14.3, 3.5)	40.4	2.55, dd (12.7, 3.4)	40.7	2.56, dd (12.5, 3.6)	40.4
19	1.09, m	46.6	1.08, m	46.6	1.06, m	47.1	1.06, m	47.1
	2.49, t (14.0)		2.49, t (14.3)		2.49, t (13.1)		2.48, t (14.1)	
20		31.1		31.1		31.1		31.1
21	1.54, m	40.7	1.55, m	40.7	1.58, m	40.7	1.59, m	40.7
	2.29, t (11.9)		2.29, t (11.9)		2.29, t (12.9)		2.29, t (12.2)	
22	5.45, dd (12.1, 5.6)	72.4	5.46, dd (12.1, 5.5)	72.4	5.46, dd (12.1, 5.7)	72.5	5.46, dd (12.2, 5.7)	72.5
23	9.48, s	209.3	9.48, s	209.3	1.12, s	27.0	1.11, s	27.0
24	1.19, s	9.5	1.19, s	9.4	0.91, s	15.6	0.91, s	15.5
25	1.05, s	15.0	1.05, s	15.0	1.01, s	14.8	1.01, s	14.8
26	0.98, s	15.9	0.98, s	15.9	0.97, s	15.9	0.97, s	15.9
27	1.52, s	26.4	1.52, s	26.4	1.50, s	26.3	1.50, s	26.3
28	3.08, d (11.0)	63.4	3.08, d (11.0)	63.4	3.08, d (11.0)	63.4	3.07, d (11.1)	63.4
	3.28, d (11.0)		3.28, d (11.0)		3.29, d (11.0)		3.29, d (11.1)	
29	0.93, s	32.2	0.93, s	32.2	0.93, s	32.2	0.93, s	32.2
30	1.07, s	23.9	1.07, s	23.8	1.07, s	23.9	1.07, s	23.9
C₂₂ Angeloyl								
1		168.3		168.3		168.3		168.3
2		128.6		128.6		128.6		128.6
3	6.09, q (7.2)	136.7	6.08, q (7.3)	136.7	6.09, q (7.4)	136.6	6.08, q (7.4)	136.7
4	1.99, d (7.2)	14.5	1.99, d (7.3)	14.5	1.99, d (7.4)	14.5	1.99, d (7.4)	14.5
5	1.92, s	19.5	1.92, s	19.5	1.92, s	19.5	1.92, s	19.5

Table S2 ¹H (500 MHz) and ¹³C (125 MHz) NMR data of the sugar moieties of compounds **1** - **4** (CD₃OD).

1		2		3		4	
$\delta_{\text{H}}, m (J \text{ Hz})$	δ_{C}	$\delta_{\text{H}}, m (J \text{ Hz})$	δ_{C}	$\delta_{\text{H}}, m (J \text{ Hz})$	δ_{C}	$\delta_{\text{H}}, m (J \text{ Hz})$	δ_{C}
glcA (at C-3)							
1 4.47, d (7.3)	103.3	4.45, d (7.4)	103.4	4.52, d (7.8)	104.5	4.53, d (7.5)	105.6
2 3.84, t (8.3)	76.7	3.71, dd (8.0, 7.4)	76.4	3.97, dd (8.8, 7.8)	77.5	3.92, t (8.2)	77.4
3 3.78, t (8.3)	82.4	3.72, t (8.0)	82.5	3.83, t (9.0)	82.7	3.79, t (8.2)	82.5
4 3.62, t (8.5)	69.6	3.58, t (8.5)	69.6	3.61, t (9.0)	70.3	3.61, t (8.5)	70.0
5 3.82, d (9.6)	75.0	3.82, d (9.5)	75.0	3.73, d (9.1)	75.3	3.78, d (9.5)	75.2
6	172.1		172.2		172.4		172.2
gal (at glcA-C-2)							
1 4.95, ^a	101.7	4.99, d (7.3)	101.4	4.98, d (7.4)	101.9	5.07, d (7.3)	101.5
2 3.52, t (8.1)	72.1	3.48, t (8.5)	72.0	3.61, t (8.1)	72.2	3.54, t (8.1)	72.1
3 3.54, dd (8.1, 3.3)	73.5	3.52, dd (8.5, 3.6)	73.7	3.55, dd (8.1, 3.2)	73.3	3.53, dd (8.1, 2.5)	74.7
4 3.84, t (3.3)	69.3	3.83, t (3.6)	69.6	3.87, t (3.2)	68.7	3.83, t (2.6)	69.1
5 3.63, m	75.2	3.64, brt (6.2)	75.1	3.66, m	75.3	3.58, m	74.7
6 3.75, dd (11.1, 5.3)	61.0	3.73, dd (11.5, 5.3)	61.1	3.69, ^a	61.0	3.65, dd (11.4, 4.7)	61.4
		3.80, dd (11.1, 3.0)		3.76, dd (11.4, 2.8)		3.80, dd (11.4, 3.0)	
Xyl (at glcA-C-3)							
1 5.00, d (6.9)	100.6	4.92, d (7.4)	100.7	5.00, d (7.1)	100.8	4.99, d (7.4)	100.7
2 3.53, dd (8.5, 6.9)	82.6	3.41, dd (8.5, 7.4)	83.7	3.54, dd (8.3, 7.1)	82.7	3.44, dd (8.3, 7.4)	83.7
3 3.65, t (8.5)	75.8	3.60, t (8.5)	76.1	3.66, t (8.3)	76.0	3.62, t (8.3)	76.1
4 3.60, m	69.5	3.59, m	69.5	3.59, m	69.4	3.58, m	69.6
5 3.19, dd (11.5, 8.5)	65.2	3.28, ^a	65.2	3.30, ^a	65.3	3.28, dm (11.4)	65.4
		3.96, dd (11.5, 5.1)		4.02, dd (11.5, 5.7)		3.94, dd (11.4, 4.5)	
glc'/xyl' (at xyl-C-2)							
1 4.64, d (7.1)	104.7	4.53, d (7.6)	106.6	4.69, d (7.3)	104.6	4.56, d (7.2)	106.0
2 3.31, dd (8.8, 7.1)	74.5	3.30, dd (9.0, 7.6)	74.8	3.33, ^a	74.3	3.31, ^a	73.4
3 3.41, t (8.8)	76.7	3.35, t (9.0)	76.5	3.42, t (8.0)	76.7	3.35, t (9.0)	76.6
4 3.37 (8.8)	70.3	3.54, m	69.6	3.37, t (8.5)	70.2	3.37, m	69.6
5 3.33, m	77.0	3.20, dd (11.2, 10.7)	65.9	3.35, m	77.0	3.21, t (11.2)	65.9
		3.97, dd (11.5, 5.4)				3.99, dd (11.2, 5.4)	
6 3.76, dd (11.2, 5.9)	61.5			3.78, dd (11.0, 5.2)	61.5		
				3.91, dm (11.0)			

^a overlapped signals

Table S3. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectroscopic data of compounds **5-7** (CD_3OD).

position	5		6		7	
	δ_{H} m (<i>J</i> in Hz)	δ_{C}	δ_{H} m (<i>J</i> in Hz)	δ_{C}	δ_{H} m (<i>J</i> in Hz)	δ_{C}
1	5.80, d (6.8)	95.5	5.85, d (6.7)	95.2	5.85, d (6.4)	95.2
3	7.50, s	152.7	7.49, s	152.7	7.48, s	152.7
4		109.4		109.4		109.3
5	3.35, m	28.6	3.38, m	28.7	3.40, m	28.4
6	2.55, dd (15.9, 7.0)	34.5	2.52, dd (15.9, 6.9)	34.5	2.54, dd (15.9, 6.9)	34.4
	2.65, dd (15.9, 6.1)		2.63, dd (15.9, 6.7)		2.60, dd (15.9, 6.4)	
7		174.4		174.5		174.4
8	5.21, dq (6.6, 4.6)	69.2	5.27, dq (6.5, 4.5)	69.0	5.32, dq (6.9, 4.5)	68.4
9	2.24, dt (6.8, 5.0)	42.8	2.30, dt (6.8, 4.5)	42.9	2.30, dt (6.9, 4.9)	42.8
10	1.00, d (6.6)	17.9	1.42, d (6.5)	17.9	1.44, d (6.5)	18.0
11		167.3		167.2		167.1
12 (OCH_3)	3.70, s	50.3	3.70, s	50.3	3.70, s	50.9
β-D-glc						
1'	4.73, d (7.9)	99.0	4.74, d (7.9)	98.7	4.75, d (7.9)	99.0
2'	3.23, dd (9.2, 7.9)	73.4	3.20, dd (9.1, 7.9)	73.3	3.22, dd (9.3, 7.9)	73.4
3'	3.40, t (9.5)	76.9	3.38, t (9.5)	77.0	3.38, t (9.5)	76.9
4'	3.30, t (9.7)	70.2	3.27, t (9.7)	70.1	3.28, t (9.7)	70.2
5'	3.33, m	77.1	3.35, m	76.5	3.33, m	77.1
6'	3.68, dd (11.8, 4.5)	61.5	3.67, dd (11.9, 4.9)	61.4	3.67, dd (11.9, 5.9)	61.5
	3.92, dd (11.8, 2.0)		3.92, dd (11.9, 2.1)		3.90, dd (11.9, 2.1)	
1''		170.9		167.4		167.3
2''	2.03, s	20.0		128.5		127.9
3''			6.91, dq (6.6, 1.2)	137.8	6.14, dq (7.2, 1.4)	138.3
4''			1.42, dd (6.6, 1.2)	13.0	2.01, dd (7.2, 1.4)	14.7
5''			1.84, d (1.2)	10.8	1.92, d (1.4)	19.5

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Figure S1. The HRESIMS of 1

Figure S2. The ^1H -NMR spectrum of **1** in CD_3OD

Figure S3. The DEPT spectrum of **1** in CD₃OD

Figure S5. The HSQC spectrum of **1** in CD₃OD

Figure S6. The HMBC spectrum of **1** in CD_3OD

Figure S7. The ^1H - ^1H ROESY spectrum of **1** in CD_3OD

Figure S8. The ^1H - ^1H TOCSY spectrum of **1** in CD_3OD

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Figure S9. The HRESIMS of 2

Figure S10. The ^1H -NMR spectrum of **2** in CD_3OD

Figure S11. The *J*-mod spectrum of **2** in CD₃OD

Figure S12. The ^1H - ^1H COSY spectrum of **2** in CD_3OD

Figure S13. The HSQC spectrum of **2** in CD₃OD

Figure S14. The HMBC spectrum of **2** in CD₃OD

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 58-58 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1

MB.137.AZTb E pic 3

18HR08 251 (8.155) AM (Cen,4, 80.00, Ar,5000.0,472.67,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00); Cm (237:268)

1: TOF MS ES+
6.15e+003

Figure S15. The ^1H - ^1H ROESY spectrum of **2** in CD_3OD

Figure S16. The HRESIMS of **3**

For Peer Review Only

Figure S17. The ¹H-NMR spectrum of **3** in CD₃OD

Figure S18. The *J*-mod spectrum of **3** in CD₃OD

For Peer Review Only

Figure S19. The ^1H - ^1H COSY spectrum of **3** in CD_3OD

Figure S20. The HSQC spectrum of **3** in CD₃OD

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Figure S21. The HMBC spectrum of **3** in CD₃OD

Figure S22. The ^1H - ^1H ROESY spectrum of **3** in CD_3OD

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Figure S23. The ^1H - ^1H TOCSY spectrum of **3** in CD_3OD

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 57-57 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1

MB.137.AZTo E pic 4

18HR09 150 (4.858) AM (Cen, 4, 80.00, Ar, 5000.0, 472.87, 0.70, LS 20); Sm (SG, 1x1.00); Sb (5.40.00); Cm (148:153)

1: TOF MS ES+
3.11e+003

Minimum:				-1.5		
Maximum:	5.0	5.0	50.0			
Mass	Calc. Mass	nDa	PPM	DBE	i-FIT	Formula
1181.5732	1181.5720	1.2	1.0	12.5	15.9	C57 H90 O24 Na

Figure S24. The HRESIMS of 4

Figure S25. The ¹H-NMR spectrum of **4** in CD₃OD

Figure S26. The *J*-mod spectrum of 4 in CD₃OD

Figure S27. The ^1H - ^1H COSY spectrum of **4** in CD_3OD

Figure S28. The HSQC spectrum of **4** in CD_3OD

Figure S30. The ^1H - ^1H ROESY spectrum of **4** in CD_3OD

Figure S31. The ^1H - ^1H TOCSY spectrum of **4** in CD_3OD

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

212 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 19-19 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1

MB.AZTb C 22-27 SF1

18HR29 78 (2.347) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00); Cm (76.82)

1: TOF MS ES+
1.31e+004

Minimum:

Maximum:

5.0

5.0

-1.5

50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
487.1418	487.1428	-1.0	-2.1	5.5	21.5	C19 H28 O13 Na

Figure S32. The HRESIMS of **5**

Figure S33. The ¹H-NMR spectrum of **5** in CD₃OD

Figure S34. The DEPT spectrum of **5** in CD₃OD

Figure S35. The ^1H - ^1H COSY spectrum of **5** in CD_3OD

Figure S36. The HSQC spectrum of **5** in CD₃OD

Figure S37. The HMBC spectrum of **5** in CD₃OD

Elemental Composition Report

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Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 22-22 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1

MB.AZTb C 22-27 SF10⁺

18HR30 45 (1.342) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5.40.00); Cm (36:50)

1: TOF MS ES+
7.39e+003

Minimum:							
Maximum:		5.0	5.0	-1.5	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
527.1733	527.1741	-0.8	-1.5	6.5	9.2	C22 H32 O13 Na	

Figure S38. The HRESIMS of 6

Figure S39. The ¹H-NMR spectrum of **6** in CD₃OD

Figure S40. The DEPTQ spectrum of **6** in CD₃OD

Figure S41. The ^1H - ^1H COSY spectrum of **6** in CD_3OD

Figure S42. The HSQC spectrum of **6** in CD₃OD

Figure S43. The HMBC spectrum of **6** in CD₃OD

Figure S44. The ^1H - ^1H ROESY spectrum of **6** in CD_3OD

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 22-22 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1
MB.AZTb C 22-27 SF10⁺
18HR30 45 (1.342) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5.40.00); Cm (36:50)

1: TOF MS ES+
7.39e+003

Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
527.1733	527.1741	-0.8	-1.5	6.5	9.2	C22 H32 O13 Na	

Figure S45. The HRESIMS of 7

Figure S46. The ^1H -NMR spectrum of **7** in CD_3OD

Figure S47. The *J-mod* spectrum of **7** in CD₃OD

Figure S48. The ^1H - ^1H COSY spectrum of **7** in CD_3OD

Figure S49. The HSQC spectrum of 7 in CD₃OD

Figure S50. The HMBC spectrum of **7** in CD₃OD