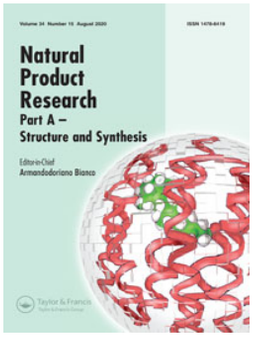

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New Oleanane-type glycosides and secoiridoid glucoside from *Aptandra zenkeri*

Michel Boni Bitchi[a,b], Faustin Aka Kabran[a], Philomène Akoua Yao-Kouassi[a], Abdulmagid Alabdul Magid[b], Dominique Harakat[c], Laurence Voutquenne-Nazabadioko[b] and Félix Zanahi Tonzibo[a]

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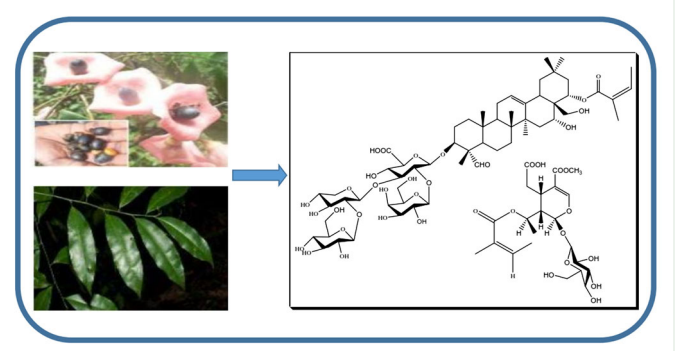
ABSTRACT

Four new saponins, camelliagenin A and B derivatives, and one new secoiridoid glucoside were isolated from the stem bark of *Aptandra zenkeri* Engl. (Aptandraceae) together with two known secoiridoid glucosides. 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*.



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

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 fruits 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

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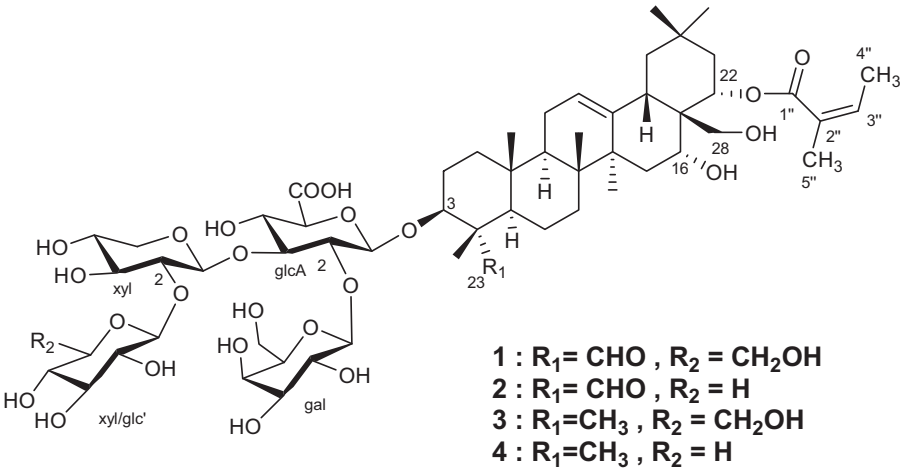

Figure 1. The structures of triterpenoid glycosides (**1**–**4**) isolated from the stem bark of Aptandra zenkeri Engl.

hepatitis and coughing (Aubréville 1959; Burkill 1997; Louis and Léonard 1948; Neuwinger 2000; Villiers 1973; List and Horhammer 1972). However, there has been no chemical or biological study reported on this plant. Only phytosterols and tocopherols were mentioned in *Aptandra sprucea* (Costa et al. 2010). As a part of a continuing study for the discovery of medicinal Ivory Cost species, seven compounds, including four new saponins, camelliagenin A and B derivatives, and one new and two known secoiridoid glucosides, 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). The known compounds were elucidated as diderroside (**6**) (Adeoye and Waigh 1983) and gonocaryoside-E (**7**) (Chan et al. 1998; Zuleta et al. 2003). Their spectroscopic data were in perfect agreement with those reported in the literature.

Compound **1** was separated as a white, amorphous powder. The molecular formula $C_{58}H_{90}O_{26}$ was deduced from the HR-ESI-MS $[M+Na]^+$ ion at *m/z* 1225.5627 (calcd 1255.5618). The ^{1}H NMR spectrum of **1** indicated the presence of six singlet methyl groups at δ_H 0.93, 0.98, 1.05, 1.07, 1.19, 1.52 (each 3H, s, H_3-29, H_3-26, H_3-25, H_3-30, H_3-24, H_3-27), a methylene and three methines bearing an oxygen function at δ_H 3.08,

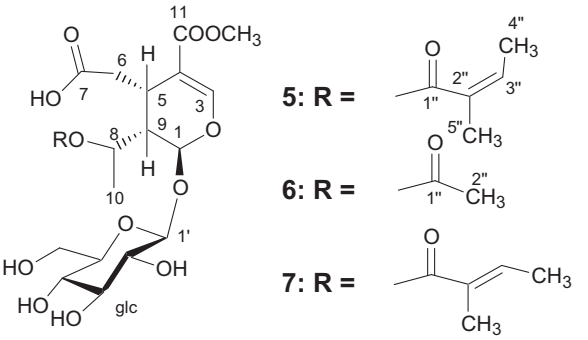

Figure 2. The structures of secoiridoid glucosides (**5**–**7**) isolated from the stem bark of Aptandra zenkeri Engl.

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 (1 H, s, H-23), which were characteristic of a polyhydroxyolean-12-ene triterpene derivative. In the HMBC spectrum, the cross-peaks observed between H-24 and δ_C 84.7 (C-3) and 209.3 (C-23) placed a secondary hydroxyl group 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 with that of camelliagenin B (Myose 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, 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_3-25 and H_3-24 on one hand and H_3-26 on the other, confirmed the β-axial orientation of these three methyl groups. The cross peaks between H-22 and H_3-30, H-22 and H-18 (δ 2.56), as well as those between H-16 and H_2-28, 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 (3β,16α,22α,28-tetrahydroxy, 23-aldehyde-olean-12-ene) (Table S1) (Myose 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 (1 H, 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 ^{1}H-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. 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 $J_{H\text{-}2,H\text{-}1}$ and $J_{H\text{-}2,H\text{-}3}$ ($\geq$ 8.1 Hz) and the small coupling constant between H-3 and H-4 ($J_{H\text{-}3,H\text{-}4} = 3.3$ 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 (δC 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, TOCSY, and HSQC experiments. The position of the sugar components was determined on the basis of the HMBC experiment, 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→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→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 $[M + Na]^+$ indicated the molecular formula of **2** to be $C_{57}H_{88}O_{25}$ (calcd 1195.5522), suggesting one methylene bearing an oxygen (-CH_2OH) less than that of **1**. The ^{1}H- and ^{13}C-NMR data of **2** were superimposable on those of **1** except for the sugar moiety (Table 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**. 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→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→2)]-β-D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin B.

Compound **3**, separated as a white, amorphous powder, was assigned a molecular formula of $C_{58}H_{92}O_{25}$ according to the HR-ESI-MS peak at *m/z* 1211.5834 $[M + Na]^+$ (calc 1211.5825). 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 (CH_3-23) in **3**. This was confirmed by a HMBC correlation between δ_H 0.91 (s) (H_3-24)/δ_C 27.0 (C-23), and the reverse one, between δ_H 1.12 (s)(H_3-23)/δ_C 15.6 (C-24). The triterpene skeleton of **3** was thus determined as the known camelliagenin A (3β,16α,22α,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. Thus, the structure of **3** was elucidated as 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.

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) consistent with a molecular formula of $C_{57}H_{90}O_{24}Na$. 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. Thus, the structure of **4** was elucidated as 3-*O*-β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→2)]-β-D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin A.

The positive HR-ESI-MS of compound **5** showed a pseudomolecular ion peak $[M+Na]^+$ at *m/z* 527.1733, in accordance with the molecular formula of $C_{22}H_{32}O_{13}$ (calcd for $C_{22}H_{32}O_{13}Na$ 527.1741). The ^{1}H NMR spectrum of **5** (Table S3) revealed signals attributed to a trisubstituted olefinic proton at δ_H 7.48 (s, H-3), an acetal proton at δ_H 5.85 (d, $J=6.4$, H-1), an oxymethine at δ_H 5.32 (dq, $J=6.9$, 4.5 Hz, H-8), an oxymethyl signal at δ_H 3.70 (s, H_3-12), two methines at δ_H 3.40 (H-5) and 2.30 (dt, $J=6.9$, 4.9 Hz, H-9), a methylene at δ_H 2.54 and 2.65 (H_2-6), and a secondary methyl at δ_H 1.00 (d, $J=6.5$ Hz, H_3-10), together with a β-anomeric proton at δ_H 4.75 (d, $J=7.9$ Hz, H-1′), suggesting **5** to be a seco-iridoid as in **6** and **7**. Full assignments of the proton and carbon resonances of the aglycone and the sugar parts of **5** were achieved by analysis of the COSY, HSQC, HMBC and ROESY spectra and were similar to those of **6** and **7** except for the acyl groups, suggesting that **5** was an ester of 7-demethyl alpigenoside (Garcia et al. 1990) or diderroside derivative (Adeoye and Waigh 1983). (Table S3). The characteristic NMR signals of 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 167.1 (C-1″), 127.9 (C-2″), 138.3 (C-3″), 14.7 (C-4″) and 19.5 (C-5″) were observed and further assigned by a combination of HSQC and HMBC experiments (Zong et al. 2015). In the HMBC experiment, long-range correlation was observed between the H-8 of 7-demethyl alpigenoside and the C-1″ (δ_C 167.1) of the angeloyl moiety, established that angeloyl esterified C-8 of the seco-iridoid unit. Thus, compound **5** was elucidated as 8-*O*-angeloyl-7-demethyl alpigenoside. 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 CD_3OD 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-C_{18}). 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-C_{18} column (Phenomenex 250 × 15 mm, Luna 5 µ) was used for semi-preparative HPLC. The eluting mobile phase consisted of H_2O with TFA (0.0025%) and CH_3CN 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 F_{254} pre-coated aluminium plates (0.2 mm, Merck). Spots were visualized through developing agent ($CHCl_3$:MeOH:H_2O, 14:6:1) and chromogenic agent (50% aq. H_2SO_4) subsequent heating.

3.2. Plant material

The stem bark of *Aptandra zenkeri* Engl. 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 3 h 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 H_2O (2 l) and successively partitioned with $CHCl_3$ (3 × 1 l), and *n*-BuOH (3 × 1 l). 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 $CHCl_3$-MeOH-H_2O 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 CH_3CN–H_2O (10–50%), in 40 min to afford 23 sub-fractions (C_1-C_{23}). Fraction C_4 (131 mg) was purified by semi-prep. HPLC using a gradient from 10% to 45% MeCN during 20 min, to yield compounds **5** (R*t* 17.2; 16 mg), **6** (R*t* 8.3; 11 mg), and **7** (R*t* 16.2; 2 mg). Fractions C_9 (250 mg) was purified by semi-prep. HPLC using an isocratic elution of 30% MeCN during 15 min, to yield compound **5** (R*t* 5.3; 43 mg). A portion of fraction E (1 g) was purified by flash chromatography over RP18, eluted by a gradient system of CH_3CN-H_2O (20% to 60%), in 40 min to afford 40 sub-fractions (E_1-E_{40}). Fractions E_{25} (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; $[\alpha]^{20}_{D}$ +8 (*c* 1, CH_3OH); HRESIMS (positive-ion mode) *m/z* 1225.5627 $[M+Na]^+$ ($C_{58}H_{90}O_{26}Na$; calcd for 1225.5618); ^{1}H NMR (CD_3OD, 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 (1 H, 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 (3 H, s, H-24), 1.05 (3H, s, H-25), 0.98 (3 H, s, H-26), 1.52 (3H, s, H-27), 3.08 (1H, d, *J* = 11 Hz), 3.28 (1H, d, *J* = 11 Hz) (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 (3 H, d, *J* = 7.2 Hz, H-4″), 1.92 (3H, s, H-5″); ^{13}C NMR (CD_3OD, 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″); ^{1}H- and ^{13}C 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; $[\alpha]^{20}_{D}$ +6 (*c* 0.81, CH_3OH); HRESIMS (positive-ion mode) *m/z* 1195.5522 $[M+Na]^+$ ($C_{57}H_{88}O_{25}Na$; calcd for 1195.5512); ^{1}H NMR (CD_3OD, 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 (3 H, d, *J* = 7.3 Hz, H-4″), 1.92 (3H, s, H-5″); ^{13}C NMR (CD_3OD, 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″); ^{1}H- and ^{13}C 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; $[\alpha]^{20}_{D}$ -5 (*c* 0.12, CH_3OH); HRESIMS (positive-ion mode) *m/z* 1211.5834 $[M + Na]^+$ ($C_{58}H_{92}O_{25}Na$; calcd for 1211.5825); ^{1}H NMR (CD_3OD, 500 MHz) δ: 1.01 (1H, m), 1.65 (1 H, 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 (1 H, brd, $J = 11.7$ Hz, H-5), 1.44 (1H, m), 1.61 (1H, m) (H-6), 1.37 (1 H, m), 1.64 (1H, m) (H-7), 1.69 (1H, m, H-9), 1.94 (2H, m, H-11), 5.36 (1 H, 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 (3 H, 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″); ^{1}H- and ^{13}C NMR data for sugar moieties (see Table S2).

3.7. Compound 4: 3-O-β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl-(1→2)]-β-D-glucuronopyranosyl-22-O-angeloyl-camelliagenin a

White, amorphous powder; $[\alpha]^{20}_{D}$ -3 (*c* 0.26, CH_3OH); HRESIMS (positive-ion mode) *m/z* 1181.5732 $[M + Na]^+$ ($C_{57}H_{90}O_{24}Na$; calcd for 1181.5720); ^{1}H 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 (3 H, s, H-24), 1.01 (3H, s, H-25), 0.97 (3 H, 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″); ^{1}H- and ^{13}C NMR data for sugar moieties (see Table S2).

3.8. Compound 5: 8-O-angeloyl-7-demethyl alpigenoside

Colorless, amorphous powder; $[\alpha]^{20}_{D}$ -90 (*c* 0.26, CH_3OH); HRESIMS (positive-ion mode) *m/z* 527.1733 $[M+Na]^+$ ($C_{22}H_{32}O_{13}Na$; calcd for 527.1741); ^1H NMR (CD_3OD, 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 (3 H, d, $J=6.5$ Hz, H-10), 3.70 (3H, s, 12-OCH_3), 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 (1 H, 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), 167.3 (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′), 167.1 (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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