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Triterpenoid saponins from the stem barks of *Chytranthus klaineanus* Radlk. ex Engl.

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ABSTRACT

In our continuing studies on saponins from Cameroonian medicinal plants, phytochemical investigation of *Chytranthus klaineanus* stem barks led to the isolation of three new oleanane-type saponins, named Klaineanosides A–C (**1–3**). Their structures were established by extensive analysis of their spectral data, mainly 1D (^1H , ^{13}C NMR, and DEPT) and 2D (COSY, HSQC, NOESY, HSQC-TOCSY, and HMBC) NMR experiments, and mass spectrometry as 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)[- β -D-xylopyranosyl(1 \rightarrow 3)- β -D-xylopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin (**1**), 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)[β -D-xylopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin (**2**), and 3-*O*- β -D-xylopyranosyl(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranosylhederagenin (**3**). These triterpene saponins **1–3** have hederagenin as aglycone with a $^{-3}\text{Rha-}^{-2}\text{Ara-}^{-3}\text{hederagenin}$ oligosaccharidic sequence usually found in Sapindaceae family.

Keywords: Sapindaceae; *Chytranthus klaineanus*; Triterpenoid saponins; Klaineanosides; NMR.

1. Introduction

The Sapindaceae family includes nearly 1900 species distributed in three subfamilies as Sapindoideae, Dodonaeoideae and Aceroideae, and about 144 genera (APG IV, 2016). These are trees, shrubs and herbaceous plants, mostly distributed in tropical and subtropical regions (Zu and Deng, 2017). Most of species are native to Australia, Asia, and Africa where they are used in traditional medicine to treat headache, diarrhea, rheumatism, pulmonary complaints, toothache, dysentery, and malaria (Burkill, 2000; Agboola et al., 2012). Triterpenoid saponins are major constituents of plants from this family (Delaude, 1993; Voutquenne et al., 2005; Cao et al., 2009; Mazzola et al 2011; Mostafa et al., 2016; Wang et al., 2017; Freitas et al., 2017; Wang Xiuling et al., 2017; Hu et al., 2018; Pertuit et al., 2018; Petit et al., 2019). *Chytranthus klaineanus* (Sapindoideae subfamily) is a tree or shrub of about 1-5 m high, found in Central Africa, from which, and to the best of our knowledge, no ethnomedicinal use is documented. Nevertheless, the antioxidant potential of the seed and leaves extracts of a related species, *C. macrobotrys*, has been reported (Jide and Bidemi, 2018). Previous phytochemical investigation of the stem barks of *C. klaineanus* revealed the presence of coumarin derivatives and one glycoside of ellagic acid (Gojayep et al., 2013). In our continuing studies of Cameroonian's saponins containing plants (Noté et al., 2009, 2013, 2016, 2017, 2018), we have investigated the saponins content of the stem barks of *C. klaineanus*.

In the present paper, we report the isolation and structure characterization of three new triterpenoid saponins, named Klaineanosides A–C (**1–3**) having hederagenin acid as aglycone.

2. Results and Discussion

The air-dried powdered stem barks of *C. klaineanus* (400 g) were extracted with aq-EtOH 70% using a sonicateur apparatus. After evaporation of the solvent, the resulting dark residue was suspended in water and partitioned against *n*-BuOH saturated with water. The *n*-BuOH phase was

then evaporated to dryness affording a brown gum which was submitted to column chromatography (CC) using Diaion HP-20 resin yielding enriched saponins fractions which were submitted to VLC using silica gel to give four main subfractions. Purification of the eluted subfractions by Semiprep-HPLC afforded three new triterpenoid saponins, named klaineanosides A– C (**1–3**) (Fig. 1).

All the isolated saponins **1–3** were obtained as white amorphous powders. The monosaccharides obtained by acid hydrolysis of each compound were identified by comparison on TLC with authentic samples as arabinose, xylose, rhamnose and glucose. The absolute configurations were determined by GC analysis to be D-for glucose and xylose and L for rhamnose and arabinose (Chaabi et al., 2010; see 3. Experimental Section). The ^1H - and ^{13}C -NMR data of the monosaccharide residues were assigned starting, either from the anomeric protons, or from the CH_3 -proton doublet of rhamnose unit, by means of COSY, HSQC-TOCSY, HSQC, NOESY, and HMBC spectra obtained for each compound. Data from these NMR experiments indicated that the sugar residues were in their pyranose form, and relatively large $^3J_{\text{H-1, H-2}}$ values 6.7 - 8.0 Hz of Glc, Xyl and Ara in their pyranose form evidenced a β -anomeric orientation for Glc and Xyl, and an α -anomeric configuration for Ara (Ishii et al., 1981). The α -anomeric configuration of the L-rhamnose unit was judged by the broad singlet of its anomeric proton and the chemical shift value of C-5 (Luo et al., 2008).

The HR-ESIMS (positive ion mode) of **klaineanoside A (1)** showed a protonated molecule peak at m/z 1309.6435 $[\text{M} + \text{H}]^+$ consistent with the molecular formula $\text{C}_{62}\text{H}_{100}\text{O}_{29}$. The ^1H NMR and ^{13}C NMR data of **1** displayed resonances due to the aglycone part characteristic for hederagenin (Table 1), a common triterpene of triterpene glycosides, which were in full agreement with literature data (Jung et al., 1993; Sarikahya and Kırmızıgül 2012; Pertuit et al., 2018; Petit et al., 2019; see Table 1). The ^1H -NMR spectrum of **1** showed six anomeric protons at δ_{H} 5.04 (d, $J = 6.7$ Hz), 5.10 (d, $J = 7.8$ Hz), 5.31 (d, $J = 7.6$ Hz), 5.34 (d, $J = 7.4$ Hz), 5.46 (d, $J = 7.9$ Hz), and

6.28 (br s), which correlated with six anomeric carbon atom signals at δ_C , 105.3, 105.4, 106.5, 106.0, 107.3, and 101.9, respectively, in the HSQC spectrum. Complete assignments of each sugar moiety were achieved by extensive analyses of 1D and 2D NMR experiments and GC analysis (see experimental Section) allowing the characterization of one α -L-arabinopyranosyl (Ara), one α -L-rhamnopyranosyl (Rha), one β -D-glucopyranosyl (Glc), and three β -D-xylopyranosyl (Xyl I, Xyl II, and Xyl III) units. The sequence of the oligosaccharide chain was obtained from the HMBC and NOESY experiments. The correlations observed in the HMBC spectrum between H-1 (δ_H 5.04) of Ara and C-3 (δ_C 81.5) of the aglycone, and in the NOESY spectrum between H-1 (δ_H 5.04) of Ara and H-3 (δ_H 4.30) of the hederagenin moiety, suggested that Ara was directly attached to C-3 of the aglycone. Moreover, the HMBC correlation observed between H-1 (δ_H 5.10) of Xyl I and C-4 (δ_C 80.5) of Ara established the connectivity between the two sugar units, which was confirmed by the NOESY correlation observed between H-4 (δ_H 4.35) of Ara and H-1 (δ_H 5.10) of Xyl I. In addition, the direct and reverse HMBC correlations observed between H-1 (δ_H 5.31) of Glc and C-3 (δ_C 86.9) of Xyl I and between H-3 (δ_H 4.07) of Xyl I and C-1 (δ_C 106.5) of Glc allowed us to locate Glc at C-3 of Xyl I (Fig. 2). On the other hand, the HMBC correlation observed between H-1 (δ_H 6.28) of Rha and C-2 (δ_C 75.7) of Ara established the connectivity between the two sugar units, which was confirmed by the NOESY correlations observed between H-2 (δ_H 4.56) of Ara and H-1 (δ_H 6.28) of Rha. Moreover, the direct and reverse HMBC correlations observed between H-1 (δ_H 5.46) of Xyl II and C-3 (δ_C 84.0) of Rha and between H-3 (δ_H 4.81) of Rha and C-1 (δ_C 107.3) of Xyl II allowed us to locate Xyl II at C-3 of Rha. In addition, the direct and reverse HMBC correlations observed between H-1 (δ_H 5.34) of Xyl III and C-3 (δ_C 86.8) of Xyl II and between H-3 (δ_H 4.20) of Xyl II and C-1 (δ_C 106.0) of Xyl III allowed us to locate Xyl III at C-3 of Xyl II. Thus, the hexasaccharide β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)[β -D-xylopyranosyl(1 \rightarrow 3)- β -D-xylopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranoside moiety was established to be linked at C-3 of the aglycone (Fig. 2).

Hence, the structure of klaineanoside A (**1**) was established as 3-*O* β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)[β -D-xylopyranosyl(1 \rightarrow 3)- β -D-xylopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin.

Extensive 2D NMR analysis of the remaining saponins **2–3** revealed that they possess all hederagenin as aglycone.

HR-ESIMS of **klaineanoside B (2)**, indicated a C₅₇H₉₂O₂₅ molecular formula, as deduced from the protonated molecule peak at *m/z* 1177.5968 [M + H]⁺ in the positive ion mode. The difference between compounds **1** and **2** (132 amu lower) was identified to be one xylose moiety, which complete assignment was achieved by extensive analyses of 1D and 2D NMR experiments. In addition, this account for the similarities between the ¹H and ¹³C NMR spectra of compounds **1** and **2** (Table 2). Instead of a hexasaccharide moiety at C-3 of hederagenin, compound **2** displayed signals for a pentasaccharide moiety attached at C-3 of the aglycone according to the analysis of 2D NMR experiments. Accordingly, klaineanoside B (**2**) was elucidated to be 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 3)- β -D-xylopyranosyl-(1 \rightarrow 4)[β -D-xylopyranosyl(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)]- α -L-arabinopyranosylhederagenin.

Klaineanoside C (3) exhibited in the HR-ESIMS a protonated molecule peak at *m/z* 1045.5612 [M + H]⁺ compatible with the molecular formula C₅₂H₈₄O₂₁. The ¹H NMR spectrum of **3** showed the presence of four anomeric proton signals at δ_H 5.03 (d, *J* = 6.7 Hz), 5.11 (d, *J* = 7.7 Hz), 5.45 (d, *J* = 7.7 Hz), and 6.28 (br s) which correlated with four anomeric carbon atom signals at δ_C , 105.2, 105.9, 107.1, and 101.8, respectively, in the HSQC spectrum. Complete assignments of each sugar were achieved by extensive 1D and 2D NMR analyses and GC analysis (see Experimental Section) allowing the characterization of one α -L-arabinopyranosyl (Ara), one α -L-rhamnopyranosyl (Rha), one β -D-glucopyranosyl (Glc), and one β -D-xylopyranosyl (Xyl) units. The connectivities between these sugar moieties were achieved by HMBC and NOESY correlations. The cross peak correlations observed in the HMBC spectrum between H-1 (δ_H 5.03)

of Ara and C-3 (δ_C 81.5) of the aglycone, and in the NOESY spectrum between H-1 (δ_H 5.03) of Ara and H-3 (δ_H 4.29) of hederagenin, suggested that Ara was directly attached to C-3 of the aglycone. Moreover, the HMBC correlation observed between H-1 (δ_H 6.28) of Rha and C-2 (δ_C 75.7) of Ara established the connectivity between the two sugar units, which was confirmed by the NOESY correlation observed between H-2 (δ_H 4.54) of Ara and H-1 (δ_H 6.28) of Rha. In addition, the HMBC correlation observed between H-1 (δ_H 5.45) of Glc and C-3 (δ_C 83.9) of Rha established the connectivity between the two sugar units, which was confirmed by the NOESY correlation observed between H-3 (δ_H 4.82) of Rha and H-1 (δ_H 5.45) of Glc. Furthermore, the direct and reverse HMBC correlations observed between H-1 (δ_H 5.11) of Xyl and C-4 (δ_C 80.9) of Glc and between H-4 (δ_H 4.31) of Glc and C-1 (δ_C 105.9) of Xyl allowed us to locate Glc at C-3 of Xyl. Consequently, the tetrasaccharide β -D-xylopyranosyl(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranosyl moiety was established to be linked at C-3 of the aglycone. Consequently, the structure of klaineanoside C (**3**) was established as acid 3-*O*- β -D-xylopyranosyl(1 \rightarrow 4)- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-rhamnopyranosyl-(1 \rightarrow 2)- α -L-arabinopyranosylhederagenin.

All the three isolated saponins **1–3**, shared hederagenin as aglycone and the $^{-3}\text{Rha-}^2\text{Ara-}^3\text{hederagenin}$ oligosaccharidic sequence. This structural feature have been often encountered in the saponins from Sapindoideae subfamily (Delaude, 1993; Kanchanapoom et al., 2001; Voutquenne, 2001; Huang et al., 2007; Asao et al., 2009; Voutquenne-Nazabadioko, 2010; Mazzola et al 2011; Hu et al., 2018; Pertuit et al., 2018; Petit et al., 2019). In addition, to the best of our knowledge, our study is the first phytochemical study on saponins from *C. klaineanus* and represents therefore a valuable contribution to the chemotaxonomy of Sapindoideae subfamily, which is known to be a rich source of triterpenoid saponins.

3. Experimental section

3.1. General experimental procedures

Optical rotations were measured on a Jasco P-2000 polarimeter. NMR experiments were performed at 298 K in pyridine-d₅ on a Bruker AVANCE 500MHz spectrometer equipped with a 5 mm Z-gradient TCI cryogenic probe. Chemical shifts are given in δ (ppm) value relative to TMS as internal standard. HRESIMS spectra were recorded on a micro TOF-ESI-TOF mass spectrometer (Agilent) operating in positive mode. Semipreparative high performance liquid chromatography (HPLC) was carried out using a LaChrom Merck Hitachi system consisting of a LaChrom L-7100 pump, an L-7455 DAD, and a D-7000 interface and employing a Phenomenex Luna 5 μ m C18(2) 100 Å, 250 \times 10 mm² column. Analytical thin-layer chromatography (TLC) was achieved on precoated silica gel plates (Merck, Kieselgel 60 F254, 0.25 mm) using UV 254 nm and a 1% vanillin/10% H₂SO₄ reagent in EtOH for visualization. Vacuum-liquid chromatography (VLC) was carried out using RP-18 and silica gel 60 (15-40 μ m).

3.2. Plant material

The stem barks of *C. klaineanus* were harvested at Eloundem, Yaoundé peripheral quarter, in Cameroon in October 2017 under the guidance of Mr. Victor Nana, botanist of the National Herbarium of Cameroon (NHC), where a voucher specimen (2338/SRFK) was deposited.

3.3. Extraction and isolation

The air-dried, powdered stems barks of *C. klaineanus* (400 g) were extracted with aq-EtOH 70% using a sonicateur apparatus. The resulting hydroalcoholic solution was then evaporated to dryness under reduce pressure to yield brown residue (30.24 g). This residue was dissolved in

ethyl acetate (300 mL), and the insoluble residue (22.08 g) was suspended in 10 mL of H₂O and partitioned in with *n*-BuOH sat. H₂O (3 x 300 mL). The *n*-BuOH soluble phase was evaporated to dryness affording 6.63 g of brown gum residue. Part of this residue (5 g) was suspended in 100 mL of water and then submitted to column chromatography (CC) using Diaion HP-20 resin, eluting with H₂O, 50% MeOH, 70% MeOH, 80% MeOH, 90% MeOH, and 100% MeOH, successively giving four main fractions (CKT1–CKT4) after TLC monitoring. The 80%-100% MeOH fraction (CKT4) was evaporated to dryness yielding a crude saponin mixture (1.21 g) that was then submitted to VLC using silica gel 60 (15–40 µm), eluted with CH₂Cl₂-MeOH (80:20) and CH₂Cl₂-MeOH-H₂O (70:30:5, 60:32:6.5) to give four main subfractions (CKT41–CKT44). Subfraction CKT43 (325 mg) was purified by semi preparative HPLC using gradient system of CH₃CN-H₂O (30 mL/min) to yield compounds **1** (*t*_R, 13.20 min, 7.9 mg), **2** (*t*_R, 13.68 min, 8.5 mg), and **3** (*t*_R, 16.16 min, 7.2 mg).

3.3.1. *Klaineanoside A (1)*

White amorphous powder; $[\alpha]_D^{25} +16.4$ (c 0.01, MeOH); ¹H NMR (C₅D₅N, 500 MHz) and ¹³C NMR (C₅D₅N, 125 MHz) data, see Tables 1 and 2; HRESIMS *m/z*: 1309.6435 [M + H]⁺ (calcd for C₆₂H₁₀₀O₂₉, 1308.6684).

3.3.2. *Klaineanoside B (2)*

White amorphous powder; $[\alpha]_D^{25} +17.5$ (c 0.01, MeOH); ¹H NMR (C₅D₅N, 500 MHz) and ¹³C NMR (C₅D₅N, 125 MHz) data, see Tables 1 and 2; HRESIMS *m/z*: 1177.5968 [M + H]⁺ (calcd for C₅₇H₉₂O₂₅, 1176.6227).

3.3.3. *Klaineanoside C (3)*

White amorphous powder; $[\alpha]^{25}_D -21.2$ (c 0.01, MeOH); ^1H NMR ($\text{C}_5\text{D}_5\text{N}$, 500 MHz) and ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$, 125 MHz) data, see Tables 1 and 2; HRESIMS m/z : 1045.5612 $[\text{M} + \text{H}]^+$ (calcd for $\text{C}_{52}\text{H}_{84}\text{O}_{21}$, 1044.5539).

3.4. Acid hydrolysis of compounds and determination of the absolute configuration of the sugar residues

Each saponin (2 mg) was hydrolyzed with 2 mL of 2 M HCl at 85 °C during 2 h. After cooling, the solvent was removed under reduced pressure. The sugar mixture was extracted from the aqueous phase (10 mL) and washed with CH_2Cl_2 (3x 5 mL). The combined CH_2Cl_2 extracts were washed with water to give after evaporation the aglycone moiety. The sugars were first analyzed by TLC over silica gel (CHCl_3 –MeOH– H_2O , 8:5:1) by comparison with standard samples. The absolute configuration of each monosaccharide was determined from GC–MS analysis of their trimethylsilylated derivatives by comparison with authentic samples using the method previously described ([Chaabi et al., 2010](#)). The following sugars were detected: D-glucose, D-xylose, L-rhamnose and L-arabinose.

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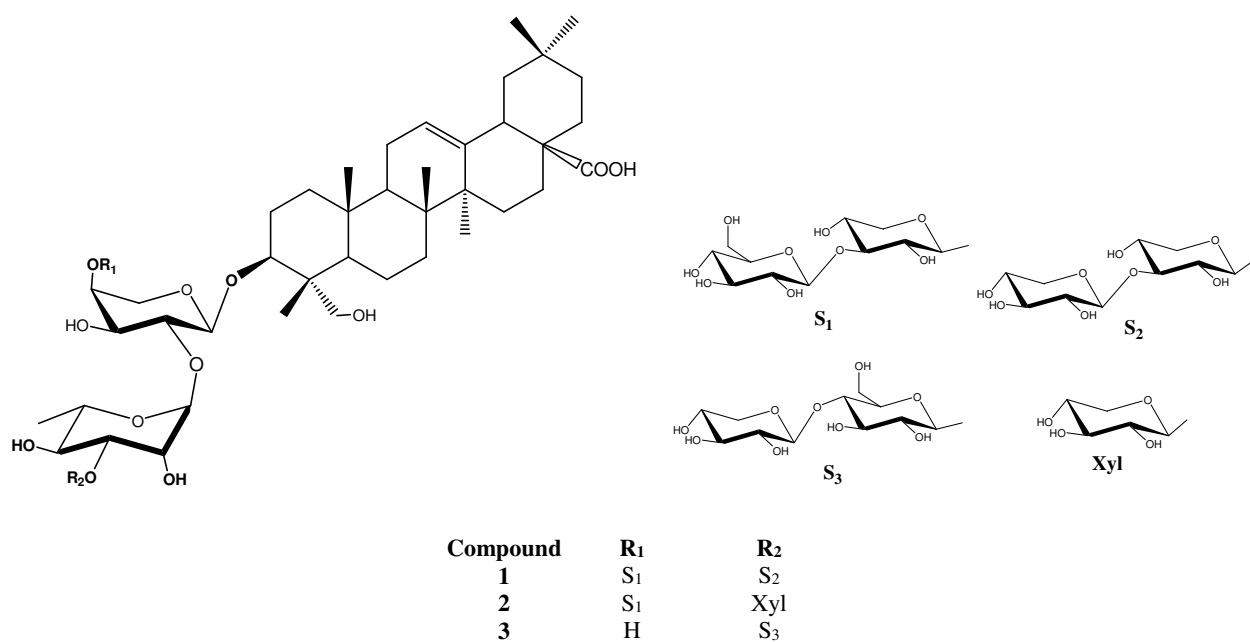


Fig.1. Structures of isolated compounds **1-3**.

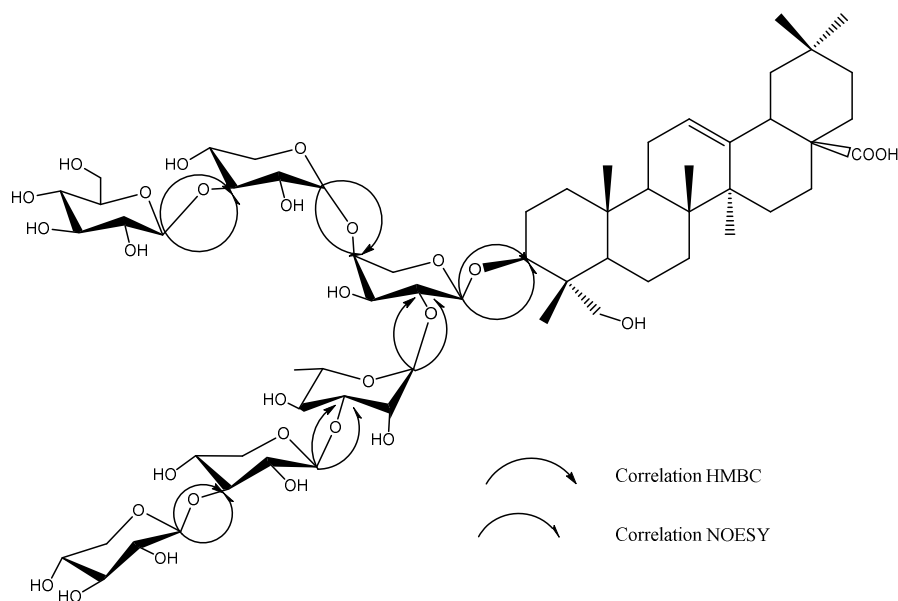


Fig.2. Key HMBC and NOESY correlations for compound **1**

Table 1. NMR spectroscopic data (500 MHz for ^1H and 125 MHz for ^{13}C) for the aglycone moieties of compounds **1-3** (δ in ppm and J in Hz)^{a)}

N°	1		2		3	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	39.4	1.08	39.4	1.08	39.3	1.07
		1.55		1.56		1.56
2	26.8	2.02	26.8	2.02	26.7	2.00
		2.26		2.24		2.23
3	81.5	4.30 (dd, 11.2, 5.1)	81.5	4.29 (dd, 11.4, 5.0)	81.5	4.29 (dd, 10.3, 5.6)
4	44.0	-	44.0	-	44.0	-
5	48.0	1.78	48.0	1.75	48.0	1.77
6	18.5	1.38	18.5	1.34	18.5	1.36
		1.75		1.74		1.75
7	33.2	1.20	33.2	1.20	33.2	1.23
		1.61		1.57		1.60
8	40.1	-	40.1	-	40.1	-
9	48.6	1.79	48.6	1.77	48.5	1.78
10	37.3	-	37.3	-	37.2	-
11	24.2	2.07	24.2	2.07	24.2	2.06
		2.14		2.11		2.09
12	123.0	5.48 br s	123.0	5.47 br s	122.9	5.46 br s
13	145.2	-	145.2	-	145.1	-
14	42.5	-	42.5	-	42.5	-
15	28.7	1.12	28.7	1.10	28.7	1.09
		2.14		2.12		2.11
16	24.2	1.93	24.2	1.92	24.0	1.92
		1.97		1.95		1.99
17	47.0	-	47.0	-	467.0	-
18	42.4	3.30 (dd, 13.9, 4.7)	42.4	3.29 (dd, 13.7, 4.5)	42.3	3.30 (dd, 13.8, 4.6)
19	46.8	1.29	46.8	1.29	46.7	1.25
		1.80		1.78		1.77
20	31.4	-	31.4	-	31.3	-
21	34.6	1.22	34.6	1.18	34.5	1.18
		1.45		1.44		1.43
22	33.6	1.81	33.6	1.82	33.6	1.80
		2.05		2.04		2.04
23	64.4	3.91	64.4	3.90	64.3	3.90
		4.31		4.31		4.30
24	14.6	1.14 (s)	14.6	1.14 (s)	14.5	1.13 (s)
25	16.5	0.95 (s)	16.5	0.95 (s)	16.4	0.94 (s)
26	17.8	1.03(s)	17.8	1.02(s)	17.8	1.02(s)
27	26.6	1.25 (s)	26.6	1.24 (s)	26.5	1.25 (s)
28	180.6	-	180.6	-	180.5	-
29	33.7	0.96 (s)	33.7	0.95 (s)	33.6	0.93 (s)
30	24.2	1.02 (s)	24.2	1.02 (s)	24.1	1.00 (s)

Assignments were based on the HMBC, HSQC, COSY and DEPT experiments. ^{a)}Overlapped ^1H NMR signals are reported without designated multiplicity; nf: not found.

Table 2. NMR spectroscopic data (500 MHz for ^1H and 125 MHz for ^{13}C) for the sugar moieties of compounds **1-3** (δ in ppm and J in Hz)^{a)}

Position	1		2		3	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}
3-O-Sugars						
Ara						
1	105.3	5.04 (d, 6.7)	105.2	5.04 (d, 6.9)	105.2	5.03 (d, 6.7)
2	75.7	4.56	75.7	4.55	75.7	4.54
3	74.5	3.99	74.3	3.98	75.5	3.97
4	80.5	4.35	80.5	4.36	70.1	4.11
5	66.9	3.66 (t, 10.7); 4.24	66.9	3.68 (t, 11.4); 4.22	66.7	3.64 (t, 11.6); 4.23 (dd, 11.6; 5.1)
Rha						
1	101.9	6.28 (br s)	101.8	6.30 (br s)	101.8	6.28 (br s)
2	72.3	4.94	72.3	4.94	72.2	4.94
3	84.0	4.81	84.0	4.81	83.9	4.82
4	73.5	4.51	73.5	4.50	73.4	4.50
5	70.0	4.71	70.0	4.71	70.0	4.70
6	18.9	1.58 (d, 6.2)	18.9	1.57 (d, 6.1)	18.8	1.56 (d, 6.1)
Xyl I						
1	105.4	5.10 (d, 7.8)	105.4	5.12 (d, 7.7)	105.9	5.11 (d, 7.7)
2	75.6	3.99	75.6	3.99	75.2	3.98
3	86.9	4.07	87.3	4.05	78.7	4.08
4	69.2	4.02	69.3	4.03	71.1	4.14
5	67.3	3.65 (t, 10.7); 4.23	67.2	3.61 (dd, 11.4; 9.7); 4.24	67.1	3.64 (t, 11.6); 4.23 (dd, 11.6; 5.1)
Glc						
1	106.5	5.31 (d, 7.6)	106.7	5.27 (d, 7.7)	107.1	5.45 (d, 7.7)
2	75.9	4.04	75.8	4.04	76.0	4.12
3	78.6	4.17	78.7	4.15	76.6	4.26
4	71.4	4.19	71.4	4.18	80.9	4.31
5	77.3	3.92	77.3	3.90	77.1	3.92
6	61.3	4.40; 4.54	61.3	4.41; 4.56	61.7	4.39; 4.52
Xyl II						
1	107.3	5.46 (d, 7.9)	107.3	5.47 (d, 8.0)		
2	76.0	4.09	76.1	4.11		
3	86.8	4.20	76.6	4.26		
4	70.2	4.12	70.2	4.12		
5	67.3	3.60 (t, 10.9); 4.18	67.8	3.72 (t, 11.2); 4.33		
Xyl III						
1	106.0	5.34 (d, 7.4)				
2	74.6	4.08				
3	76.6	4.24				
4	69.5	4.11				
5	67.8	3.74 (t 7.8); 4.33 (dd, 11.6; 5.0)				

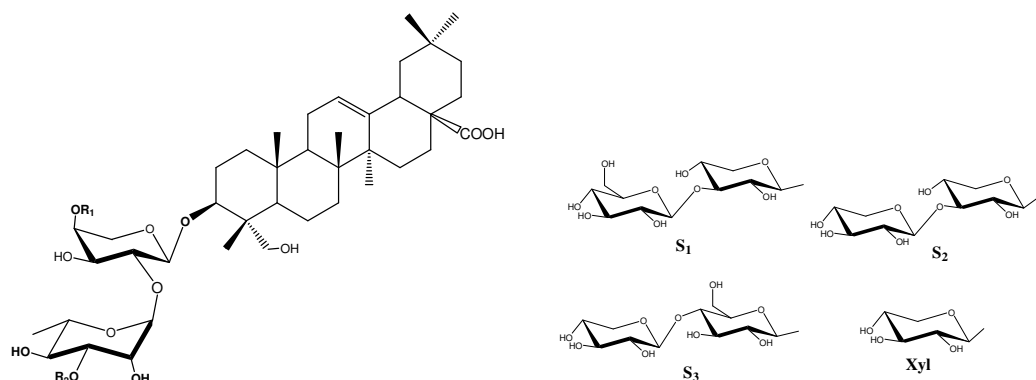
Assignments were based on the HMBC, HSQC, COSY and DEPT experiments.

^{a)}Overlapped ^1H NMR signals are reported without designated multiplicity.

Triterpenoid saponins from the stem barks of *Chytranthus klaineanus* Radlk. ex Engl.

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Graphical Abstract



Compound	R ₁	R ₂
1	S ₁	S ₂
2	S ₁	Xyl
3	H	S ₃