New triterpenoid saponins from the stem bark of Hallea ledermannii

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New triterpenoid saponins from the stem bark of *Hallea ledermannii*

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Abstract

Twenty-three triterpenoid saponins (**1-23**) have been isolated from the aquoeus and ethyl acetate fractions of the stem bark of *Hallea ledermannii*. Among them, nine (**1-9**) are newly described, some of them containes uncommun natural 6-deoxy-D-allofuranose, 6-deoxy-D-allopyranose, and 6-deoxy-D-pyranose as a sugar moiety. This is the first report of the isolation and structural elucidation of these compounds from *H. ledermannii*. The chemical structure of the compounds was determined using NMR and HRMS data.

Keywords: *Hallea ledermannii*, Rubiaceae, Triterpenoid saponins.

Introduction

The Hallea genus belongs to the Rubiaceae family. It is better known under the synonym of Mitragyna and can also be called: Fleroya or Nauclea. In general, plants of the genus Hallea are trees or shrubs with opposite leaves [1]. Mitragyna genus have been used in traditional medicine to treat many deseases such as fever, malaria, diarrhea, inflammation and hypertension [2]. According to prior investigations, many species possess antitumor, cardiovascular disease and antibacterial activities [2, 3]. Phytochemical research has showed that alkaloids, triterpenoids and flavonoids were the main compounds in Mitragyna genus [4-6]. *Hallea ledermannii* (K. Krause) Verdc., (Rubiaceae), is a large tree of swamp forests, up to 35 m hight [7]. In Côte d'Ivoire, the aqueous decoction of the stem bark of *H.*

ledermannii is orally used to treat infections [8] and malaria [9]. Previous pharmacological studies evaluated the hypertensive, antioxidant and antidiabetic *activities* of *Hallea ledermannii* extracts [10-12]. From the phytochemical point of view, very few studies have been carried out on this plant.

The aim of this study is to isolate and characterize the chemical constituents from *H. ledermannii.* Thus, this paper reports by spectroscopic analysis, the structural elucidation of nine new triterpenoid glycosides, together with fourteen known triterpenoid glycosides from the stem barks of *H. ledermannii.*

Results and discussion

The aqueous and ethyl acetate fractions of the stem bark of *Hallea ledermannii* were subjected to multiple column chromatographic to give twenty three compounds **1–23** including nine undescribed triterpenoid glycosides(**1-9**) (Fig.1). The structure of isolated compounds was made by HR-ESI-MS, 1D, and 2D-NMR analysis. The spectroscopic data of the known triterpene saponins were in perfect agreement with those reported in the literature. In order to determine the sugar composition in these compounds, acid hydrolysis of a part of the saponin mixture generated seven sugar units in the aqueous layer, identified after purification and measurement of their optical rotation as D-(glucose, fucose, quinovose, 6-deoxy-allo*furanose,* 6-deoxy-allo*pyranose* and xylose) and L-rhamnose.

The known compounds (**10-23**) has been identified as quinovic acid-3-*O*-*β*-D-quinovopyranoside (**10**) [13], quinovic acid-3-*O*-*β*-D-fucopyranoside (**11**) [14], quinovic acid 3-*O*-*β*-D-glucopyranoside (**12**), quinovic acid-3-*O*-*β*-D-6-deoxyglucopyranosyl-28-*O*-*β*-D-glucopyranoside (**13**), quinovic acid-28-*O*-*β*-D-glucopyranoside (**14**) [15], quinovic acid-3-*O*-*β*-D-glucopyranosyl-28-*O*-*β*-D-glucopyranoside (**15**) [16], quinovic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-β-D-fucopyranosyl-28-*O*-*β*-D-glucopyranoside (**16**), quinovic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-L-rhamnopyranosyl-28-*β*-D-glucopyranoside (**17**), quinovic acid-3-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopyranosyl-28-*O*-*β*-D-glucopyranoside (**18**) [17], quinovic acid-3-*β*-*O*-D-6-deoxy-allopyranoside (**19**) [18], quinovic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranoside (**20**) [14], cincholic acid 3-*O*-*β*-D-6-deoxy-glucopyranosyl-28-*O*-β-D-glucopyranoside (**21**) [19], cincholic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-fucopyranoside (**22**) and cincholic acid-3-*O*-*β*-D-glucopyranosyl(1→4)-*β*-D-fucopyranosyl-28-*O*-*β*-D-glucopyranoside (**23**) [20].

Identification of compounds **1-9**

Compounds **1**-**9** were isolated as white amorphous powders. The analysis of their NMR spectra, as well as the acid hydrolysis allowed to attribute each sugar and their attachment to

the identified genin. The D and L configuration of sugars was established after hydrolysis analysis and chiral analytical HPLC and by comparison with authentic monosaccharide samples.

Compounds 1-5

The ^{1}H-NMR spectrum of compounds (**1-5**) showed six 3-H singlets of methyl groups, nine methylene groups, a double doublet at 5.62 indicating an olefinic proton (H-12), a double doublet ranging from 3.08 to 3.17 attributable to H-3 proton (Table 1). These data together with characteristic peaks in the ^{13}C-NMR spectrum at δ_C 130.9 (C-12), 133.9 to 133.2 (C-13), 179.1 (C-27), 177.9 -181.5 (C-28), indicated that the compounds (**1-5**) belongs to pentacyclic triterpene acids [21]. The presence of two carboxyl groups unambiguously indicated that they had a quinovic acid [18] skeleton. The NMR spectra of compounds (**1-5**) also displayed anomeric protons ((Table 2) which sequences are described as follows.

Compound **1** and **2** were assigned a molecular formula of $C_{42}H_{66}O_{14}$, as determined from their HRESIMS m/z: at m/z 791.4220 $[M-H]^{3-}$ and 793.4382 $[M-H]^{-}$ respectively.

The ^{1}H NMR and ^{13}C spectra of compounds **1** and **2**, each showed two anomeric protons at 4.38 and 5.40 and at 4.60 and 5.40 respectively (Table 2). Eight-protons from spin-spin coupling were defined from each anomeric protons at δ_H 4.38 and at δ_H 4.60 respctively. The analysis of their HSQC, and HMBC spectra and coupling constants led to identify uncommun 6-deoxy-β-allofuranose [22, 23] and 6-deoxy-β-allopyranose [18, 24] units for **1** and **2** respectively. Their β configurations were given on the basis of the *J* coupling constants > 7 Hz and were confirmed by the NOESY correlations between the β-axial protons H-1'/H-2'. The second sugar moieties with anomeric protons at δ_H 5.40 (d, *J* = 8.2 Hz) and at δ_H 5.40 (d, *J* = 8.1 Hz) appeared on the ^{1}H NMR spectra of **1** and **2** to be a β-glucopyranose respectively (Table 2). The HMBC correlations observed between the anomeric protons of **1** and **2** at δ_H 4.38 and 4.60 to δ_C 90.1 and 90.7 respectively, indicated their *O*-linked to the aglycone at C-3; whereas the HMBC correlations between the protons δ_H 5.40 and δ_C 177.9 (C-28) showed that the glucose moieties of **1** and **2** were linked to the aglycone at C-28 position. Thus, naturally occurring scarce compounds were identified as quinovic acid-3β-*O*-6-deoxy-β-D-allofuranosyl-28-*O*-*β*-D-glucopyranoside and quinovic acid-3β-*O*-6-deoxy-β-D-allopyranosyl-28-*O*-*β*-D-glucopyranoside for **1** and **2** respectively.

The HR-ESI-MS of compound **3** showed a quasi-molecular anion at m/z 779.4219 $[M-H]^{-}$, corresponding to a molecular formula of $C_{41}H_{64}O_{14}$, with14 mass units less than **1** and **2**. The ^{1}H- and ^{13}C-NMR data of **3** were similar to those of **1** except for the replacement of the 6-deoxy furanose moiety in **1** by the xylose moiety in **3** (Table 2). The HMBC correlations from H-1' xyl at δ_H 4.25 (d, *J* = 7.6 Hz) to C-3 at δ_C 90.6 and H-1'' glc at δ_H 5.40 (d, *J* = 8.2 Hz) to C-28 (δ_C 177.9) confirmed the *O*-linkage of the xylose to C-3 and the glucose to C-28.

Consequently, the structure of **3** was determined to be quinovic acid-3-*O*-*β*-D-xylopyranosyl-28-*O*-*β*-D-glucopyranoside.

The ^{1}H NMR, HSQC and COSY spectra of compound **4** led the idenfication of three sugars from their anomeric protons at δ_H 4.68 (d, *J* = 7.8 Hz), 5.40 (d, *J* = 8.1 Hz) and 4.39 (d, *J* = 7.8 Hz), attributed to two β-glucopyranoses and one 6-deoxy-*β*-glucopyranose respectively (Table 2). In HMBC spectrum, a disaccharide was identified by the correlation between δ_H 4.68 (H-1‴) and δ_C 81.0 (C-2'). In addition, δ_H 5.40 (H-1") correlated with δ_C 177.9 (C-28), and the disaccharide attached to the aglycone through a *β*-quinovose linkage by H-1' correlation with with C-3 (91.5 ppm). In accordance with its quasi-molecular anion at m/z 779.4219 $[M-H]^-$, the structure of compound **4** was established as quinovic acid-3-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-quinovopyranosyl-28-*O*-*β*-D-glucopyranoside.

Compound **5** gave in ESI negative mode an ion peak at m/z 793.4370 $[M-H]^-$, related to the formula $C_{42}H_{66}O_{14}$ similar to **1**. Its ^{1}H NMR spectrum showed two doublets integrating one proton at δ_H 4.70 (H-1', *J* = 1.3 Hz) and at 4.59 (H-1", *J* = 7.8 Hz) characteristic of the osidic units of *α*-L-rhamnopyranose and *β*-D-glucopyranose respectively (Table 2).
Unequivocal information from the HMBC experiment indicated correlations between H-1' and C-3 (90.8 ppm), H-1" (δ_H 4.59) and C-4' (83.6 ppm). Thus, compound **5** was elucidated as quinovic acid 3-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-L-rhamnopyranoside.

Compound 6-8.

The NMR spectra of these compounds showed 30 carbons (Table 3) in the aglycone part, including six methyl groups for H-23, H-24, H-25, H-26, H-29 and H-30, one olefinic proton for H-12, two characteristic carboxyl carbons C-27 and C-28. All spectroscopic evidence supported the presence of cincholic acid aglycone for **6-8**. The difference between these compounds is in the sugar part. Thus the sugar moieties of each compound is described as follows.

The ^{1}H NMR spectrum of **6** showed, two anomeric protons at δ_H 4.40 (H-1', d, *J* = 7.8 Hz) and δ_H 4.68 (H-1", d, *J* = 7.8 Hz) (Table 4), identified as *β*-D-quinovose and *β*-D-glucopyranoside respectively by COSY and HSQC spectrum analysis. The disaccharide *β*-D-glucopyranosyl-(1→4)-*β*-D-quinovopyranoside was determined by HMBC correlation between gluc-H-1" and qui-C-4' (δ_C 82.0) and was attached to the aglycone through a β-quinovose linkage by H-1' correlation to C-3 (90.8 ppm). The compound **6** was elucidated as cincholic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-quinovopyranoside, in agreement with its quasi-molecular anion at m/z 793.4377 $[M-H]^-$, corresponding to a molecular formula of $C_{42}H_{65}O_{14}$.

The molecular formula $C_{42}H_{66}O_{11}$, of compound **7** was obtained by HR-EI-MS at m/z 793.4380 $[M-H]^-$. Its ^{1}H NMR spectrum showed, two osidic units at δ_H 4.70 (H-1', *J* = 1.3 Hz) and 4.60 (H-1", *J* = 7.8 Hz), characteristic of *α*-L-rhamnopyranose and *β*-D-glucopyranose

respectively (Table 4). The osidic sequences of sugar moieties was the same as those obtained in the disaccharide of compound **5**. The structure of **7** was thus proposed based on the data described and named cincholic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-L-rhamnopyranoside.

Compound **8** was assigned to the molecular formula $C_{48}H_{76}O_{19}$ from its negative HRESIMS, which exhibited a molecular ion peak $[M-H]^-$ at m/z 955.4903, suggesting the gain of one hexose unit than **7**. Inspection of the NMR data indicated that **8** contained the same disaccharide chain of *β*-D-glucopyranosyl-(1→4)-*α*-L-rhamnopyranoside linked to C-3 position of the aglycone, compared to **7** (Table 4). The other sugar linked to C-28 was identified as a *β*-D-glucopyranose. The compound **8** was described as cincholic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-*α*- L-rhamnopyranosyl-*28*-*β*-D-glucopyranoside.

The molecular formula of compound **9** was determined to be $C_{53}H_{86}O_{22}$ on the basis of HR-ESI-MS (m/z 1073.5526 $[M-H]^-$, calcd for $C_{53}H_{86}O_{22}$, 1073.5532).
^{1}H NMR and HSQC spectra (Tables 3 and 4) displayed six singlet signals at δ_H 1.02 (H-23), 0.84 (H-24), 0.88 (H-25), 0.93 (H-26), 0.91 (H-29), 0.95 (H-30) belonging to six methyl groups (Table 3). The ^{13}C NMR spectral data showed 29 carbon resonances and 24 osidic carbons characteristic to the 27-nor-triterpenoid glycoside (Table 3). Two olefinic quaternary carbons at δ_C 130.0 (C-13) and 138 (C-14), and a carboxylic acid carbon at 178.2 (C-28) illustrated the pyrocincholic acid skeleton [25]. In addition, ^{1}H NMR spectrum displayed 4 anomeric protons at δ_H 4.30 (d, *J* = 7.8 Hz, H-1'), 5.42 (d, *J* = 8.1 Hz, H-1''), 4.79 (dd, *J* = 8.8 ; 7.8 Hz, H-1‴) and 4.32 (d, *J* = 7.8 Hz, H-1'''') (Table 4). The HSQC and COSY spectra were used, starting with H-1' to identify one *β*-D-quinovopyranose and three *β*-D-glucopyranose parts starting with H-1'', H-1‴ and H-1''''. An unambiguous determination of the sequence and linkage sites was obtained from the HMBC experiment, showing cross peak correlations between H-1' (δ_H 4. 30) and C-3 (δ_C 90.8), H-1''(δ_H 5.42) and C-28 (δ_C 178.2), H-1''' (δ_H 4.79) and C-2'' (δ_C 78.7), and H-1'''' (δ_H 4. 32) and C-6'' (δ_C 69.5). Therefore, the structure pyrocincholic acid-3*β*-*O*-*β*-D-quinovopyranosyl-28-*O*-*β*-D-glucopyranosyl-(1→6)-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucopyranoside was assigned to compound **9**.

Material and methods

General experimental procedures

NMR experiments were carried out in MeOH-d4 on Bruker Avance DRX III 500 instruments. HR-ESI-MS experiments were performed using a Micromass Q-TOF micro instrument. Analytical TLC was performed on precoated silica-gel 60 F_{254} Merck and spots were observed under UV light at 254 and 365 nm or visualized by spraying the dried plates

with 50% H_2SO_4, followed by heating. Silica gel 60 (63-200 mesh, Merck) was used for column chromatography. Extracts were fractionned first on dianion HP-20 resin. HPLC was performed on a Dionex apparatus equipped with an ASI-100 autosampler, an Ultimate 3000 pump, a diode array detector UVD 340S and Chromeleon software. Interchim column (C18 - HQ, 5 µm, 250 x 10 mm) was used for semi-preparative HPLC or preparative HPLC (PLC) with binary gradient eluent (H_2O (filtred at 0.22 with TFA); CH_3CN) and a flow rate of 4 mL/min in semi-preparative HPLC and 20 mL/min in PLC; the chromatogram was monitored at 205, 210, 254 and 365 nm.

Plant material

Hallea ledermannii leaves were collected in November 2018 at Adiopodoumé (Abidjan) in the South region of Côte d'Ivoire (located at 5°20'12" N et 4°7'57" W) and authenticated at the floristic center of University Félix HOUPHOUËT-BOIGNY (Abidjan, Ivory Coast), where a voucher specimen with number UCJ 015307 was deposited.

Extraction and isolation

The dried and powdered stem bark (200 g) of *H. ledermannii* was extracted with MeOH/H_2O (80/20). The hydromethanolic extract was concentrated to obtain a crude extract (24 g), which was dissolved in water (0.2 L) and successively partitioned with dichloromethane and ethyl acetate. The aqueous and ethyl acetate phase were evaporated to yield an aqueous and ethyl acetate fractions.

The aqueous fraction (20 g) was separated into five subfractions (HP1, HP2, HP3, HP4 and HP5) on dianion HP-20 resin, eluated by the AcOEt/MeOH/H_2O.

The HP3 fraction (4.8 g) was chromatographed on normal silica gel eluated with DCM/MeOH/H_2O (90/10/0) to DCM/MeOH/H_2O (60/40 /7) to give fourteen subfractions (F_1-F_{14}).

Fraction F_6 (129.6 mg) was purified in PLC eluting with MeCN / H_2O to give compounds **1** (Rt = 34.06 min ; 3.0 mg) and **12** (Rt = 14.28 min ; 18.0 mg).

Fraction F_8 (880.9 mg) was subjected to flash chromatography on normal silica eluted with the DCM/MeOH to yield 9 subfractions numbered F_{8a} to F_{8i}. The subfraction F_{8h} (463.0 mg) was purified by PLC eluted with MeCN / H_2O to yield compounds **3** (Rt = 19.89 min ; 1.1 mg), **2** (Rt = 23.15 min ; 2.0 mg), **6** (Rt = 21.27 min ; 2.3 mg), **13** (Rt = 21.05 min ; 13.1 mg), **21** (Rt = 21.05 min ; 1.5 mg) and **22** (Rt = 21.19 min ; 18.0 mg). The subfraction F_{8g} (159.1 mg) was purified in semi-prep eluted with MeCN/H_2O to give compounds **14** (Rt = 19.89 min; 1.5 mg) and **15** (Rt = 10.59 min; 6.8 mg).

Fraction F_{11} (360.9 mg) was purified on semi-prep eluted with MeCN / H_2O to afford compounds **5** (Rt = 21.98 min; 1.3 mg), **8** (Rt = 18.44 min; 3.8 mg), **16** (Rt = 19.07 min; 11.3 mg), **17** (Rt = 21.01 min ; 2.5 mg) and **23** (Rt = 17.65 min; 5.7 mg).

Fraction F_{12} (157 mg) was purified in PLC eluting with MeCN/H_2O to give compound **18** (Rt = 10.44 min; 2.2 mg).

Fraction F_{14} (909.9 mg) was purified in semi-prep eluted with MeCN / H_2O to afford compound **9** (Rt = 23.92 min; 6.8 mg).

Fraction HP4 (1.5 g) was chromatographed on normal silica gel eluated with DCM/MeOH/H_2O (90/10/0) to (70 /30/5). Thirteen subfractions (Fa–Fm) were obtained.

Subfraction F_f (278 mg) was purified in semi-prep eluated with MeCN/H_2O to give compound **19** (Rt = 27.53 min ; 3.0 mg).

Subfraction F_i (153 mg) was purified in semi-prep eluated with MeCN/H_2O to give compound **4** (Rt = 32.89 min ; 3.0 mg), **7** (Rt = 31.60 min ; 1.3 mg) and **20** (Rt = 28.38 min ; 7.5 mg).

The ethyl acetate fraction (1.35 g) was subjected to flash chromatography on normal silica eluted with DCM/AcOEt and AcOEt/MeOH mixtures. Ten fractions were obtained. Fraction F_5 (121.8 mg) was purified in PLC eluted with MeCN/H_2O to give compounds **10** (Rt = 44.47 min; 21.7 mg) and **11** (Rt = 44.47 min; 20.3 mg).

Quinovic acid-3β-*O*-6-deoxy-β-D-allofuranosyl-28-*O*-*β*-D-glucopyranoside (**1**)

White amorphous powder, $[\alpha]_D^{20}$ +22 (*c* 0.150, MeOH), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra data, see Table 1 and Table 2, HR-ESI-MS *m/z* 791.4220 $[M-3H]^{3-}$ (calcd $C_{42}H_{63}O_{14}$, 791.4218)

Quinovic acid-3β-*O*-6-deoxy-β-D-allopyranosyl-28-*O*-β-D-glucopyranoside (**2**)

White amorphous powder, $[\alpha]_D^{20}$+20 (*c* 0.050, MeOH), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra data, see Table 1 and Table 2, HR-ESI-MS *m/z* 793.4382 $[M-H]^-$ (calcd $C_{42}H_{65}O_{14}$, 793.4374).

Quinovic acid-3-*O*-*β*-D-xylopyranosyl-28-*O*-*β*-D-glucopyranoside (**3**)

White amorphous powder, $[\alpha]_D^{20}$+ 22 (*c* 0.100, MeOH), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra data, see Table 1 and Table 2, HR-ESI-MS *m/z* 779.4219 $[M-H]^-$ (calcd $C_{41}H_{63}O_{14}$, 779.4218).

Quinovic acid-3-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-quinovopyranosyl-28-*O*-*β*-D-glucopyranoside (**4**)

White amorphous powder, $[\alpha]_D^{20}$+ 41.6 (*c* 0.480, MeOH) ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD spectra data, see Table 1 and Table 2, HR-ESI-MS *m/z* 955.4903 $[M-H]^-$ (calcd $C_{48}H_{75}O_{19}$, 955.4903).

Quinovic acid 3-*O*-*β*-D-glucopyranosyl-(1→4)-α-L-rhamnopyranoside (**5**)

White amorphous powder, $[\alpha]_D^{20}$+ 35 (*c* 0.508, MeOH), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra data, see Table 1 and Table 2, HR-ESI-MS *m/z* 793.4370 $[M-H]^-$ (calcd $C_{42}H_{65}O_{14}$, 793.4374).

Cincholic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-β-D-quinovopyranoside (**6**)

White amorphous powder, $[\alpha]_D^{20}$+ 0.0 (*c* 0.65, MeOH), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra data, see Table 3 and Table 4, HR-ESI-MS *m/z* 793.4377 $[M-H]^-$ (calcd $C_{42}H_{65}O_{14}$, 793.4374).

Cincholic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-L-rhamnopyranoside (**7**)

White amorphous powder, $[\alpha]_D^{20}$- 1.5 (c 0.065, $CHCl_3$), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra data, see Table 3 and Table 4, HR-ESI-MS *m/z* 793.4374 $[M-H]^-$ (calcd $C_{42}H_{65}O_{14}$, 793.4374).

Cincholic acid-3-*O*-*β*-D-glucopyranosyl-(1→4)-α-L-rhamnopyranosyl-28-β-D-glucopyranoside (**8**)

White amorphous powder, $[\alpha]_D^{20}$+ 9.5 (*c* 0.190, MeOH), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (125 MHz, CD_3OD) spectra data, see Table 3 and Table 4, HR-ESI-MS *m/z* 955.4911 $[M-H]^-$ (calcd $C_{48}H_{75}O_{19}$, 955.4903).

Pyrocincholic acid-3-*O*-*β*-D-quinovopyranosyl-28-*O*-*β*-D-glucopyranosyl-(1→6)-[*β*-D-glucopyranosyl-(1→2)]-*β*-D-glucopyranoside (**9**)

White amorphous powder, $[\alpha]_D^{20}$+6.7 (*c* 0.340, MeOH), ^{1}H NMR (500 MHz, CD_3OD) and ^{13}C NMR (150 MHz, CD_3OD) spectra data, see Table 3 and Table 4, HR-ESI-MS *m/z* 1073.5526 $[M-H]^-$ (calcd $C_{53}H_{85}O_{22}$, 1073.5532).

Acid hydrolysis of saponin mixture

The crude saponin mixture (100 mg) was refluxed with 300 ml of 2 N TFA for 3 h. The sapogenin was extracted with EtOAc (300 ml), and evaporated to dryness. The aqueous layer was freeze-dried. Seven sugars were identified with authentic samples by TLC as D-(glucose, fucose, quinovose, 6-deoxy-allo*furanose,* 6-deoxy-allo*pyranose* and xylose) and L-rhamnose.

Conclusion

Twenty-three saponins have been isolated from *Hallea ledermannii*. Sixteen were derivated from quinovic acid (**1-5, 10-20**), six from cinchonic acid (**6**-**8** and **21-23**) and one from

pyrocinchonic acid (**9**). This is the first report of triterpenoid saponins from *H. ledermannii,* among them (**1-9**) are newly described in the literature.

This study will contribute to a better understanding of the correlation of the described structures and the claim medicinal and pharmacological activities of this plant. Therefore, biological studies of isolated compounds are being evaluated to make this plant an effective source of pharmaceuticals.

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Appendix A. Supplementary data

Supplementary data to this article can be found online

Declaration of Conflicting Interests

The authors declare that there are no competing interests or personal relationships that could influence the work reported in this article.

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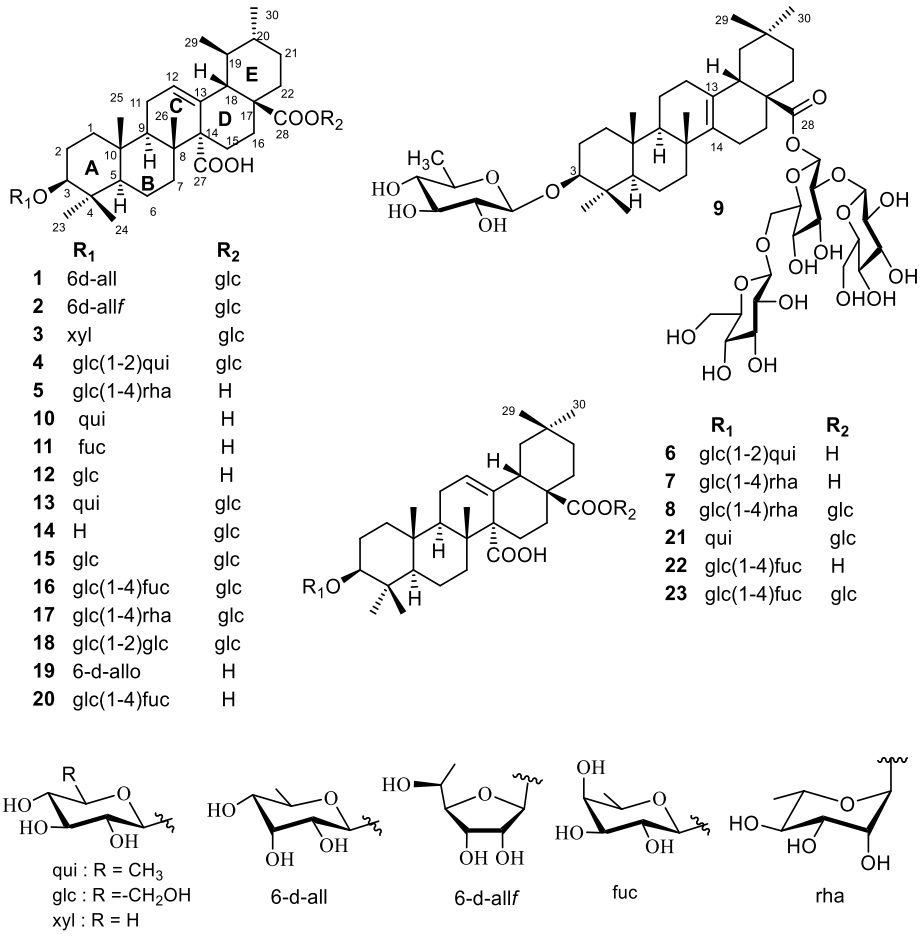

Figure 1 : Triterpenoid saponins isolated from stem bark of *H. ledermannii*

Table 1 : ^{1}H and ^{13}C NMR spectroscopic data of the aglycone moieties of compounds **1**- **5** (in CD_3OD)

	1		**2**		**3**		**4**		**5**	
	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	δ_H m (J_{Hz})	δ_C
1	1.02 m ; 1.69 m	39.7	0.97 m ; 1.69 m	40.0	1.02 m; 1.70 m	39.9	1.04 m ; 1.71	40.0	1.00 m; 1.69 m	39.9
2	1.70 m ; 1.93 m	27.9	1.63 dt (13.3; 3.2) 1.85 m	27.1	1.69 m 1.83 m	27.2	1.72 m; 1.96 m	27.2	1.65 m ; 1.79 m	27.2
3	3.17 d (11.5; 4.5)	90.1	3.08 dd (11.8;4.7)	90.7	3.10 dd (11.5; 4.4)	90.6	3.17 dd (11.5;4.5)	91.4	3.10 dd (11.8; 4.7)	90.8
4	-	40.1	-	40.1	-	40.1	-	40.4	-	40.1
5	0.71 d (11.3)	56.6	0.73 d (11.6)	57.0	0.75 d (11.2)	56.9	0.73 d (11.7)	57.0	0.74 d (12.2)	57.0
6	1.35 m 1.51 m	19.2	1.35 dt (13.6, 2.6) 1.51 td (13.6;3.2)	19.3	1.34 dt (13.1; 2.6) 1.52 td (13.1; 3.2)	19.3	1.34 td (13.1; 3.5) 1.50 dt (13.1;3.4)	19.3	1.35 m ; 1.51 m	19.3
7	1.21 m 1.67 m	38.1	1.21 m 1.63 dt (13.3; 3.2)	38.0	1.19 dt (13.3; 3.5) 1.64 dt (13.5; 3.4)	38.0	1.20 td (13.7; 4.2) 1,70 m	38.0	1.21 m ; 1.65 m	38.0
8	-	40.8	-	40.8	-	40.8	-	40.8	-	40.7
9	2.21 dd (11.5;5.3)	48.0	2.21 dd (11.3;5.1)	48.1	2.21 dd (11.4; 6.0)	48.1	2.20 dd (11.3;5.3)	48.1	2.23 dd (12.1; 5.1)	48.9
10	-	37.8	-	37.8	-	37.8	-	37.8	-	37.8
11	1.90 m ; 1.98 m	23.8	1.93 m ; 1.97 m	23.9	1.93 m ; 1.97 m	23.9	1.92 m ; 1.98 m	23.9	1.92 m; 1.95 m	23.8
12	5.62 dd (5.0; 2.3)	130.9	5.62 dd (4.7; 2.5)	130.9	5.62 dd (5.0; 2.5)	130.9	5.62 dd (4.4; 2.7)	130.9	5.61 dd (4.8; 2.2)	130.5
13	-	133.3	-	133.3	-	133.2	-	133.3	-	133.9
14	-	57.3	-	57.3	-	57.3	-	57.3	-	57.3
15	1.78 m 2.10 m	26.4	1.77 m 2.10 td (14.5; 3.2)	26.4	1.75 m 2.09 td (13.5; 3.4)	26.4	1.76 m 2.08 td (13.3; 3.4)	26.4	1.70 m; 2.06 m	26.5
16	1.77 m; 2.06 m	25.8	1.70 m; 2.06 m	25.8	1.70 m; 2.03 m	25.8	1.77 m; 2.04 m	25.8	1.73 m; 2.05 m	25.7
17	-	48.6	-	48.9	-	48.9	-	49.4	-	48.9
18	2.29 d (10.5)	55.3	2.29 d (10.5)	55.3	2.29 d (10.7)	55.3	2.29 d (10.7)	55.3	2.25 d (10.5)	55.5
19	0.98 m	40.2	0.98 m	40.3	0.95 m	40.3	0.98 m	40.4	0.98 m	40.4
20	1.01 m	38.1	1.01 m	38.3	1.02 m	38.3	1.01 m	38.2	1.01 m	38.3
21	1.29 m ; 1.51 m	31.1	1.29 m ; 1.51 m	31.1	1.25 m; 1.46 m	31.2	1.29 m ; 1.49 m	31.2	1.25 m, 1.46 m	31.2
22	1.61	37.0	1.61; 1.71 m	37.0	1.60 td (13.5, 3.5); 1.74 m	37.0	1.62 td (13.4; 4.0)	37.0	1.60 td (13.5; 3.6); 1.71 m	37.6
23	1.00 s	28.7	1.01 s	28.6	1.01 s	28.5	1.04 s	28.4	0.98 s	28.5
24	0.81 s	16.9	0.82 s	17.1	0.82 s	17.1	0.82 s	17.0	0.79 s	17.0
25	0.96 s	16.8	0.97 s	16.9	0.97 s	17.0	0.97 s	17.0	0.90 s	16.9
26	0.88 s	18.9	0.89 s	19.2	0.89 s	19.2	0.88 s	19.2	0.89 s	19.1
27	-	179.1	-	179.1	-	179.1	-	179.1	-	179.1
28	-	177.9	-	177.9	-	177.9	-	177.9	-	181.5
29	0.92 d (5.6)	18.1	0.91 d (6.3)	18.3	0.92 d (6.2)	18.1	0.92 d (5.7)	19.1	0.90 d (6.3)	18.2
30	0.93 d (5.6)	21.5	0.92 d (6.0)	21.5	0.93 d (5.9)	21.5	0.91 d (5.7)	21.5	0.92 d (6.0)	21.5

Table 2 : ^{1}H and ^{13}C NMR spectroscopic data of the sugar moieties of compounds **1**-**5** (in CD_3OD).

	1		**2**		**3**		**4**		**5**	
	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	δ_H m (J_{Hz})	δ_C
	6-d-all*f* – in 3		**6-d-all – in 3**		**xyl in 3**		**qui in 3**		**rha-in 3**	
1'	4.38 d (7.9)	107.7	4.60 d (8.0)	104.1	4.25 d (7.6)	107.5	4.39 d (7.8)	105.4	4.70 d (1.3)	104.1
2'	4.10 dd (7.9; 1.6)	79.0	3.31 m	72.9	3.16 dd (9.0; 7.9)	75.5	3.51 t (8.2)	81.0	3.84 dd (3.5; 1.3)	72.3
3'	3.85 dd (9.7; 1.6)	79.0	3.4 t (2.9)	73.3	3.27 t (9.0)	78.0	3.49 t (8.5)	78.5	3.86 dd (9.1; 3.5)	72.6
4'	3.32 m	73.6	3.13 dd (9.5; 2.9)	74.4	3.45 m	71.2	2.99 t (8.5)	71.6	3.60 t (9.1)	83.6
5'	3.37 m	71.2	3.70 m	70.3	3.17 t (11.2) ; 3.81 dd (11.2; 5.4)	66.7	3.26 m	77.7	3.75 dq (9.1; 6.2)	68.6
6'	1.40 d (6.4)	18.1	1.21 d (6.2)	18.1			1.25 d (6.2)	18.1	1.30 d (6.2)	18.0
	glc-en 28		**glc-en 28**		**glc-en 28**		**glc-en 28**		**glc in 4 -rha**	
1''	5.40 d (8.2)	95.6	5.40 d (8.1)	95.6	5.40 d (8.2)	95.6	5.40 d (8.1)	95.6	4.59 d (7.8)	105.7
2''	3.31	73.9	3.31 m	73.9	3.31 m	73.9	3.31 m	73.9	3.23 dd (8.8; 7.8)	76.1
3'	3.40 t (9.4)	78.6	3.40 t (9.3)	78.3	3.40 t (9.1)	78.3	3.34 t (8.5)	78.3	3.36 t (8.8)	78.2
4''	3.35 t (9.4)	71.2	3.35 t (9.3)	71.2	3.37 t (9.1)	71.3	3.35 t (8.5)	71.2	3.29 t (8.8)	71.5
5''	3.34 m	78.3	3.34 m	78.6	3.33 m	78.7	3.32 m	78.6	3.25 ddd (7.7; 5.5; 2.5)	78.2
6''	3.68 dd (12.5;4.2)	62.5	3.68 dd (12.4; 5.1)	62.5	3.67 dd (12.1; 4.6)	62.5	3.68 dd (12.1, 5.4)	62.5	3.68 dd (11.9; 5.5)	62.7
	3.80 dd (12.5;1.9)		3.80 dd (12.4; 1.8)		3.81 dd (12.1; 1.8)		3.80 dd (12.1, 1.2)		3.84 dd (11.9; 2.5)	
							glc in 2 qui			
1'''							4.68 d (7.8)	104.4		
2'''							3.20 dd (8.7, 7.8)	76.3		
3'''							3.40 t (8.7	77.9		
4'''							3.17 t (8.7)	71.9		
5'''							3.23 m	78.3		
6'''							3.60 dd (12.1, 5.9)	63.1		
							3.81 dd (12.1, 2.8)			

Table 3 : ^{1}H and ^{13}C NMR spectroscopic data of the aglycone moiety of compounds **6-9** (in CD_3OD)

	6		**7**		**8**		**9**	
	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	1.01 m ; 1.66 m	39.9	1.01 m; 1.66 m	39.9	1.00 m ; 1.67 m	39.8	0.93 m; 1.74 m	39,4
2	1.70 m ; 1.89 m	27.0	1.70 m; 1.85 m	27.2	1.69 m; 1.77 m	26.6	1.70 td (13.5, 3.5) 1.79 m	27,2
3	3.10 dd (11.6;4.5)	90.8	3.10 dd (11.6;4.5)	90.8	3.04 dd (11.4; 4.5)	90.3	3.11 dd (11.8, 4.8)	90,8
4	-		-	40.1	-	40.1	-	40,2
5	0.71 d (12.1)	57.2	0.71 d (12.1)	57.1	0.74 d (11.9)	56.8	0.78 dd (12.0; 1.8)	57,1
6	1.35 m 1.53 m	19.2	1.35 m 1.53 m	19.3	1.35 m 1.50 dt (12.8; 3.5)	19.4	1.49 m; 1.70 m	19,6
7	1.24 m 1.65 m	38.7	1.24 m 1.65 m	37.9	1.23 td (13.3; 2.8) 1.55 dt (13.3; 3)	37.8	1.14 dt (13.5; 3.7) 1.83 m	40,8
8	-	40.7	-	40.6	-	40.7	-	38,9
9	2.10 dd (11.6 ;5.7)	48.3	2.10 dd (11.6;5.7)	48.0	2.09 m	48.1	0.97 dd (12.6 ; 1.6)	57,7
10	-	37.9	-	37.9	-	37.9	-	38,2
11	1.92 m ; 1.94 m	24.0	1.92 m; 1.94 m	23.9	1.90 m ; 1.95 m	24.0	1.42 m; 1.55 m	18,9
12	5.6 br s	127.9	5.64 br s	127.5	5.65 t (3.5)	127.8	1.78 m; 2.23 m	32,7
13	-	137.3	-	137.8	-	137.4	-	131,1
14	-	57.1	-	57.1	-	57.2	-	138,0
15	1.67 m ; 2.06 m	25.1	1.67 m ; 2.06 m	25.5	1.67 m ; 2.06 m	25.6	1.96 m; 2.22 m	22,0
16	1.65 m; 2.04 m	25.6	1.65 m; 2.04 m	25.1	1.75 m; 2.09 m	25.1	1.80 m; 1.94 m	24,0
17	-	48.6	-	48.6	-	48.9	-	46,5
18	2.89 dd (13.4;3.7)	44.6	2.89 dd (13.4;3.7)	44.7	2.90 dd (13.5; 3.4)	44.6	2.41 dd (12.3, 3.5)	40,3
19	1.11 m ; 1.40 t (13.5)	44.6	1.11 m ; 1.40 t (13.5)	44.7	1.12 m	44.6	1.06 m ; 1.50 m	42,4
20	-	31.6	-	31.6	1.40 t (14.3)	31.6	-	31,4
21	1.19 m ; 1.35 m	34.7	1.19 m; 1.35 m	34.8	1.20 m ; 1.32 m	34.7	1.22 m ; 1.47 m	35,1
22	1.51 m ; 1.75 td (13.5 ; 3.5)	32.7	1.51 m ; 1.75 td (13.5;3.5)	33.3	1.55 td (12.1; 3.5); 1.73 m	32.7	1.58 m; 1.80 m	32,0
23	1.02 s	28.5	1.02 s	28.4	0.91 s	28.7	1.02 s	28,3
24	0.82 s	17.0	0.82 s	16.9	0.78 s	17.0	0.84 s	16,8
25	0.97 s	16.9	0.97 s	16.8	0.97 s	16.9	0.88 s	17,1
26	0.92 s	17.4	0.92	18.9	0.88 s	19.0	0.93 s	21,5
27	-	180.0	-	179.8	-	180.0	-	
28	-	181.0	-	181.7	-	178.0	-	178,2
29	0.87 s	33.6	0.87 s	33.6	0.87 s	33.6	0.91 s	33,2
30	0.92 s	24.0	0.89 s	24.0	0.92 s	24.0	0.95 s	25,6

Table 4 : ^{1}H and ^{13}C NMR spectroscopic data of the sugar moieties of compounds **6-9** (in CD_3OD).

	6		**7**		**8**		**9**	
	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
	qui-in 3		**rha-in 3**		**rha-in 3**		**Qui – in 3**	
1'	4.40 d (7.8)	107.0	4.70 d (1.3)	104.1	4.69 brs	104.2	4.30 d (7.8)	106.6
2'	3.58 dd (9.0 ; 7.8)	82.0	3.83 dd (3.5 ; 1.3)	72.3	3.83 dd (3.5 ; 1.0)	72.3	3.21 t (8.5)	75.9
3'	3.50 t (9.0)	79.1	3.86 dd (9.1 ; 3.5)	72.6	3.85 dd (9.1 ; 3.5)	72.5	3.24 m	77.9
4'	3.00 t (9.0)	77.8	3.60 t (9.1)	83.6	3.61 t (9.1)	83.6	2.99 t (9.2)	77.0
5'	3.30 m	73.8	3.75 dq (9.1 ; 6.2)	68.6	3.78 dq (8.9 ; 6.2)	68.6	3.25 m	73.0
6'	1.28 d (6.2)	19.2	1.30 d (6,2)	16.6	1.30 d (6.2)	18.0	1.26 d (6,2)	18.2
	glc in 2 -qui		**glc in 4 -rha**		**glc in 4 -rha**		**glc1 in 28**	
1"	4.68 d (7.8)	105.9	4.60 d (7.8)	105.7	4.57 d (7.8)	105.7	5.42 d (8.1)	94.0
2"	3.21 dd (8.5 ; 7.8)	75.9	3.21 dd (8.9 ; 7.8)	76.1	3.20 dd (8.9 ; 7.8)	76.1	3.62 t (8.1)	78.7
3"	3.35 m	78.3	3.36 t (8.9)	78.2	3.40 t (8.9)	78.2	3.65 t (8.1)	78.6
4"	3.17 t (8.9)	71.5	3.30 t (8.9)	71.5	3.30 t (8.9)	71.4	3.49 t (8.1)	70.7
5"	3.25 m	78.1	3.26 ddd (7.7; 5.5; 2.5)	78.2	3.24 ddd (7.2; 4.9; 1.9)	78.0	3.50 m	75.7
6"	3.62 dd (12.0 ; 5.5)	62.8	3.68 dd (11.9; 5.5)	62.7	3.68 dd (11.5 ; 4.9)	62.7	3.77 dd (11.5, 3.5)	69.5
	3.81 dd (12.0 ; 2.2)		3,84 dd (11.9 ; 2.5)		3.84 dd (11.5 ; 1.9)		4.11 dd (11.5, 1.1)	
					glc-in 28		**glc in 2 –glc1**	
1‴					5.40 d (8.2)	95.6	4.79 d (7.8)	104.0
2‴					3.34 t (8.2)	73.9	3.23 dd (8.8, 7.8)	75.9
3‴					3.35 t (8.2)	78,3	3.36 t (8.8)	78.0
4‴					3.36 t (8.2)	71.1	3.21 t (8.8)	72.3
5‴					3.40 m	78.7	3,25 m	78.2
6‴					3.70 dd (12.0; 5.5)	62.4	3.66 brd (11.5)	63.5
					3.84 dd (12.0; 2.7)		3.90 dd (11.5, 2.4)	
							glc in 6–glc1	
1⁗							4.32 d (7.8)	104.7
2⁗							3.23 t (7.8)	75.1
3⁗							3.30 m	78.0
4⁗							3.27 t (8.9)	71.6
5⁗							3.25 m	78.0
6⁗							3.64 brd (11.9)	62.8
							3.85 dd (11.9, 2.5)	