Antibacterial Ellagic Acid Derivatives and Other Constituents from *Pancovia pedicellaris*

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Two new ellagic acid derivatives, named panconosides A (**1**) and B (**2**) were isolated from *Pancovia pedicellaris* together with eleven known compounds (**3** – **13**). The structures of **1** and **2**, as well as those of the known compounds were established by spectroscopic methods and by comparison with previously reported data. Compounds **1** and **2** were tested *in vitro* for their antibacterial potential against six strains of microorganisms: *Micrococcus luteus*, *Streptococcus ferus*, *Streptococcus minor*, *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas agarici*. They were found to exhibit moderate antibacterial activity against all the tested strains compared to standard drugs.

Key words: Pancovia pedicellaris, Sapindaceae, Ellagic Acid Derivatives, Panconosides A and B, Antibacterial Activity

Introduction

Plants of *Pancovia* genus (Sapindaceae) are trees or shrubs generally found in tropical or subtropical regions. In Cameroon, they are used in traditional medicine for the treatment of several ailments such as skin diseases, dysentery and rheumatism [1]. Previous phytochemical studies on plants of this family reported the presence of various classes of secondary metabolites including flavonoids, coumarins, ellagic acid, and saponins as major constituents [2 – 5]. Some of these compounds were shown to exhibit interesting pharmacological properties including antiplasmodial, haemolytic and antioxidant activities [5 – 7]. *Pancovia pedicellaris* Radlk & Gilg is a tree or shrub of about 5 – 10 m high, found in Central Africa [1]. No previous reports on the chemical constituents or biological properties of this species have been reported. As part of our ongoing search for bioactive metabolites from Cameroonian plants, we recently investigated extracts from the leaves and the stem bark of *P. pedicellaris*. In this paper, we report the results of these investigations which led to two new ellagic acid derivatives, panconosides A (**1**) and B (**2**), together with eleven known compounds identified as 3,3′,4′-tri-*O*-methylellagic acid 4-*O*-β-D-glucopyranoside (**3**), allantoin (**4**), L-quebrachitol (**5**), stigmasterol (**6**), umbelliferone (**7**), scopoletin (**8**), 8′-*epi*-cleomiscosin A (**9**), 3-oxotirucalla-7,24-dien-21-oic acid (**10**), benjaminamide (**11**), 3-*O*-β-D-glucopyranosylstigmasterol (**12**), and 7-oxostigmasteryl-3-*O*-β-D-glucopyranoside (**13**).

Results and Discussion

The air-dried, powdered leaves and stem bark of *P. pedicellaris* were extracted separately with MeOH. The crude extract from the leaves obtained after concentration was further extracted with *n*-hexane, and the MeOH soluble fraction subjected to successive column chromatography over silica gel to yield five compounds, including the two new ellagic acid derivatives, *i. e.* the panconosides A (**1**) and B (**2**), 3,3′,4′-tri-*O*-methylellagic acid 4-*O*-β-D-glucopyranoside (**3**) [8], allantoin (**4**) [9], and L-quebrachitol (**5**) [10].

The crude MeOH extract obtained from the stem bark was extracted with EtOAc, and the EtOAc-soluble fraction subjected to repeated column chromatography over silica gel. This process yielded

Table 1. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) data for **1** and **2** in [D$_6$]DMSO.

Position	**1**		**2**	
	δc	δ_H [m, J (Hz)]	δc	δ_H [m, J (Hz)]
1	112.8		112.6	
2	141.7		141.7	
3	142.2		142.4	
4	152.1		151.6	
5	112.6	7.90 (s)	112.2	7.83 (s)
6	114.2		114.2	
7	158.6		158.6	
1′	113.1		113.1	
2′	141.6		141.6	
3′	141.3		141.3	
4′	154.8		154.8	
5′	108.0	7.63 (s)	108.0	7.65 (s)
6′	113.3		113.3	
7′	158.8		158.8	
1″	101.3	5.40 (d, J = 8.2)	99.0	5.46 (d, J = 7.5)
2″	72.0	3.63 (m)	76.7	3.63 (m)
3″	78.0	5.17 (t, J = 9.4)	77.5	3.46 (m)
4″	67.9	3.55 (m)	70.1	3.24 (t, J = 8.8)
5″	77.4	3.65 (br s)	77.7	3.56 (br t, J = 8.8)
6″a	60.6	3.73 (dd, J = 11.3; 5.1)	60.8	3.65 (m)
6″b		3.57 (m)		3.48 (m)
1‴	120.4		100.7	5.26 (d, J = 1.3)
2‴	109.3	7.04 (s)	70.9	3.37 (br s)
3‴	145.9		70.8	3.72 (m)
4‴	138.6		72.3	3.18 (t, J = 9.4)
5‴	145.9		69.0	3.70 (m)
6‴	109.3	7.04 (s)	18.5	1.11 (d, J = 6.3)
7‴	165.9			
3-OMe	62.2	4.10 (s)	62.2	4.11 (s)
3′-OMe	61.8	4.06 (s)	61.8	4.05 (s)
4′-OMe	57.2	4.01 (s)	57.2	4.01 (s)

the known compounds stigmasterol (**6**) [11], umbelliferone (**7**) [12], scopoletin (**8**) [13], 8′-*epi*-cleomiscosin A (**9**) [14], 3-oxotirucalla-7,24-dien-21-oic acid (**10**) [15], benjaminamide (**11**) [16], 3-*O*-β-D-glucopyranosylstigmasterol (**12**) [11], and 7-oxostigmasteryl-3-*O*-β-D-glucopyranoside (**13**) [17]. The known compounds **3**–**13** were identified by analysis of their MS, ^{1}H and ^{13}C NMR data as well as by comparison with previously reported data and authentic samples.

Compound **1** was obtained as beige crystals and gave a positive reaction with ferric chloride, indicating its phenolic nature. It also responded positively to the Molish test, suggesting that it was a glycoside. Its elemental composition $C_{30}H_{26}O_{17}$, with 18 degrees of unsaturation, was deduced from its HRMS ((+)-ESI) which exhibited a pseudo-molecular ion peak $[M+Na]^+$ at *m/z* = 681.10664 (calculated *m/z* = 681.10991). Its UV spectrum (λ_{max} = 255, 280 and 355 nm) was similar to that of ellagic acid derivatives, suggesting that this compound has an ellagic acid skeleton [18, 19]. The IR spectrum displayed characteristic absorptions for hydroxy groups (3420 cm^{-1}), lactone functions (1748 cm^{-1}), aromatic C=C groups (1611 cm^{-1}), and glycosidic C–O bonds (1085 cm^{-1}). The broad band-decoupled ^{13}C NMR spectrum (Table 1) of compound **1** displayed only 28 carbon signals which were sorted by DEPT and HSQC techniques into eight methines including three aromatic methine carbons and five oxymethine carbons, one oxymethylene, fifteen quaternary aromatic carbons including two carbonyls of α, β-unsaturated lactone groups at δ = 158.6 and 158.8 [8], one ester carbonyl group at δ = 165.9 and three methoxy carbons at δ = 57.2, 61.8, and 62.2, respectively. The fact that only 28 carbon signals were observed in the ^{13}C NMR spectrum of **1** compared to the 30 carbons of the molecular formula was very significant and suggested that it possessed a unit of symmetry. The ^{1}H and ^{13}C NMR spectra (Table 1) also indicated the presence of a sugar residue. The signals at δ = 101.3, 78.0, 77.4, 72.0, 67.9, and 60.6 in the ^{13}C NMR spectrum suggested that the sugar moiety in **1** was a glucopyranoside [8]. The coupling constant between the anomeric protons H-1″ [δ = 5.40 (d, J = 8.2 Hz)] and H-2″ [δ = 3.63 (m)] corresponded to two *trans* diaxial protons, suggesting a chair conformation of the carbohydrate moiety with the C-1″ and C-2″ substituents in equatorial position and indicating the presence of a β-glucoside. Its ^{1}H NMR spectrum (Table 1) showed also four aromatic protons as singlets at δ = 7.90 (s, H-5), 7.63 (s, H-5′), and 7.04 (s, H-2‴/H-6‴) and three methoxy groups (δ = 4.01, 4.06 and 4.10). The 28 carbon signals observed in the ^{13}C NMR of compound **1** include, besides glucopyranosyl and methoxy carbons, those for the two 7-carbon units of an ellagic acid skeleton and those for another highly oxygenated phenyl ring attributed to a gallic acid moiety with the carbonyl group at δ = 165.9 [20]. The

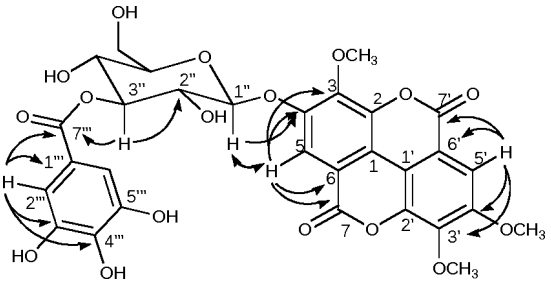

Fig. 1. Selected HMBC (→) and NOESY (↔) correlations in compound **1**.

ellagic acid moiety was confirmed by its HMBC correlations, in particular those from H-5 (δ = 7.90) to C-3, C-4, C-6 and C-7 and from H-5′ (δ = 7.63) to C-3′, C-4′, C-6′ and C-7′. The location of the methoxy groups at C-3′, C-4′ and C-3 of the ellagic acid skeleton was also deduced from correlations observed between the methoxy protons at δ = 4.01 (OMe-4′), 4.06 (OMe-3′) and 4.10 (OMe-3) and C-4′ (δ = 154.8), C-3′ (δ = 141.3) and C-3 (δ = 142.2), respectively. The presence of the gallic acid moiety was confirmed by the two-proton singlet signal observed at δ = 7.04 indicating a 3, 4, 5-trihydroxy substitution pattern in one of the aromatic rings in **1**. The aromatic methine H-2‴ (δ = 7.04) showed no HMBC correlations with the ellagic acid skeleton, but with C-1‴, C-3‴, C-4‴ and C-7‴, supporting the existence of the gallic acid unit. To establish the connectivity between the ellagic acid moiety and the glucose on one hand and between the sugar and the gallic acid moiety on the other hand, use was made of observed HMBC correlations in compound **1** (Fig. 1). The correlation observed from the anomeric proton H-1″ (δ = 5.40) to C-4 (δ = 152.1) clearly indicates that the glucose unit was linked to C-4 of the aglycon (ellagic acid skeleton). Those from the proton H-3″ (δ = 5.17) of the glucose moiety to C-7‴ (δ = 165.9, carbonyl group), C-2″ (δ = 72.0) and C-4″ (δ = 67.9) suggest that the galloyl unit was linked to the glucose moiety across C-3″ (δ = 78.0). Additionally, the location of the glucose substituent was further confirmed by the observation of an NOE between the anomeric proton H-1″ (δ = 5.40) and H-5 (δ = 7.90) in the NOESY spectrum. Thus compound **1** was determined as 3,3′,4′-tri-*O*-methylellagic acid 4-*O*-(3″-galloyl)-β-D-glucopyranoside, named panconoside A.

Compound **2** was obtained as yellow crystals. Its molecular formula $C_{29}H_{32}O_{17}$ was determined from HRMS ((+)-ESI) which showed the pseudo-molecular ion peak at *m/z* = 675.15354 $[M+Na]^+$ (calculated *m/z* = 675.15686) corresponding to 14 degrees of unsaturation. It responded positively to the Molish test, suggesting its glycoside nature. Its UV spectrum (λ_{max} = 255, 360 nm) was similar to that of ellagic acid derivatives, suggesting that compound **2** like compound **1** had an ellagic acid skeleton [18, 19]. The IR spectrum displayed characteristic absorptions for hydroxy groups (3430 cm^{-1}) and lactone functions (1749 cm^{-1}), aromatic C=C groups (1600 cm^{-1}), and glycosidic C–O bonds (1090 cm^{-1}). The broad band-decoupled ^{13}C NMR of compound **2** showed 29 carbon signals which were sorted by DEPT and HSQC experiments into twelve methine groups including two aromatic methine carbons and ten oxymethine carbons, one oxymethylene, twelve quaternary aromatic carbons, including two lactone carbons and six oxygen-bearing carbons, and three methoxy groups as well as one methyl group at δ = 18.5 (Table 1). The NMR spectroscopic data of **2** were similar to those of compound **1**, but lacked signals for a gallic acid moiety. Its ^1H NMR spectrum exhibited in addition to signals for an ellagic acid moiety [δ = 7.83 (s, H-5) and 7.65 (s, H-5′)], and a glucopyranosyl group, five oxygen-bearing methine protons, along with a doublet methyl proton signal [δ = 1.11 (d, *J* = 6.3 Hz)] indicating the presence of a 6-deoxy sugar. The second sugar unit was easily determined as rhamnose through analysis of chemical shifts and coupling constant patterns of its proton signals (Table 1) which were connected by a ^1H-^1H COSY spectrum. In addition, the set of chemical shifts observed at δ = 100.7, 70.9, 70.8, 72.3, 69.0, and 18.5 (C-1‴ to C-6‴) resembled the corresponding signals of substituted rhamnose glycosides [18]. The anomeric protons (H-1″, H-1‴) of the sugar units were observed at δ = 5.46 (d, *J* = 7.5 Hz, H-1″) and 5.26 (d, *J* = 1.3 Hz, H-1‴) and attributed to glucose and rhamnose, respectively. The values of the coupling constants suggest the β configuration for glucose [8] and α for rhamnose [18]. The junction between the rhamnose and glucose and between the glucose and the ellagic acid moiety were made using the correlations observed in the HMBC spectrum (Fig. 2). In particular, those observed from the anomeric protons [H-1″ (δ = 5.46)] to C-4 (δ = 151.6) and [H-1‴ (δ = 5.26)] to C-2″ (δ = 76.7) indicated that the glucose was linked to the aglycon at position C-4, and the rhamnose to glucose at position C-2″ ($C_{1‴}$-O-$C_{2″}$ junction), respectively. In the NOESY experiment, the observation of an NOE between H-5 (δ = 7.83) and H-1″ (δ = 5.46) supported the location of the glucose unit. Acid hydrolysis of

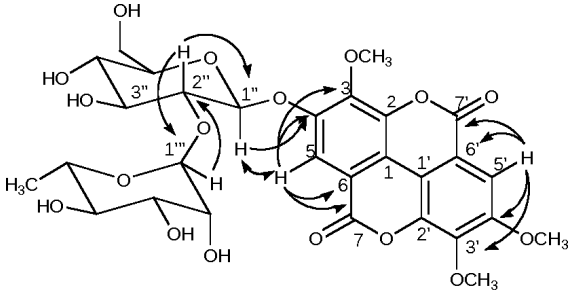

Fig. 2. Selected HMBC (→) and NOESY (↔) correlations in compound **2**.

Tested compound	MIC (μg mL^{-1}) Tested microorganisms					
	M. luteus	*E. coli*	*P. agarici*	*S. ferus*	*B. subtilis*	*S. minor*
Leaves[a]	156.25	39.06	78.12	78.12	78.12	39.06
Stem[a]	19.53	9.76	9.76	156.25	78.12	19.53
1	78.12	78.12	39.06	39.06	78.12	39.06
2	na	78.12	78.12	na	na	na
Ampicillin	0.01	nt	nt	1.95	3.90	3.90
Gentamicin	nt	2.44	3.90	nt	nt	nt

Table 2. *In vitro* antibacterial activity of compounds **1**, **2** and extracts.

[a] = extract; na = not active; nt = not tested.

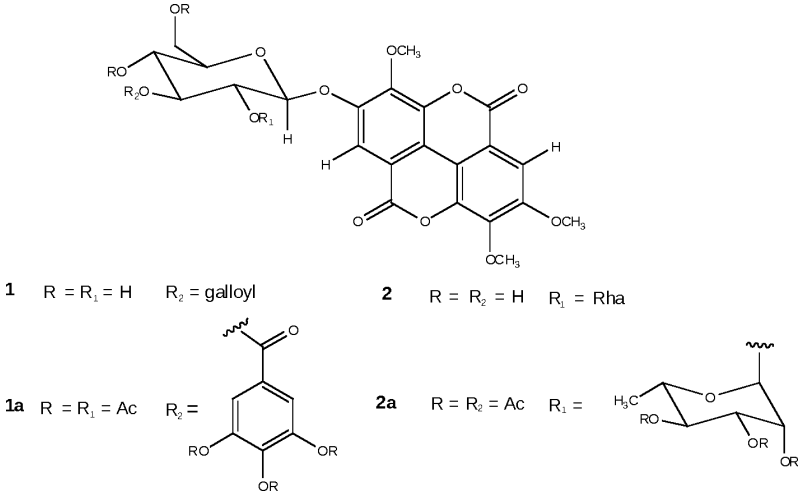

Fig. 3. Structures of compounds **1**, **1a**, **2** and **2a**.

compound **2** gave glucose, rhamnose and 3,3′,4′-tri-*O*-methylellagic acid, which were identified on TLC by comparison with known samples of glucose and rhamnose using *n*-BuOH-Me_2CO-H_2O (4 : 5 : 1), and NMR data for the aglycon. The three methoxy groups at δ = 4.01 (OMe-4′), 4.05 (OMe-3′) and 4.11 (OMe-3) correlate with C-4′, C-3′ and C-3 carbons of the aglycon. Thus, the structure of **2** was established as 3, 3′,4′-tri-*O*-methylellagic acid 4-*O*-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside, named panconoside B.

Acetylation of compounds **1** and **2** afforded the peracetylated derivatives **1a** and **2a** (Fig. 3).

The antibacterial activity of compounds **1** and **2** was evaluated in an antibacterial assay against 6 strains of microorganisms, *Micrococcus luteus*, *Streptococcus ferus*, *Streptococcus minor*, *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas agarici* (Table 2), by the agar well diffusion method [21, 22]. Compound **1** displayed a moderate antibacterial effect expressed as minimum inhibitory concentration (MIC) against all strains. In particular, *P. agarici*, *S. ferus* and *S. minor* were the most inhibited (MIC = 39.06 μg mL^{-1}). Compound **2** also showed moderate activity against *E. coli* and *P. agarici* (MIC = 78.12 μg mL^{-1}). The methanolic extract of the leaves exhibited antibacterial potency with MIC values of 39.06, 78.12 and 156.23 μg mL^{-1}. The EtOAc extract of the stem bark showed a remarkable antibacterial effect with the best value of MIC against *E. coli* and *P. agarici* (MIC = 9.76 μg mL^{-1}) close to that of gentamycin used as standard drug (Table 2). These results provide promising baseline information for the potential use of these crude extracts in the treatment of bacterial infections.

Although ellagic acid has already been isolated from the Sapindaceae family [4], this is the first report of its derivatives in this family. Despite the moderate antibacterial potency of compounds **1** and **2**, several ellagic acid derivatives isolated from plants exhibit antiplasmodial, cytotoxic, antioxidant, and α-glucosidase inhibitory activities [4, 20, 23, 24]. All these results highlight the potency of this class of secondary metabolites and suggest potential uses of plants from the genus *Pancovia* in medicine.

Experimental Section

General

Melting points were determined on a Büchi-540 melting point apparatus. UV spectra were measured on a Spectronic

Unicam Spectrophotometer. Optical rotations were measured in DMSO solution on a Jasco Digital Polarimeter (model DIP-360). IR spectra were determined on a JASCO FT/IR-410 spectrometer. HRMS ((+)-ESI) were run on a Bruker FT-ICR: APEX III (7.0 T). ^{1}H and ^{13}C NMR spectra were run on a Bruker DRX spectrometer equipped with 5 mm ^{1}H and ^{13}C probes operating at 500 and 125 MHz, respectively, with TMS as internal standard. Silica gels (Merck, 230 – 400 and 70 – 230 mesh) were used for column chromatography, while pre-coated aluminum silica gel 60 F_{254} sheets were used for TLC with different mixtures of *n*-hexane, EtOAc, CH_2Cl_2, and MeOH as eluents; spots were visualized under UV lamps (254 and 365 nm) or by heating after spraying with 50 % H_2SO_4 reagent.

Plant material

The stem bark and leaves of *P. pedicellaris* were collected in April 2008 from Mount Kala in the Central Region of the Republic of Cameroon. The plant was identified by Mr. Nana Victor, plant taxonomist at the National Herbarium of Cameroon, where a voucher specimen (Nr. 2741 / SRFCam) has been deposited.

Extraction and isolation

The air-dried and powdered stem bark (2.5 kg) and leaves (2 kg) of *P. pedicellaris* were extracted separately with MeOH (5 L) at r. t. for 48 h and filtered. The filtrate was concentrated to dryness under vacuum to give 120 g and 50 g of crude extract, respectively.

The MeOH extract from the stem bark was extracted selectively with EtOAc. The EtOAc-soluble fraction was evaporated to dryness under vacuum to give a dry residue (40 g) which was then subjected to column chromatography over silica gel (Merck, 230 – 400 mesh) and eluted with a gradient mixture of *n*-hexane/EtOAc and EtOAc/MeOH of increasing polarity. Ninety column fractions, each containing 200 mL, were collected and combined according to their TLC profiles on pre-coated silica gel 60 F_{254} plates developed with *n*-hexane/EtOAc mixtures to yield 3 fractions (F_{1-3}). Fraction F_1 was subjected to CC over silica gel (Merck, 70 – 230 mesh) eluted with an *n*-hexane/EtOAc mixture (9.5 : 0.5 to 7 : 3). This resulted in the isolation of stigmasterol (**6**) (15 mg), 3-oxotirucalla-7, 24-dien-21-oic acid (**10**) (16 mg) and umbelliferone (**7**) (56 mg). Fraction F_2 was also subjected to successive CC (Merck, 70 – 230 mesh) and eluted with a mixture of *n*-hexane and EtOAc (6 : 4) to give scopoletin (**8**) (903 mg) and benjaminamide (**11**) (32 mg). Fraction F_3 was eluted with an *n*-hexane/EtOAc mixture of increasing polarity (5 : 5 to 1 : 9) to yield 8′-*epi*-cleomiscosin (**9**) (10 mg), 3-*O*-β-D-glucopyranosylstigmasterol (**12**) (900 mg) and 7-oxostigmasteryl-3-*O*-β-D-glucopyranoside (**13**) (11 mg).

The crude MeOH extract from the leaves was dissolved in MeOH (500 mL) and washed with *n*-hexane (5 × 500 mL). After concentration, this yielded 30 g of a hexane-soluble fraction and 17 g of a MeOH fraction. This latter fraction was subjected to silica gel (Merck, 230 – 400 mesh) flash chromatography and eluted with gradient *n*-hexane/EtOAc and EtOAc/MeOH mixtures in the order of increasing polarity. Thirty-five fractions, each containing 250 mL, were collected and combined according to their TLC profiles on pre-coated silica gel 60 F_{254} plates developed with *n*-hexane/EtOAc and CH_2Cl_2/MeOH to yield 3 main fractions (F'_{1-3}). Fraction F'_1 was subjected to CC over silica gel (Merck, 70 – 230 mesh) and eluted with a CH_2Cl_2/MeOH mixture (9.8 : 0.2 to 8 : 2) to yield panconoside A (**1**) (15 mg) and 3,3′,4′-tri-*O*-methylellagic acid 4-*O*-β-D-glucopyranoside (**3**) (80 mg). Fraction F'_2 was subjected to CC over silica gel (Merck, 70 – 230 mesh) with a CH_2Cl_2/MeOH mixture (9.5 : 0.5 to 8 : 2) to yield panconoside B (**2**) (500 mg) and allantoin (**4**) (855 mg). Fraction F'_3 yielded L-quebrachitol (**5**) (725 mg) by column chromatography separation over silica gel using the mixture CH_2Cl_2/MeOH (7 : 3).

Antibacterial assays

In vitro antibacterial activity screening of the crude extracts and of compounds **1** and **2** were determined by the agar well diffusion method as described in previous reports [22, 23].

*Acid hydrolysis of compound **2***

A solution of 7 mg of compound **2** in 10 mL MeOH/H_2O (1 : 1) mixed with 5 mL 2N HCl was refluxed at 100 °C for 3 h. After evaporation of the organic solvent under vacuum and threefold extraction of the aqueous phase with EtOAc, the aglycon was identified as 3,3′,4′-tri-*O*-methylellagic acid by NMR techniques. The neutralized aqueous portion resulted in the detection of glucose and rhamnose by comparison with standard sugar samples on TLC plates using *n*-BuOH/Me_2CO/H_2O (4 : 5 : 1) as solvents and using $(NH_4)_6Mo_7O_{24}Ce(SO_4)_2H_2SO_4$ reagent for visualization.

*Acetylation of Panconosides A (**1**) and B (**2**)*

Panconoside A (**1**) (4 mg) or B (**2**) (8 mg) was dissolved in dry pyridine (0.5 mL), and Ac_2O (1.0 mL) was added. The mixture was stirred overnight at r. t. After the usual work-up, filtration on a short silica gel column yielded the acetylated derivative **1a** (5 mg) or **2a** (10 mg).

*Panconoside A [3,3′,4′-tri-O-methylellagic acid 4-O-(3″-galloyl)-β-D-glucopyranoside] (**1**)*

Beige crystals, m. p. 247 – 249 °C. – UV/Vis (MeOH): λ_{max} ($\lg \varepsilon_{max}$) = 255 (3.42), 280 (3.43), 355 (3.44) nm. –

$[\alpha]_D^{20}$ = +66.6° (*c* = 0.3, DMSO). – IR (KBr): ν_{max} = 3420 (O–H), 1748 (C=O), 1611 (C=C), 1356, 1085 (C – O) cm^{-1}. – ^1H NMR ([D$_6$]DMSO) and ^{13}C NMR ([D$_6$]DMSO) spectroscopic data, see Table 1. – MS (EI, 70 eV): *m/z* (%) = 344 (100), 329 (17), 286 (12). – HRMS ((+)-ESI): *m/z* = 681.10664 (calcd. 681.10991 for $C_{30}H_{26}O_{17}Na$, $[M+Na]^+$).

*Panconoside B [3,3′,4′-tri-O-methylellagic acid 4-O-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside] (**2**)*

Yellow crystals, m. p. 257 – 259 °C. – UV/Vis (MeOH): λ_{max} (lg ε_{max}) = 255 (3.71), 360 (2.47) nm. – $[\alpha]_D^{20}$ = −80.0° (*c* = 0.5, MeOH). – IR (KBr): ν_{max} = 3430 (O–H), 1749 (C=O), 1600 (C=C), 1090 cm^{-1}. – ^1H NMR ([D$_6$]DMSO) and ^{13}C NMR ([D$_6$]DMSO) spectroscopic data, see Table 1. – MS (EI, 70 eV): *m/z* (%) = 344 (100), 329 (20), 286 (17). – HRMS ((+)-ESI): *m/z* = 675.15354 (calcd. 675.15686 for $C_{29}H_{32}O_{17}Na$, $[M+Na]^+$).

*Panconoside A peracetate (**1a**)*

Yellow amorphous powder. – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.03, 2.07, 2.10, 2.21, 2.32 (6 × s, 18 H, CO*Me*), 3.50 (br s, 1H, 5″-H), 4.06 (s, 3H, OMe), 4.09 (m, 1H, 6″b-H), 4.15 (s, 3H, OMe), 4.24 (s, 3H, OMe), 4.29 (m, 1H, 6″a-H), 5.27 (d, *J* = 7.6 Hz, 1H, 1″-H), 5.31 (t, *J* = 9.4 Hz, 1H, 3″-H), 5.54 (m, 1H, 4″-H), 5.57 (m, 1H, 2″-H), 7.73 (s, 1H, 5′-H), 7.78 (s, 2H, 2‴/6‴-H), 7.96 (s, 1H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2, 20.6 (all CO*Me*), 56.9 (OMe), 62.0 (2 × OMe), 62.3 (C-6″), 68.0 (C-4″), 70.7 (C-2″), 72.7 (C-5″), 73.4 (C-3″), 100.0 (C-1″), 108.0 (C-5′), 112.5 (C-5), 112.7 (C-1), 113.0 (C-1′), 113.7 (C-6′), 115.4 (C-6), 122.6 (C-2‴/6‴), 126.7 (C-1‴), 139.4 (C-4‴), 141.4 (C-3′), 141.6 (C-2′), 141.9 (C-2), 143.3 (C-3), 143.6 (C-3‴/5‴), 151.5 (C-4), 154.9 (C-4′), 158.4 (C-7), 158.7 (C-7′), 163.6 (C-7‴), 166.4 (C=O), 167.5 (C=O), 169.3 (C=O), 169.5 (C=O), 170.9 (C=O).

*Panconoside B peracetate (**2a**)*

Yellow amorphous powder. – ^1H NMR (500 MHz, $CDCl_3$): δ = 1.15 (d, *J* = 6.3 Hz, 3H, 6‴-Me), 1.98, 2.00, 2.06, 2.09, 2.13, 2.16 (6 × s, 18 H, CO*Me*), 3.89 (br t, *J* = 8.8 Hz, 1H, 5″-H), 3.96 (m, 1H, 2″-H), 4.06 (s, 3H, OMe), 4.10 (m, 1H, 6″b-H), 4.15 (m, 1H, 5‴-H), 4.18 (m, 1H, 6″a-H), 4.21 (s, 1H, 2‴-H), 4.23 (s, 3H, OMe), 4.28 (s, 3H, OMe), 5.05 (m, 1H, 3‴-H), 5.08 (m, 1H, 4″-H), 5.10 (m, 1H, 3″-H), 5.16 (d, *J* = 1.3 Hz, 1H, 1‴-H), 5.30 (d, *J* = 7.5 Hz, 1H, 1″-H), 5.40 (t. *J* = 9.4 Hz, 1H, 4‴-H), 7.71 (s, 1H, 5′-H), 7.86 (s, 1H, 5-H). – ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.5 (C-6‴), 20.6, 20.7, 20.8, 20.9 (all CO*Me*), 56.9 (OMe), 61.9 (C-6″), 62.0 (OMe), 62.2 (OMe), 67.2 (C-5‴), 68.3 (C-4″), 68.4 (C-3‴), 70.1 (C-2‴), 70.9 (C-4‴), 72.4 (C-2″), 74.2 (C-3″), 76.4 (C-5″), 97.7 (C-1″), 99.3 (C-1‴), 107.9 (C-5′), 112.2 (C-5), 112.6 (C-1), 113.1 (C-1′), 113.7 (C-6′), 115.2 (C-6), 141.2 (C-3′), 141.4 (C-2), 141.9 (C-2′), 143.3 (C-3), 150.2 (C-4), 154.8 (C-4′), 158.4 (C-7), 158.6 (C-7′), 169.7 (C=O), 169.8 (C=O), 169.9 (C=O), 170.1 (C=O), 170.2 (C=O), 170.7 (C=O).

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