



## Acylated farnesyl diglycosides from *Guioa crenulata*

Abdulmagid Alabdul Magid, Laurence Voutquenne, Marc Litaudon, Catherine Lavaud

### ► To cite this version:

Abdulmagid Alabdul Magid, Laurence Voutquenne, Marc Litaudon, Catherine Lavaud. Acylated farnesyl diglycosides from *Guioa crenulata*. *Phytochemistry*, 2005, 66 (23), pp.2714-2718. <10.1016/j.phytochem.2005.09.009>. <hal-00019118>

**HAL Id: hal-00019118**

**<https://hal.science/hal-00019118v1>**

Submitted on 25 Nov 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

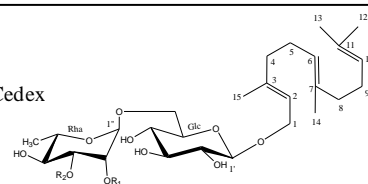
## Acylated farnesyl diglycosides from *Guioa crenulata*

Abdulmagid Alabdul Magid<sup>a</sup>, Laurence Voutquenne<sup>a\*</sup>, Marc Litaudon<sup>b</sup> and Catherine Lavaud<sup>a</sup>

<sup>a</sup> Laboratoire de Pharmacognosie, FRE CNRS 2715, IFR 53 Biomolécules, Bât. 18, BP 1039, Reims Cedex 51079, France.

<sup>b</sup> Institut de Chimie des Substances Naturelles du CNRS, 91190 Gif-sur-Yvette, France.

Chemical investigation of the hydromethanolic extract of the leaves of *Guioa crenulata* has led to the isolation and characterisation of four new farnesyl diglycosides named guiosides **I**, **II**, **III** and **IV**, along with three known flavonol glycosides and one trimeric proanthocyanidin possessing a doubly-linked structure.



R <sub>1</sub>	R <sub>2</sub>
H	H
H	CH <sub>3</sub> CO-
CH <sub>3</sub> CO-	H
CH <sub>3</sub> CO-	CH <sub>3</sub> CO-

## Acylated farnesyl diglycosides from *Guioa crenulata*

Abdulmagid Alabdul Magid<sup>a</sup>, Laurence Voutquenne<sup>\*a</sup>, Marc Litaudon<sup>b</sup> and Catherine Lavaud<sup>a</sup>.

<sup>a</sup> Laboratoire de Pharmacognosie, FRE CNRS 2715, IFR 53 Biomolécules, Bât. 18, BP 1039, Reims Cedex 51079, France.

<sup>b</sup> Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif-sur-Yvette, France.

<sup>\*</sup> Corresponding author :

Tel.: +33-3-26-91-82-08;

Fax: +33-3-26-91-35-96.

E-mail address: Laurence.voutquenne@univ-reims.fr (L. Voutquenne).

## Abstract

Chemical investigation of the hydromethanolic extract of the leaves of *Guioa crenulata* has led to the isolation and characterisation of four new farnesyl diglycosides named guiosides **I**, **II**, **III** and **IV**, along with three known flavonol glycosides and one trimeric proanthocyanidin possessing a doubly linked structure. The structures of these compounds have been determined on the basis of spectroscopic studies and chemical evidence. The ethanolic and ethyl acetate extracts of the leaves showed no cytotoxic activity and no activity against acetylcholinesterase.

Key words: *Guioa crenulata*, Sapindaceae, farnesyl glycoside, acyclic sesquiterpene, kaempferol, quercetin, proanthocyanidin trimers.

## 1. Introduction

The Sapindaceae family, a tropical and subtropical woody family, are represented by 150 genera (about 2000 species) distributed into two subfamilies (Sapindoideae and Dodonaeoideae (Delaude, 1993; Mabberley, 1997). Many members of this family e.g. *Pometia*, *Dodonaea* and *Sapindus* have attracted the attention of various authors from phytochemical and biological properties. Sapindaceae generally contain saponins. Many species contain in their leaves flavonoids, phenolic acids and tannins (proanthocyanidins) (Umadevi and Daniel, 1991). The genus *Guioa* (Sapindoideae) is represented by nine species which are distributed in New Caledonia and Australia (De Kok, 2002). No previous chemical work has been reported on this genus. In a continuation of our chemotaxonomic studies on the constituents of plants of the Sapindaceae family, we have examined the leaves of *Guioa crenulata* Radlk., a tree of moderate size (height of about 5 m) which growing in New Caledonia.

The leaves of *Guioa crenulata* Radlk. were collected at Mont Mandjélia in New Caledonia. This species was selected by the CNRS (ICSN) France in a screening program for potential cytotoxic compounds from plants growing in New Caledonia. The ethanolic and ethyl acetate extracts of the leaves were tested in a preliminary biological screening. No in vitro cytotoxic activity was revealed against P.388 cells, no activity was detected with the tubulin test and on topoisomerase I and no inhibition activity against acetylcholinesterase was observed.

This paper reports on the isolation and the structural determination of three known flavonoids glycosides (**1** – **3**), a known trimeric proanthocyanidin possessing a doubly linked structure (**4**) and four new acyclic sesquiterpene glycosides (**5** – **8**) named **guiosides I, II, III** and **IV** from the leaves of *Guioa crenulata* Radlk..

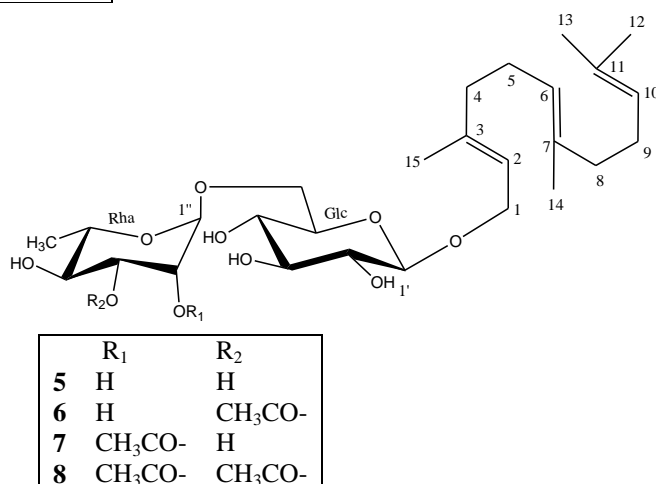
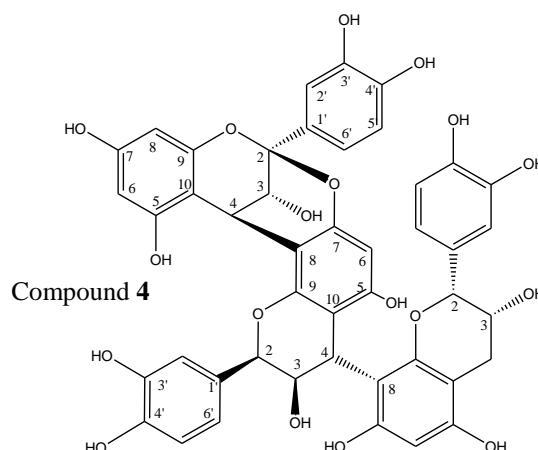
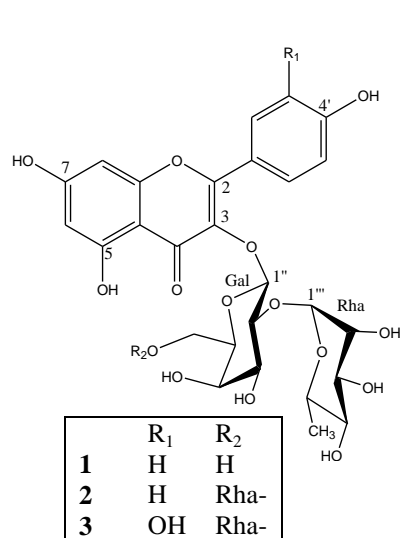
## 2. Results and discussion

The air-dried leaves were defatted with hexane and the defatted drug was extracted with 80 % aq. methanol. The hydromethanolic extract was concentrated and the residue was suspended in water and extracted with ethyl acetate to afford two fractions: aqueous fraction and ethyl acetate fraction. The aqueous fraction was subjected to a column chromatography over Sephadex LH-20, which was eluted successively with water, 50% aqueous methanol and methanol. Fractions eluted with 50% aqueous methanol were further purified by silica gel and column chromatography finally by HPLC semi-preparative over C-18 to afford three flavonoids glycosides **1**, **2**, **3** and one trimeric proanthocyanidin **4**. The ethyl acetate fraction was purified using column chromatography over silica gel, C-18 and by HPLC semi-preparative over RP 18 to afford four new acyclic sesquiterpene glycosides (**5** – **8**).

The monosaccharides obtained by the acid hydrolysis of the crude extract, were identified as rhamnose, glucose and galactose by TLC and their absolute configuration was determined to be D for glucose and galactose and L for rhamnose by measurement of the optical rotation of each purified sugar, consistent with the stereochemistry of naturally occurring

monosaccharides. Three known flavonol glycosides were isolated and identified by comparison of their spectral data (NMR, MS and UV) with the literature values as 3-*O*-[ $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)- $\beta$ -D-galactopyranosyl] kaempferol (**1**) (Yasukawa et Takido., 1987) 3-*O*-[2,6-di-*O*- $\alpha$ -L-rhamnopyranosyl- $\beta$ -D-galactopyranosyl] kaempferol (**2**) (Yasukawa et Takido, 1987; De Simone et al., 1990; Yasukawa et al., 1990; Brun et al., 1999; Dini et al., 2004) and 3-*O*-[2,6-di-*O*- $\alpha$ -L-rhamnopyranosyl- $\beta$ -D-galactopyranosyl] quercetin (**3**) (Yasukawa et al., 1989; Yasukawa et al., 1990; Brun et al., 1999, Dini et al., 2004).

The isolated proanthocyanidin (**4**) epicatechin-(4 $\beta$  $\rightarrow$ 8, 2 $\beta$  $\rightarrow$ O $\rightarrow$ 7)-epicatechin-(4 $\alpha$  $\rightarrow$ 8)-epicatechin (cinnamtannin B1) was identified from its 1D and 2D NMR data and by comparison of its spectral data (NMR, MS, CD, UV and  $[\alpha]_D$ ) with the literature values (Nonaka et al., 1983; Baldé et al., 1991; Baldé et al., 1993; Kohei et al., 2001).



Compound **5** was a diglycoside as shown by the presence in the  $^{13}\text{C}$  NMR spectrum of two signals at  $\delta_{\text{C}}$  102.2 and 102.4 which were correlated in HSQC spectrum with two anomeric protons at  $\delta_{\text{H}}$  4.77 and 4.29, respectively (Table 1). COSY and HSQC experiments allowed complete assignment of all protons and carbons for each sugar units. A  $\beta$ -D-glucose unit was identified starting from anomeric proton at  $\delta_{\text{H}}$  4.29 (*d*,  $J_{1-2}$  = 7.8 Hz), on the basis of its large coupling constants. The second unit with anomeric proton at  $\delta_{\text{H}}$  4.77 (*d*,  $J_{1-2}$  = 1.7 Hz) was identified as L-rhamnose with its methyl group at  $\delta_{\text{H}}$  1.29 (*d*,  $J_{5-6}$  = 6.3 Hz) and  $\delta_{\text{C}}$  18.1 (Table 1). It is known that  $^1J_{\text{H-C}} < 165$  Hz and  $\delta_{\text{C}5} > 73.1$  ppm indicate a  $\beta$  configuration for L-rhamnose, and  $^1J_{\text{H-C}} > 165$  Hz and  $\delta_{\text{C}5} < 70.0$  ppm indicate an  $\alpha$  configuration (Kasai et al., 1979; Backinowsky et al., 1980; Massiot et Lavaud, 1995; Delay et al., 1997). The chemical shift of carbon 5 at  $\delta_{\text{C}}$  69.8 and the coupling constant  $^1J_{\text{C-H}}$  at 170 Hz for the anomeric carbon showed that this rhamnose was in  $\alpha$  configuration. The positive electrospray ionization ESI-MS of compound **5** showed an ion peak at  $m/z$  531  $[\text{M}+\text{H}]^+$ . Further analysis of the  $^{13}\text{C}$  NMR spectrum revealed the presence of three olefinic methines at  $\delta$  121.3, 125.1 and 125.4 correlated in HSQC spectrum with three protons at  $\delta$  5.39 (*ddq*, 7.8-6.4-1.3), 5.14 (*ddq*, 8.3-6.4-1.3) and 5.11 (*tq'*, 7-1.4), respectively. The resonance of four methyl groups attached on three olefinic quaternary carbons were observed together with four methylenes and one oxymethylene. Examination of the interaction of these groups on HSQC, COSY, and HMBC spectra led to the assignment of the aglycone as farnesol, an acyclic sesquiterpene. The chemical shifts of both methyl carbons, C-14 and C-15 at  $\delta_{\text{C}}$  16.1 and 17.8, respectively and those of C-4 and C-8 at  $\delta_{\text{C}}$  40.7 and 40.9, respectively are very similar to the values observed for (2*E*, 6*E*)-farnesol (Kasai et al., 1986; Tanaka, 1991). Only one methyl resonance appeared above  $\delta$  20 in the  $^{13}\text{C}$  NMR spectrum of compound **5**, this was particularly indicative for the stereochemistry *E* of the double bonds of the farnesyl group (Numata et al., 1992). The absence of a signal in the region  $\delta$  30-33 in the  $^{13}\text{C}$  NMR spectrum of compound **5** rules out

the other possible stereochemistry configuration (*2E*, *6Z*), (*2Z*, *6Z*), or (*2Z*, *6E*) for the farnesyl moiety (Tanaka, 1991). The deshielding of C-1 ( $\delta$  66.0) of the aglycone and C-6' ( $\delta$  68.0) of glucose suggested the points of linkage of sugar units. Cross peaks were observed in the HMBC experiment between the H-1'' of rhamnose ( $\delta$  4.77) and C-6' of glucose ( $\delta$  68.0) and between H-1' of glucose ( $\delta$  4.29) and C-1 of the aglycone ( $\delta$  66.0). These results led to the assignment of compound **5** as 1-*O*-[ $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranosyl] all-*trans*-farnes-1-ol, named **guioside I**.

The positive ESI-MS spectrum of compound **6** showed a pseudomolecular ion peak at  $m/z$  595  $[M+Na]^+$  and suggesting a supplementary acetyl group (42 *amu*) compared to compound **5**. The  $^1H$  and  $^{13}C$  NMR spectra of compound **6** showed signals for an acetyl group at  $\delta_H$  2.12 (3H, *s*) and  $\delta_C$  21.1 (CH<sub>3</sub>) and 172.9 (CO). Two anomeric carbons were detected at 102.0 and 102.3 in the  $^{13}C$ -NMR spectrum, attached to doublets at  $\delta_H$  4.78 and 4.30, respectively in the HSQC experiment. Complete assignments of each glycosidic proton system were achieved by analysis of COSY and HSQC experiments. The first unit with anomeric proton at  $\delta_H$  4.30 (*d*,  $J=7.8$  Hz) and with its methylene carbons C-6' at  $\delta_C$  68.1 was identified as  $\beta$ -D-glucose (Table 1). The second glycosidic unit with anomeric proton at  $\delta_H$  4.78 (*d*,  $J=1.8$ ) was identified as  $\alpha$ -L-rhamnose which possessed a deshielded H-3 at  $\delta_H$  4.96 indicating the position of acetylation. The deshielding of C-6' of glucose suggested the point of linkage of the rhamnose as in compound **5** (Table 1). The sequence of the glycosidic chain in compound **6** was achieved by analysis of HMBC experiment. The HMBC spectrum showed cross peaks between C-1 ( $\delta$  66.0) of farnesol and H-1' of glucose ( $\delta$  4.30), between C-6' ( $\delta$  68.1) of glucose and H-1'' of esterified rhamnose ( $\delta$  4.78), and between H-3'' ( $\delta$  4.96) of this rhamnose and carbonyl ( $\delta$  172.5) of the acetyl group. Thus, compound **6** is 1-*O*-[(3-*O*-acetyl)- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranosyl] all-*trans*-farnes-1-ol, named **guioside II**.



The spectral data of compound **7** obtained from the positive ESI-MS ( $m/z$  595  $[M+Na]^+$ ) and NMR experiments were almost the same as those of compound **6** except for the position of the acetyl group on the rhamnose moiety, which suggested that compounds **6** and **7** were two regioisomers with all-*trans*-farnes-1-ol aglycone. The  $^1H$ - $^{13}C$  long-range correlations of the down-field shifted methine proton at  $\delta_H$  5.07 (H-2'') with the carbonyl of acetyl group at  $\delta_C$  172.9, in HMBC spectrum, suggested that the acetyl esterified the rhamnose in position 2''. The other correlations between C-1 ( $\delta$  66.1) of farnesol and H-1' of glucose ( $\delta$  4.29,  $d$ ,  $J=7.8$ ), between C-6' ( $\delta$  67.8) of glucose and H-1'' of esterified rhamnose ( $\delta$  4.80,  $d$ ,  $J=1.3$ ), led to the assignment of compound **7** as 1-*O*-[2-*O*-acetyl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranosyl] all-*trans*-farnes-1-ol, named **guioside III**.

The positive ESI-MS spectrum of compound **8** showed a pseudomolecular ion peak at  $m/z$  661  $[M+2Na]^+$  suggesting the presence of a supplementary acetyl group compared to compounds **6** and **7**. The  $^1H$  and  $^{13}C$  NMR data of compound **8** were closely comparable to those of **5**, **6** and **7** except for the signals of rhamnose moiety and the presence of two methyl acetate ( $\delta_H$  2.03 and 2.11 and  $\delta_C$  20,8 and 20,7) (Table 1). The  $\alpha$ -L-rhamnose possessed two deshielded protons H-2'' and H-3'' at  $\delta$  5.26 and 5.09, respectively, indicating the position of the two acetyl groups. Thus, compound **8** was determined to be 1-*O*-[2,3-di-*O*-acetyl- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranosyl] all-*trans*-farnes-1-ol, named **guioside IV**.

Similar glycosides of all-*trans*-farnes-1-ol with four monosaccharide units (two rhamnose units and one xylose unit linked to a glucose unit at the C-2, C-3 and C-6, respectively) have been reported in another Sapindaceae species, *Lepisanthes rubiginosa* (Adesanya et al., 1999). Triglycosides of 12-hydroxy-all-*trans*-farnes-1-ol have been also reported in many species of the genus *Sapindus* (Sapindaceae), *S. mukurossi* (Kasai et al., 1986), *S. trifoliatu*s (Kasai et

al., 1988) and *S. delavayi* (Wong et al., 1991) with the same sugar glucose and rhamnose. But, to our knowledge, **guiosides I-IV** are the first natural isolated farnesyl diglycosides.

### **3. Experimental**

#### ***3.1. General experimental procedures***

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance DRX in  $\text{CD}_3\text{OD}$  ( $^1\text{H}$  at 500 MHz and  $^{13}\text{C}$  at 125 MHz). 2D NMR experiments were performed using standard Bruker microprograms (XWIN-NMR version 2.6 software). ESI-MS experiments were performed using a Bruker Esquire LC-MS instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. UV spectra were obtained using a PHILIPS PU 8720 spectrophotometer, whereas CD spectra were recorded with a Jasco J-810 spectropolarimeter. CC was carried out on Sephadex LH-20 (Pharmacia Biotech AB, Uppsala, Sweden), Kieselgel 60 (63-200 mesh) Merck or LiChroprep RP-18 (40-63  $\mu\text{m}$ ) Merck. HPLC was performed on a Dionex apparatus equipped with an ASI-100 autosampler, a P580 pump, a diode array detector UVD 340S and a Chromeleon<sup>®</sup> software. A C-18 reversed phase column (201SP510, 250x10 mm, 5 $\mu$ , 90 Å, Dionex, vydac, France) was used for semi-preparative HPLC with a binary gradient elution (solvent A:  $\text{H}_2\text{O}$ , pH 2.4 with 0.0025 % TFA, solvent B: MeCN) at 25°C, and a flow rate of 3  $\text{ml}\cdot\text{min}^{-1}$ , the chromatogram was monitored at 205 and 210 nm. TLC was performed on Kieselgel 60 F<sub>254</sub> Merck<sup>®</sup>, with  $\text{CHCl}_3$ -MeOH- $\text{H}_2\text{O}$ .

#### ***3.2. Plant material***

The leaves of *G. crenulata* Radlk. were collected at Mont Mandjélia in New Caledonia in December 1999 and authenticated by M. Litaudon of the ICSN-CNRS-91198 Gif-sur-Yvette, France (Herbarium number LIT 1002 ).

#### ***3.3. Extraction and isolation***

The powdered air-dried leaves (72 g) were defatted by extraction with hexane (500 ml) at room temperature. The residue was macerated in 20 % aq. Methanol (700 ml) for 3h and then boiled under reflux for 3 h. The hydromethanolic extract was filtered, and then concentrated to maximum. This residue was suspended in H<sub>2</sub>O (150 ml) and partitioned in a separatory funnel between H<sub>2</sub>O and ethyl acetate (3x150 ml) affording an ethyl acetate soluble fraction (7.3 g) and a H<sub>2</sub>O soluble fraction (12.1 g).

The aqueous fraction (12 g) was dissolved in H<sub>2</sub>O and applied to a Sephadex LH-20 column (30x750 mm). The adsorbed materials were eluted successively with H<sub>2</sub>O, 50% aq.MeOH and MeOH. Twenty-two fractions (**I-XXII**), 250 ml each, were collected and monitored by silica TLC with the eluent CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (70:30:5).

**Fraction I** (1.5 g) was subjected to a silica gel CC (27x270 mm) using a gradient of CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (95:5:0 to 60:40:7), fractions of 100 ml were collected. Frs. [22-27] eluted with CHCl<sub>3</sub>-MeOH (7:3) and frs. [28-32] eluted with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (70:30:1) gave 214 mg of compound **4** in pure form (yield 0.297).

**Fraction VI** (1 g) was subjected to a silica gel CC (25x250 mm) using a gradient of CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (8:2:0 to 60:40:7), fractions of 50 ml were collected. Frs. [16-32] eluted with CHCl<sub>3</sub>-MeOH (7:3) gave 500 mg of pure compound **2** (yield 0.694 %). Frs. [52-55] eluted with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (60:40:7) were further purified by a semi-prep. HPLC, using 21% B in an isocratic elution to give compound **3** at *R*<sub>t</sub> 7.8 min (8 mg) and compound **2** at *R*<sub>t</sub> 9.4 min (14 mg).

**Fractions VIII and XI** (240 mg) were subjected to silica gel CC (15x160 mm) using a gradient of CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (8:2:0 to 70:30:5), fractions of 5 ml were collected. Frs. [13-39] eluted with CHCl<sub>3</sub>-MeOH (75:25) were purified by a semi-prep. HPLC, with 21% B in an isocratic elution to give 3 mg of compound **1**.

A part of the ethyl acetate fraction (5 g) was subjected to a reversed phase RP-18 vacuum liquid chromatography (VLC) (50x50 mm) and eluted successively with 40, 80 % aqueous methanol and MeOH. Three fractions (**A**, **B**, **C**) of 250 ml were collected and monitored by silica TLC with the eluent CHCl<sub>3</sub>-MeOH (8:2).

A part of the fraction **B** (700 mg) eluted with MeOH-H<sub>2</sub>O (40:60) was subjected to a reversed phase RP-18 CC (22x180 mm) using a gradient of MeOH-H<sub>2</sub>O (6:4 to 10:0), fractions of 10 ml were collected. **Frs. [26-33]** eluted with MeOH-H<sub>2</sub>O (7:3) were subjected to a silica gel CC (15x130) using a gradient of CHCl<sub>3</sub>-MeOH (95:5 to 7:3), fractions of 5 ml were collected. **Frs. [24-27]** eluted with CHCl<sub>3</sub>-MeOH (85:15) were purified by a semi-prep. HPLC using a linear gradient (35 to 50 % **B**) during 30 min and give compounds **5**, **6** and **7** at *R<sub>t</sub>* 21.9 min (6 mg), 26.4 min (14 mg) and *R<sub>t</sub>* 27.3 min (6 mg), respectively.

**Frs. [37-49]** eluted with MeOH-H<sub>2</sub>O (8:2) was subjected to a silica gel CC (10x100) using a gradient of CHCl<sub>3</sub>-MeOH (100:0 to 9:1), fractions of 5 ml were collected. **Frs. [1-4]** eluted with CHCl<sub>3</sub> contains 4 mg of compound **8**.

### 3.4. Acid hydrolysis

200 mg of the 80% aqueous extract of the leaves was refluxed with 30 ml of 2N HCl for 4h30. The mixture was extracted with EtOAc (3x15 ml). The acid aqueous layer was neutralised with 0.5 M NaOH and freeze-dried. Three sugars were identified with authentic samples by TLC in MeCOEt/isoPrOH/Me<sub>2</sub>CO/H<sub>2</sub>O (20:10:7:6) as rhamnose, glucose and galactose. After a TLC prep. of sugar mixture (100 mg) in this solvent, the optical rotation of each purified sugar was measured.

### 3.5. compound **5**, guioside **I**

C<sub>27</sub>H<sub>46</sub>O<sub>10</sub>, transparent glassy material. [ $\alpha$ ]<sub>D</sub> -44.1 (MeOH, *c* 1). ESI-MS (positive ion mode): *m/z* 531 [M+H]<sup>+</sup>. <sup>1</sup>H and <sup>13</sup>C NMR data (CD<sub>3</sub>OD): see Table 1.

### 3.6. compound 6, guiosideII

C<sub>29</sub>H<sub>48</sub>O<sub>11</sub>, transparent glassy material.  $[\alpha]_D$  -28.5 (MeOH, *c* 1), ESI-MS (positive ion mode): *m/z* 573 [M+H]<sup>+</sup>, 595 [M+Na]<sup>+</sup>. <sup>1</sup>H and <sup>13</sup>C NMR data (CD<sub>3</sub>OD): see Table 1.

### 3.7. compound 7, guiosideIII

C<sub>29</sub>H<sub>48</sub>O<sub>11</sub>, transparent glassy material.  $[\alpha]_D$  -24.3 (MeOH, *c* 0.58), ESI-MS (positive ion mode): *m/z* 595 [M+Na]<sup>+</sup>. <sup>1</sup>H and <sup>13</sup>C NMR data (CD<sub>3</sub>OD): see Table 1.

### 3.8. compound 8, guiosideIV

C<sub>31</sub>H<sub>50</sub>O<sub>12</sub>, transparent glassy material.  $[\alpha]_D$  -31.5 (MeOH, *c* 0.33), ESI-MS (positive ion mode): *m/z* 661 [M+2Na]<sup>+</sup>. <sup>1</sup>H and <sup>13</sup>C NMR data (CD<sub>3</sub>OD): see Table 1.

## References

- Adesanya, S.A., Martin, M.T., Hill, B., Dumontet, V., Tri, M.V., Sévenet, T., Païs, M., 1999. Rubiginoside, a farnesyl glycoside from *Lepisanthes rubiginosa*. *Phytochemistry* 51, 1039-1041.
- Backinowsky, L., Balan, N.F., Shashkov, A.S., Kochetkov, N.K., 1980. Synthesis and <sup>13</sup>C NMR spectra of  $\beta$  and  $\alpha$ -L-rhamnopyranosides. *Carbohydrate Research* 84, 225-235.
- Baldé, A.M., Pieters, L.A., Gergely, A., Kolodziej, H., Claeys, M., Vlietinck, A.J., 1991. A-type proanthocyanidins from stem-bark of *Pavetta owariensis*. *Phytochemistry* 30, 337-342.
- Baldé, A.M., De Bruyne, T., Pieters, L., Claeys, M., Vanden Berghe, D., Vlietinck, A., 1993. Proanthocyanidins from stem bark of *Pavetta owariensis*. NMR study of acetylated trimeric proanthocyanidins possessing a doubly-linked structure, *Journal of Natural Products* 56, 1087-1088.
- Brun, G., Dijoux, M.G., David, B., Mariotte, A.M., 1999. A new flavonol glycoside from *Catharanthus roseus*. *Phytochemistry* 50, 167-169.
- De Kok, R., 2002. Are plant adaptations to growing on serpentine soil rare or common? A

- few case studies from New Caledonia, *Adansonia* 24, 229-238.
- Delaude, C., 1993. Les Sapindaceae et leur saponins, *Bull. Soc. Roy. Sc. Liège* 62, 93-120.
- De Simone, F., Dini, A., Pizza, C., Saturnino, P., Schettino, O., 1990. Two flavonol glycosides from *Chenopodium quinoa*. *Phytochemistry* 29, 3690-3692.
- Delay, C., Gavin, J.A., Aumelas, A., Bonnet, P.A., Roumestand, C., 1997. Isolation and structure elucidation of a highly haemolytic saponin from the Merck saponin extract using high-enhanced NMR techniques, *Carbohydrate Research* **302**, 67-78.
- Dini, I., Tenore, G.C., Dini, A., 2004. Phenolic constituents of *Kancolla* seeds. *Food Chemistry* 84, 163-168.
- Kasai, R., Nishi, M., Mizutani, K., Miyahara, I., Moriya, T., Miyahara, K., Tanaka, O., 1988. Trifolioside II, an acyclic sesquiterpene oligoglycoside from pericarps of *Sapindus trifoliatius*. *Phytochemistry* 27, 2209-2211.
- Kasai, R., Fujino, H., Kuzuki, T., Wong, W. H., Goto, C., Yata, N., Tanaka, O., Yasuhara, F., Yamaguchi, S., 1986. Acyclic sesquiterpene oligoglycosides from pericarps of *Sapindus mukurossi*. *Phytochemistry* 25, 871-876.
- Kasai, R., Okihara, M., Asakawa, J., Mizutani, K., Tanaka, O., 1979.  $^{13}\text{C}$  NMR study of  $\alpha$  and  $\beta$ -anomeric pairs of D-mannopyranosides and L-rhamnopyranosides. *Tetrahedron* 35, 1427-1432.
- Kohei, K., Chiharu, W., Hanani, E., Mansur, U., Toshiko, S., 2001. Studies on the Constituents of Bark of *Parameria laevigata* Moldenke. *Chem. Pharm. Bull.* 49, 551-557.
- Mabberley, D.J., 1997. The Plant-book: a Portable Dictionary of the Vascular Plants, second ed. Cambridge University Press, Cambridge.
- Massiot, G., Lavaud, C., 1995. Structural Elucidation of Saponins. Studies in Natural Products Chemistry 15, 187-224, Ed. Atta-ur-Rahman, Amsterdam.

- Nonaka, G.I., Morimoto, S., Nishioka, I., 1983. Tannins and related compounds. Part 13. Isolation and Structures of Trimeric, Tetrameric, and pentameric Proanthocyanidins from Cinnamon. *J. Chem. Soc. Perkin Trans. I* 9, 2139-2145.
- Numata, A., Kanbara, S., Takahashi, C., Fujiki, R., Yoneda, M., Usami, Y., Fujita, E., 1992. A cytotoxic principle of the brown alga *Sargassum tortile* and structures of chromenes. *Phytochemistry* 31, 1209-1213.
- Tanaka, Y., 1991. Ruber and related Polyphenols, Methods in plant biochemistry 7 (terpenoids), 519-536, Series editors Dey, P. M., Harborne, J. B., (Academic Press Limited, London).
- Umadevi, I. and Daniel, M., 1991. Chemosystematics of the Sapindaceae. *Feddes Repertorium* 102, 607-612.
- Wong, W.H., Kasai, R., Choshi, W., Nakagawa, Y., Mizutani, K., Ohtani, K., Tanaka, O., 1991. Acyclic sesquiterpene oligoglycosides from pericarps of *Sapindus delavayi*. *Phytochemistry* 30, 2699-2702.
- Yasukawa, K., Takido, M., 1987. A flavonol glycoside from *Lysimachia mauritiana*. *Phytochemistry* 26, 1242-1226.
- Yasukawa, K., Sekine, H., Takido, M., 1989. Two flavonol glycosides from *Lysimachia fortunei*. *Phytochemistry* 28, 2215-2216.
- Yasukawa, K., Ogawa, H., Takido, M., 1990. Two flavonol glycosides from *Lysimachia nummularia*. *Phytochemistry* 29, 1707-1708.

Table 1:  $^{13}\text{C}$  (125 MHz) and  $^1\text{H}$  (500 MHz) NMR chemical shifts of compounds **5-8** in  $\text{CD}_3\text{OD}$ .

	<b>5</b>		<b>6</b>		<b>7</b>		<b>8</b>	
Position	$\delta_{\text{H}}, m, J \text{ Hz}$	$\delta_{\text{C}}$	$\delta_{\text{H}}, m, J \text{ Hz}$	$\delta_{\text{C}}$	$\delta_{\text{H}}, m, J \text{ Hz}$	$\delta_{\text{C}}$	$\delta_{\text{H}}, m, J \text{ Hz}$	$\delta_{\text{C}}$
1	4.25 ( <i>dd</i> , 11.9-7.8)	66.0	4.26 ( <i>dd</i> , 11.9-7.9)	66.0	4.25 ( <i>dd</i> , 11.8-7.9)	66.1	4.26 ( <i>dd</i> , 11.7-7.6)	66.1
	4.31 ( <i>dd</i> , 11.9-6.4)	-	4.31 ( <i>dd</i> , 11.9-6.3)	-	4.30 ( <i>dd</i> , 11.8-7.3)	-	4.30 ( <i>dd</i> , 11.7-6)	-
2	5.39 ( <i>ddq</i> , 7.8-6.4-1.3)	121.3	5.39 ( <i>td</i> , 6.4-1.3)	121.2	5.39 ( <i>t</i> , 6.4)	121.4	5.39 ( <i>tm</i> , 6.3)	121.3
3	-	142.4	-	142.6	-	142.4	-	142.5
4	2.09 ( <i>m</i> )	40.7	2.08 ( <i>tm</i> , 6.4)	40.7	2.09 ( <i>m</i> )	40.7	2.09 ( <i>m</i> )	40.7
5	2.16 ( <i>ddd</i> , 14.9-6.4-2.1)	27.4	2.15 ( <i>tm</i> , 7.4)	27.4	2.15 ( <i>ddm</i> , 14.7- 7.3)	27.4	2.15 ( <i>tm</i> , 6.8)	27.4
6	5.14 ( <i>ddq</i> , 8.3-6.4-1.3)	125.1	5.15 ( <i>td</i> , 6.9-1.2)	125.2	5.15 ( <i>t</i> , 6.9)	125.1	5.15 ( <i>td</i> , 6.7-1.1)	125.2
7	-	136.3	-	136.3	-	136.3	-	136.3
8	2.00 ( <i>ddm</i> , 8.1-7)	40.9	2.00 ( <i>tm</i> , 8.1)	40.9	2.00 ( <i>ddm</i> , 7.9-7)	40.9	2.01 ( <i>tm</i> , 7.3)	40.9
9	2.09 ( <i>m</i> )	27.8	2.10 ( <i>m</i> )	27.8	2.10 ( <i>m</i> )	27.8	2.10 ( <i>m</i> )	27.8
10	5.11 ( <i>td'</i> , 7-1.4)	125.4	5.11 ( <i>td'</i> , 7.1-1.5)	125.4	5.11 ( <i>t</i> , 7.1)	125.4	5.12 ( <i>td'</i> , 7-1.4)	125.4
11	-	132.1	-	132.1	-	132.1	-	132.1
12	1.69 ( <i>q</i> , 1.2)	25.9	1.69 ( <i>d</i> , 1.1)	25.9	1.69 ( <i>s</i> )	25.9	1.69 ( <i>s</i> )	25.9
13	1.62 ( <i>s</i> )	17.8	1.62 ( <i>s</i> )	17.8	1.62 ( <i>s</i> )	17.8	1.62 ( <i>s</i> )	17.8
14	1.63 ( <i>d</i> , 1.1)	16.1	1.63 ( <i>d</i> , 1)	16.1	1.63 ( <i>s</i> )	16.1	1.63 ( <i>s</i> )	16.1
15	1.73 ( <i>d</i> , 1.1)	16.6	1.73 ( <i>d</i> , 1)	16.6	1.73 ( <i>s</i> )	16.6	1.73 ( <i>s</i> )	16.6
$\beta$ -D-Glc								
1'	4.29 ( <i>d</i> , 7.8)	102.4	4.30 ( <i>d</i> , 7.8)	102.3	4.29 ( <i>d</i> , 7.8)	102.5	4.31 ( <i>d</i> , 7.8)	102.5
2'	3.19 ( <i>dd</i> , 9-7.8)	75.0	3.20 ( <i>dd</i> , 9-7.8)	75.0	3.19 ( <i>dd</i> , 9-7.9)	75.0	3.21 ( <i>dd</i> , 8.9-7.9)	75.0
3'	3.36 ( <i>t</i> , 9)	78.1	3.36 ( <i>t</i> , 9)	78.1	3.35 ( <i>t</i> , 9)	78.1	3.36 ( <i>t</i> , 8.9)	78.1
4'	3.29 ( <i>dd</i> , 9.6-8.9)	71.6	3.30 ( <i>dd</i> , 9.4-9)	71.7	3.29 ( <i>dd</i> , 9.4-9)	71.6	3.30 ( <i>t</i> , 8.9)	71.7
5'	3.37 ( <i>ddd</i> , 9.6-6-1.8 )	76.8	3.40 ( <i>ddd</i> , 9.6-6.3-1.8)	76.9	3.38 ( <i>ddd</i> , 9.2-6.2-1.7)	77.0	3.37 ( <i>ddd</i> , 9.6-6.3-1.7)	76.9
6'a	3.62 ( <i>dd</i> , 11.1-6)	68.0	3.63 ( <i>dd</i> , 11.2-6.3)	68.1	3.65 ( <i>dd</i> , 11.3-6.2)	67.8	3.67 ( <i>dd</i> , 11.3-6.4)	68.2
6'b	4.00 ( <i>dd</i> , 11.1-1.8)		4.03 ( <i>dd</i> , 11.2-1.8)	-	3.99 ( <i>dd</i> , 11.3-1.6)	-	4.03 ( <i>dd</i> , 11.3-1.7)	-
$\alpha$ -L-Rha-								
1''	4.77 ( <i>d</i> , 1.7)	102.2	4.78 ( <i>d</i> , 1.8)	102.0	4.80 ( <i>d</i> , 1.3)	99.2	4.82 ( <i>d</i> , 1.6)	99.4
2''	3.86 ( <i>dd</i> , 3.4-1.7)	72.2	4.02 ( <i>dd</i> , 3.4-1.8)	69.8	5.07 ( <i>dd</i> , 3.6-1.6)	74.0	5.26 ( <i>dd</i> , 3.4-1.7)	71.2
3''	3.68 ( <i>dd</i> , 9.5-3.4)	72.3	4.96 ( <i>dd</i> , 9.8-3.4)	75.7	3.86 ( <i>dd</i> , 9.6-3.6)	70.5	5.09 ( <i>dd</i> , 9.9-3.4)	73.2
4''	3.39 ( <i>t</i> , 9.5)	74.0	3.59 ( <i>t</i> , 9.7)	71.3	3.36 ( <i>t</i> , 9.6)	74.2	3.51 ( <i>t</i> , 9.8)	71.4
5''	3.68 ( <i>m</i> )	69.8	3.79 ( <i>dq</i> , 9.6-6.2)	69.9	3.72 ( <i>dq</i> , 9.5-6.2)	69.8	3.85 ( <i>dq</i> , 9.5-6.2)	69.8
6''	1.29 ( <i>d</i> , 6.3)	18.1	1.31 ( <i>d</i> , 6.2)	18.1	1.29 ( <i>d</i> , 6.2)	18.1	1.32 ( <i>d</i> , 6.2)	18.0
2''acetate								
CH <sub>3</sub> -					2.10 ( <i>s</i> )	20.9	2.03 ( <i>s</i> )	20.8
C=O					-	172.9	-	171.7
3''acetate								
CH <sub>3</sub> -			2.12 ( <i>s</i> )	21.1			2.11 ( <i>s</i> )	20.7
C=O			-	172.5			-	172.1

Glc= $\beta$ -D-glucopyranosyl, Rha= $\alpha$ -L-rhamnopyranosyl



