



## New Flavonol Glycoside from the Leaves of *Ventilago africana*

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Diane Patricia Apie Gossan, Abdulmagid Alabdul Magid, Philomène Akoua Yao-Kouassi, Damien Le Faucheur, Antoine Ahibo Coffy, et al.. New Flavonol Glycoside from the Leaves of *Ventilago africana*. Natural Product Communications , 2015, 10 (11), pp.1934578X1501001. 10.1177/1934578X1501001103 . hal-03407986

**HAL Id: hal-03407986**

**<https://hal.univ-reims.fr/hal-03407986>**

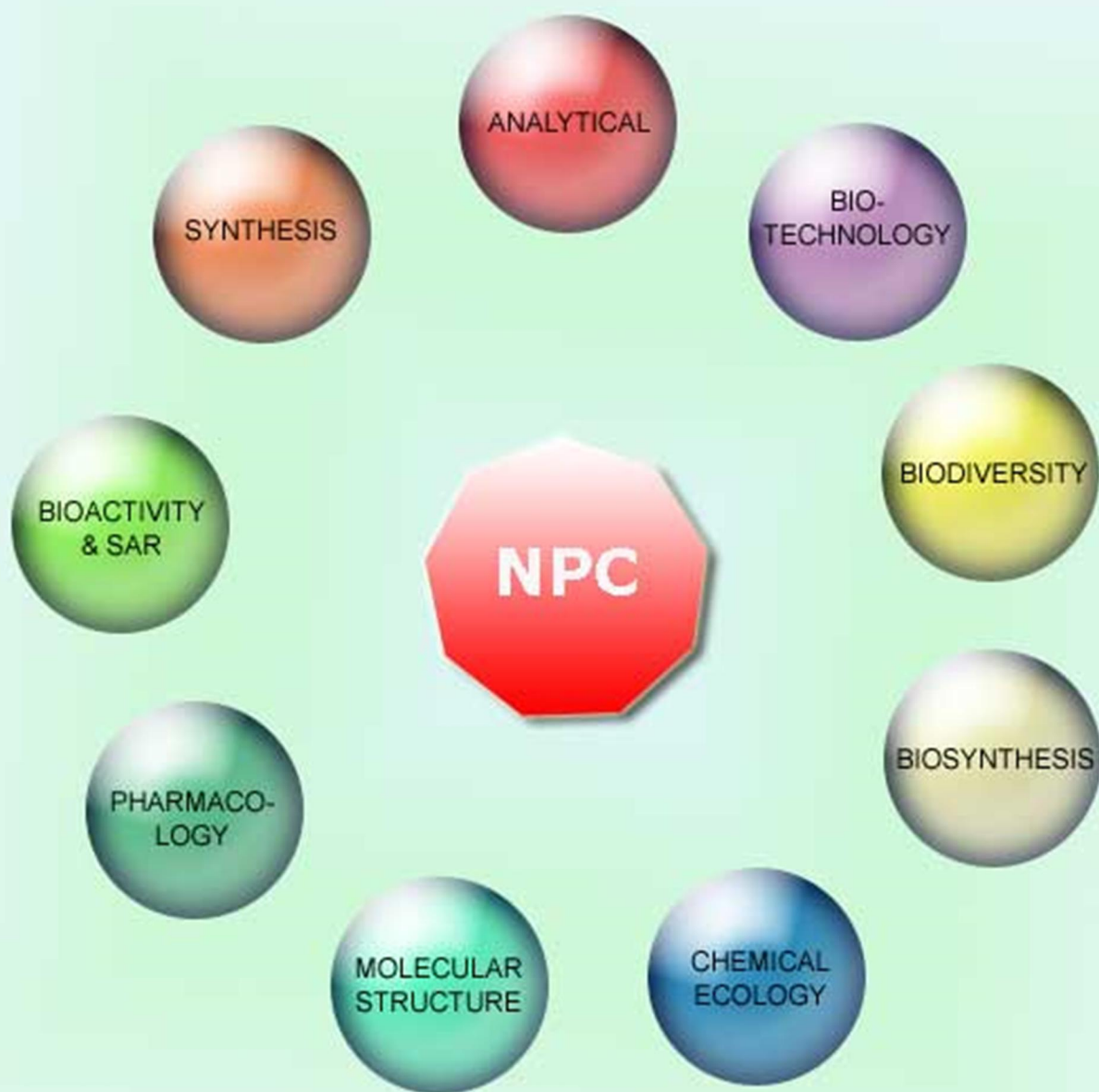
Submitted on 28 Oct 2021

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# NATURAL PRODUCT COMMUNICATIONS

An International Journal for Communications and Reviews Covering all  
Aspects of Natural Products Research



Volume 10. Issue 11. Pages 1797-2018. 2015  
ISSN 1934-578X (printed); ISSN 1555-9475 (online)  
[www.naturalproduct.us](http://www.naturalproduct.us)

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New Flavonol Glycoside from the Leaves of *Ventilago africana*Diane Patricia Apie Gossan<sup>a,b</sup>, Abdulmagid Alabdul Magid<sup>\*a</sup>, Philomène Akoua Yao-Kouassi<sup>b</sup>, Damien Le Faucheur<sup>a</sup>, Antoine Ahibo Coffy<sup>b</sup>, Dominique Harakat<sup>c</sup> and Laurence Voutquenne-Nazabadioko<sup>a</sup><sup>a</sup>ICMR-UMR CNRS 7312, Groupe Isolement et Structure, Campus Sciences, Bat. 18, BP 1039, 51687 Reims Cedex 2, France<sup>b</sup>Laboratoire de Chimie Organique Biologique, 01 BPV 34 Abidjan 01, Université Félix-Houphouët Boigny d'Abidjan-Cocody, Côte d'Ivoire<sup>c</sup>ICMR-UMR CNRS 7312, Service Commun d'Analyses, Campus Sciences, Bat. 18, BP 1039, 51687 Reims Cedex 2, France

abdulmagid.alabdulmagid@univ-reims.fr (A. Alabdul Magid)

Received: June 21<sup>st</sup>, 2015; July 30<sup>th</sup>, 2015

A new flavonol diglycoside, rhamnocitrin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-galactopyranoside, was isolated from the leaves of *Ventilago Africana*, in addition to 11 known flavonoids. Their structures were determined by spectroscopic methods including 1D- and 2D-NMR, and HR-ESI-MS analysis. The isolated compounds were evaluated for their antioxidant activity by using DPPH radical-scavenging assay. Compounds 4, 7-9 have discrete to good antioxidant potential with EC<sub>50</sub> values ranging from 20.9 to 40.4  $\mu$ M, compared with ascorbic acid (EC<sub>50</sub> 60  $\mu$ M) used as positive control.

**Keywords:** *Ventilago africana*, Rhamnaceae, Flavonoids; DPPH free radical scavenging activity.

*Ventilago africana* Exell is a liane with a thick, soft, woody stem belonging to the family Rhamnaceae [1]. It is distributed in evergreen forests, especially marshy sites and mangroves, from Guinea-Bissau to Nigeria, and across the Congo basin to Uganda and Angola [2]. *V. africana* has been used in traditional medicine for the treatment of *dysmenorrhea* and as a febrifuge [2]. Previous chemical studies of the genus *Ventilago* have shown the presence of a variety of anthraquinones, naphthoquinones, quinones, and benzoisochromanquinones [3]. In the course of our search for interesting bioactive substances in nature, the 80% aqueous methanol extract of the leaves of *V. africana* was investigated. As a result, a new flavonol diglycoside was identified, together with eleven known flavonoids. Free radical scavenging activities of the isolated compounds are also described in this paper.

The *n*-BuOH-soluble fraction of the 80% MeOH extract of the leaves of *V. africana* was separated by a combination of chromatographic methods to obtain a new flavonol diglycoside **1**, in addition to eleven known compounds (**2**-**12**) (Figure 1). Compounds **2**-**12** were elucidated as kaempferol-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside (**2**) [4], kaempferol-3-*O*-(2,6-di-*O*- $\alpha$ -L-rhamnopyranosyl- $\beta$ -D-glucopyranoside (**3**) [5], kaempferol-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-galactopyranoside (**4**) [6], rhamnocitrin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside (**5**) [6], rhamnocitrin-3-*O*-(2,6-di-*O*- $\alpha$ -L-rhamnopyranosyl- $\beta$ -D-glucopyranoside (**6**) [7], quercetin (**7**) [8], quercetin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside (**8**) [9], quercetin-3-*O*-(2,6-di-*O*- $\alpha$ -L-rhamnopyranosyl- $\beta$ -D-glucopyranoside (**9**) [9], rhamnetin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside (**10**) [10], isorhamnetin 3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside (**11**) [10], and rhamnazin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside (**12**) [11]. To the best of our knowledge, this is the first report of flavonoids in the genus *Ventilago*.

Compound **1** was isolated as an amorphous, yellow powder, and its molecular formula was determined to be C<sub>28</sub>H<sub>32</sub>O<sub>15</sub> by HR-ESI-MS

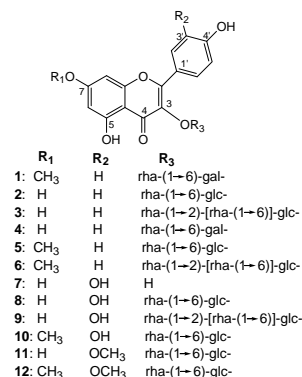


Figure 1: Chemical structure of compounds **1**-**12**, isolated from *V. africana*.

from the ion at *m/z* 631.1636 [M + Na]<sup>+</sup> (C<sub>28</sub>H<sub>32</sub>O<sub>15</sub>Na, calcd 631.1639). The UV spectrum revealed absorption bands at 266 and 346 nm, suggesting a flavonol skeleton. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** comprised resonances corresponding to aromatic and glycosidic protons and carbons, and an OCH<sub>3</sub> ( $\delta$ <sub>C</sub> 56.5;  $\delta$ <sub>H</sub> 3.92). Four aromatic doublets corresponded to H-6 [ $\delta$ <sub>H</sub> 6.38 (1H, *J* = 1.1 Hz)], *meta*-coupled with H-8 [ $\delta$ <sub>H</sub> 6.65 (1H, *J* = 1.1 Hz)] on the A ring, and to H-2', H-6' [ $\delta$ <sub>H</sub> 8.14 (2H, *J* = 8.0 Hz)], *ortho*-coupled with H-3', H-5' [ $\delta$ <sub>H</sub> 6.92 (2H, *J* = 8.0 Hz)] on the B ring. Full identification of the aglycone was finally achieved by 2D-NMR spectroscopy. The HMBC correlation between  $\delta$ <sub>H</sub> 3.92 (OCH<sub>3</sub>) and  $\delta$ <sub>C</sub> 167.5 (C-7) placed the OCH<sub>3</sub> at C-7 of the aglycone, which led to the rhamnocitrin structure (7-methoxy 3,5,4'-trihydroxy-flavone) [7]. Furthermore, two anomeric proton resonances corresponding to *O*-linked sugars were displayed in the <sup>1</sup>H NMR spectrum as two doublets at  $\delta$ <sub>H-1''</sub> 5.10 (d, *J* = 7.8 Hz) and  $\delta$ <sub>H-1'''</sub> 4.54, *J* = 1.2 Hz. Based on the results of acid hydrolysis of the flavonoids mixture, the magnitudes of their *J*<sub>1,2</sub> coupling constants and the analysis of 1D and 2D-NMR data, the sugar units were elucidated as  $\beta$ -D-galactopyranose ( $\delta$ <sub>H-1''</sub> 5.10;  $\delta$ <sub>C-1''</sub> 105.3) and  $\alpha$ -L-rhamnopyranose ( $\delta$ <sub>H-1'''</sub> 4.54;  $\delta$ <sub>C-1'''</sub> 101.9) [12]. The  $\beta$ -D-gal was characterized by the

large coupling constants  $J_{H-1,H-2}$  and  $J_{H-2,H-3}$  ( $> 7.8$  Hz) and the small coupling constant  $J_{H-3,H-4}$  (3.3 Hz), whereas the  $\alpha$ -L-rha was characterized by the small coupling constants  $J_{H-1,H-2}$  (1.2 Hz) and its methyl group at  $\delta_{H-6}$  1.20 (d,  $J = 6.0$  Hz) and  $\delta_{C-6}$  18.0. The glycosidic linkage was established by the HMBC correlations between  $\delta_{H-1''}$  5.10 and  $\delta_C$  135.8 (C-3) and between  $\delta_{H-1'''}$  4.54 and  $\delta_{C-6''}$  67.5, indicating that the galactose unit was located at C-3 of the aglycone and the rhamnose unit was attached to C-6 of galactose. Thus, **1** was characterized as rhamnocitrin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)]- $\beta$ -D-galactopyranoside.

In order to assess the antioxidative properties of **1-12**, the radical scavenging activity of these compounds on DPPH was measured. According to the results, summarized in Table 1, compounds **4**, **7**, **8**, and **9** exhibited a good antioxidant potential ( $EC_{50}$  values ranging from 20.9 to 40.4  $\mu$ M) compared with ascorbic acid, which was used as a positive control ( $EC_{50}$  60  $\mu$ M) (Table 1).

Compounds **7-10** were found to be active, which indicated that the di-OH substitution at 3' and 4' of the B-ring is particularly important to the antiradical activity of a flavonoid. Compounds **2** and **4** shared a common aglycone mono-OH substituted in the B-ring. The only difference was the nature of the disaccharide chain linked at C-3, rha-(1 $\rightarrow$ 6)-glc- (**2**) and rha-(1 $\rightarrow$ 6)-gal- (**4**), suggesting that the galactose might contribute to the antioxidant activity.

**Table 1:** DPPH radical scavenging activity of compounds **1-12**.

Compds	$EC_{50} \pm S.D.$ ( $\mu$ M)	Compds	$EC_{50} \pm S.D.$ ( $\mu$ M)
<b>1</b>	- <sup>a</sup>	<b>8</b>	40.2 $\pm$ 0.7
<b>2</b>	- <sup>a</sup>	<b>9</b>	36.5 $\pm$ 0.6
<b>3</b>	- <sup>a</sup>	<b>10</b>	65.5 $\pm$ 1.9
<b>4</b>	40.4 $\pm$ 0.9	<b>11</b>	- <sup>a</sup>
<b>5</b>	- <sup>a</sup>	<b>12</b>	- <sup>a</sup>
<b>6</b>	- <sup>a</sup>	Ascorbic acid <sup>b</sup>	60.2 $\pm$ 1.2
<b>7</b>	20.9 $\pm$ 0.5		

<sup>a</sup> 50% inhibition not achieved at the concentration of 200  $\mu$ g/mL. <sup>b</sup> Used as a positive control.

Comparison of the antioxidant activity of compounds **1** with **4** and **8** with **10** indicated that the methoxy group at C-7 in **1** or **10** decreased activity. The free 3'-OH was also found to be important for antioxidant activity by comparison of the antioxidant activity of **8** (3'-OH) with **11** (3'-OCH<sub>3</sub>). The same result was found by comparison of activity of **10** and **12**. Thus, the hindrance effect (methoxy groups at C-7 and/or C-3'), the nature of the saccharide chain linked at C-3, and the B ring OH substitution (4'-OH or 3',4'-di-OH) in the flavonoid structures are determinant in the scavenging of free radicals.

## Experimental

**General:** NMR, Bruker Avance DRX III 500; HR-ESI-MS, Micromass Q-TOF micro instrument; Optical rotations, Perkin-Elmer 341 polarimeter; UV, Shimadzu UV-2450 spectrophotometer in MeOH; TLC, pre-coated silica-gel 60 F<sub>254</sub>; CC, Kieselgel 60 (63-200 mesh) or LiChroprep RP-18 (40-63  $\mu$ m); Flash chromatography, Grace Reveleris system with dual UV and ELSD detection equipped with a 12g RP-C<sub>18</sub> column. The mobile phase was water and methanol with a flow rate of 30 mL/min and the effluents were monitored at 205, 225, 250, and 360 nm. HPLC was performed on a Dionex apparatus equipped with an ASI-100 autosampler, an Ultimate 3000 pump, a diode array detector UVD 340S and a Chromeleon software. RP-C<sub>18</sub> column (Phenomenex 250x15 mm, Luna 5 $\mu$ ) was used for semi preparative HPLC with a binary gradient eluent (H<sub>2</sub>O (pH 2.4 with TFA); MeCN) and a flow rate of 6 mL/min; the chromatogram was monitored at 205, 225, 250, and 350 nm. Absorbance values in the DPPH free radical

scavenging assay were read on a Fluostar omega microplate reader (BMG labtech).

**Plant material:** The leaves of *V. africana* were collected in Adiopodoumé, Ivory Coast, in January 2011. A voucher specimen (Aké-Assi-21254) has been deposited in the herbarium of the National Center of Floristics of FHB University of Cocody (Ivory Coast).

**Extraction and isolation:** The powdered dry leaves of *V. africana* (800 g) were percolated with 14 L of 80% MeOH. After methanol evaporation and concentration to 2 L, the aqueous residue was successively partitioned with light petroleum, CH<sub>2</sub>Cl<sub>2</sub>, and *n*-BuOH. The *n*-BuOH extract (43.8 g) was subjected to Diaion HP20 macroporous adsorbent resin CC using a MeOH-H<sub>2</sub>O gradient (25, 50, 75, and 100% MeOH) to yield fractions I-IV, successively. Fraction II (9.7 g) was subjected to RP-C<sub>18</sub> CC with a gradient system of MeOH-H<sub>2</sub>O (25-45% MeOH) to afford 12 fractions (B<sub>1</sub>-B<sub>12</sub>). Further purification of B<sub>4</sub> (0.42 g) (eluted with MeOH-H<sub>2</sub>O, 3:7) by RP-C<sub>18</sub> chromatography using a MeOH-H<sub>2</sub>O gradient (6:4-7:3) and then by semi-prep HPLC (14% MeCN) afforded compounds **9** (*rt* 10.9 min, 9 mg), **8** (*rt* 11.9 min, 10 mg), and **3** (*rt* 14.0 min, 19 mg). Further purification of B<sub>7</sub> (0.61 g) (eluted with MeOH-H<sub>2</sub>O, 35:65) by RP-C<sub>18</sub> chromatography using a MeOH-H<sub>2</sub>O gradient (5:5-6:4) and then by semi-prep HPLC using a binary gradient (16-20% MeCN in 30 min) yielded compounds **4** (*rt* 16.5 min, 5 mg), **2** (*rt* 17.5 min, 26 mg), and **11** (*rt* 20.4 min, 4 mg). Fraction III (12 g) was subjected to silica gel VLC eluted successively with CHCl<sub>3</sub>-MeOH-H<sub>2</sub>O (95:5:0, 9:1:0, 85:15:0, 8:2:0, 75:25:0, 7:3:0.5) to yield fractions C<sub>1</sub>-C<sub>6</sub>. Fraction C<sub>2</sub> (0.28 g) was further separated by RP-C<sub>18</sub> CC eluted with a gradient of MeOH:H<sub>2</sub>O (4:6-8:2) to afford 16 mg of **13** and 33 mg of **7**. Fraction C<sub>4</sub> (0.84 g) was further purified by RP-C<sub>18</sub> flash chromatography using a binary gradient (30-80% MeOH in 60 min) and then by semi-prep HPLC (27-32% MeCN in 50 min) to afford compound **5** (*rt* 12.5 min, 11 mg). Fraction C<sub>6</sub> (1.1 g) was further purified by RP-C<sub>18</sub> VLC and then by semi-prep HPLC (24-26% MeCN in 50 min) to yield compounds **6** (*rt* 11.1 min, 12 mg) and **12** (*rt* 13.3 min, 8 mg) or isocratic elution with 14% MeCN to give compounds **10** (*rt* 13.8 min, 10 mg) and **1** (*rt* 21.3 min, 11 mg).

## Rhamnocitrin-3-*O*- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 6)]- $\beta$ -D-galactopyranoside (**1**)

$[\alpha]_D$ : -27.2 (*c* 0.13, MeOH).

UV/Vis  $\lambda_{max}$  (MeOH) nm (Abs.): 266 (0.58), 348 (0.50).

<sup>1</sup>H NMR (500 MHz, MeOH-*d*<sub>4</sub>): 1.20 (1H, d,  $J = 6.0$  Hz, H-6''), 3.30 (1H, t,  $J = 9.4$  Hz, H-4''), 3.42 (1H, dd,  $J = 10.3$ -6.1 Hz, H-6''), 3.51 (1H, dd,  $J = 9.4$ -3.2 Hz, H-3''), 3.54 (1H, m, H-5''), 3.56 (1H, dd,  $J = 9.0$ -3.3 Hz, H-3''), 3.60 (1H, dd,  $J = 3.2$ -1.2 Hz, H-2''), 3.64 (1H, brdt,  $J = 6.1$  Hz, H-5''), 3.74 (1H, dd,  $J = 10.3$ -5.5 Hz, H-6''), 3.79 (1H, d,  $J = 3.2$  Hz, H-4''), 3.82 (1H, dd,  $J = 9.0$ -7.8 Hz, H-2''), 3.92 (3H, s, 7-OMe), 4.54 (1H, d,  $J = 1.2$  Hz, H-1''), 5.10 (1H, d,  $J = 7.8$  Hz, H-1''), 6.38 (1H, s, H-6), 6.65 (1H, s, H-8), 6.92 (2H, d,  $J = 8.0$  Hz, H-3',5'), 8.14 (2H, d,  $J = 8.0$  Hz, H-2',6').

<sup>13</sup>C NMR (125 MHz MeOH-*d*<sub>4</sub>): 18.0 (CH<sub>3</sub>, C-6''), 56.5 (7-OCH<sub>3</sub>), 67.5 (CH<sub>2</sub>, C-6''), 69.7 (CH, C-5''), 70.2 (CH, C-4''), 72.1 (CH, C-2''), 72.3 (CH, C-3''), 73.0 (CH, C-2''), 73.9 (CH, C-4''), 75.0 (CH, C-3''), 75.4 (CH, C-5''), 93.3 (CH, C-8), 99.2 (CH, C-6), 101.9 (CH, C-1''), 105.3 (CH, C-1''), 106.5 (C, C-10), 116.2 (CH, C-3',5'), 122.6 (C, C-1'), 132.6 (CH, C-2',6'), 135.8 (C, C-3), 158.5 (C, C-9), 159.7 (C, C-2), 162.0 (C, C-4'), 163.8 (C, C-5), 167.5 (C, C-7), 179.8 (C, C-4).

HR-ESI-MS: *m/z* [M + Na<sup>+</sup>] calcd for C<sub>28</sub>H<sub>32</sub>O<sub>15</sub>Na: 631.1639; found: 631.1636.

**Acid hydrolysis:** Acid hydrolysis of the *n*-BuOH soluble fraction was realized as previously described [13]. Briefly, 1 g was refluxed with 50 mL of 2M HCl for 4 h. After extraction with ethyl acetate (3 x 30 mL), the aqueous layer was evaporated to furnish the monosaccharide residue (300 mg). Three sugars were identified as D-glucose, D-galactose and L-rhamnose by comparison with authentic samples on TLC and by measurement of the optical rotation of each purified sugar.

**DPPH free radical scavenging assay:** The scavenging activity of isolated compounds against DPPH was investigated by spectrophotometric methodology, as previously described [13]. Briefly, 5  $\mu$ L of either the standard or sample solutions (dissolved in DMSO) was mixed with 95  $\mu$ L of DPPH solution (158  $\mu$ M, dissolved in absolute EtOH). After mixing gently and incubating for

30 min at 37°C, the optical density was measured at  $\lambda$  515 nm. The percentage of absorbance inhibition at  $\lambda$  515 nm was calculated using the following equation: % inhibition  $[(Ab_{\text{control}} - Ab_{\text{sample}})/Ab_{\text{control}}] \times 100$ . DPPH solution in EtOH was used as a control. The curve of the % scavenging activity against the concentration of sample was prepared by the MSeExcel based program to obtain the EC<sub>50</sub>. All the tests were conducted in triplicate. The experimental data were expressed as mean  $\pm$  standard deviation.

**Acknowledgments** - The authors are grateful to CNRS, Conseil Régional Champagne Ardenne, Conseil Général de la Marne, and Ministry of Higher Education and Research (MESR), and to the PLANET CPER project for financial support.

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