

# A New Flavonol Glycoside from *Tristemma hirtum* (Melastomataceae)

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Abstract – Chemical investigation of the plant *Tristemma hirtum* P. Beauv (Melastomataceae) resulted to the isolation of a new flavonol glycoside named quercetin-7-*O*- $\alpha$ -*D*-arabinofuranoside (1), together with nine known compounds including 3'-hexadecanoyl-2'-(9aZ)-tetradecanoyl-glycerol 1'-*O*-[ $\beta$ -*D*-galactopyranosyl-(1"  $\rightarrow$  6")- $\alpha$ -*D*-galactopyranoside] (2), arjunolic acid (3),  $\beta$ -sitosterol-3-*O*- $\beta$ -*D*-glucopyranoside (4), terminolic acid (5), quercetin (6), asiatic acid (7), maslinic acid (8), 1 $\beta$ -*O*-galloylpedunculagin (9) and 6-hydroxyapigenin 7-*O*- $\beta$ -*D*-glucopyranoside (10) from the methanol extract using normal and reversed phase column chromatography. The structures of these compounds were determined by comprehensive interpretation of their spectral data mainly including 1D- 2D-NMR (<sup>1</sup>H-<sup>1</sup>H COSY, HSQC, and HMBC) spectroscopic and ESI-TOF-MS mass spectrometric analysis.

Keywords - Tristemma hirtum, Melastomataceae, flavonol glycoside

# Introduction

Melastomataceae are among the most abundant and diversified groups of plants throughout the tropics in the world, mainly widespread in many regions of Africa and West Cameroon. They are predominantly pantropical plants, including approximately 163 genera and 4300 species.<sup>1</sup> Many species of this family are known by their different uses in folk medicine as antioxidant,<sup>2,3</sup> antihypertensive,<sup>4</sup> antihyperglycemic,<sup>5</sup> hemostatic<sup>6</sup> and antihepatitis drugs.7 Antiinflammatory,6 antimicrobial,3,8 and cytotoxic effects<sup>2</sup> have also been investigated. Cumulative phytochemical studies of Melastomataceae plants have indicated an abundance of polyphenols9, flavonoids10, fatty acids, steroids, and free triterpenoids.<sup>11</sup> A great variety of natural compounds found in this family and their pharmacological properties prompted us to study the chemical constituents of Tristemma hirtum P. Beauv.

As a rare species, T. hirtum is widely used in the West

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Region of Cameroon for the treatment of typhoid, skin diseases, hemorrhoids and pregnancy control as declared by the ethnical population. Despite of the traditional use of this plant, no scientific report or information was found in the literature regarding either its biologica activity or its chemical constituents. In our continuous investigation of secondary metabolites from Cameroonian medicinal plants belonging to Melastomataceae family<sup>3</sup>, the present study was undertaken in order to characterize the chemical constituents of the aerial part of this plant. The study led the isolation and structural elucidation of ten to compounds from both ethyl acetate and *n*-butanol soluble fractions of its methanol extract, amongst which one new flavonol glycoside (1) and nine known compounds (2-10)were characterized.

### **Experimental**

**General experimental procedures** – UV spectra were recorded using a PhotoLab 6600 UV-VIS 143320661 2.17-WTW-2.20 and the IR spectra were recorded as KBr discs on a Shimadzu FTIR-8400S. The <sup>1</sup>H-NMR, COSY, HMQC and HMBC spectra were performed in deuterated solvents on a Bruker DRX-500 Spectrometer at 500 MHz/125 MHz and on a Bruker AVANCE 700 spectro-

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meter (Bruker, Germany) at 700 MHz/175 MHz. All chemical shifts ( $\delta$ ) are given in ppm units with reference to tetramethylsilane (TMS) as an internal standard, and the coupling constants (J) are in Hz. ESI mass spectra were carried out on an Agilent 6210 ESI-TOF mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Column chromatography was performed using 70 - 230 mesh and 230 - 400 mesh silica gel 60 (Merck), and sephadex LH-20. Fractions were monitored by TLC using Merck pre-coated silica gel sheets (60 F<sub>254</sub>), and spots were visualized under UV light (254 and 365 nm) and by spraying with 50% H<sub>2</sub>SO<sub>4</sub> and heating at 110 °C.

**Plant material** – The aerial part of *Tristemma hirtum* P. Beauv (Melastomataceae) was collected in the Bamboutos sub-division, Bangang village near Mbouda (West Region of Cameroon) in January 2015. The plant was identified at the Cameroon National Herbarium, Yaoundé, Cameroon by comparison with an existed specimen (33937/HNC).

**Extraction and isolation** – The air-dried plant of *Tristemma hirtum* P. Beauv (3 kg) were extracted three times (each time for 24 h) by maceration with MeOH (15 L) at room temperature. The filtrate obtained was concentrated under reduced pressure to yield a dark crude extract (543.3 g). A part of this extract (519 g) was suspended in water (500 mL) and successively extracted with EtOAc and *n*-BuOH which were concentrated to dryness under reduced pressure to afford EtOAc (130 g) and *n*-BuOH (136 g) fractions, respectively.

A part of the EtOAc extract (100 g) was subjected to column chromatography (CC) over silica gel using hexane-EtOAc (95:5  $\rightarrow$  0:100) and EtOAc-MeOH (100:0  $\rightarrow$  70:30) to afford 64 fractions of 300 mL each. These fractions were combined on the basis of their TLC profiles into six main fractions  $F1 \rightarrow F6$ . Fraction F6 (6.5 g) was rechromatographed on silica gel column using the tertiary system of EtOAc-MeOH-H<sub>2</sub>O (90:10:5) to afford ten sub-fractions (F6<sub>a</sub>-F6<sub>i</sub>). Subfraction F6<sub>i</sub> (200 mg) was further purified on the reverse phase (RP-18) column chromatography, eluting with MeOH- $H_2O$  (95:5) to yield compound 2 (58.9 mg). Fraction F5 (21 g) was subjected to column chromatography over sephadex LH-20 using MeOH as the eluent to yield 3 (98 mg) as well as a complex mixture which was purified using a system of n-hexane-EtOAc (20:80) to yield 4 (6.1 mg) and 5 (8.4 mg). Fraction F3 (15 g) was rechromatographed on silica gel column with hexane-EtOAc (40:60) to afford four sub-fractions ( $F3_a$ - $F3_d$ ). Compound 6 (40 mg) was crystalized from sub-fractions F3<sub>a</sub> (150 mg) in MeOH. The subfraction F3<sub>d</sub> was subjected to CC over sephadex LH-

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Table 1. <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz) and <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 125 MHz) data of compound 1 (J in Hz)

Position	Chemical shift	
	$\delta_{ m C}$	$\delta_{ m H}$
2	158.0	
3	131.9	
4	173.5	
5	164.4	
6	99.2	6.24 (1H, <i>br s</i> )
7	161.3	
8	94.1	6.42 (1H, <i>br s</i> )
9	157.8	
10	104.6	
1'	121.8	
2'	116.1	7.55 (1H, <i>br s</i> )
3'	148.0	
4'	158.1	
5'	115.2	6.93 (1H, <i>d</i> , <i>J</i> = 8.4 Hz)
6'	121.9	7.52(1H, <i>br s</i> )
1''	108.2	5.49 (1H, <i>br s</i> )
2"	82.5	4.35 (1H, <i>br s</i> )
3"	78.0	3.92 (1H, <i>m</i> )
4''	84.7	3.87 (1H, <i>m</i> )
5"	60.7	3.50 (1H, <i>m</i> ) 3.53(1H, <i>m</i> )

20 gel using MeOH and then purified on silica gel column using hexane-EtOAc (40:60) as eluent to yield 1 (18.4 mg), 7 (14 mg) and 8 (10.6 mg). Fraction F4 (11 g) was subjected to sephadex LH-20 gel column chromatography to obtain 3 sub-fractions (F4a-F4c). Sub-fraction  $F4_c$  (350 mg) was purified on the reverse phase silica (RP-18) column chromatography eluting with MeOH- $H_2O$  (30:70) to yield compound 9 (25 mg). Subfractions  $(F6_a-F6_i)$  (6 g) were combined mainly on the basis of TLC to a part of *n*-BuOH extract (100 g). The resulting fraction was subjected to column chromatography over silica gel eluted with (EtOAc-MeOH with increasing polarity) to yield five main fractions (A-E). Fraction C (EtOAc-MeOH 80:20) (8.8 g) was subjected to sephadex LH-20 gel column chromatography to obtain 10 (125 mg) upon recrystallization from MeOH and a mixture C2.

**Compound (1)** – Yellow amorphous powder. UV  $\lambda_{max}$  (MeOH) nm: 229, 306, 351; IR  $\nu_{max}$  (KBr) cm<sup>-1</sup>: 3292, 1730, 1589, 1500, 1370; ESIMS (positive mode) *m/z*: 434.9 [M+H]<sup>+</sup> and ESIMS (negative mode) *m/z*: 432.9 [M-H]<sup>-</sup> (molecular formula C<sub>20</sub>H<sub>18</sub>O<sub>11</sub>); <sup>1</sup>H and <sup>13</sup>C NMR: see Table 1.

3'-hexadecanoyl-2'-(9aZ)-tetradecanoylglycerol 1'-O- $[\beta$ -D-galactopyranosyl- $(1'' \rightarrow 6'')$ - $\alpha$ -D-galactopyranoside] (2) – Yellow oil. ESIMS (positive mode): m/z 863.4  $[M+H]^+$  (C<sub>45</sub>H<sub>82</sub>O<sub>15</sub>). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{H}$ : 0.90 (3H, t, J = 7.1 Hz), 0.90 (3H, t, J = 7.1 Hz) 1.30 (2H, m), 1.20 - 1.40 (4H, m), 1.63 (2H, m), 2.06 (2H, m), 2.34 (4H, t, J = 6.9 Hz), 3.94 - 3.51 (4H, m), 3.92 - 3.73 (4H, m), 3.97 (1H, d, J = 5.4 Hz, H<sub>a</sub>-1'), 3.75 (1H, d, J = 2.2 Hz, H<sub>b</sub>-1'), 4.45 (1H, d, J = 12.2 Hz, H<sub>a</sub>-3'), 4.23  $(1H, d, J = 6.6 \text{ Hz}, H_{b}-3'), 4.26 (1H, d, J = 9.4 \text{ Hz}, H-1''),$ 4.88 (1H; d, J = 3.7 Hz, H-1""), 5.26 (1H, m, H-2'), 5.37 (2H, m); <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 125 MHz):  $\delta_{\rm C}$  173.7, 173.3, 103.9 (C-1"), 73.3 (C-2"), 70.0 (C-3") 71.2 (C-4"), 71.3 (C-5"), 66.4 (C-6"), 99.2 (C-1""), 68.9 (C-2""), 71.1 (C-3""), 73.2 (C-4"'), 69.8 (C-5"'), 61.5 (C-6"'), 67.4 (C-1'), 70.3 (C-2'), 62.5 (C-3').

**Arjunolic acid (3)** – White powder. <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{\rm H}$ : 3.68 (1H, m, H-2), 3.34 (1H, *d*, *J* = 7.8 Hz, H-3), 5.23 (1H, *m*, H-12), 3.26 (1H, *d*, *J* = 11.4 Hz, H-23a), 3.50 (1H, *d*, *J* = 11.4 Hz, H-23b), 0.70 (3H, *s*, H-24), 0.83 (3H, *s*, H-25), 1.06 (3H, *s*, H-26), 1.29 (3H, *s*, H-27), 0.90 (3H, *s*, H-29), 0.95 (3H, *s*, H-30); <sup>13</sup>C (CD<sub>3</sub>OD, 125 MHz)  $\delta_{\rm C}$ : 47.5 (C-1),69.8 (C-2), 78.2 (C-3), 44.3 (C-4), 48.5 (C-5), 19.2 (C-6), 33.6 (C-7), 40.7(C-8), 48.3 (C-9), 38.9 (C-10), 24.1 (C-11), 123.6 (C-12), 145.4 (C-13),42.5 (C-14), 29.0 (C-15), 24.5 (C-16), 47.1 (C-17), 43.0 (C-18), 44.5(C-19), 31.5 (C-20), 34.0 (C-21), 33.5 (C-22), 66.3 (C-23), 14.1 (C-24),17.8 (C-25), 17.6 (C-26), 26.6 (C-27), 182.1 (C-28), 32.1 (C-29), 24.8 (C-30).

β-Sitosterol-3-O-β-D-glucopyranoside (4) – White powder. <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{\text{H}}$ : 0.66 - 1.25 (CH<sub>3</sub> groups), 3.50 (1H, *m*, H-3), 5.35 (1H, *m*, H-5) for aglycone; 5.02 (1H, *d*, *J* = 7.5 Hz, H-1') representing the anomeric proton of the sugar; <sup>13</sup>C (CD<sub>3</sub>OD,125 MHz)  $\delta_{\text{C}}$ : 37.3 (C-1), 30.2 (C-2), 78.5 (C-3), 39.2 (C-4), 140.8 (C-5), 121.7 (C-6),31.9 (C-7), 31.9 (C-8), 51.2 (C-9), 36.5 (C-10), 21.1 (C-11), 39.8 (C-12), 42.3 (C-13), 56.8 (C-14), 24.3 (C-15), 28.3 (C-16), 56.0 (C-17), 11.9(C-18), 19.4 (C-19), 36.2 (C-20), 18.8 (C-21), 33.9 (C-22), 26.1 (C-23), 45.9 (C-24), 29.2 (C-25), 19.8 (C-26), 19.3 (C-27), 23.1 (C-28), 12.2(C-29) for aglycone, 102.5 (C-1'), 75.3 (C-2'), 78.6 (C-3'), 71.6 (C-4'),78.1 (C-5'), 62.5 (C-6') for sugar moiety.

**Terminolic acid (5)** – White powder. ESIMS (positive mode): m/z 527.3 [M+Na]<sup>+</sup> (C<sub>30</sub>H<sub>48</sub>O<sub>6</sub>Na). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 700 MHz)  $\delta_{\rm H}$ : 3.52 (1H, m, H-2), 3.10 (1H, m, H-3), 4.26 (1H, m, H-6), 5.22 (1H, m, H-12), 3.20 (1H, m, H-23a), 3.40 (1H, m, H-23b), 0.92 (3H, s, H-24), 1.28 (3H, s, H-25), 0.98 (3H, s, H-26), 1.06 (3H, s, H-27), 0.89

(3H, *s*, H-29), 0.89 (3H, *s*, H-30).<sup>13</sup>C-NMR (CD<sub>3</sub>OD, 175 MHz)  $\delta_{C}$ : 49.3 (C-1), 67.7 (C-2), 76.2 (C-3), 44.2 (C-4), 47.2 (C-5), 66.2 (C-6), 40.1 (C-7), 39.5 (C-8), 47.9 (C-9), 37.2 (C-10), 23.1 (C-11), 122.2 (C-12), 144.0 (C-13), 42.1 (C-14), 27.5 (C-15), 27.6 (C-16), 47.0 (C-17), 42.5 (C-18), 47.1 (C-19), 31.5 (C-20), 33.6 (C-21), 34.0 (C-22), 65.1 (C-23), 16.3 (C-24), 18.6 (C-25), 18.3 (C-26), 26.2 (C-27), 179.1 (C-28), 33.5 (C-29), 24.5 (C-30).

**Quercetin (6)** – Yellow powder. ESIMS (positive mode): m/z 302.2 [M+H]<sup>+</sup> (C<sub>15</sub>H<sub>10</sub>O<sub>7</sub>). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{\rm H}$ : 7.75 (1H, d, J = 2.1 Hz, H-2'), 7.65 (1H, dd, J = 8.5 Hz, H-6'), 6.90 (1H, d, H-5'), 6.40 (1H, d, J = 2.0Hz, H-8), 6.19 (1H, d, H-6). <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta_{\rm C}$ : 176.2 (C-4), 164.1 (C-2), 161.1(C-4'), 157.1 (C-7), 147.5 (C-9), 146.5 (C-5), 144.7 (C-3'), 135.8 (C-3), 123.3 (C-1'), 120.3 (C-6'), 115.1 (C-5'), 114.5 (C-2'), 103.2 (C-10), 98.2 (C-6), 93.2 (C-8).

Asiatic acid (7) – White powder. <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{\text{H}}$ : 3.67 (1H, *m*, H-2), 3.37 (1H, *d*, *J* = 9.2 Hz, H-3), 5.28 (1H, *m*, H-12), 2.88 (1H,*d*, *J* = 11.3 Hz, H-18), 3.29 (1H, *m*, H-23a), 3.52 (1H, *m*, H-23b), 0.71 (3H, *s*, H-24), 0.84 (3H, *s*, H-25), 0.87 (3H, *s*, H-26), 1.16 (3H, *s*, H-27), 0.82 (3H, *d*, *J* = 6.7 Hz, H-29), 0.88 (3H, *d*, *J* = 7.0 Hz, H-30).<sup>13</sup>C-NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta_{\text{C}}$ : 46.8 (C-1), 70.4 (C-2), 77.3 (C-3), 42.5 (C-4), 46.3 (C-5), 19.2 (C-6), 33.7 (C-7), 40.5 (C-8), 48.9 (C-9), 37.2 (C-10), 23.5 (C-11), 126.3 (C-12), 139.1 (C-13), 42.6 (C-14), 29.0 (C-15), 24.5 (C-16), 47.1 (C-17), 41.6 (C-18), 37.5 (C-19), 37.8 (C-20), 31.6 (C-21), 35.4 (C-22), 65.1 (C-23), 13.4 (C-24), 17.6 (C-25), 18.5 (C-26), 22.9 (C-27), 175.2 (C-28), 21.4 (C-29), 17.5 (C-30).

**Maslinic acid (8)** – White powder. <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{\text{H}}$ : 3.64 (1H, *m*, H-2), 2.93 (1H, *d*, *J* = 7.5 Hz, H-3), 5.28 (1H, *m*, H-12), 2.87 (1H, *m*, H-18), 0.83 (1H, *s*, H-23), 1.03 (3H, *s*, H-24), 1.28 (3H, *s*, H-25), 0.98 (3H, *s*, H-26), 1.18 (3H, *s*, H-27), 0.96 (3H, *s*, H-29), 0.93 (3H, *s*, H-30). <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta_{\text{C}}$ : 47.5 (C-1), 68.6 (C-2), 83.2 (C-3), 40.5 (C-4), 55.1 (C-5), 19.5 (C-6), 33.9 (C-7), 39.5 (C-8), 47.9 (C-9), 37.1 (C-10), 23.1 (C-11), 121.9 (C-12), 144.2 (C-13), 42.1 (C-14), 27.5 (C-15), 27.6 (C-16), 39.4 (C-17), 41.8 (C-18), 47.2 (C-19), 31.6 (C-20), 34.9 (C-21), 33.8 (C-22), 16.2 (C-23), 28.9 (C-24), 15.5 (C-25), 16.3 (C-26), 23.7 (C-27), 180.1 (C-28), 34.5 (C-29), 26.5 (C-30).

**1***β***-O-galloylpedunculagin** (9) – Yellowish powder. ESIMS (negative mode): m/z 935.0 [M-H]<sup>-</sup> (C<sub>41</sub>H<sub>28</sub>O<sub>26</sub>). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{\rm H}$ : glucose moiety - 6.14 (1H, d, J = 8.5 Hz, H-1), 5.21 (1H, dd, J = 3.6, 9.9 Hz, H-2), 5.48 (1H, t, J = 9.7 Hz, H-3), 5.21 (1H, m, H-4), 4.38 (1H, m, H-5), 3.92 (1H, m, H-6a), 5.37 (1H, dd,

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*J* = 6.6, 13.1 Hz, H-6b); 7.12 (2H, *s*, galloyl-H), 6.64 (1H, *s*, C-3 HHDP moiety), 6.41 (1H, *s*, C-6 HHDP moiety), 6.55 (1H, *s*, C-3' HHDP moiety), 6.70 (1H, *s*, C-6' HHDP moiety); <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta_{C}$ : glucose moiety - 91.6 (C-1), 75.5 (C-2), 76.8 (C-3), 68.2 (C-4), 72.7 (C-5), 62.3 (C-6). 120.0; C-1 galloyl moiety - 109.9, 147.0, 140.0, 147.0, 109.9, 166.2 (ester); C-2 HHDP moiety - 115.5, 124.0, 108.0, 145.8, 137.5, 144.0, 169.7 (ester); C-3 HHDP - 115.5, 124.0, 108.0, 145.8, 137.5, 144.0, 170.8 (ester); C-4 HHDP moiety - 116.7, 124.0, 108.0, 146.0, 137.6, 144.4, 169.3 (ester); C-6 HHDP moiety - 115.5, 124.0, 146.3, 137.5, 144.1, 169.8 (ester).

6-Hydroxyapigenin-7-*O*-β-D-glucopyranoside (10) – Yellow powder. ESIMS (negative mode): m/z 446.9 [M-H]<sup>-</sup> and ESIMS (positive mode): m/z 448.9 [M+H]<sup>+</sup> (C<sub>21</sub>H<sub>20</sub>O<sub>11</sub>). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz)  $\delta_{\rm H}$ : 7.94 [2H, *d*, *J* = 8.8 Hz, H-2', 6'], 7.02 (1H, *s*, H-8), 6.94 [2H, *d* (BB'), H-3', 5'], 6.84 (1H, *s*, H-3), 5.01 (1H, *d*, *J* = 7.5 Hz, H-1"), 3.48 (1H, *d*, *J* = 2.1 Hz, H-6"a), 3.76 (1H, *d*, *J* = 3.9 Hz, H-6"b), 3.46 – 3.36 (*m*, H-2", 3", 5"), 3.46 (1H, *dd*, *J* = 9.2, 9.2 Hz, H-4"); <sup>13</sup>C-NMR (CD<sub>3</sub>OD, 125 MHz)  $\delta_{\rm C}$ : 182.9 (C-4), 164.5 (C-2), 161.7(C-4'), 149.5 (C-9), 151.8 (C-7), 147.0 (C-5), 130.9 (C-6), 128.4 (d, C-2'/C-6'), 121.3 (C-1'), 115.9 (C-3', 5'), 106.2 (C-10), 102.9 (C-3), 101.4 (C-1"), 94.5 (C-8), 75.5 (C-5"), 70.3 (C-3"), 76.5 (C-2"), 78.1 (C-4"), 61.0 (C-6").

### **Result and Discussion**

A dry aerial part of *T. hirtum* (3 kg) was extracted with methanol. The crude extract (519 g) suspended in water was successively extracted with EtOAc and *n*-BuOH to yield 130 g and 136 g of EtOAc and *n*-BuOH extracts,



Fig. 1. Chemical structures of compounds isolated from T. hirtum.

respectively. Parts of EtOAc and *n*-BuOH fractions were subjected to column chromatography over silica gel and sephadex LH-20 gel to yield ten secondary metabolites (**1 - 10**) (Fig. 1). Nine among them were identified as 3'hexadecanoyl-2'-(9aZ)-tetradecanoylglycerol 1'-*O*-[ $\beta$ -*D*galactopyranosyl-(1" $\rightarrow$ 6")- $\alpha$ -*D*-galactopyranoside] (**2**),<sup>12</sup> arjunolic acid (**3**),<sup>3</sup>  $\beta$ -sitosterol-3-*O*- $\beta$ -*D*-glucopyranoside (**4**),<sup>13</sup> terminolic acid (**5**),<sup>14</sup> quercetin (**6**),<sup>15</sup> asiatic acid (**7**),<sup>16</sup> maslinic acid (**8**),<sup>17</sup> 1 $\beta$ -*O*-galloylpedunculagin (**9**)<sup>18</sup> and 6-hydroxyapigenin-7-*O*- $\beta$ -*D*-glucopyranoside (**10**)<sup>19</sup> by spectroscopic means and comparison with reported data.

Compound (1) was isolated as a yellow amorphous powder. The molecular formula C<sub>20</sub>H<sub>18</sub>O<sub>11</sub> was suggested by HRESIMS (positive mode) with a  $[M+H]^+$  peak at m/z434.9235 and HRESIMS (negative mode) with a [M-H]<sup>-</sup> peak at m/z 432.9123 indicating the molecular formula  $C_{20}H_{18}O_{11}$ . An important ion peak was observed at m/z $301.9 [M+H-133.1228]^+$ , corresponding to the perdition of a pentose sugar moiety ( $C_5H_9O_4$ ). The <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 500 MHz) spectrum (Table 1) confirmed many of the above features and revealed a set of quercetin signals and arabinofuranose moiety. The presence of quercetin was suggested by the following signals: two broad single at  $\delta_{\rm H}$  6.24 (1H, br s, H-6) and 6.42 (1H, br s, H-8); an ABX spin system due to the aromatic ring protons at  $\delta_{\rm H}$  6.93 (1H, d, J = 8.4 Hz, H-5'), 7.52 (1H, dd, J = 8.4, 2.1 Hz, H-6') and 7.55 (1H, br s, H-2').<sup>16</sup>

The total assignment of the <sup>1</sup>H-NMR [( $\delta_{\rm H}$  5.49, br s, H-1"), 4.35 (1H, br s, H-2"), 3.92 (1H, m, H-3"), 3.87 (1H, *m*, H-4"), 3.50 (1H, *m*, H<sub>a</sub>-5" and 3.53 (1H, *m*, H<sub>b</sub>-5") and <sup>13</sup>C-NMR [ $\delta_{\rm C}$  108.2 (C-1"), 84.7 (C-4"), 82.5 (C-2"), 78.0 (C-3") and 60.7 (C-5")] data of the pentose moiety (Fig. 2), were achieved on the basis of the HSQC, HMBC and <sup>1</sup>H-<sup>1</sup>H COSY correlations. The two downfield carbon signals at  $\delta_{\rm C}$  84.7 and 82.5 compared to the literature suggests it to be an arabinofuranose moiety rather than the arabinopyranosyl form.<sup>20</sup> This sugar was shown to be attached C-7 of guercetin from the HMBC correlation between  $\delta_H$  5.49 (H-1") and  $\delta_C$  161.3 (C-7). Furthermore, the D-configuration for this sugar was assumed based on Massiot and Lavaud's assertion regarding this configuration commonly found for this monosaccharide in natural products from plant kingdom.<sup>21</sup> Therefore, its α-anomeric configuration was able to be determined from the singlet nature of its anomeric proton.<sup>20</sup> Consequently, the structure of compound 1 was determined as quercetin 7-O-a-Darabinofuranoside. It is important to mention that the homologue of this compound (quercetin 7-O- $\alpha$ -Darabinopyranoside) has previously been reported from various sources including Reaumuria soongarica (Tama-



Fig. 2. Selected HMBC and COSY <sup>1</sup>H-<sup>1</sup>H correlations of compound 1.

ricaceae).<sup>22</sup> To the best of our knowledge, compound 1 has not been isolated from a natural source.

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