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### New chromone derivative terminalianone from African plant *Terminalia brownii* Fresen (Combretaceae) in Tanzania

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## New chromone derivative terminalianone from African plant *Terminalia brownii* Fresen (Combretaceae) in Tanzania

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A new chromone derivative named terminalianone (**1**) was isolated from the African plant, *Terminalia brownii* Fresen (Combretaceae) in Tanzania. Its structure was determined to be 7-hydroxy-3-[6'-hydroxyphenyl-2'-oxo-ethyl]chromone by FAB-MS and NMR spectral data.

**Keywords:** *Terminalia brownii* Fresen; Combretaceae; chromone; 7-hydroxy-3-[6'-hydroxyphenyl-2'-oxo-ethyl]chromone

### 1. Introduction

The African plant, *Terminalia brownii* Fresen (Combretaceae), is found in many regions of Africa. It has different vernacular names in different places such as 'orbukoi' in Maasai of Tanzania and *kuuku*, *muwuku* in Kamba of Kenya. Traditional healers in Africa have used *Combretum* and *Terminalia* species due to their anti-infective effect, including antibacterial, antifungal, and antiparasitic activities [1–4]. The Combretaceae family is the source of a wide range of tannins, flavonoids, terpenoids, and stilbenoids. It was reported that the leaves, barks, and fruits of *Terminalia arjuna*, *Terminalia bellerica*, *Terminalia chebula*, and *Terminalia muelleri*; the leaves and fruits of *Phyllanthus emblica*; and the seeds of *Syzygium cumini* were found to have high total phenolic contents and high antioxidant activity [5]. Various types of flavonoids detected from

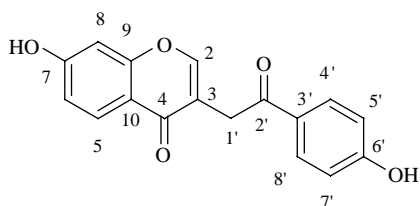
the members of the Combretaceae family include arjunolone, flavones, bicalein, quercetin, kempferol, pelargonin, and resveratrol-3-*O*- $\beta$ -D-rutinoside [6–9].

In this study, a new chromone was isolated from *T. Brownii* Fresen in Tanzania, and its structural elucidation is described (Figure 1).

### 2. Results and discussion

Preparative HPLC of polyphenols on octa decyl silyl (ODS) with 33% CH<sub>3</sub>CN–H<sub>2</sub>O afforded a new compound (**1**). Compound **1** showed a quasi-molecular ion at *m/z* 297.0766 [M + H]<sup>+</sup> compatible with the formula of C<sub>17</sub>H<sub>13</sub>O<sub>5</sub> by positive ion high-resolution FAB-MS. Thus, the molecular formula of **1** was deduced to be C<sub>17</sub>H<sub>12</sub>O<sub>5</sub>. The acetylation of compound **1** provided a diacetate derivative and indicated the presence of two hydroxyl groups in the molecule. The <sup>1</sup>H NMR spectral data for **1**

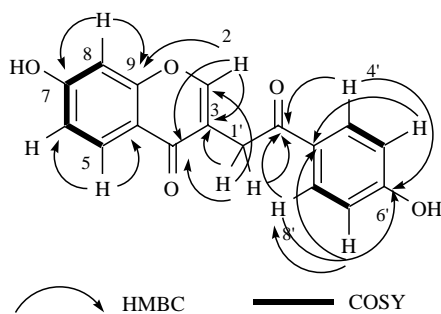
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Figure 1. Structure of compound **1**.

showed two methylene protons and eight methine protons, including one singlet, six doublet, and one double doublet signals (Table 1). The  $^1\text{H}$  NMR signals at  $\delta$  6.88 (2H, d,  $J = 9.0\text{ Hz}$ ) and 7.99 (2H, d,  $J = 9.0\text{ Hz}$ ) were assigned to an AA'BB' spin system of a 1,4-disubstituted phenyl group. The signals of ABX spin system at  $\delta$  6.85 (1H, d,  $J = 2.5\text{ Hz}$ ), 6.92 (1H, dd,  $J = 8.5, 2.5\text{ Hz}$ ), and 7.91 (1H, d,  $J = 8.5\text{ Hz}$ ) indicated the presence of a 1,3,4-trisubstituted phenyl group. They were confirmed by  $^1\text{H}$ - $^1\text{H}$  COSY experiment (Figure 2). The  $^{13}\text{C}$  NMR and DEPT experiments revealed one  $\text{sp}^3$  methylene, eight methines, and eight quaternary carbons, including two hydroxyl substituted carbons ( $\delta$  164.0 and 164.6) and two carbonyl carbons ( $\delta$  178.8 and 197.4) as shown in Table 1. The complete assign-

Table 1.  $^1\text{H}$  (500 MHz) and  $^{13}\text{C}$  (125 MHz) NMR spectral data for **1** in  $\text{CD}_3\text{OD}$ .

Position	$\delta_{\text{C}}$	$\delta_{\text{H}}$	
2	156.1	8.05	s
3	120.2		
4	178.8		
5	128.1	7.91	d (8.5)
6	116.3	6.92	dd (8.5, 2.5)
7	164.0		
8	103.4	6.85	d (2.5)
9	160.3		
10	117.6		
1'	35.4	4.10 (2H)	s
2'	197.4		
3'	129.8		
4'	132.1	7.99	d (9.0)
5'	116.3	6.88	d (9.0)
6'	164.6		
7'	116.3	6.88	d (9.0)
8'	132.1	7.99	d (9.0)

Figure 2. Key HMBC and COSY correlations of compound **1**.

ments of direct  $^1\text{H}$ - $^{13}\text{C}$  connections were established by HSQC experiment. The long-range  $^1\text{H}$ - $^{13}\text{C}$  correlations were analyzed by HMBC experiment. The HMBC correlations from H-2 ( $\delta$  8.05) to C-3 ( $\delta$  120.2), C-4 ( $\delta$  178.8), and C-9 ( $\delta$  160.3); from H-8 ( $\delta$  6.85) to C-7 ( $\delta$  164.0) and C-9 ( $\delta$  160.3); from H-5 ( $\delta$  7.91) to C-10 ( $\delta$  117.6) and C-6 ( $\delta$  116.3) revealed the presence of a 3-substituted-7-hydroxychromone moiety in **1** (Figure 2). The remaining structural moiety was elucidated to be a *para*-hydroxyphenyl-2-oxo-ethyl by HMBC correlations. The HMBC correlations from H-1' ( $\delta$  4.10) to C-2' ( $\delta$  197.4), from H-4' and H-8' ( $\delta$  7.99) to C-2' ( $\delta$  197.4) and C-6' ( $\delta$  164.6), from H-5' and H-7' ( $\delta$  6.88) to C-3' ( $\delta$  129.8) were consistent with a *para*-hydroxyphenyl-2-oxo-ethyl moiety (Figure 2). Furthermore, the HMBC correlations from H-1' ( $\delta$  4.10) to C-2 ( $\delta$  156.1), C-3 ( $\delta$  120.2), and C-4 ( $\delta$  178.8) revealed that this structural moiety was substituted at the C-3 position of 7-hydroxychromone ring as shown in Figure 1. Therefore, the structure of **1** was determined to be 7-hydroxy-3-[6'-hydroxyphenyl-2'-oxo-ethyl]chromone, named terminalianone.

### 3. Experimental

#### 3.1 General experimental procedures

The positive ion FAB-MS spectra were recorded using a JEOL JMS-HX 110A

mass spectrometer with *m*-nitrobenzyl alcohol as a matrix. The  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were measured with a Varian UNITY INOVA 500 spectrometer in  $\text{CD}_3\text{OD}$  with TMS as an internal standard. Preparative HPLC was performed on a Shimadzu LC-6AD with a Shimadzu SPD-6AV spectrophotometer set at 280 nm. The column used was a  $250 \times 10$  mm i.d.,  $10\text{-}\mu\text{m}$  LiChrospher RP-18 (e) (Cica-Merck, Darmstadt, Germany).

### 3.2 Plant material

The barks of *T. brownii* Fresen were collected by Maasai in Arusha, Tanzania, in July 2005. A voucher specimen (2005TZ01) has been deposited at Mukogawa Women's University, Nishinomia, Japan.

### 3.3 Extraction and isolation

The air-dried and powdered plants (6.94 g) were extracted with 100 ml of water at  $100^\circ\text{C}$  for 15 min. The extract was centrifuged at 3000 rpm/min for 5 min, and the supernatant was collected. Polyphenols were separated by preparative HPLC on LiChrospher RP-18 with 33%  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  at a flow rate of 2.0 ml. Compound **1** (5 mg) was obtained from the peak at a retention time of 22 min.

#### 3.3.1 Compound **1**

Compound **1**, powder was UV (MeOH)  $\lambda_{\text{max}}$ : 280 nm.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data: see Table 1. HR-ESI-MS:  $m/z$

297.0766  $[\text{M} + \text{H}]^+$  (calcd for  $\text{C}_{17}\text{H}_{13}\text{O}_5$ , 297.0759).

### 3.4 Acetylation of **1**

About 0.5 mg of **1** was dissolved in 0.5 ml of dry pyridine. Then, 0.5 ml of acetic anhydride was added to this solution and the solution was allowed to stand for 5 h at room temperature. After that, the reaction product was extracted with ether by adding water.

*Diacetate of 1*. Positive ion FAB-MS:  $m/z$  403.0800  $[\text{M} + \text{Na}]^+$  (calcd for  $\text{C}_{21}\text{H}_{16}\text{O}_7\text{Na}$ , 403.0793).

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