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## Coumarins and other constituents from *Deverra battandieri*

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## ABSTRACT

Three undescribed coumarin derivatives, pituranthosin A-C (**1-3**), along with nineteen known compounds were isolated and identified from the chloroform and ethyl acetate fractions of the hydroalcoholic extract of *Deverra battandieri* (Apiaceae). The structures of the compounds were established by interpretation of their spectral data using 1D-NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT experiments), 2D-NMR (COSY, NOESY, HSQC and HMBC), HRESIMS, and by comparison with the literature data.

### *Keywords.*

Apiaceae, *Deverra battandieri*, coumarin, furanocoumarin, Saharan medicinal plants

## 1. Introduction

The members of the Apiaceae family are well-known producers of coumarins (Caesar and Cech, 2016; Matos et al., 2015) and furanocoumarins (Dueholm et al., 2015; Sarker and Nahar, 2017; Bruni et al., 2019). Coumarins are recognized to exhibit valuable biological properties such as analgesic, anti-inflammatory, antibacterial, antiviral, antifungal, and antiproliferative (Dehghan et al., 2017; Hashita and Dharmesh, 2018; Hassan et al., 2016; Song et al., 2017; Zhu and Jiang, 2018), apart from their well-known photosensitizing properties (Kasperkiewicz et al., 2016). The genus *Deverra* D.C. (Apiaceae) is spread in the Mediterranean region including the Arabic peninsula; it consists of seventeen species of which nine are accepted (Dobignard and Chatelain, 2011; Downie et al., 2010). Several members of the *Deverra* genus are used in folk medicine to treat asthma, rheumatism, digestive difficulties, urinary infections, and scorpion stings (Attia et al., 2011; Benchelah et al., 2000; Boukef, 1986; Guetat et al., 2019; Hammiche and Maiza, 2006). *Deverra battandieri* (Maire) Podlech [syn. *Pituranthos battandieri* (Maire)] is a traditional medicinal plant and a native species of the Sahara Desert of North Africa, particularly in Morocco and Algeria (Quezel and Santa, 1963; El Oualidi et al., 2012). Previously, antioxidant properties and phytochemical study on the polar fractions of *D. battandieri* led to the isolation of coumarins: xanthotoxol, 8-(6',7'-dihydroxygeranyloxy)-psoralen, the flavonoid: isorhamnetin 3-O-β-D-glucopyranoside, and mannitol (Esseid et al., 2017).

Following a systematic study of Saharan medicinal plants collected in Algeria (Boumaraf et al., 2017; Hammoud et al., 2018), this report describes the isolation and structural elucidation of three previously undescribed coumarin derivatives (**1-3**) (Figure 1), nine known coumarins (**4-12**) (Figure S1), and additional ten known compounds from extracts of *D. battandieri* collected in Bechar region of southern Algeria.

## 2. Results and discussion

Purification of the chloroform (CHCl<sub>3</sub>) and ethyl acetate (EtOAc) extracts of the hydroalcoholic (80:20) extract from the aerial parts of *Deverra battandieri* by column chromatography afforded three new furanocoumarin derivatives, pituranthosins A-C (**1-3**). The known furanocoumarins: 8-[(*R*)-6',7'-dihydroxygeranyloxy]psoralen (**4**) (Ito et al., 1998; Row et al., 2006), xanthotoxol (**5**) (He et al., 2007), xanthotoxin (**6**) (Harkar et al., 1984), (*R*)-(+)-heraclenin (**7**) (Setzer et al., 2003), (*R*)-(+)-byakangelicol (**8**) (Setzer et al., 2003), (*R*)-(+)-byakangelicin (**9**) (Ngwendson et al., 2003), phellopterin (**10**) (Kang et al., 2008); and the coumarins (*R*)-(+)-marmin (**11**) (Coates and Melvin, 1970) and rutaretin (**12**) (Lemmich and Shabana, 1984) were also isolated. Several other known compounds such as vanillin (Youssef and Frahm, 1995), vanillic acid (Kwon and Lee, 2001),  $\beta$ -hydroxypropiovanillone (Karonen et al., 2004), isorhamnetin (Spinola and Castilho, 2016), apigenin (Kouichi et al., 2011), and biochanin A (Agrawal and Bansal, 1989) were isolated along with the mixtures: stigmasterol and  $\beta$ -sitosterol (50-50%) (Hammoud et al., 2018), daucosterol and stigmasterol 3-*O*- $\beta$ -glucopyranoside (72-28%) (Voutquene and Lavaud, 1999). The structures of these known compounds were confirmed by comparison of their spectroscopic data (MS and <sup>1</sup>H- and <sup>13</sup>C-NMR) with the literature.

Pituranthosin A (**1**) was isolated as a yellowish powder and its molecular formula was determined as C<sub>23</sub>H<sub>28</sub>O<sub>6</sub> by its pseudo molecular peak on positive HRESIMS *m/z* 423.1773 [M+Na]<sup>+</sup> (calcd. for C<sub>23</sub>H<sub>28</sub>O<sub>6</sub>Na, 423.17781) indicating ten degrees of unsaturation. The <sup>1</sup>H NMR spectrum (Table 1) showed characteristic aromatic signals for two independent AB systems at  $\delta_H$  8.03 (d, *J* = 9.6 Hz, 1H), 6.38 (d, *J* = 9.6 Hz, 1H), and 7.90 (d, *J* = 2.2 Hz, 1H), 6.96 (d, *J* = 2.2 Hz, 1H), and a singlet at  $\delta_H$  7.57 (s, 1H) ppm indicating a psoralen type furanocoumarin nucleus (Adams et al., 2006). Additional <sup>1</sup>H NMR signals revealed the presence of two methyls on a quaternary carbon at  $\delta_H$  1.10 and 1.05 ppm, one methyl on a

double bond at  $\delta_{\text{H}}$  1.66 (s, 3H), one oxygenated methylene at  $\delta_{\text{H}}$  5.03 (d br,  $J = 6.9$  Hz, 2H), one oxygenated methine at  $\delta_{\text{H}}$  3.26 (dd,  $J = 10.5, 1.8$  Hz, 1H), and two aliphatic methylenes among other signals, indicating the presence of a geranyl group as a substituent in the furanocoumarin core. Both the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR (Tables 1 and 2) spectral data of compound **1** were close to those of 8-[(6',7'-dihydroxy-3',7'-dimethyl-2'-octenyl)oxy]psoralen (Ito et al., 1998) with additional  $^1\text{H}$ -NMR signals at  $\delta_{\text{H}}$  3.40 (qd,  $J = 7.0, 1.7$  Hz, 2H) and 1.12 (t,  $J = 7.0$  Hz, 3H) ppm assignable to an ethoxyl group, which revealed that compound **1** was an *O*-ethyl derivative. To determine the position of the geranyl and ethoxyl groups, the HMBC (Figure 2) experiment was useful. Thus, connectivity observed between the protons of the signal at  $\delta_{\text{H}}$  3.40 ppm (qd,  $J = 7.0, 1.7$  Hz, 2H) and the quaternary carbon at  $\delta_{\text{C}}$  78.32 helped us to situate the ethoxy group at C-7'. Besides, correlations between the protons in C-1' at  $\delta_{\text{H}}$  5.03 (d br,  $J = 7.6$  Hz, 2H) and C-8 at  $\delta_{\text{C}}$  132.29, and between the proton at  $\delta_{\text{H}}$  7.57 (s, 1H, H-5) and the carbons C-4 ( $\delta_{\text{C}}$  146.75) and C-10 ( $\delta_{\text{C}}$  107.96) led us to link the geranyl group at C-8 position in the central core. The presence of the furanocoumarin nucleus was further supported by its ultraviolet (UV) spectrum which showed a typical absorption maximum at 310 nm due to aromatic  $\pi$ - $\pi^*$  transition. Being well-known that the psoralen derivatives are known to be potential photosensitizers (Kitamura et al., 2005) this observation is extensive to the undescribed furanocoumarin derivatives isolated from *D. battandieri* (Figure 3b). This Compound (**1**) was found optically active with  $[\alpha]_{\text{D}}^{20} +8.8$ ;  $[\alpha]_{578}^{20} +9.7$ ;  $[\alpha]_{546}^{20} +10.3$  (c 1.365 g/100 ml, MeOH). The positive value of the optical rotation agreed with the (*R*) configuration of the chiral center at C-6' (Edegger et al., 2004; Wang et al., 2018). Therefore, the structure of **1** was determined to be 8-[(*R*)-6'-hydroxy-7'-ethoxygeranyloxy]psoralen.

Compound (**2**) was obtained as a yellowish solid with a molecular formula of  $\text{C}_{24}\text{H}_{28}\text{O}_6$  deduced from the positive HRESIMS  $m/z$  435.1780  $[\text{M}+\text{Na}]^+$  (calcd. for  $\text{C}_{24}\text{H}_{28}\text{O}_6\text{Na}$ , 435.1784) and indicated eleven degrees of unsaturation in it. The  $^1\text{H}$ -NMR data (Table 1) of **2**,

was very similar to that of **1**, suggesting that the two compounds were closely related in structure. The major difference is that **2** has two additional C-methyl resonances and lacked the ethyl group. A detailed comparison of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR signals of **1** and **2** (Tables 1 and 2) revealed that the signals due to ethoxy group at  $\delta_{\text{H}}$  3.40 (qd,  $J = 7.0, 1.7$  Hz, 2H) and 1.12 (t,  $J = 7.0$  Hz, 3H) ppm of **1** have been replaced by signals due to an acetonide group seen at  $\delta_{\text{H}}$  1.36 (s, 3H),  $\delta_{\text{C}}$  28.90;  $\delta_{\text{H}}$  1.23 (s, 3H),  $\delta_{\text{C}}$  27.15, and  $\delta_{\text{C}}$  107.64. Thus, compound **2** was determined to be 8-[6',7'-dihydroxygeranyloxy]psoralen acetonide and was named pituranthosin B.

Compound (**3**) differs in the side chain at C-8 from compounds **1** and **2**. Its UV spectrum showed a maximum absorption at 312 nm due to the characteristic aromatic  $\pi$ - $\pi^*$  transition of furanocoumarins (Figure 3d) (Kitamura et al., 2005). The positive HRESIMS spectrum of **3** showed a pseudomolecular ion  $[\text{M}+\text{Na}]^+$  at  $m/z$  411.1419 matching the molecular formula  $\text{C}_{21}\text{H}_{24}\text{O}_7$  (calcd for  $\text{C}_{21}\text{H}_{24}\text{O}_7\text{Na}$ : 411.1420) and indicating a compound containing ten unsaturations. The NMR data of **3** (Tables 1 and 2) was similar to those of citraurancoumarin B, a furanocoumarin, with the presence of a 2,6,7-trihydroxy-7-methyl-3(10)-methyleneoctan-1-oxy group at the C-5 position (Xiong et al., 2016). HMBC experiment of compound **3** allowed to identify the differences between compound **3** and citraurancoumarin B. Thus, HMBC correlations between the proton at position C-5 ( $\delta_{\text{H}}$  7.59) with C-4 ( $\delta_{\text{C}}$  146.75), and C-10 ( $\delta_{\text{C}}$  107.98) and the HMBC correlation between C-8 ( $\delta_{\text{C}}$  132.97) and the protons of the oxygenated methylene C-1' ( $\delta_{\text{H}}$  4.61 – 4.54, 2H) confirmed the side chain at C-8. The stereochemistry was not determined due to the small amount of compound isolated. Therefore, compound **3** was characterized as 8-[2',6',7'-trihydroxy-7'-methyl-3'(10')-octaenyloxy]psoralen and was named pituranthosin C.

Initially, compound **1** seemed to be an artifact but during the isolation process and chromatographic separation, no ethanol solvent was used (see Experimental). Pituranthosin B

**2** can be an artifact obtained from compound **4** and was generated with the use of acetone in the fractionation process. However, no harsh conditions were used in the isolation process of **2**. The formation of **2** was not observed while incubating compound **4** with acetone for 24 h. These facts suggested that compounds **1** and **2** are indeed undescribed secondary metabolites. The number of coumarins reported from *Deverra* species are few; for example, *D. triradiata* reported the presence of pituranthoside, *S-trans*-marmin, xanthotoxol, umbelliferone, isopimpinellin, and bergapten (Halim et al, 1995); *D. deanudata* reported the coumarins: bergapten, isoimperatorin, nodakenetin, osthol, and oxypeucedanin (Aloui et al., 2015), and the polar extracts of *D. battandieri* reported xanthotoxol and 8-(6',7'-dihydroxygeranyloxy)-psoralen (Esseid et al., 2017). The high concentrations of coumarins found in this medicinal plant are potentially responsible for the wide variety of traditional benefits reported from this Saharan plant.

### **3. Experimental**

#### *3.1. General Procedure*

Optical rotations were measured using a Perkin Elmer model 341. UV spectra were recorded using a Shimadzu model (190-3200 nm, UV-3101PC) or Shimadzu model UV-1700 spectrophotometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained by Bruker model Avance AMX-400 and AMX-500 MHz spectrometers (Bruker BioSpin, Rheinstetten, Germany) with standard pulse sequences operating at 400 and 500 MHz for <sup>1</sup>H and 100 and 125 MHz for <sup>13</sup>C, respectively. MeOH-*d*<sub>4</sub>, DMSO-*d*<sub>6</sub>, or CDCl<sub>3</sub> were used as solvents with TMS as internal standard. Chemical shifts ( $\delta$ ) are reported in ppm and coupling constants (*J*) are reported in Hz. High resolution mass spectra (HRESIMS) were performed on an Agilent 6520 Accurate Mass Q-TOF (Agilent Corporation, Santa Clara, CA, USA), a  $\mu$ -QToF spectrometer (Bruker Daltonics, Wissembourg, France) with a LCT Premier XE Micromass Waters spectrometer in positive ionization mode (Waters Corporation) and a Bruker Maxis 4G (CRMPO Université de

Rennes 1). Column chromatography (CC) were carried out with silica gel Fluka (cat. 60737, 40-63  $\mu\text{m}$ ), silica gel 60 (Merck 230-400 mesh) and Sephadex LH-20 (Sigma-Aldrich). Column fractions were monitored by TLC silica gel 60 F<sub>254</sub> (Merck), 0.2 mm, Macherey Nagel (cat. 818-333) by detection with a spraying reagent  $\text{CH}_3\text{CO}_2\text{H}-\text{H}_2\text{O}-\text{H}_2\text{SO}_4$  (80:16:4) followed by heating at 100 °C. Preparative TLC was carried out on silica gel 60 PF<sub>254+366</sub> (20 cm $\times$ 20 cm, 1 mm thickness, Analtech cat. 02014). Solvents such as  $\text{CHCl}_3$ , toluene, EtOAc, and MeOH are reagent grade and were purchased from VWR (Fontenay-sous-bois, France); acetonitrile is HPLC grade and was purchased from Fisher Scientific; Milli-Q water (18.2 M $\Omega$ ) was generated by Millipore synergy System (Molsheim, France).

### 3.2. Plant material

The aerial parts from *Deverra battandieri* (Maire) Podlech [syn. *Pituranthos battandieri* Maire] (Quezel and Santa, 1963; Ozenda, 1958; El Oualidi et al., 2012), an endemic species of the Algerian-Moroccan Sahara, were harvested near the hydraulic dam of Djorf Torba in the Wilaya of Bechar in Southern Algeria (GPS coordinates 30°31'0" N and 2°45'0" W) during the flowering stage in April 2010. The plant material was authenticated by M. Mohamed Benabdelhakem, Director of the nature preservation agency, Bechar. A voucher specimen (PBA 54/04/10) was deposited at the Herbarium of the VARENBIOMOL Research Unit, University Frères Mentouri Constantine 1.

### 3.3. Extraction and isolation

Air-dried aerial parts (3350 g) of *D. battandieri* Maire (Apiaceae) were macerated three times (1000 ml/each) at room temperature with MeOH-H<sub>2</sub>O (80:20, v/v) for 48 h. After filtration, the filtrate was concentrated to reach a volume for around 1000 ml, then it was added additional H<sub>2</sub>O (1300 ml). The resulting solution was extracted successively with petroleum ether,  $\text{CHCl}_3$ , EtOAc, and *n*-BuOH. The organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and

concentrated in vacuum up to 35°C to obtain the following partition extracts: petroleum ether (0.9 g), CHCl<sub>3</sub> (17 g), EtOAc (12 g), and *n*-BuOH (70 g), respectively. The CHCl<sub>3</sub> extract was fractionated by column chromatography (230-400 mesh silica gel; *n*-hexane-EtOAc step gradients, and then with increasing percentages of acetone) to give 31 fractions (F<sub>1</sub>-F<sub>31</sub>) which were obtained by combining the fractions based on TLC analysis. Following purification of fraction F<sub>3</sub> (150.4 mg) (*n*-hexane/EtOAc 88:12) by crystallization in MeOH and a little amount of CHCl<sub>3</sub>, a mixture of β-sitosterol and stigmasterol (50-50%) (27 mg) was isolated. Fraction F<sub>9</sub> (276.8 mg) (*n*-hexane/EtOAc 80:20) was chromatographed on a silica gel column (*n*-hexane/EtOAc 7:3) to yield 16 sub-fractions (subF<sub>1</sub>-subF<sub>16</sub>). SubF<sub>11</sub> (50 mg) was chromatographed on preparative silica gel TLC (CHCl<sub>3</sub> 100%; two elutions) to afford xanthotoxin (**6**) (4 mg), phellopterin (**10**) (5 mg), and vanillin (8 mg). Fraction F<sub>11</sub> (75.1 mg) (*n*-hexane/EtOAc 78:22) was chromatographed on preparative silica gel TLC (CHCl<sub>3</sub>/acetone 19:1) to afford xanthoxol (**5**) (30.8 mg). Purification of fraction F<sub>13</sub> (280 mg) (*n*-hexane/EtOAc 70:30) on preparative plates of silica gel (CHCl<sub>3</sub>/acetone 19:1) yielded 8-[(*R*)-6'-hydroxy-7'-ethoxygeranyloxy] psoralen named pituranthosin A (**1**) (7 mg). Fraction F<sub>18</sub> (1.5 g) (*n*-hexane/EtOAc 50:50) was chromatographed on a silica gel column (*n*-hexane/EtOAc) to yield 27 sub-fractions (subF<sub>1</sub>-subF<sub>27</sub>). SubF<sub>6</sub> (62 mg) (*n*-hexane/EtOAc 85:15) was subjected to preparative plates of silica gel TLC (CHCl<sub>3</sub>/acetone 98:2) to afford 8-[6',7'-dihydroxygeranyloxy]psoralen acetone named pituranthosin B (**2**) (8 mg). SubF<sub>21</sub> (45 mg) (*n*-hexane/EtOAc 50:50) was chromatographed using preparative plates of silica gel TLC (CHCl<sub>3</sub>/acetone 9:1) and purified on a Sephadex LH-20 column to yield (*R*)-(+)-marmin (**11**) (9 mg), (*R*)-(+)-heraclenin (**7**) (11 mg), and rutaretin (**12**) (8 mg). SubF<sub>24</sub> (32 mg) (*n*-hexane/EtOAc 30:70) gave (*R*)-(+)-byakangelicol (**8**) (10 mg) after purification by crystallization in MeOH. Fraction F<sub>20</sub> (766 mg) (*n*-hexane/EtOAc 45:55) yielded, (*R*)-(+)-byakangelicin (**9**) (536.5 mg) after purification by crystallization in MeOH/CHCl<sub>3</sub>. Fraction F<sub>24</sub>

(184.5 mg) (*n*-hexane/EtOAc 20:80) gave 8-[2,6,7-trihydroxy-7-methyl-3(10)-octaenyloxy]psoralen named pituranthosin C (**3**) (2 mg) after purification on preparative plates of silica gel (CHCl<sub>3</sub>/acetone 9:1 three elutions). The concentration of fraction F<sub>25</sub> (543.8 mg) (*n*-hexane/EtOAc 15:85) yielded a yellowish precipitate which was washed with CHCl<sub>3</sub>/MeOH to give a mixture of daucosterol and stigmasterol 3-*O*-β-glucopyranoside at 72 and 28%, respectively (158 mg). The EtOAc extract (10 g) was chromatographed on a silica gel column (230-400 mesh silica gel; CHCl<sub>3</sub>-acetone step gradients and then with increasing percentages of MeOH) to yield 43 fractions (F<sub>1</sub>-F<sub>43</sub>) based on their TLC behavior. Fraction F<sub>9</sub> (99 mg) (CHCl<sub>3</sub>/acetone 98:2) was subjected to preparative TLC on silica gel (CHCl<sub>3</sub>/acetone 9:1 two elutions) to give isorhamnetin (20 mg). Fraction F<sub>11</sub> (173 mg) (CHCl<sub>3</sub>/acetone 93:7) was submitted to preparative silica gel TLC (CHCl<sub>3</sub>/acetone 9:1) and purified over Sephadex LH-20 column eluted with MeOH to afford vanillic acid (7 mg) and β-hydroxypropiovanillone (4.5 mg). Fraction F<sub>14</sub> (148 mg) (CHCl<sub>3</sub>/acetone 90:10) gave apigenin (10 mg) after purification on preparative plates of silica gel (CHCl<sub>3</sub>/acetone 9:1). Fraction F<sub>17</sub> (71 mg) (CHCl<sub>3</sub>/acetone 88:12) was submitted to preparative plates of silica gel TLC (CHCl<sub>3</sub>/acetone 9:1) and purified on a Sephadex LH-20 column to afford 8-[(*R*)-6',7'-dihydroxygeranyloxy]psoralen (**4**) (9 mg). Biochanin A (10 mg) was obtained from fraction F<sub>21</sub> (124 mg) (CHCl<sub>3</sub>/acetone 85:15) following purification on preparative silica gel plates (CHCl<sub>3</sub>/acetone 8:2).

8-[(*R*)-6'-hydroxy-7'-ethoxygeranyloxy]psoralen (**1**): yellow powder;  $[\alpha]_D^{20} +8.8$  (c 1.3, MeOH); <sup>1</sup>H-NMR (400 MHz, MeOH-*d*<sub>4</sub>) and <sup>13</sup>C-NMR (100 MHz, MeOH-*d*<sub>4</sub>) spectroscopic data, see Tables 1 and 2; HRESIMS *m/z*: 423.1773 [M+Na]<sup>+</sup> (calcd for C<sub>23</sub>H<sub>28</sub>NaO<sub>6</sub>, 423.17781), *m/z*: 439.1515 [M+K]<sup>+</sup> (calcd for C<sub>23</sub>H<sub>28</sub>KO<sub>6</sub>, 439.15175).

8-[6',7'-dihydroxygeranyloxy]psoralen acetonide (**2**): yellow powder;  $[\alpha]_D^{25}$  0 (c 0.5, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H-NMR (MeOH-*d*<sub>4</sub>, 500 MHz) and <sup>13</sup>C-NMR (MeOH-*d*<sub>4</sub>, 125 MHz) spectroscopic data, see Tables 1 and 2; HRESIMS *m/z*: 435.1780 [M+Na]<sup>+</sup> (calcd for C<sub>24</sub>H<sub>28</sub>O<sub>6</sub>Na, 435.1784).

8-[2',6',7'-trihydroxy-7'-methyl-3'(10')-octaenyloxy]psoralen (**3**): yellow powder; <sup>1</sup>H-NMR (400 MHz, MeOH-*d*<sub>4</sub>); <sup>13</sup>C-NMR (100 MHz, MeOH-*d*<sub>4</sub>) spectroscopic data, see Tables 1 and 2; HRESIMS *m/z*: 411.1419 [M+Na]<sup>+</sup> (calcd for C<sub>21</sub>H<sub>24</sub>O<sub>7</sub>Na, 411.1420).

### 3.4 HPLC-UV profiling of the chloroform fraction of *D. battandieri*

The HPLC system included a Beckman HPLC system with Beckman 507E auto sampler, a 126 solvent delivery module, 166 single wavelength detector with the serial number: KA1B3VW. The detection was performed at 275 nm for UV active components. The analysis was carried on a C18 nucleosil column (5μm, 250 x 4.6 mm) which was protected by security guard cartridge and was maintained at a constant room temperature of 25 °C. The mobile phases consisted of eluent A: 0.1 % formic acid in water, and eluent B: MeOH. Gradient was applied (A:B, 10-70-70-10% MeOH) (0-10-20-21-33 min). The total run time was 55 min. The flow rate was kept at 1.0 mL/min and the injection volume was 20 μL. Peak identity of the individual peaks was assigned by retention time (RT) values based on comparison with the standards and spiked authentic standard to the sample.

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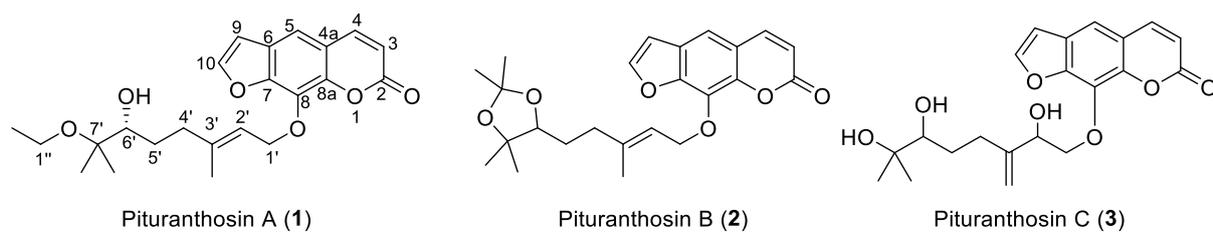
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**Table 1:**  $^1\text{H}$  NMR data of **1-3** (MeOH- $d_4$ ).  $\delta$  in ppm,  $J$  (Hz) in parentheses.

	<b>1</b>	<b>2</b>	<b>3</b>
<b>Position</b>	$\delta_{\text{H}}$ ( $J$ )	$\delta_{\text{H}}$ ( $J$ )	$\delta_{\text{H}}$ ( $J$ )
2			
3	6.38, d (9.6)	6.36, d (9.6)	6.40, d (9.6)
4	8.03, d (9.6)	8.05, d (9.6)	8.05, d (9.6)
5	7.57, s	7.53, s	7.59, s
9	7.90, d (2.2)	7.88, d (2.2)	7.91, d (2.2)
10	6.96, d (2.2)	6.94, d (2.2)	6.97, d (2.2)
1'	5.03, d br (7.6)	5.01, dd (7.2, 1.6)	4.61 – 4.54, m
2'	5.65-5.55, m	5.62 – 5.53, m	4.46, ddd (11.0, 8.3, 5.7)
4'	2.24, ddd (14.2, 9.9, 4.7) 2.08 – 1.95, m	2.18, ddd (11.4, 9.7, 5.3) 2.09 – 1.97, m	2.56-2.38, m 2.31-2.19, m
5'	1.58, dddd (13.7, 9.9, 6.9, 1.8) 1.27 – 1.17, m	1.52-1.45, m 1.45-1.30, m	1.50, ddd (13.6, 6.8, 3.1) 1.89-1.78, m
6'	3.26 (dd, $J$ = 10.5, 1.8)	3.58, dd (9.3, 3.6)	3.25, m, overlapped
8'	1.10, s	1.16, s	1.18, s
9'	1.05, s	1.03, s	1.16, s
10'	1.66, s	1.67, s	5.05, s 5.27, s
1''	3.40, qd (7.0, 1.7)		
2''	1.12, t (7.0)	1.36, s	
3''		1.23, s	

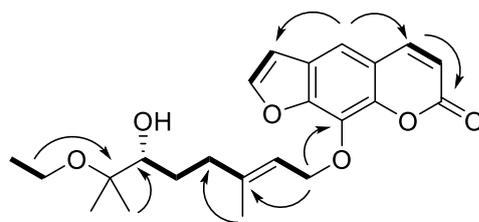
**Table 2:**  $^{13}\text{C}$  NMR data of **1-3** (MeOH- $d_4$ ).  $\delta$  in ppm

	<b>1</b>	<b>2</b>	<b>3</b>
<b>Position</b>	$\delta_{\text{C}}$	$\delta_{\text{C}}$	$\delta_{\text{C}}$
2	162.75, C	162.67, C	162.74, C
3	114.93, CH	114.84, CH	115.04, CH
4	146.75, CH	146.56, CH	146.75, CH
4a	117.94, C	117.64, C	118.07, C
5	115.19, CH	114.93, CH	115.01, CH
6	127.72, C	127.47, C	127.98, C
7	150.21, C	149.80, C	149.21, C
8	132.29, C	132.10, C	132.97, C
8a	144.98, C	144.81, C	144.36, C
9	148.48, CH	148.09, CH	148.55, CH
10	107.96, CH	107.82, CH	107.98, CH
1'	70.22, CH <sub>2</sub>	70.59, CH <sub>2</sub>	74.73, CH <sub>2</sub>
2'	120.74, CH	120.88, CH	77.98, CH
3'	144.95, C	143.77, C	149.93, C
4'	37.66, CH <sub>2</sub>	37.45, CH <sub>2</sub>	30.69, CH <sub>2</sub>
5'	30.37, CH <sub>2</sub>	28.37, CH <sub>2</sub>	30.80, CH <sub>2</sub>
6'	77.07, CH	83.64, CH	78.97, CH
7'	78.32, C	81.30, C	73.80, C
8'	21.98, CH <sub>3</sub>	26.30, CH <sub>3</sub>	25.07, CH <sub>3</sub>
9'	21.04, CH <sub>3</sub>	23.39, CH <sub>3</sub>	25.67, CH <sub>3</sub>
10'	16.46, CH <sub>3</sub>	16.79, CH <sub>3</sub>	112.11, CH <sub>2</sub>
1''	57.67, CH <sub>2</sub>	107.64, C	
2''	16.56, CH <sub>3</sub>	28.90, CH <sub>3</sub>	
3''		27.15, CH <sub>3</sub>	



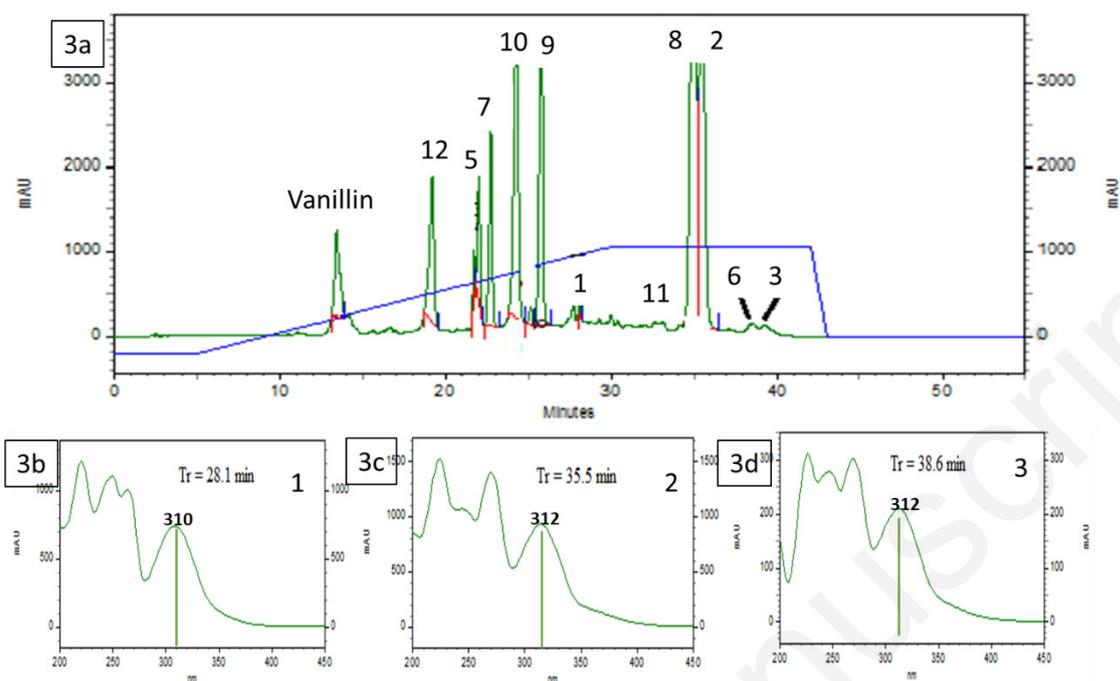
**Figure 1.** Undescribed furanocoumarins isolated from *Deverra battandieri*

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**Figure 2.** Selected COSY (bold bond) and HMBC (H→C) correlations for compound **1**.

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**Figure 3.** 3a) HPLC/UV (275 nm) chromatographic profile of the  $\text{CHCl}_3$  extract of the aerial parts of *D. battandieri*. Column nucleosil HD-18 (5 $\mu\text{m}$ , 250 x 4.6 mm). Phase: 0.1% formic acid in milli-Q  $\text{H}_2\text{O}$ -ACN. Gradient: (10-35-35-10-10 % ACN) (0-5-30-43-55 min). Flow 1 mL  $\text{min}^{-1}$ ; injection volume: 20  $\mu\text{L}$ ; 3b) UV spectrum of compound 1; 3c) UV spectrum of compound 2; 3d) UV spectrum of compound 3.