

## A Novel Compound From *Ceratostigma Minus*

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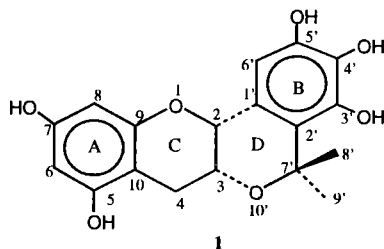
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**Abstract:** A novel compound, plumbocatechin A **1**, was isolated from the whole plant of *Ceratostigma minus*. The structural elucidation of **1** was mainly achieved by 2D-NMR techniques.

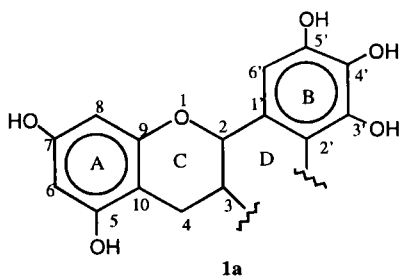
**Keywords:** *Ceratostigma minus*; Plumbocatechin A.



Previous papers have reported the isolation of several compounds, plumbasides A-C, plumbagin, quercetin, myricetin, quercetin 3-O-glucoside, myricetin 3-O-rhamnoside and maltol-O-glucoside from *Ceratostigma minus*<sup>1,2</sup>. The continuation of our research work for bioactive compounds have led to the isolation of a novel compound, plumbocatechin A **1**. The structure elucidation of **1** were made by 2D-NMR techniques.

Plumbocatechin A **1** was obtained as an amorphous powder. EIMS clearly revealed the molecular weight to be 346 and HREIMS established its elemental formula as C<sub>18</sub>H<sub>18</sub>O<sub>7</sub>. The <sup>13</sup>C-NMR spectrum exhibited 18 resolved signals, comprising 2xCH<sub>3</sub>, 1xCH<sub>2</sub>, 5xCH and 10 quaternary carbons, as distinguished by DEPT spectra. Eighteen proton signals were present in the <sup>1</sup>H-NMR spectrum and five proton signals at δ7.5-8.5 ppm disappeared in the D<sub>2</sub>O exchange experiment, indicating that compound **1** contains five exchangeable protons. This result was consistent with the fact revealed by DEPT spectrum. The IR spectrum did not show the presence of carbonyl group, suggesting that five exchangeable protons are assignable to hydroxyl groups. Two aromatic rings were

inferred by the chemical shifts of twelve carbon signals at the aromatic range in the  $^{13}\text{C}$ -NMR spectrum. The aromatic region of the  $^1\text{H}$ -NMR spectrum showed a classic pattern for a 1,2,3,5-tetrasubstituted aromatic ring [5.77 (1H, d,  $J=2.3\text{Hz}$ ), 5.97 (1H, d,  $J=2.3\text{Hz}$ )] and a pentasubstituted aromatic ring (6.46, 1H, s). The above information suggested that the chemical formulation of compound **1** is  $\text{C}_{18}\text{H}_{13}\text{O}_2(\text{OH})_5$ . IR absorption bands at  $3402\text{cm}^{-1}$  for hydroxyls, and 1629, 1608 and  $1517\text{cm}^{-1}$  for aromatic ring suggested that **1** is likely a phenolic compound. Consideration of two aromatic rings accounted for a total of 8 of the 10 degrees of unsaturation required for this formula. The remaining degrees of unsaturation was assumed to result from the presence of two additional oxygen-containing heterocycles. Interpretation of  $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT, HMQC (**Table 1**) and  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectra led to the proposal of the partial structure **1a**, with only a  $-\text{OC}(\text{CH}_3)_2$  group left unaccounted for. The connection of the two parts was made on the basis of the chemical shifts of C-3, C-2' and C-7'. The planar structure of **1** was thus proposed and further confirmed by H-2 $\beta$  correlating with C-9, H-3 $\beta$  with C-7', and H-8' and H-9' with both C-2' and C-7' in the HMBC spectrum. The C-1' was assigned to  $\delta 125.40$  and C-2' to 122.28, as H-8' and H-9' appear to exhibit HMBC cross peaks to C-2' only, whereas H-6' and H-2 $\beta$  correlate with both. Although their chemical shifts are very close, C-7 and C-9 were respectively assigned to  $\delta 157.23$  and 157.31 based on H-2 $\beta$  HMBC cross peak correlating with C-9 only, and H-6 HMBC cross peaks with C-7 and C-5, and H-8 HMBC cross peaks with C-7 and C-9, whereas H-6 and H-8 did not correlate with C-9 and C-5, respectively.



In an attempt to determine the stereochemistry of C-2 and C-3, a NOESY experiment was performed. The strong correlation between H-2 $\beta$  and H-3 $\beta$  indicated a cis-configuration. H-3 $\beta$  correlating with both H-4 $\alpha$  and H-4 $\beta$  inferred that H-3 $\beta$  takes an equatorial bond as the C-ring is probably taking a chair-conformation. Also consistent with the structure **1**, a correlation was observed between H-2 $\beta$  and H-4 $\beta$  which is taking axial, indicating that H-2 $\beta$  is axial, and C-ring is definitely taking a chair conformation. H-2 $\beta$  and H-6' are shown to be very close in space by a long range correlation between two protons.

Plumbocatechin A **1**,  $\text{C}_{18}\text{H}_{18}\text{O}_7$  (HRMS, found 346.1371, requires 346.1384), amorphous powder, IR (KBr)  $\nu_{\text{max}}\text{cm}^{-1}$ : 3402, 1629, 1602, 1517 1645 and 1143;  $^1\text{H}$ -NMR (acetone- $d_6$ ) 8.45 (<1H, brs., OH), 8.15 (<1H, s, OH), 7.93 (<1H, s, OH), 7.70 (<1H, brs., OH), 7.45 (<1H, brs., OH), 4.40 (1H, s, H-2 $\beta$ ), 4.22 (1H, dd,  $J=1.6, 5.1\text{Hz}$ , H-3 $\beta$ ), 2.85 (1H, dd,  $J=5.1, 17.5\text{Hz}$ , H-4 $\beta$ ), 2.76 (1H, dd,  $J=1.6, 17.5\text{Hz}$ , H-4 $\alpha$ ), 5.77 (1H, d,  $J=2.3\text{Hz}$ , H-6), 5.97 (1H,  $J=2.3\text{Hz}$ , H-8), 6.46 (1H, s, H-6'), 1.60 (3H, s,  $\text{CH}_3$ -7' $\beta$ ), 1.54

(3H, s, CH<sub>3</sub>-7'α). EIMS *m/z* (%): 346[M]<sup>+</sup>(55), 331[M-CH<sub>3</sub>]<sup>+</sup>(100). 193 (95), 149 (35) and 139 (77). <sup>13</sup>CNMR (acetone-d<sub>6</sub>): 71.68 (C-2), 63.83 (C-3), 26.30 (C-4), 156.76 (C-5), 95.69 (C-6), 157.23 (C-7), 95.94 (C-8), 157.31 (C-9), 99.47 (C-10), 125.40 (C-1'), 122.28 (C-2'), 143.01 (C-3'), 134.17 (C-4'), 144.37 (C-5'), 109.53 (C-6'), 75.60 (C-7'), 24.56 (C-8') and 28.91 (C-9').

**Table 1.** Long range <sup>1</sup>H-<sup>13</sup>C Correlation Data from the HMBC of Compound 1

<sup>1</sup> H	J <sub>2</sub>	J <sub>3</sub>
2B	C-1'	C-9, C-3
3B	C-4	C-7'
4	C-10, C-3	C-5
6	C-5, C-7	C-10, C-8
8	C-7, C-9	C-8, C-10
6'	C-1'	C-2
8'	C-7'	C-2'
9'	C-7'	C-2,

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