

## Short communication

2-Carboxy-dihydrostilbene and flavan glycosides from *Desmodium heterocarpon*

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## ABSTRACT

A new 2-carboxy-dihydrostilbene glucoside, 2-carboxy-3,5,4'-trihydroxydihydrostilbene 3-O- $\beta$ -D-glucopyranoside (**1**) and a new flavan diglycoside, (2S)-5,7,4'-trihydroxyflavan 7-O- $\beta$ -D-apiofuranosyl-(1 $\rightarrow$ 6)-O- $\beta$ -D-glucopyranoside (**3**) were isolated from the aerial portion of Thai origin *Desmodium heterocarpon* together with five known compounds, lunularic acid 4'-O- $\beta$ -D-glucopyranoside (**2**), vitexin (**4**), isovitexin (**5**), (-)-*epi*-catechin 3-O- $\beta$ -D-glucopyranoside (**6**), and (-)-*epi*-afzelachin 3-O- $\beta$ -D-glucopyranoside (**7**). The structure determinations were based on physical data and spectroscopic evidence including 1D- and 2D-NMR experiments. The presence of 2-carboxy-dihydrostilbene derivatives from this species added the information data of this compound-type to the plant kingdom.

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## 1. Introduction

*Desmodium heterocarpon* (L.) DC., a member of the family Fabaceae, is commonly found in the paddy field during the raining season in North-eastern Thailand. Previous phytochemical investigation of this plant reported the isolation of several compounds such as triterpenoids, steroids and flavonoids (Huang et al., 2010). In the biological properties, the antioxidant activities of phenolic components from plant extract have been reported (Tsai et al., 2011). This present study describes the isolation and structure identification of seven glycosides including a new 2-carboxy-dihydrostilbene derivative glucoside (**1**) and a new flavan diglycoside (**3**) from the water soluble fraction of the aerial portion of this plant in addition to five known compounds (**2**, **4**–**7**).

## 2. Results and discussion

The methanolic extract of the aerial portions of *D. heterocarpon* was partitioned between Et<sub>2</sub>O and H<sub>2</sub>O. The aqueous soluble fraction was separated by combination of chromatographic methods to provide a new glucoside of dihydrostilbenic acid (**1**)

and a new flavan diglycoside (**3**) (Fig. 1) along with five known compounds. The known compounds were identified to be lunularic acid 4'-O- $\beta$ -D-glucopyranoside (**2**) (Fang et al., 2012), vitexin (**4**), isovitexin (**5**) (Agrawal and Bansal, 1989), (-)-*epi*-catechin 3-O- $\beta$ -D-glucopyranoside (**6**) (Morimoto et al., 1985), and (-)-*epi*-afzelachin 3-O- $\beta$ -D-glucopyranoside (**7**) (Morimoto et al., 1988). All known compounds were identified by comparison of physical data with literature values and from spectroscopic evidence.

Compound **1** was isolated as an amorphous powder. The molecular formula was determined to be C<sub>21</sub>H<sub>24</sub>O<sub>10</sub> by high resolution electrospray time-of-flight (HR-ESI-TOF) mass spectrometric analysis. The <sup>1</sup>H NMR spectrum revealed the presence of a pair of *meta*-coupled aromatic protons at  $\delta_H$  6.12 and 6.16 (each 1H, d, *J* = 2.5 Hz), a set of AA'BB' aromatic ring at  $\delta_H$  6.64 and 7.05 (each 2H, d, *J* = 8.4 Hz), two methylenes at  $\delta_H$  2.63 (2H, dd, *J* = 8.2, 8.1 Hz) and 3.18 (2H, m) in addition to an anomeric proton signal at  $\delta_H$  4.77 (1H, d, *J* = 7.7 Hz). The <sup>13</sup>C NMR spectrum showed that this compound contained two aromatic ring systems, two methylene carbons, one carboxyl group for the aglycone moiety, as well as one  $\beta$ -D-glucopyranosyl moiety. The NMR spectral data (Table 1) indicated that the structure of this compound was related to lunularic acid 4'-O- $\beta$ -D-glucopyranoside (**2**). This compound has one oxygen atom more than compound **2**, suggesting the presence of an additional hydroxyl group on the aromatic ring. The structure assignment was based on the analyzing results from 2D-NMR spectroscopic methods including COSY, NOESY, HMQC and HMBC.

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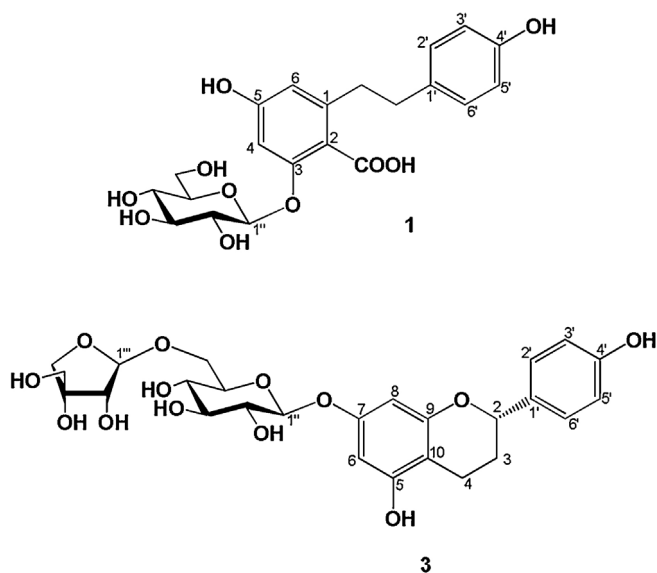


Fig. 1. Structures of compounds 1 and 3.

In the HMBC spectrum (Fig. 2), the significant correlations were found from methylene protons at  $\delta_H$  3.18 (H<sub>2</sub>- $\alpha$ ) to an aryl methine carbon at  $\delta_C$  108.2, and two non-protonated aryl carbons at  $\delta_C$  112.2 and 147.0, ascribable to C-6, C-2 and C-1, respectively. The chemical shift of a methine carbon at  $\delta_C$  101.3 was assigned to locate at C-4 position of the aromatic ring due to the coupling constant between  $\delta_H$  6.12 (H-6) and 6.16 (H-4) with  $J=2.5$  Hz, and was also confirmed by the HMBC correlation from  $\delta_H$  6.12 (H-6) to this carbon atom. The oxy-aryl carbon at  $\delta_C$  159.0 was placed at C-3 position since the HMBC correlation was observed only from  $\delta_H$  6.16 (H-4). The appearance of the HMBC correlations from  $\delta_H$  6.12 (H-6) and 6.16 (H-4) to the oxy-aryl carbon at  $\delta_C$  166.2 indicated that this carbon atom was C-5 position. The remaining oxy-aryl carbon at  $\delta_C$  155.4 was belonged to C-4' position of the other aromatic ring, supporting by the HMBC correlations from  $\delta_H$  7.05

(H-2',6') and 6.64 (H-3',5'). The sugar unit was assigned to be linked at C-3 position, deduced from the HMBC correlation from the anomeric proton at  $\delta_H$  4.77 (H-1'') to C-3 ( $\delta_C$  159.0). Also the NOESY correlation was only observed between H-1'' and H-4 (Fig. 2), confirming the sugar unit to C-3 position. Consequently, the structure of this compound was elucidated to be 2-carboxy-3,5,4'-trihydroxydihydrostilbene 3-O- $\beta$ -D-glucopyranoside.

Compound 3 was isolated as an amorphous powder. The molecular formula was determined to be C<sub>26</sub>H<sub>32</sub>O<sub>13</sub> by high resolution electrospray time-of-flight (HR-ESI-TOF) mass spectrometric analysis. The <sup>1</sup>H NMR spectrum revealed the presence of two sugar units from the anomeric signals at  $\delta_H$  4.70 (1H, d,  $J=7.6$  Hz) and 4.80 (1H, d,  $J=3.1$  Hz), a pair of *meta*-coupled aromatic protons at  $\delta_H$  5.96 and 6.8 (each 1H, d,  $J=2.5$  Hz), and a set of AA'BB' aromatic ring at  $\delta_H$  6.74 and 7.19 (each 2H, d,  $J=8.4$  Hz) in addition to a broad double signal at  $\delta_H$  4.86 (1H,  $J=9.3$  Hz) and multiplets at  $\delta_H$  1.88 (1H), 2.03 (1H) and 2.53 (2H). In the <sup>13</sup>C NMR spectrum, 11 carbon signals belonging to the sugar part could be identified to be a  $\beta$ -D-apiofuranosyl-(1  $\rightarrow$  6)-O- $\beta$ -D-glucopyranosyl unit by comparing chemical shifts with the reported data (Kanchanapoom et al., 2002). The remaining 15 carbon atoms were consistent with a flavonoid skeleton. The partial connectivities of C-2 to C-3 and C-4 were deduced from COSY and HMQC analysis, indicating that the aglycone of this compound was a flavan (Sauvain et al., 1994). In the HMBC spectrum, the correlation from the anomeric proton at  $\delta_H$  4.70 (H-1'' Glc) to C-7 ( $\delta_C$  156.7) indicated the location of the sugar moiety to this carbon atom. Besides, the NOESY spectrum provided further confirmation of the sugar unit to C-7 position from the cross peak correlation of H-1'' Glc with  $\delta_H$  5.96 (H-6) and 6.08 (H-8) as shown in Fig. 2. The absolute configuration at C-2 position was established to be S from the CD spectrum, which showed extreme values for  $\Delta\epsilon$  (nm)  $-1.63$  (272), relating to the data of 2S-configured compounds (Baba et al., 1986; Antus et al., 2001; Yang et al., 2010; Zhong et al., 2013). Consequently, the structure of this compound was identified as (2S)-5,7,4'-trihydroxyflavan 7-O- $\beta$ -D-apiofuranosyl-(1  $\rightarrow$  6)-O- $\beta$ -D-glucopyranoside.

Table 1  
NMR spectroscopic data of compounds 1 and 2 (<sup>1</sup>H NMR, 400 MHz and <sup>13</sup>C NMR, 100 MHz).

Position	1 Proton	1 Carbon	2 Carbon
1		147.0	145.0
2		112.2	118.2
3		159.0	163.8
4	6.16 (1H, d, $J=2.5$ Hz)	101.3	114.5
5		166.2	130.1
6	6.12 (1H, d, $J=2.5$ Hz)	108.2	119.5
1'		133.4	136.4
2', 6'	7.05 (2H, d, $J=8.4$ Hz)	129.5	129.2
3', 5'	6.64 (2H, d, $J=8.4$ Hz)	115.1	116.0
4'		155.4	155.5
$\alpha$	3.18 (2H, m)	38.2	37.9
$\beta$	2.63 (2H, dd, $J=8.2, 8.1$ Hz)	37.3	37.3
COOH		173.1	173.0
Glc-1''	4.77 (1H, d, $J=7.7$ Hz)	100.1	100.7
2''	3.13-3.20 (1H)	73.5	73.3
3''	3.30-3.38 (1H)	76.9	76.7
4''	3.13-3.20 (1H)	70.0	69.8
5''	3.21-3.29 (1H)	77.2	77.0
6''	3.40-3.50 (1H)	61.0	60.8
	3.66 (1H, br d, $J=11.5$ Hz)		

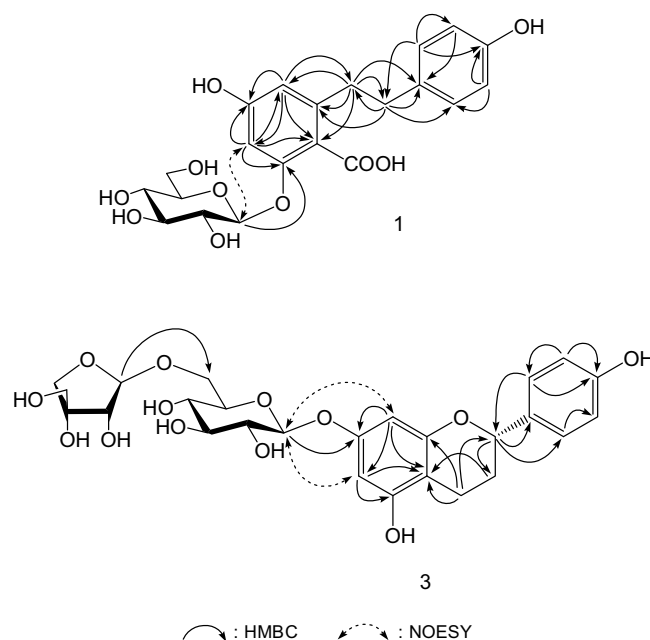


Fig. 2. HMBC and NOESY correlations of compounds 1 and 3.

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