doi:10.15625/2525-2518/57/2/13098



STRUCTURAL ELUCIDATION OF GLYCOSIDES FROM THE SEEDS OF ENTADA PHASEOLOIDES GROWING IN THUA THIEN HUE

Le Canh Viet Cuong¹, Le Thi Lien¹, Nguyen Phuc Khanh Nhi¹, Tran Phuong Ha¹, Le Tuan Anh¹, Masayoshi Arai², Hoang Le Tuan Anh^{1, 3, *}

¹Mientrung Institute for Scientific Research, Vietnam Academy of Science and Technology (VAST), 321 Huynh Thuc Khang, Hue city, Thua Thien Hue, Viet Nam

²*Research Center for Drug Discovery, Graduate School of Pharmaceutical Sciences, Osaka University, Osaka 565-0871, Japan*

³Graduate University of Science and Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi, Viet Nam

^{*}Email: *hoangletuananh@hotmail.com*

Received: 14 September 2018; Accepted for publication: 13 March 2019

Abstract. *Entada phaseoloides* (L.) Merr. belongs to Fabaceae family and is widely distributed throughout Viet Nam, Thailand, Malaysia, Indonesia, Philippines, China, New Guinea, and Australia. In Vietnamese traditional medicine, the seeds of *Entada phaseoloides* were used for the treatment of stomachache, haemorrhoids and hernia diseases. In this article, we report the isolation and structural elucidation of four glycosides from the water extract of seeds of *E. phaseoloides* including phaseoloideside C (1), phaseoloideside E (2), acanthoside D (3), and 1-(3,4,5-trimethoxyphenyl)prop-7-en-9-ol-O-(6"O- α -L-arabinopyranosyl)- β -D-glucopyranoside (4). To the best of our knowledge, compounds 3-4 are isolated from *E. phaseoloides* for the first time.

Keywords: Entada phaseoloides, Fabaceae, saponin, phaseoloideside C, phaseoloideside E, and acanthoside D.

Classification numbers: 1.1.1; 1.1.6.

1. INTRODUCTION

Entada is a genus of the Fabaceae family comprising 30 species in the world and 3 species in Viet Nam (*Entada phaseoloides, Entada, pursaetha*, and *Entada glandulosa*) [1, 2]. *Entada phaseoloides* is a woody climber distributed throughout Viet Nam, Thailand, Malaysia, Indonesia, Philippines, China, New Guinea, and Australia. The seeds of *E. phaseoloides* have been used as the folk medicine to treat stomachache, haemorrhoids, and hernia [2]. Pharmacological studies on extracts and isolated compounds from this plant displayed cytotoxic [1, 3], antidiabetic [4, 5], antioxidant [6, 7], antimicrobial [6, 8], antivirus [9] and anti-

inflamatory [10] activities. Besides, studies on chemical constituents of *E. phaseoloides* showed the presence of triterpenoid saponins [1, 3, 10-14], sulfur-containing amides [15-17], phenylacetic acid derivatives [9, 18] and flavonoids [8]. Herein, we reported the isolation and chemical structural elucidation of four glycosides from the seeds of *E. phaseoloides*.

2. MATERIAL AND METHODS

2.1. Plant Materials

The seeds of *E. phaseoloides* (L.) Merr. were collected in Nam Dong, Thua Thien Hue, Viet Nam, in August 2017 and identified by Dr. Vu Tien Chinh, Vietnam National Museum of Nature, VAST. A voucher specimen (MISR-2017-03) was deposited at Mientrung Institute for Scientific Research, VAST.

2.2. General experimental procedures

All NMR spectra were recorded on a Bruker AM500 FT-NMR spectrometer (500 MHz for ¹H-NMR and 125 MHz for ¹³C-NMR). The HR-ESI-MS spectra were obtained using an AGILENT 6550 iFunnel Q-TOF LC/MS system. Plant sample was extracted on a JP. Selecta 300867 sonicator. Column chromatography was performed using a silica gel (Kieselgel 60, 70-230 mesh and 230-400 mesh, Merck) or RP-18 resins (150 μ m, Fuji Silysia Chemical Ltd.), thin layer chromatography (TLC) using a pre-coated silica-gel 60 F₂₅₄ (0.25 mm, Merck) and RP-18 F_{254S} plates (0.25 mm, Merck).

2.3. Extraction and isolation

The seeds of E. phaseoloides (7.5 kg) were extracted with methanol (15 L x 3 times) under sonication at 50 0 C for 3 h to give the methanol extract (EP, 850 g), which was then suspended in water (2 L) and partitioned with dichloromethane and ethyl acetate to yield dichloromethane (EPD, 50.0 g), ethyl acetate (EPE, 8.0 g), and water (EPW, 792.0 g) extracts. The water extract (EPW) was chromatographed on a Diaion HP-20P column and eluted with water to remove sugars and ionic compounds, then with increasing concentration of methanol in water (25 %, 50 %, 75 %, and 100 %) to yield four fractions, EPW1-EPW4, respectively. The EPW2 fraction was chromatographed on a silica gel column and eluted with mixtures of dichloromethane/methanol (20/1 \rightarrow 1/1, v/v) to yield five fractions, EPW2A- EPW2E. The EPW2C fraction was applied to a RP-18 column and eluted with acetone/water (1/2, v/v) to give two sub-fractions, EPW2C1-EPW2C2. Compound 1 (20 mg) was yielded by the purification of the EPW2C2 sub-fraction on a silica gel column using dichloromethane/methanol/water (2.5/1/0.1, v/v/v). The EPW2C1 sub-fraction was chromatographed on a silica gel column, eluted with dichloromethane/methanol/water (2/1/0.1, v/v/v) to obtain compound 2 (50.0 mg). The EPW2D fraction was separated by RP-18 column chromatography and eluted with methanol/water (1/2.5, v/v) to obtain three sub-fractions, EPW2D1-EPW2D3. The EPW2D1 sub-fraction continued to be chromatographed on silica gel column and eluted with dichloromathane/acetone/water (1/2.5/0.1, v/v/v) to yield compound 3 (8 mg). Finally, the EPW2D3 sub-fraction was further chromatographed on silica gel column and eluted with dichloromathane/acetone/water (1/2/0.1, v/v/v) to furnish compound 4 (6 mg).

Phaseoloideside C (1): White amorphous powder; HR-ESI-MS: m/z 1544.7095 [M+H]⁺ (C₇₀H₁₁₃NO₃₆, M = 1544); ¹H-NMR (500 MHz, CD₃OD- d_4) and ¹³C-NMR (125 MHz, CD₃OD- d_4) see Table 1.

Phaseoloideside E (2): White amorphous powder; HR-ESI-MS: 1586.7206 $[M+H]^+$ (C₇₂H₁₁₅NO₃₇, M = 1586); ¹H-NMR (500 MHz, CD₃OD-*d*₄) and ¹³C-NMR (125 MHz, CD₃OD-*d*₄) see Table 1.

Acanthoside D (3): White amorphous powder; ¹H-NMR (500 MHz, CD₃OD- d_4 in D₂O), δ (ppm): 6.76 (4H, s, H-2, 2', 6, 6'), 4.93 (2H, dd, J = 1.5, 7.0 Hz, H-7, 7'), 3.27 (2H, m, H-8, 8'), 4.00 (2H, dd, J = 3.0, 8.5 Hz, H_a-9, H_a-9'), 4.35 (2H, dd, J = 7.0, 8.5 Hz, H_b-9, H_b-9'), 4.85 (2H, d, J = 9.0, Glc-H-1, 1'), 3.27 (2H, m, Glc-H-2, 2'), 3.49 (2H, m, Glc-H-3, 3'), 3.55 (2H, m, Glc-H-4, 4'), 3.52 (2H, m, Glc-H-5, 5'), 3.78 (2H, dd, J = 2.0, 12.0 Hz, Glc-H_a-6, 6'), 3.72 (2H, dd, J = 5.0, 12.0 Hz, Glc-H_b-6, 6'), 3.88 (12H, s, OCH₃-3, 3', 5, 5'); ¹³C-NMR (125 MHz, CD₃OD- d_4 in D₂O), δ (ppm): 134.8 (C-1, 1'), 104.7 (C-2, 2', 6, 6'), 154.0 (C-3, 3', 5, 5'), 86.9 (C-7, 7'), 55.0 (C-8, 8'), 72.8 (C-9, 9'), 104.6 (Glc-C-1, 1'), 75.1 (Glc-C-2, 2'), 77.7 (Glc-C-3, 3'), 70.5 (Glc-C-4, 4'), 77.1 (Glc-C-5, 5'), 61.8 (Glc-C-6, 6'), 57.2 (OCH₃-3, 3', 5, 5').

1-(3,4,5-Trimethoxyphenyl)prop-7-en-9-ol-*O***-(6***"-O***-***α***-L-arabinopyranosyl)***β***-D-glucopyranoside (4)**: Colourless oil; ¹H-NMR (500 MHz, CD₃OD-*d*₄), δ (ppm): 6.76 (2H, s, H-2, 6), 6.65 (1H, d, *J* = 15.5 Hz, H-7), 6.32 (1H, dt, *J* = 6.0, 15.5 Hz, H-8), 4.34 (1H, dd, *J* = 6.0, 13.0 Hz, H-9a), 4.51 (1H, dd, *J* = 6.0, 13.0 Hz, H-9b), 4.39 (1H, d, *J* = 7.5 Hz, H-1'), 3.28 (1H, dd, *J* = 7.5, 9.0 Hz, H-2'), 3.33 (1H, m, H-3'), 3.82 (1H, m, H-4'), 3.38 (1H, m, H-5'), 4.13 (1H, dd, *J* = 2.0, 11.5 Hz, H-6'a), 3.76 (1H, dd, *J* = 6.0, 11.5 Hz, H-6'b), 4.36 (1H, d, *J* = 6.5 Hz, H-1''), 3.48 (1H, m, H-2''), 3.54 (1H, m, H-3''), 3.90 (1H, m, H-4''), 3.63 (1H, m, H-5''a), 3.55 (1H, m, H-5''b), 3.87 (6H, s, OCH₃-3, 5), 3.78 (3H, s, OCH₃-4); ¹³C-NMR (125 MHz, CD₃OD-*d*₄), δ (ppm): 134.4 (C-1), 105.0 (C-2, 6), 154.6 (C-3, 5), 139.0 (C-4), 133.7 (C-7), 126.4 (C-8), 69.5 (C-9), 103.4 (C-1'), 75.1 (C-2'), 78.0 (C-3''), 71.7 (C-4'), 76.9 (C-5'), 69.4 (C-6'), 105.2 (C-1''), 72.4 (C-2''), 74.2 (C-3''), 70.8 (C-4''), 66.7 (C-5''), 56.7 (OCH₃-3, 5), 61.2 (OCH₃-4).

3. RESULTS AND DISCUSSION

Compound 1 was obtained as a white amorphous powder. Its molecular formula was determined as $C_{70}H_{113}NO_{36}$ from pseudo-molecular ion peak at m/z 1544.7095 [M+H]⁺ (calcd. for $C_{70}H_{114}NO_{36}$, 1544.7121) in the HR-ESI-MS. The ¹H-NMR spectrum of 1 observed signals of the protons of seven tertiary methyl groups at $\delta_{\rm H}$ 0.77, 0.87, 0.90, 0.98, 0.99, 1.00, and 1.34 (each, 3H, s); a trisubstituted olefinic proton at $\delta_{\rm H}$ 5.44 (1H, brs), and two oxymethine groups at $\delta_{\rm H}$ 3.87 (1H, brs) and 4.33 (1H, brd, J = 3.0 Hz), which suggested to be an entagenic acid aglycon [19, 20]. Besides, signals of seven anomeric protons were showed at $\delta_{\rm H}$ 4.48 (1H, d, J =8.0 Hz), 4.49 (1H, d, J = 7.5 Hz), 4.57 (1H, d, J = 6.5 Hz), 4.65 (1H, d, J = 8.0 Hz), 4.97 (1H, d, J = 3.0 Hz), 5.37 (1H, d, J = 3.5 Hz) and 5.43 (1H, d, J = 8.0 Hz), suggesting the presence of seven sugar moieties. The ¹³C-NMR and DEPT of **1** showed the presence of 70 carbons including 2 carbonyls, 7 non-protonated, 36 methine, 17 methylene and 8 methyl carbons (Table 1). The signals of the carbonyl carbon (δ_C 173.2) and the methyl group (δ_H 1.96 (s), δ_C 23.2) in the HSQC spectrum suggested the presence of an acetyl group. The downfield chemical shift of C-3 ($\delta_{\rm C}$ 91.1) and upfield chemical shift of C-28 ($\delta_{\rm C}$ 176.8) were displayed in ¹³C-NMR spectrum, which suggested that compound 1 was a bidesmosidic glycoside of entagenic acid with two oligosaccharides linked at C-3 and C-28 [21]. Complete assignments of each sugar proton system were accomplished by analysis of ¹H-¹H COSY spectrum, while the carbons were

assigned from HSQC and HMBC spectra (Table 1). The coupling constant and chemical shift of the protons and carbons of the sugar moieties suggested the presence of one 2-(acetylamino)-2deoxy- β -glucopyranosyl (GlcNAc), one terminal β -glucopyranosyl (Glc1), one α arabinopyranosyl (Ara), one terminal β -xylopyranosyl (Xyl), one β -glucopyranosyl (Glc2), one α -apiopyranosyl (Api1) and one terminal α -apiopyranosyl (Api2) units (Figure 1). The sequence within the sugar chain at C-3 was determined by HMBC experiments. The key HMBC correlation between proton H-1 (δ_H 4.48) of GlcNAc and carbon C-3 (δ_C 91.1) of aglycon determined that the GlcNAc was linked to C-3 of aglycon (Figure 2). The important HMBC correlations between proton H-1 ($\delta_{\rm H}$ 4.65) of Glc1 and carbon C-4 ($\delta_{\rm C}$ 80.6) of GlcNAc, proton H-1 ($\delta_{\rm H}$ 4.57) of Ara and carbon C-6 ($\delta_{\rm C}$ 68.3) of GlcNAc, and between proton H-1 ($\delta_{\rm H}$ 4.49) of Xyl and carbon C-3 ($\delta_{\rm C}$ 83.1) of Ara showed the location of Glc1 at C-4 of GlcNAc, of Ara at C-6 of GlcNAc, and of Xyl at C-3 of Ara (Figure 2). In the same way, the other sugar chain at C-28 was determined by the key HMBC correlations of proton H-1 (δ_H 5.43) of Glc2 with carbon C-28 (δ_C 176.8) of aglycon, proton H-1 (δ_H 5.37) of Api1 with carbon C-2 (δ_C 79.9) of Glc2, and proton H-1 ($\delta_{\rm H}$ 4.97) of Api2 with carbon C-5 ($\delta_{\rm C}$ 71.4) of Api1 (Figure 2). Detailed analysis of HR-ESI-MS, 1D, 2D-NMR, and comparison with published data allowed us to determine compound 1 as phaseoloideside C [19].



Figure 1. Chemical structures of compounds 1-4.

Compound **2** was obtained as a white amorphous powder. Its molecular formula was determined as $C_{72}H_{115}NO_{37}$ from pseudo-molecular ion peak at m/z 1586.7206 [M+H]⁺ (calcd. for $C_{72}H_{116}NO_{37}$, 1586.7226) in the HR-ESI-MS. Its ¹H-NMR spectrum indicated the signals of nine methyl groups at δ_H 0.79, 0.83, 0.91, 0.96, 0.98, 1.03, 1.32, 1.96, and 2.07 (each, 3H, s), a trisubstituted olefinic proton at δ_H 5.40 (1H, brs), two oxymethine groups at δ_H 3.86 (1H, brs) and 4.33 (1H, brd, J = 3.5 Hz), and seven anomeric protons at δ_H 4.48 (1H, d, J = 8.5 Hz), 4.49 (1H, d, J = 7.5 Hz), 4.57 (1H, d, J = 6.5 Hz), 4.65 (1H, d, J = 8.0 Hz), 4.69 (1H, d, J = 8.0 Hz), 5.28 (1H, d, J = 3.0 Hz) and 5.47 (1H, d, J = 7.5 Hz). The ¹³C-NMR and DEPT of **2** displayed the signals of 72 carbons: 10 non-protonated (including 3 carbonyls), 37 methine, 16 methylene, and 9 methyl carbons (Table 1). The signals of two carbonyl carbons at δ_C 173.2, 172.7 and two methyl groups [(δ_H 1.96 (s) and δ_C 23.2; δ_H 2.07 (s) and δ_C 20.8] in the HSQC spectrum suggested the presence of two acetyl groups. By comparing ¹H- and ¹³C-NMR data, the structure of **2** can be similar with that of phaseoloideside C (**1**). However, the differences between them

are the component of sugar units of oligosaccharide chain at C-28 and an additional acetyl group. It was confirmed by the key HMBC correlations of proton H-1 (δ_H 5.47) of Glc2 with carbon C-28 (δ_C 176.9), proton H-1 (δ_H 4.69) of Xyl2 with carbon C-2 (δ_C 80.3) of Glc2, and proton H-1 (δ_H 5.28) of Api with carbon C-3 (δ_C 85.6) of Xyl2. Moreover, the HMBC correlation between proton H-6 (δ_H 4.20, 4.29) of Glc2 and acetyl group at δ_C 172.7 (C=O) showed the position of acetyl group at C-6 through an ester bond (Figure 2). All NMR assignments of **2** were confirmed by detailed analyses of HSQC and HMBC spectra, which are in good agreement with those reported in literature [11]. Consequently, compound **2** was identified as phaseoloideside E.

Similarly, detailed analysis of ¹H-, ¹³C-NMR data as well as comparison of them with the literature values led to the identification of compounds **3** and **4** as acanthoside D [22] and 1-(3,4,5-trimethoxyphenyl)prop-7-en-9-ol-O-(6"O- α -L-arabinopyranosyl)- β -D-glucopyranoside [23].

С	${\delta_C}^{\#1}$	Compound 1		С	${\delta_C}^{\#2}$	Compound 2	
		${\delta_C}^{a,b}$	$\delta_{H}^{\ a,c}$			${\delta_C}^{a,b}$	$\delta_{H}^{a,c}$
			(mult., J in Hz)				(mult., J in Hz)
1	37.1	37.6	1.72 (m)	1	37.1	37.5	1.72 (m)
2	26.5	27.0	1.69 (m) 1.90 (m)	2	26.7	27.0	1.69 (m) 1.90 (m)
3	89.7	91.1	3.14 (dd, 4.0, 11.5)	3	89.7	91.1	3.14 (dd, 4.0, 11.5)
4	39.3	40.0	-	4	39.3	40.0	-
5	55.6	56.8	0.77 (m)	5	55.8	56.8	0.76 (m)
6	19.0	19.6	1.40 (m)	6	19.1	19.6	1.37 (m)
			1.52 (m)				1.53 (m)
7	39.0	39.9	1.01 (m)	7	39.1	39.9	0.97*
			1.65 (m)				1.63 (m)
8	42.1	42.2	-	8	41.6	42.2	-
9	47.5	48.3	1.54 (m)	9	47.5	48.3	1.54 (m)
10	37.2	38.0	-	10	37.1	38.0	-
11	24.1	24.7	1.92 (m)	11	24.1	24.7	1.88 (m)
12	124.8	125.8	5.44 (brs)	12	125.0	125.8	5.40 (brs)
13	144.7	144.9	-	13	144.6	144.8	-
14	47.9	48.5	-	14	47.7	48.5	-
15	68.9	69.3	3.87 (brs)	15	68.9	69.3	3.86 (brs)
16	79.1	79.5	4.33 (d, 3.0)	16	78.9	79.2	4.33 (brd, 3.5)
17	48.7	48.5	-	17	48.7	48.5	-
18	42.1	42.6	2.97 (dd, 4.0, 14.5)	18	41.9	42.5	3.02 (brd, 10.5)

Table 1. The ¹H- and ¹³C-NMR data of **1-2** and reference compounds.

19	46.7	47.4	1.02 (m)	19	46.7	47.1	1.02 (m)
			2.32 (t, 13.5)				2.33 (t, 13.0)
20	30.9	31.3	-	20	30.9	31.4	-
21	36.0	36.5	1.19 (m)	21	36.3	36.5	1.18 (m)
			1.97 (m)				1.98 (m)
22	31.9	32.0	1.92 (m)	22	31.7	32.3	1.84 (m)
							1.97 (m)
23	28.2	28.6	0.98 (s)	23	28.1	28.6	0.98 (s)
24	17.1	17.1	0.77 (s)	24	17.1	17.1	0.79 (s)
25	15.8	16.2	0.99 (s)	25	15.8	16.3	0.96 (s)
26	18.1	18.3	0.87 (s)	26	18.1	18.5	0.83 (s)
27	20.8	20.5	1.34 (s)	27	20.8	20.5	1.32 (s)
28	175.7	176.8	-	28	176.1	176.9	-
29	33.4	33.4	0.90 (s)	29	33.4	33.4	0.91 (s)
30	24.6	24.8	1.00 (s)	30	24.5	24.9	1.03 (s)
GlcNAc				GlcNAc			
1	104.5	105.0	4.48 (d, 8.0)	1	104.6	105.0	4.48 (d, 8.5)
2	57.6	57.3	3.74 (m)	2	59.0	57.3	3.72 (m)
3	73.9	73.9	3.64 (dd, 8.5, 10.5)	3	73.9	73.9	3.64 (m)
4	81.0	80.6	4.04 (t-like, 8.0)	4	80.9	80.6	4.03 (m)
5	75.1	75.1	3.51 (m)	5	75.1	75.1	3.54 (m)
6	68.2	68.3	3.95 (m)	6	68.3	68.3	3.95 (m)
			4.13 (m)				4.12 (dd, 6.0, 12.0)
CH_3 (Ac)	23.7	23.2	1.96 (s)	CH_3 (Ac)	23.8	23.2	1.96 (s)
C=O (Ac)	170.0	173.2	-	C=O	170.1	173.2	-
Glc1				Glc1			
1	104.5	104.3	4.65 (d, 8.0)	1	104.5	104.3	4.65 (d, 8.0)
2	74.8	74.9	3.32 (t-like, 8.0)	2	75.0	74.9	3.32 (m)
3	78.8	77.9	3.38 (m)	3	78.6	77.9	3.38 (m)
4	71.3	71.4	3.88 (m)	4	71.6	71.4	3.35 (m)
5	78.7	77.7	3.45 (m)	5	78.4	77.7	3.44 (m)
6	62.3	62.4	3.70 (m)	6	62.4	62.4	3.72 (m)
			3.88 (m)				3.88 (m)
Ara				Ara			
1	103.5	103.6	4.57 (d, 6.5)	1	103.5	103.6	4.57 (d, 6.5)
2	73.2	73.9	3.74 (m)	2	73.2	73.9	3.74 (m)
3	83.4	83.1	3.76 (m)	3	83.9	83.1	3.75 (m)
4	68.5	71.1	3.38 (m)	4	68.9	71.1	3.39 (m)

5	66.4	66.5	3.54 (m)	5	66.4	66.5	3.55 (m)
			3.87 (m)				3.87 (m)
Xyl				Xyl1			
1	107.0	107.6	4.49 (d, 7.5)	1	107.9	107.6	4.49 (d, 7.5)
2	76.7	76.4	3.28 (m)	2	74.8	76.4	3.28 (m)
3	78.9	78.0	3.38 (m)	3	78	78.0	3.38 (m)
4	71.0	71.1	3.50 (m)	4	70.8	70.8	3.50 (m)
5	67.5	67.4	3.28 (m)	5	67.5	67.3	3.27 (m)
			11.5)				4.08 (dd, 0.0, 11.3)
Glc2				Glc2			
1	94.5	94.7	5.43 (d, 8.0)	1	93.3	93.6	5.47 (d, 7.5)
2	80.1	79.9	3.53 (m)	2	80.1	80.3	4.30 (brd, 10.5)
3	78.6	78.4	3.55 (m)	3	78.4	78.4	3.67 (m)
4	70.9	71.4	3.39 (t-like, 8.5)	4	70.4	69.8	3.37 (m)
5	78.2	78.4	3.33 (m)	5	78.2	78.4	3.64 (m)
6	62.5	62.4	3.70 (m)	6	64.2	64.5	4.20 (dd, 5.0, 12.0)
			3.80 (m)				4.29 (brd, 10.5)
CH_3 (Ac)	-	-	-	CH_3 (Ac)	20.8	20.8	2.07 (s)
C=O (Ac)	-	-	-	C=O (Ac)	170.8	172.7	-
Api1				Xyl2			
1	110.9	110.9	5.37 (d, 3.5)	1	105.7	105.3	4.69 (d, 8.0)
2	78.0	78.7	4.00 (m)	2	75.9	75.9	3.43 (m)
3	80.4	80.4	-	3	85.0	85.6	3.41 (m)
4	75.2	75.2	3.78 (m)	4	69.5	69.0	3.56 (m)
	71.6	71.4	4.11 (III)	5	(7.2)	(()	2.20 ()
5	/1.0	/1.4	3.75 (m)	5	07.2	00.9	3.20 (m) 3.96 (m)
Api2				Арі			
1	110.8	110.8	4.97 (d, 3.0)	1	111.5	111.2	5.28 (d, 3.0)
2	77.6	77.9	3.93 (d, 3.0)	2	77.9	77.9	4.00 (d, 3.0)
3	80.4	80.4	-	3	80.5	80.5	-
4	75.1	75.2	3.78 (m)	4	75.2	75.3	3.62 (m)
			4.00 (m)				
5	65.5	65.5	3.60 (d, 2.0)	5	65.6	65.3	3.82 (m)
							4.14 (m)

Structural elucidation of four glycosides from the seeds of Entada phaseoloides...



Figure 2. Key HMBC correlations of compounds 1-2.

4. CONCLUSIONS

The phytochemical study on the water extract of the seeds of *Entada phaseoloides* (L.) Merr. led to the isolation of four compounds including phaseoloideside C (1), phaseoloideside E (2), acanthoside D (3), and 1-(3,4,5-trimethoxyphenyl)prop-7-en-9-ol-O-(6"-O- α -L-arabinopyranosyl)- β -D-glucopyranoside (4). Their chemical structures were elucidated by HR-ESI-MS data, 1D, 2D-NMR spectra analysis and in comparison with those reported in the literature. To the best of our knowledge, this is the first report of isolation of compounds **3-4** from this plant.

REFERENCES

- 1. Hui X., Zhinan M., Guangzhong Y., Shasha M., Xinzhou Y., Peng Z., Jizhou W. -Triterpene saponins from *Entada phaseoloides*, Helv. Chim. Acta **96** (2013) 1579-1589.
- 2. Chi V. V. The Dictionary of Medicinal Plants in Viet Nam. Medical Publishing House, Hanoi 1 (2012) 115-116 (in Vietnamese).
- 3. Xiong H., Ding X., Yang X., Yang G. Z., Mei Z. N. Triterpene saponins from the stems of *Entada phaseoloides*, Planta Med. **80** (2014) 710-718.
- Zheng T., Shu G., Yang Z., Mo S., Zhao Y., Mei Z. Antidiabetic effect of total saponins from *Entada phaseoloides* (L.) Merr. in type 2 diabetic rats, J. Ethnopharmacol. 139 (2012) 814-821.
- Ikram M., Babar Z. U., Taufiqual Islam A. M., Chowdhury A., Uddin M. E., Islam M. R., Islam S. - Antidiabetic and hypolipidemic effects of the different fractions of methanolic extracts of *Entada phaseoloides* (L.) Merr. in alloxan induced diabetic mice, IJPSR 2 (2011) 3160-3165.
- Rashid M., Kuddus R., Faruque O., Rumi F., Quadir M. A., Rashid M. A. Antioxidant, cytotoxic, membrane stabilizing and antimicrobial activities of bark and seed of *Entada phaseoloides* (L.) Merr.: A medicinal plant from chittagong hill tracts, J. Pharm. Nutri.Sci. 1 (2011) 171-176.
- 7. Dong Y., Shi H., Yang H., Peng Y., Wang M., Li X. Antioxidant phenolic compounds from the stems of *Entada phaseoloides*, Chem. Biodivers. **9** (2012) 68-79.

- Li K., Xing S., Wang M., Peng Y., Dong Y., Li X. Anticomplement and antimicrobial activities of flavonoids from *Entada phaseoloides*, Nat. Prod. Commun. 7 (2012) 867-871.
- 9. Chen L., Zhang Y., Ding G., Ba M., Guo Y., Zou Z. Two new derivatives of 2, 5dihydroxyphenylacetic acid from the kernel of *Entada phaseoloides*, Molecules **18** (2013) 1477-1482.
- Xiong H., Zheng Y., Yang G., Wang H., Mei Z. Triterpene saponins with antiinflammatory activity from the stems of *Entada phaseoloides*, Fitoterapia 103 (2015) 33-45.
- 11. Mo S., Xiong H., Shu G., Yang X., Wang J., Zheng C., Xiong W., Mei Z. -Phaseoloideside E, a novel natural triterpenoid saponin identified from *Entada phaseoloides*, induces apoptosis in Ec-109 esophageal cancer cells through reactive oxygen species generation, J. Pharmacol. Sci. **122** (2013) 163-175.
- 12. Okada Y., Shibata S., Kamo O., Okuyama T. ¹³C NMR spectral studies of entagenic acid to establish its structure. Chem. Pharm. Bull. **36** (1988) 5028-5030.
- Okada Y., Shibata S., M. J. Javellana A. N. A., Kamo O. Entada saponins (ES) II and IV from the bark of *Entada phaseoloides*. Chem. Pharm. Bull. 36 (1988) 1264-1269.
- 14. Okada Y., Shibata S., Ikekawa T., Javellana A. M. J., Kamo O. Entada saponin-III, a saponin isolated from the bark of *Entada phaseoloides*, Phytochemistry **26** (1987) 2789-2796.
- Ikegami F., Shibasaki I., Ohmiya S., Ruangrungsi N., Murakoshi I. Entadamide A, a new sulfur-containing amide from *Entada phaseoloides* seeds, Chem. Pharm. Bull. 33 (1985) 5153-5154.
- Ikegami F., Ohmiya S., Ruangrungsi N., Sakai S. I., Murakoshi I. Entadamide B, a second new sulphur-containing amide from *Entada phaseoloides*, Phytochemistry 26 (1987) 1525-1526.
- Ikegami F., Sekine T., Duangteraprecha S., Matsushita N., Matsuda N., Ruangrungsi, N., Murakoshi I. - Entadamide C, a sulphur-containing amide from *Entada phaseoloides*. Phytochemistry 28 (1989) 881-882.
- 18. Singh O., Ali M., Akhtar N. Phenolic acid glucosides from the seeds of *Entada* phaseoloides Merill, J. Asian Nat. Prod. Res. **13** (2011) 682-687.
- 19. Xiong H., Mei Z., Yang G., Mo S., Yang X., Zhang P., Wu J. Triterpene saponins from *Entada phaseoloides*, Helv. Chim. Acta **96** (2013) 1579-1589.
- 20. Xiong H., Ding X., Yang X. Z., Yang G. Z., Mei Z. N. Triterpene saponins from the stems of *Entada phaseoloides*, Planta Med. **80** (2014) 710-718.
- Nzowa, L. K., Barboni, L., Teponno, R. B., Ricciutelli, M., Lupidi, G., Quassinti, L., Bramucci, M., Tapondjou, L. A. - Rheediinosides A and B, two antiproliferative and antioxidant triterpene saponins from *Entada rheedii*, Phytochemistry **71** (2010) 254-261.
- 22. Kaneko T., Ohtani, K. Kasai, R. Yamasaki K., Nguyen M. D. *n*-Alkyl glycosides and phydroxybenzoyloxy glucose from fruits of *Crescentia cujete*, Phytochemistry **47** (1998) 259-263.
- 23. Sugimoto S., Matsunami K., Otsuka H. Medicinal plants of Thailand. II: chemical studies on the seed kernels of *Entada rheedei* Sprengel, J. Nat. Med. **66** (2012) 552-557.