Vietnam Journal of Chemistry, International Edition, **54**(6): 678-682, 2016
DOI: 10.15625/0866-7144.2016-00386

Megastigmans and other compounds from *Antidesma hainanensis* Merr.

Le Canh Viet Cuong[1], Do Thi Trang[1], Nguyen Xuan Nhiem[1], Pham Hai Yen[1], Bui Huu Tai[1], Hoang Le Tuan Anh[1], Le Mai Huong[2], Chau Van Minh[1], Phan Van Kiem[1*]

[1]*Institute of Marine Biochemistry, Vietnam Academy of Science and Technology (VAST)*

[2]*Institute of Natural Products Chemistry, VAST*

Received 28 June 2016; Accepted for publication 8 December 2016

Abstract

Four megastigmans 7-megastigmene-3-ol-9-one 3-*O*-[α-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside] (**1**), alangionoside L (**2**), alangioside (**3**), ampelopsisionoside (**4**), and other constituents as N–*trans*-feruloyloctopamide (**5**), *trans*-linalool-3,6-oxide-β-D-glucopyranoside (**6**), 5α,8α-dipioxiergosta-6,22-diene-3β-ol (**7**), and (Z)-2-hexenyl β-D-glucopyranoside (**8**) were isolated from the methanol extract of the *Antidesma hainanensis* leaves. Their chemical structures were successfully determined using NMR and ESI-MS analysis as well as in comparison with the reported data. This is the first report of these compounds from Euphorbiaceae family.

Keywords. *Antidesma hainanensis*, Euphorbiaceae, megastigman.

1. INTRODUCTION

Antidesma is a genus of tropical plants belonging to Euphorbiaceae family and comprises about 100 species in the world and 29 species in Vietnam [1]. The study of the chemical composition showed this genus contains alkaloids, coumarinolignans, megastigmanes, lignan glucosides, benzopyranones, ferulic acid, and particularly is rich in polyphenols, in addition to oil. Biological activity of this genus and pure substances extracted from this genus has been studied, such as antifungal, cytotoxic, and antioxidant activities [2]. However, no public announcement about the chemical composition and biological activity of *A. hainanensis* has been reported up to now. As part of our ongoing chemical investigations on the genus *Antidesma*, we report herein the isolation and structure elucidation of eight compounds from the methanol extract of the *A. hainanensis* leaves.

2. MATERIAL AND METHODS

2.1. Plant Material

The leaves of *Antidesma hainanensis* Merr. were collected in Tamdao, Vinhphuc province, Vietnam, in December, 2014 and identified by Dr. Nguyen Quoc Binh, Vietnam National Museum of Nature. A voucher specimen was deposited at Institute of Marine Biochemistry, VAST.

2.2. General experimental procedures

All NMR spectra were recorded on a Bruker AM500 FT-NMR spectrometer (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR). NMR measurements, including ^{1}H-, ^{13}C-NMR, HSQC, and HMBC experiments, were carried out using 5-mm probe tubes at temperature of 22.2^{o}C. ESI-MS spectra were recorded on Agilent 1100. Column chromatography was performed using a silica gel (Kieselgel 60, 70-230 mesh and 230 - 400 mesh, Merck) or RP-18 resins (150 µm, Fuji Silysia Chemical Ltd.), thin layer chromatography (TLC) using a pre-coated silica-gel 60 F_{254} (0.25 mm, Merck) and RP-18 F_{254S} plates (0.25 mm, Merck).

2.3. Extraction and isolation

The dried leaves of *A. hainanensis* (3.7 kg) were extracted in MeOH three times using sonicator to yield 330 g of a dark solid extract, which was then suspended in water and successively partitioned with *n*-hexane, dichloromethane and ethyl acetate (EtOAc) to give *n*-hexane (AH1, 70 g), dichloromethane (AH2, 85 g), EtOAc (AH3, 62 g),

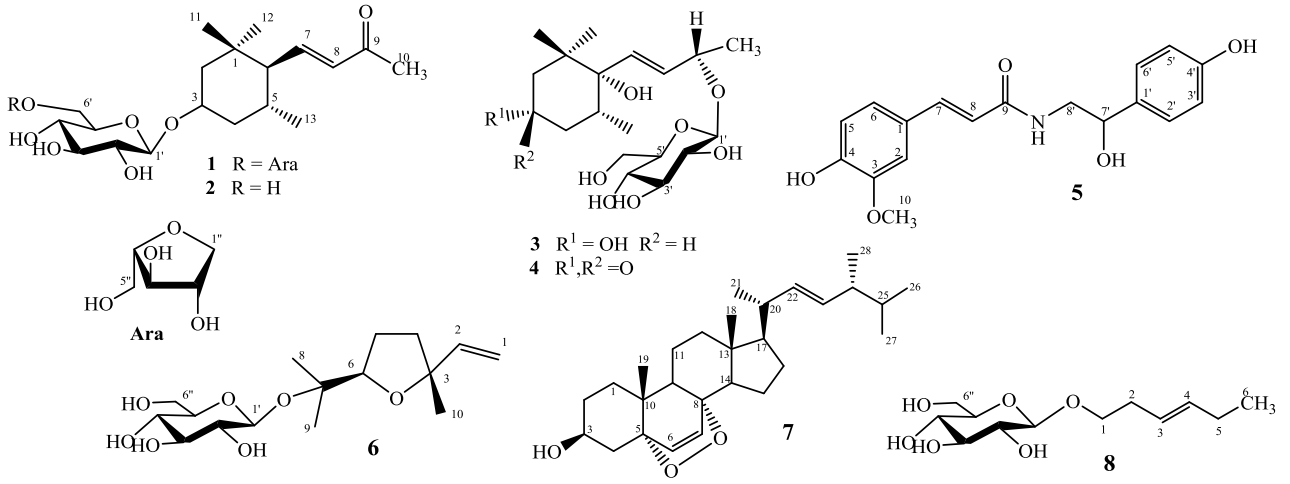

Figure 1: Chemical structures of compounds **1**-**8**

and water layers (AH4, 110 g) after removal solvent *in vacuo*. The AH2 fraction (85 g) was chromatographed on a YMC column eluting with acetone/water (1/3, v/v) to give four smaller fractions (AH2A-AH2D). The AH2D fraction (15g) was chromatographed on a silica gel column eluting with dichloromethane/acetone (20/1, v/v) to yield compound **7** (AH25, 5.0 mg). The AH3 fraction (62g) was chromatographed on a YMC column eluting with methanol/water (1/1.5, v/v) to give four smaller fractions (AH3A-AH3D). The AH3B fraction was chromatographed on a silica gel column eluting with dichloromethane/methanol/water (10/1/0.05) to yield compound **3** (AH8, 5.0mg), 4 (AH5, 5mg), and **5** (AH4, 8.0 mg). The AH3D fraction was chromatographed on a silica gel column eluting with dichloromethane/methanol/water (10/1/0.05) to yield compound **6** (AH11, 14.0mg). The water layer (AH4, 110g) was chromatographed on a Diaion HP-20 column eluting with water to remove sugar component, then increasing concentration of methanol in water (25, 50, 75, and 100 %) to give four fractions, AH4**A**-AH4**D**, respectively. The AH4C fraction was chromatographed on a silica gel column eluting with dichloromethane/methanol (gradient from 100/1-0/1, v/v) to give four fractions (AH4B**1**-AH4B4). The AH4B3 (15g) was chromatographed on a silica gel column eluting with dichloromethane/methanol /water (1/3/1, v/v/v) to yield 5 subtractions (AH4BB3**A**- AH4BB3**E**. The AH4B3D was chromatographed on a silica gel column eluting with dichloromethane/ acetone/water (1/1/0.1, v/v/v) to yield compounds **1** (AH20, 6.0 mg) and **8** (AH19, 5 mg). The AH4B3E was chromatographed on a silica gel column eluting with dichloromethane/acetone/water (1/1.5/0.05, v/v/v) to yield compound **2** (AH14, 12.0 mg).

7-Megastigmene-3-ol-9-one 3-*O*-[*α*-L-arabino-furanosyl-(1→6)-*β*-D-glucopyranoside] (1) [3]**:** Amorphous solid. ESI-MS m/z 527 $[M+Na]^+$ ($C_{24}H_{40}O_{11}$). ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 1.23 (1H, t, *J* = 12.5 Hz, H_a-2), 1.89 (1H, m, H_b-2), 3.89 (1H, m, H-3), 1.09 (1H, m, H_a-4), ; 2.19 (1H, m, H_b-4), 1.79 (1H, m, H-5), 1.60 (1H, t, *J* = 10.5 Hz, H-6), 6.68 (1H, dd, *J* = 10.0, 16.0 Hz, H-7), 6.09 (1H, d, *J* = 16.0 Hz, H-8), 2.28 (3H, s, H-10), 0.97 (3H, s, H-11), 0.92 (3H, s, H-12), 0.86 (3H, d, *J* = 6.5 Hz, H-13), 4.39 (1H, d, *J* = 7.5 Hz, H-1'), 3.15 (1H, dd, *J* = 7.5, 8.5 Hz, H-2'), 3.37 (1H, t, *J* = 8.5 Hz, H-3'), 3.28 (1H, t, *J* = 8.5 Hz, H-4'), 3.48 (1H, m, H-5'), 3.62 (1H, dd, *J* = 5.5, 12.0 Hz, H_a-6'), 3.99 (dd, *J* = 2.5, 12.0 Hz, H_b-6'), 5.01 (1H, s, H-1"), 4.04 1H, H-2"), 3.84 (1H, dd, *J* = 3.0, 6.0 Hz, H-3"), 4.02 (1H, m, H-4"), 3.67 (1H, dd, *J* = 5.5, 12.0 Hz, H_a-5"), 3.76 (1H, dd, *J* = 3.0, 12.0 Hz, H_b-5"). ^{13}C-NMR (125 MHz, $CDCl_3$), see table 1.

Alangionoside L (2) [4]: ESI-MS m/z 373 $[M+H]^+$ ($C_{19}H_{32}O_7$). ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 1.21 (1H, d, *J* = 12.5 Hz, H_a-2), 1.90 (1H, 1H, ddd, *J* = 2.0, 4.0, 12.5 Hz, H_b-2), 3.94 (1H, m, H-3), 1.08 (1H, d, *J* = 12.0 Hz, H_a-4), 2.18 (1H, m, H_b-4), 1.76 (1H, m, H-5), 1.60 (1H, t, *J* = 10.5 Hz, H-6), 6.68 (1H, dd, *J* = 10.5, 16.0 Hz, H-7), 6.10 (1H, d, *J* = 16.0 Hz, H-8), 2.28 (3H, s, H-10), 0.96 (3H, s, H-11), 0.91 (3H, s, H-12), 0.86 (3H, d, *J* = 6.5 Hz, H-13), 4.38 (1H, d, *J* = 7.5 Hz, H-1'), 3.15 (1H, dd, *J* = 7.5, 9.0 Hz, H-2'), 3.37 (1H, t, *J* = 9.0 Hz, H-3'), 3.29 (1H, t, *J* = 9.0 Hz, H-4'), 3.31 (1H, m, H-5'), 3.68 (1H, ddd, *J* = 1.0, 4.0, 11.5 Hz, H_a-6'), 3.89 (1H, dd, *J* = 1.0, 11.5 Hz, H_b-6'). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm), see table 1.

Alangioside (3) [5]: ESI-MS m/z 391 $[M+H]^+$ ($C_{19}H_{34}O_8$). ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 1.42 (1H, m, H_a-2), 1.66 (1H, d, *J* = 12.0 Hz, H_b-2), 3.82 (1H, m H-3), 1.40 (1H, m H_a-4), 1.69 (1H, d, *J* = 5.5 Hz, H_b-4), 1.95 (1H, m, H-5), 5.63 (1H, d, *J* = 16.0 Hz, H-7), 5.81 (1H, dd, *J* = 7.0, 16.0 Hz, H-8), 4.42 (1H, t, *J* = 6.0 Hz, H-9), 1.32 (3H, d, *J* = 6.0 Hz, H-10), 1.00 (3H, s, H-11), 0.91 (3H, s, H-12), 0.83 (3H, d, *J* = 7.0 Hz, H-13), 4.36 (1H, d, *J* = 7.5 Hz, H-1'), 3.19 (1H, dd, *J* = 7.5, 8.5 Hz, H-2'), 3.36 (1H, t, *J* = 8.5 Hz, H-3'), 3.34 (1H, overlapped, H-4') 3.24 (1H, m, H-5'), 3.67 (1H, dd, *J* = 5.0, 12.0 Hz, H_a-6'), 3.85(1H, dd, *J* = 3.0, 12.0 Hz, H_b-6'). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm), see table 1.

Ampelopsisionoside (4) [5]: ESI-MS: *m/z* 423 $[M+Cl]^-$. ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 1.84 (1H, dd, *J* = 2.0, 13.5 Hz, H_a-2), 2.89 (1H, d, *J* = 13.5 Hz, H_b-2), 2.14 (1H, m, H_a-4), 2.47 (1H, dd, *J* = 13.5, 13.5 Hz, H_b-4), 2.29 (1H, m, H-5), 5.75 (1H, d, *J* = 16.0 Hz, H-7), 5.92 (1H, dd, *J* = 7.0, 16.0 Hz, H-8), 4.47 (1H, m, H-9), 1.34 (3H, d, *J* = 6.0 Hz, H-10), 0.95 (3H, s, H-11), 1.00 (3H, s, H-12), 0.92 (3H, d, *J* = 6.5 Hz, H-13), 4.37 (1H, d, *J* = 7.5 Hz, H-1'), 3.21 (1H, dd, *J* = 7.5, 9.0 Hz, H-2'), 3.67 (1H, t, *J* = 9.0 Hz, H-3'), 3.32 (1H, t, *J* = 9.0 Hz, H-4'), 3.25 (1H, m, H-5'), 3.67 (1H, dd, *J* = 5.5, 12.0 Hz, H_a-6'), 3.85 (1H, dd, *J* = 2.5, 12.0 Hz, H_b-6'). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm), see table 1.

N–*trans*-feruloyloctopamide (5) [6]: Colorless oil. ESI-MS: *m/z* 328 $[M-H]^-$; *m/z* 364 $[M+Cl]^-$; *m/z* 366 $[M+Cl+2]^-$ ($C_{18}H_{19}NO_5$). ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 7.14 (1H, br s, H-2), 6.81 (1H, d, *J* = 8.0 Hz, H-5), 7.04 (1H, br d, *J* = 8.0 Hz, H-6), 7.46 (1H, d, *J* = 16.0 Hz, H-7), 6.48 (1H, d, *J* = 16.0 Hz, H-8), 7.24 (1H, d, *J* = 8.5 Hz, H-2′),6.79 (1H, d, *J* = 8.5 Hz, H-3′), 6.79 (1H, d, *J* = 8.5 Hz, H-5′), 7.24 (1H, d, *J* = 8.5 Hz, H-6′), 4.74 (1H, dd, *J* = 4.5, 7.5 Hz, H-7′), 3.55 (1H, dd, *J* = 4.5, 13.5 Hz, H_a-8′), 3.46 (1H, dd, *J* = 7.5, 13.5 Hz, H_b-8′), 3.90 (3H, s, 3-OCH_3). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm), see table 1.

***trans*-Linalool-3,6-oxide-*β*-D-glucopyranoside (6)** [7]: ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 5.02 (1H, dd, *J* = 1.5, 11.0, H_a-1), 5.24 (1H, dd, *J* =1.5, 17.5, H_b-1), 6.00 (1H, dd, *J* = 11.0, 17.5, H-2), 1.85 (1H, m, H_a-4), 1. 95 (1H, m, H_b-4), 1.80 (1H, m, H_a-5), 2.00 (1H, m, H_b-5), 4.08 (1H, dd, *J* = 6.5, 8.5, H-6), 1.24 (3H, s, H-8), 1.28 (3H, s, H-9), 1.36 (3H, s, H-10), 4.53 (1H, d, *J* = 7.5 Hz, H-1'), 3.31 (1H, dd, *J* = 7.5, 9.0 Hz, H-2'), 3.39 (1H, t, 9.0 Hz, H-3'), 3.29 (1H, t, 9.0 Hz, H-4'), 2.29 (1H, m, H-5'), 3.66 (1H, dd, *J* =5.0, 12.0, H_a-6'), 3.83 (1H, dd, *J* = 2.5, 12.0, H_b-6'). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm), see table 1.

5*α*,8*α*-Dipioxyergosta-6,22-diene-3*β*-ol (7) [8]: ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 3.97 (1H, m, H-3), 6.24 (1H, d, *J* = 8.5 Hz, H-6), 6.50 (1H, d, *J* = 8.5 Hz, H-7), 0.83 (3H, s, H-18), 0.88 (3H, s, H-19), 1.00 (3H, d, *J* = 6.5 Hz, H-21), 5.14 (1H, dd, *J* = 7.0, 15.0 Hz, H-22), 5.23 (1H, (1H, dd, *J* = 7.0, 15.0 Hz, H-23), 0.81 (3H, d, *J* = 6.5 Hz, H-26), 0.84 (3H, d, *J* = 6.5 Hz, H-27), 0.92 (3H, d, *J* = 6.5 Hz, H-28). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm): 30.1 (C-1), 34.7 (C-2), 66.5 (C-3), 39.4 (C-4), 82.2 (C-5), 135.4 (C-6), 130.8 (C-7), 79.4 (C-8), 51.1 (C-9), 37.0 (C-10), 20.6 (C-11), 37.0 (C-12), 44.6 (C-13), 51.7 (C-14), 23.4 (C-15), 28.6 (C-16), 56.2 (C-17), 12.9 (C-18), 18.2 (C-19), 39.7 (C-20), 20.9 (C-21), 135.2 (C-22), 132.3 (C-23), 42.8 (C-24), 33.1 (C-25), 19.6 (C-26), 19.9 (C-27), 17.6 (C-28).

(Z)-2-hexenyl *β*-D-glucopyranoside (8) [9]: ^{1}H-NMR (500 MHz, CD_3OD) δ (ppm): 3.88 (2H, m, H-1), 2.39 (2H, q, *J* = 7.0 Hz, H-2), 5.47 (1H, m, H-3), 5.39 (1H, m, H-4), 2.09 (1H, m, H-5), 0.98 (2H, t, *J* = 7.0 Hz, H-6), 4.29 (1H, d, *J* = 7.5 Hz, H-1′), 3.19 (1H, dd, *J* = 7.5, 8.5 Hz, H-2′), 3.37 (1H, t, *J* = 8.5 Hz, H-3′), 3.30 (1H, t, *J* = 8.5 Hz, H-4′), 3.27 (1H, m, H-5′), 3.69 (1H, dd, *J* = 5.5, 12.0, Hz, H_a-6′), 3.57 (1H, dd, *J* = 7.0, 12.0 Hz, H_b-6′). ^{13}C-NMR (125 MHz, CD_3OD) δ (ppm): 70.5 (C-1), 28.8 (C-2), 134.5 (C-3), 125.8 (C-4), 21.5 (C-5), 14.6 (C-6), 104.3 (C-1′), 75.1 (C-2′), 77.9 (C-3′), 71.6 (C-4′), 78.1 (C-5′), 62.7 (C-6′).

3. RESULTS AND DISCUSSION

Compound **1** was obtained as an amorphous solid. The ^{1}H-NMR spectra of compound **1** showed the signals of a *trans* double bond at 6.68 (1H, dd, *J* = 10.0, 16.0 Hz) and 6.09 (1H, d, *J* = 16.0 Hz), three methyl singlets at 2.28 (3H), 0.97 (3H) and 0.92 (3H), and one methyl doublet at 0.86 (*J* = 6.5 Hz). Beside, two sugar units were identified at the signals from 3.0 to 5.0 ppm, including two anomeric protons at 4.39 (1H, d, *J* = 7.5 Hz) and at 5.01 (1H, s) of a glucopyranose and a arabinofuranose, respectively [3]. The ^{13}C-NMR and DEPT spectra of **1** exhibited 13 signals of the megastigman aglycone, including one ketone carbon at 200.9, the double bond at 151.9 and 134.6, four methyl carbon at 21.6, 21.8, 26.9 and 31.8 ppm; six glucopyranosyl carbon signals at 68.2, 72.0, 75.0, 75.8 and 102.9, and five arabinofuranosyl carbon signals at 63.1, 79.0, 83.1, 86.0 and 109.9 ppm [3]. The downfield shifted of glucose C-6′ (δ_C 68.2) was well consistent with the data in literature [3], confirming the arabinofuranosyl linked at C-6′. All the NMR data of **1** were compared with the corresponding data of 7-megastigmene-3-ol-9-one 3-*O*-[α-L-arabino-

furanosyl-(1→6)-*β*-D-glucopyranoside] and found to match well [3]. Furthermore, the molecular formula

Table 1: ^{13}C-NMR data for compounds **1**-**6** and reference compounds

C	1		2		3		4		5		6	
	$^{\#}\delta_C$	$\delta_C{}^{a,b}$	$^{@}\delta_C$	$\delta_C{}^{a,b}$	$^{\$}\delta_C$	$\delta_C{}^{a,b}$	$^{\&}\delta_C$	$^{a,b}\delta_C$	$^{*}\delta_C$	$^{a,b}\delta_C$	$^{\%}\delta_C$	$^{a,b}\delta_C$
1	36.4	36.3	36.4	36.3	40.8	40.5	43.9	44.0	128.10	128.3	112.2	112.2
2	47.7	47.6	47.7	47.6	46.0	45.9	52.4	52.4	111.23	111.6	145.2	145.3
3	75.8	76.6	75.4	75.4	67.5	67.4	214.9	215.0	148.59	149.3	84.6	84.6
4	43.5	43.4	43.5	43.4	40.0	39.9	45.9	46.2	149.21	149.9	38.5	38.6
5	31.9	31.9	32.0	32.0	35.6	35.3	37.7	37.8	116.04	116.5	28.4	28.4
6	59.1	59.1	59.1	59.1	78.5	78.2	77.8	78.1	122.64	123.3	86.9	86.9
7	151.8	151.9	151.8	151.8	133.7	135.8	133.7	134.0	140.72	142.3	80.6	80.6
8	134.6	134.6	134.7	134.6	135.6	133.7	134.8	134.9	119.73	118.6	24.0	24.0
9	200.8	200.9	200.8	200.8	78.0	78.1	77.6	77.8	167.30	169.5	20.8	20.9
10	27.0	26.9	27.0	26.9	21.5	21.5	21.4	21.5	56.10	56.4	26.2	26.2
11	21.8	21.8	21.8	21.8	25.4	25.3	24.8	25.0				
12	31.8	31.8	31.8	31.8	26.3	26.2	25.2	25.3				
13	21.6	21.6	21.6	21.6	16.6	16.5	16.3	16.5				
1'	103.0	102.9	102.8	102.8	102.3	102.5	102.5	102.6	135.09	134.7	98.7	98.7
2'	75.1	75.0	75.1	75.1	75.1	75.4	75.1	75.3	128.00	128.5	75.1	75.1
3'	78.0	78.0	78.1	78.1	78.0	78.0	77.8	78.1	115.70	116.1	77.8	77.9
4'	72.1	72.0	71.8	71.7	71.3	71.5	71.3	71.6	157.51	158.1	71.7	71.7
5'	76.7	75.8	77.9	77.9	77.8	77.9	77.7	78.0	115.70	116.1	77.6	77.6
6'	68.2	68.2	62.9	62.8	62.6	62.6	62.5	62.7	128.00	128.5	62.7	62.8
7'									73.63	73.6		
8'									48.72	48.5		
1"	110.0	109.9										
2"	83.2	83.1										
3"	79.0	78.9										
4"	86.0	86.0										
5"	63.1	63.1										

[a]Measured in CD_3OD, [b]125 MHz, $^{\#}\delta_C$ of 7-megastigmene-3-ol-9-one 3-*O*-[*α*-L-arabinofuranosyl-(1→6)-*β*-D-glucopyranoside] [3]; $^{@}\delta_C$ of alangionoside L [4]; $^{\$}\delta c$ of alangioside [5]; $^{\&}\delta c$ of ampelopsisionoside [5]; *δc of N–*trans*-feruloyloctopamide [6]; $^{\%}\delta c$ of *trans*-linalool-3,6-oxide-*β*-D-glucopyranoside [7].

of **1** was confirmed by the exhibition of a pseudo ion peak at *m/z* 527 $[M+Na]^+$ in the ESIMS, corresponding to $C_{24}H_{40}O_{11}$. This compound was first isolated from *Schisandra rubriflora* in 2005, however, this is the first report of **1** from Euphorbiaceae family.

Compound **5** was obtained as colorless oil. The ESIMS of 5 showed a pseudo-molecular ion peak at *m/z* 328 $[M-H]^-$, corresponding to the molecular formula of $C_{18}H_{19}NO_5$. The ^{1}H-NMR, ^{13}C-NMR and DEPT spectra of compound **5** showed signals of a para substituted benzene ring at δ_H 7.24 and 6.79 (each, 2H, d, *J* = 8.5 Hz)/δ_C 128.5 and 116.1; a 1,3,4-trisubstituted benzene ring at δ_H 7.14 (1H, brs), 6.81 (1H, d, *J* = 8.0), 7.04 (1H, d, *J* = 8.0); a trans double bond was confirmed at δ_H 7.46 (1H, *J* = 16.0 Hz), 6.48 (1H, *J* = 16.0 Hz)/ δ_C 142.3/118.6; a N-C=O group at δ_c 169.5 and one methoxy group at δ_H 3.90 (3H, s)/δ_c 56.4; one oximethine group at δ_H 4.74/ δ_C 73.6 and one methylene carbon connected to N atom at δ_H 3.55/3.46 and δ_C 48.5 [6]. The above assigned proton and carbon signals were done by the analysis of HSQC and HMBC spectra of **5**. In the HSQC spectrum, protons at δ_H 7.46, 6.48, and 4.74 had cross peaks with carbons at δ_C 142.3, 118.6, and 73.6, respectively, while two protons at δ_H 3.55 and 3.46 had cross peaks with one carbon at δ_C 48.5. In the HMBC spectrum, correlations between proton

H-7 (δ_H 7.46) and carbons C-9 (δ_C 169.5)/C-1 (δ_C 128.3)/C-2 (δ_C 11.6)/C-6 (δ_C 123.3) confirmed the double bond linked to the 1,3,4-trisubstituted benzene ring and carbonyl group; while proton H-7' (δ_H 4.74) had HMBC correlations with carbons C-8' (δ_C 48.5)/C-1' (δ_C 134.7)/C-2' (δ_C 128.5) confirming this carbon linked to the other benzene ring. The methoxy group was confirmed at C-3 by the HMBC observation of cross peak from δ_H 3.90 to C-3 (δ_C 149.3). As shown in the table 1, all chemical shifts of carbon signals in the ^{13}C-NMR spectra of **5** were similar to those of N–*trans*-feruloyloctopamide [6].

Compound **6** was obtained as amorphous powder. The NMR spectra of **6** exhibited signals of the monoterpene aglycone and a glucopyranosyl sugar, including a double bond and three methyl groups. In the ^{1}H NMR spectrum, a cyclic structure was found from the appearance of a multiplet signal of two methylene groups at δ_H 1.85/1.95 (H-4) and 1.80/2.00 (H-5). A double doublet proton signal (δ_H 6.00, J = 11.0, 17.0 Hz, H-2,) and two AB-type proton signals (δ_H 5.02, H_a-1 and 5.24, H_b-1) indicated the existence of a terminal vinyl group [10]. Three methyl group signals were at δ_H 1.24, 1.28, and 1.36 (H-8, H-9, and H-10 respectively). The above evidence suggested that the aglycone moiety of **6** was assumed to be linalool-3,6-oxide [7, 10]. In addition, the NMR data of glucopyranosyl moiety was very similar to the corresponding published data [7, 10] with the *axial* configuration of the anomeric proton (H-1', δ_H 4.53, J = 7.5 Hz). Furthermore, HMBC correlation from H-1' to C-7 (δ_C 80.6) confirmed that the sugar linked to C-7 of the aglycone. All the assigned proton and carbon signals were taken by detail analysis of HSQC and HMBC spectra of **6**. Consequently, compound **6** was identified as *trans*-linalool-3,6-oxide-*β*-D-glucopyranoside.

The remaining compounds were identified as (-)-alangionoside L (**2**) [4], alangioside (**3**) [5], ampelopsisionoside (**4**) [5], 5*α*,8*α*-dipioxicholest-6,22-diene-3*β*-ol (**7**) [8], and (Z)-2-hexenyl *β*-D-glucopyranoside (**8**) [9] by comparing their NMR data with the data in reported literature and further confirmed by HSQC and HMBC spectra. This is the fist report of these compounds from *Antidesma hainanensis.*

Acknowledgment. *This research was supported by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.01-2013.05. The authors would like to thank Dr. Nguyen Quoc Binh, Vietnam National Museum of Nature for the plant identification.*

REFERENCES

1. V. V. Chi. *Dictionary of Medicinal Plants in Vietnam.* Medical Publishing House, Hanoi, 441-442 (2012).
2. Dictionary of Natural Products on CD-ROM, Version 15:1, Copyright @ 1982-2015 Chapman & Hall/CRC.
3. Gan-Peng Li, Jing-Feng Zhao, Yong-Qiang Tu, Xiao-Dong Yang, Hong-Bin Zhang and Liang Li. *Chemical constituents of Schisandra rubriflora Refd. et Wils*, Journal of Integrative Plant Biology, **47(3)**, 362-367 (2005).
4. Hideaki Otsuka, Masami Yao, Kenji Kamada, and Yoshio Takeda. Alangionoside G-M: *Glycosides of megastigmane derivatives from the leaves of Alangium premnifolium*, Chemical and Pharmaceutical Bulletin, **43(5)**, 754-759 (1995).
5. Simona De Marino, Nicola Borrone, Franco Zollo, Angela Ianaro, Paola Di Meglio, and Maria Iorizzi. *Megastigmane and phenolic components from Laurus nobilis L. leaves and their inhibitory effects on nitric oxide production*, Journal of Agricultural and Food Chemistry, **52**, 7525-7531 (2004).
6. Russell R. King, and Larry A. Calhoun. *Characterization of cross-linked hydroxycinamic acid amides isolated from potato common scab lesions*, Phytochemistry, **66**, 2468-2473 (2005).
7. Yong-Li Li, Ji-Gang Zhang, Ping Yu, Bei-Lei Ke, Ji Ye, Xian-Wen Yang, Hui-Zi Jin, Wei-Dong Zhang. *New Monoterpenes, Diterpenes, and Lignans from Abies recurvate*, Planta Med, **78**, 1574-1578 (2012).
8. Jian-Min Yue, Shao-Nong Chen, Zhong-Wen Lin, Han-Dong Sun. *Sterol from the fungus Lactarium volemus*, Phytochemistry, **56**, 801-806 (2001).
9. Kenji Mizutani, Masamichi Yuda, Osamu Tanaka, Yuh-Ichirou Saruwatari, Tohru Fura. Ming-Ru Jia, Yi-Kui Ling, and Xui-Feng Pu. *Chemical studies on Chinese traditional medicine, Dangshen. I. isolation of (Z)-3-and (E)-2-Hexenyl β-D-Glucosides*, Chemical and Pharmaceutical Bulletin, **36(7)**, 2689-2690 (1998).
10. Lihua Jiang, Hiroshi Kojima, Kumi Yamada, Akio Kobayashi, and Kikue Kubota. *Isolation of some glycosides as aroma precursors in young leaves of Japanese pepper* (*Xanthoxylum piperitum* DC.), J. Agric. Food Chem., **49**, 5888-5894 (2001).

Corresponding author: **Phan Van Kiem**
Institute of Marine Biochemistry Vietnam Academy of Science and Technology
18 Hoang Quoc Viet, Caugiay, Hanoi, Viet Nam
E-mail: phankiem@yahoo.com.