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Phenolic Compounds from *Dendrobium Nobile* Lindl.

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Abstract

*Dendrobium nobile Lindl.(Orchidaceae), Vietnamese name as Hoang thao dui ga is an epiphytic plant on high tree branches. It grows widely in humid mountainous areas in Vietnam. The plant is used to treat fever, dry mouth, dry throat, increase vitality in traditional medicine. In the course of study on chemical composition of Dendrobium nobile Lindl. in Vietnam, this paper describes the extraction and structure evaluation of five known compounds, including E-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one (**1**) together with ferulic acid (**2**), 4-hydroxy cinnamic acid (**3**) umbellic acid (**4**) and 3-(4-hydroxyphenyl) propionic acid (**5**). The stems of this plant were collected, identified, dried and extracted in different polarity solvents. These substances were isolated from the ethyl acetate and water fractions of methanol extract on the basis of column chromatography. Their structures were identified based on spectroscopic evaluation and comparison of corresponding authentic compounds. This is the first report of compound **1** from the Dendrobium genus.*

Keywords: *Dendrobium nobile* Lindl., phenolic, acid.

1. Introduction

Over the past 80 years, more than 40 species of the *Dendrobium* genus have been studied. Previous reports on the chemical components of the *Dendrobium* genus have revealed that this genus was abundant of aromatic compounds, sesquiterpenoids, alkaloids and polysaccharides [1]. A large number of aromatic compounds, represented as bibenzyl, phenanthrene, fluorenone and coumarin have been isolated from the genus *Dendrobium*. Common bibenzyls were present in many different species of *Dendrobium*. For example, moscatilin and gigantol were isolated from nearly 20 species of *Dendrobium*. The naturally occurring phenanthrenes in *Dendrobium* species occured as hydroxyl and/or methoxy substituted 9,10-dihydro or dehydro derivatives. The number of hydroxyl and methoxy in the molecules also ranged from 3 to 6 groups. Fluorenone and coumarin were present in much lower amounts than bibenzyl and phenanthrene in *Dendrobium*. Alkaloids were the first groups extracted and structurally determined from the genus *Dendrobium*. Up to now, there are many different alkaloid skeletons, which are sesquiterpene, indolizidine, pyrrolidine, phthalide and imidazole frames found. Sesquiterpenoids are also commonly found in the genus *Dendrobium* and are mostly found in *Dendrobium nobile* Lindl. (*D.nobile)* and *D.moniliforme*. Picrotoxane was the most common sesquiterpenoid. In addition, alloaromadendrane, cyclocopacamphane, cadinene and muurolene, have also been found in the genus. Polysaccharides always presented in large amounts in the genus *Dendrobium*, such as *D. officinale*. Bioactivity studies also demonstrated that *Dendrobium* has comprehensive biological activities, related to immunity, nervous, cardiovascular, endocrine, digestive and urinary systems [1,2,3]. Especially, polysaccharides have demonstrated multi-purpose uses, such as: boost immunity, antitumor, antioxidant.

D.nobile, Vietnamese name as Hoang thao dui ga, is an epiphytic species, distributes throughout the mountainous areas of the northern and central provinces. The stem is about 0.3-0.6 m high and slightly flattened. Leaves are 12 cm long, 2-3 cm wide. The inflorescences grow in clusters of 2-4 flowers on peduncles 2-3 cm long. Flowers are very beautiful with oval lip wings, 4-5 cm long, 3 cm wide rolled into a funnel in the flower, and the flower throat has a purple point. The plant was used in traditional medicine to help replenish the body's fluids. *D.nobile*'s alkaloid-based functional foods are used to increase strength for sport activities. Phytochemical studies reported some remarkable classes of substances in this plant (Fig. 1). The basic alkaloids of the plant are dendrobine, salts of dendrobine, nobilonine, dendramine, and dendrine, in which dendrobine, nobilonine were the main alkaloid components of the plant. The sesquiterpenes includes copacamphane, picrotoxane and cyclocopacamphane skeretons. Phenathrenes and bibenzyls were isolated as well. In addition, *D.nobile* also contained phenolic acids such as 4-hydroxybenzoic acid, vanillic acid, syringic acid, ferulic acid [1,4,5].

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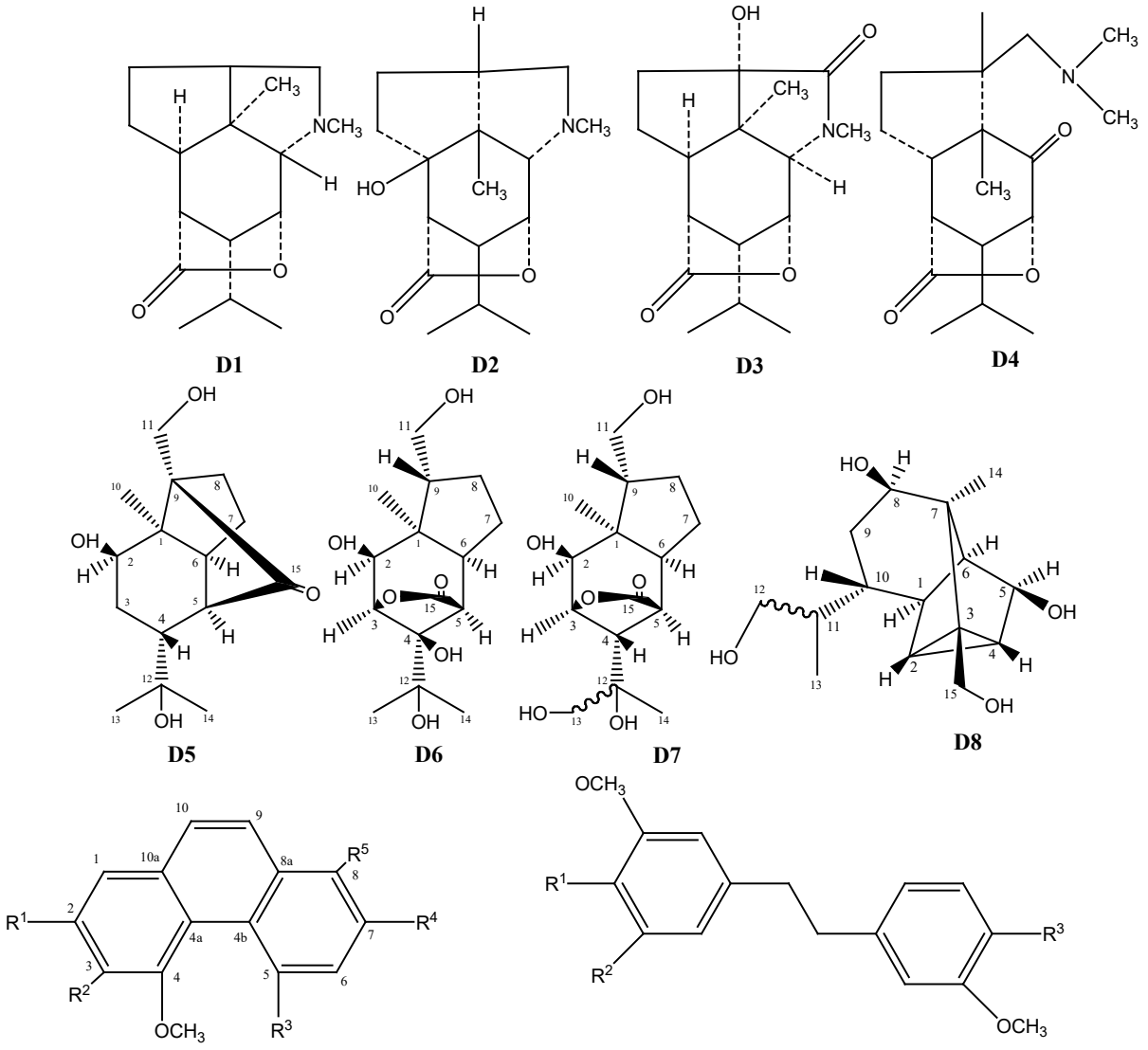


D9 $R_1 = R_3 = OH$, $R_2 = R_5 = OCH_3$, $R_4 = H$
D10 $R_1 = OCH_3$, $R_2 = R_4 = OH$, $R_3 = R_5 = H$
D11 $R_1 = R_2 = R_3 = OH$, $R_4 = R_5 = H$
D12 $R_1 = H$, $R_2 = R_3 = OH$
D13 $R_1 = H$, $R_2 = OH$, $R_3 = OCH_3$
D14 $R_1 = R_3 = OH$, $R_2 = OCH_3$

Fig. 1. Some compounds were isolated from *Dendrobium nobile* Lindl.

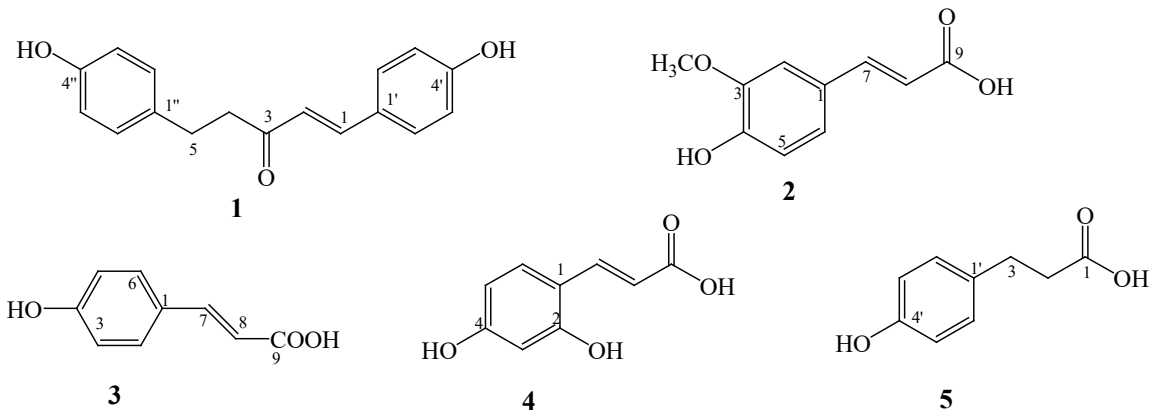


Fig. 2. The chemical structures of compounds **1-5**

However, in Vietnam, the studies have only focused on the ecology of the genus *Dendrobium* such as the clonal propagation process, the development of buds and flowers, the fertilization process, etc. [6], [7]. Researches on *D.nobile* have not concentrated on its chemical composition. In this paper, 5 phenolic compounds (Fig. 2) were isolated and characterised of from this species in Vietnam.

2. Materials and Methods

2.1. Plant Materials

The stems of *Dendrobium nobile* Lindl. (Fig. 3) were collected in Bo Trach mountain, Quang Binh province in April 2016. The plant samples were then preserved to create specimens and identified by Dr. Bui Van Thanh (Institute of Ecology and Biological Resources - Vietnam Academy of Science and Technology (VAST). As the result, this plant was *Dendrobium nobile* Lindl., belonged to the *Dendrobium* genus, the Orchidaceae family. A voucher specimen (DN1) was deposited at the Institute of Ecology and Biological Resources, VAST.

Fig. 3. *Dendrobium nobile* Lindl.

2.2. General Experimental Procedures

The extracted residues were analyzed and separated based on chromatographic methods. isolated compounds were identified based on modern analytical methods 1D, 2D-NMR, ESI-MS.

Column chromatography was performed using silica gel (Kieselgel 60, 70-230 mesh and 230 - 400 mesh, Merck) as stationary phase or RP-18 resins (150 µm, Fuji Silysia Chemical Ltd.) as reversed phase.

Thin layer chromatography (TLC) was performed using a pre-coated silica-gel 60 F_{254} (0.25 mm, Merck) and RP-18 F_{254S} plates (0.25 mm, Merck). NMR spectra were recorded on a Agilent 400 MR NMR spectrometer (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR). Chemical shifts (δ) are reported in parts per million (ppm). The abbreviations used to report the data are s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br. (broad).

ESI mass spectra were recorded on an AGILENT 1200 series LC-MSD Ion Trap.

Melting point was measured on a Cole-Parmer Instrument electrothermal melting point apparatus, serial number R216000334.

Plant sample was extracted with methanol using Vevor Ultrasonic model JPS-100A.

2.3. Extraction and Isolation

The cleaned stems of *D.nobile* was cut in small pieces, dried and grinned. The dried powders of *D.nobile* stems (5.0 kg) were sonicated with methanol at room temperature (3 times × 10 L, each 1 h). The extracts were collected, filtered and distilled to recover the solvent under reduced pressure to obtain 280.0 g of methanol extract (DN). This residue was suspended in water and extracted with dichloromethane and ethyl acetate, respectively. The dichloromethane, ethyl acetate extracts were distilled to recover the solvent under reduced pressure to obtain dichloromethane fraction (DN1, 150.0 g), ethyl acetate fraction (DN2, 32.0 g) and water residue. The DN2 fraction was objected on silica gel chromatographic column with a dichloromethane/methanol gradient elution system (100/0 → 0/100, v/v) to obtain 8 fractions (E1- E8). The E2 fraction was chromatographed on the RP-C18 silica gel column with acetone/water elution system (1/1, v/v) as diluted solvent to obtain two sub-fractions (E2A- E2B). The E2A sub-fraction was continued to be chromatographed on the RP-C18 silica gel column with the methanol/water elution system (1/1.5, v/v) to give the compound **3** (13.0 mg). The E2B sub-fraction was continued to be objected to silica gel chromatographic column with the eluent system of *n*-hexane/dichloromethane/methanol (7/10/1, v/v/v) to obtain compound **1** (8.0 mg). The E4 fraction was chromatographed on a silica gel chromatographic column with the elution system of n-hexane/dichloromethane/methanol (5/10/1, v/v/v) to obtain 2 E4A- E4B fractions. Compound **5** (6.0 mg) was obtained after purification of fraction E4B by reversed phase RP-18 chromatography column with acetone/water elution system (1.5/1, v/v). The aqueous solution was evaporated to remove ethyl acetate to yield water residue, which was then objected on a Diaion HP-20 column, removed sugar with water, then gradually increased the concentration of methanol in water (25, 50, 75 and 100% methanol) to obtain 4 fractions, W1 - W4. The W4 fraction was put on a normal phase silica gel chromatographic column with dichloromethane/methanol/water elution system (6/1/0.05, v/v/v) to obtain 3 fractions (W4A- W4C). Compound **2** (18.0 mg), compound **4** (20.0 mg) was

obtained after purification of the W4C fraction by reverse phase RP-18 chromatography column with methanol/water elution system (1/1.5, v/v). Column chromatography performances were monitored by thin layer chromatography (see Fig. 4). The separated compounds were structurally determined by 1D, 2D-NMR, MS spectroscopy methods.

***E*-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one (1)**: White amorphous powder; ESI-MS *m/z* 268.3 $[M]^+$, $C_{17}H_{16}O_3$.

^{1}H-NMR ((400 MHz, CD_3OD), δ (ppm): 7.36 (2H, d, J = 8.4 Hz, H-2', H-6'), 7.29 (1H, d, J = 15.6 Hz, H-1), 6.99 (2H, d, J = 8.4 Hz, H-2", H-6"), 6.76 (2H, d, J = 8.4 Hz, H-3', H-5'), 6.66 (2H, d, J = 8.4 Hz, H-3", H-5"), 6.37 (1H, d, J = 15.6 Hz, H-2), 3.27 (1H, t, J = 7.2 Hz, H-4), 2.61 (1H, t, J = 7.4 Hz, H-5).

^{13}C-NMR (100 MHz, CD_3OD), δ (ppm): 165.3(C-3), 158.8 (C-4'), 155.6 (C-4"), 138.5 (C-1), 125.9 (C-1'), 129.5 (C-1"), 129.5 (2C, C-2", C-6"), 129.2 (2C, C-2', C-6'), 118.8 (C-2), 115.7 (2C, C-3', C-5'), 115.1 (2C, C-3", C-5"), 40.7 (C-4), 34.5 (C-5).

(*E*)-Ferulic acid (2): Colorless crystal; mp 170 °C; ESI-MS *m/z* 195.4 $[M+H]^+$, $C_{10}H_{10}O_4$.

^{1}H-NMR (400 MHz, CD_3OD), δ (ppm): 7.16 (1H, d, J = 2.0 Hz, H-2), 7.04 (1H, dd, J = 2.0, 8.4 Hz, H-6), 6.79 (1H, d, J = 8.4 Hz, H-5), 6.29 (1H, d, J = 16.0 Hz, H-8), 3.87 (3H, s, 3-O$\underline{C}H_3$).

^{13}C-NMR (100 MHz, CD_3OD), δ (ppm): 171.0 (C-9), 150.5 (C-3), 149.3 (C-4), 146.9 (C-7), 127.8 (C-1), 124.0 (C-6), 116.4 (C-5), 115.9 (C-8), 111.6 (C-2), 56.4 (3-O$\underline{C}H_3$).

4-hydroxy cinamic acid (3): Colorless crystal; mp 213 °C; ESI-MS *m/z* 165.05 $[M+H]^+$, $C_9H_8O_3$.

^{1}H-NMR (400 MHz, CD_3OD), δ (ppm): 7.59 (1H, d, J = 16.0 Hz, H-7), 7.45 (1H, d, J = 2.0 Hz, H-2), 7.45 (1H, d, J = 8.4 Hz, H-6), 6.81 (1H, d, J = 8.4 Hz, H-3), 6.81 (1H, d, J = 8.4 Hz, H-5), 6.28 (1H, d, J = 16.0 Hz, H-8).

^{13}C-NMR (100 MHz, CD_3OD), δ (ppm): 171.2 (C-9), 161.1 (C-4), 146.6 (C-7), 131.1 (C-2), 131.1 (C-6), 127.3 (C-1), 116.8 (C-3), 116.8 (C-5), 115.7 (C-8).

Umbellic acid (4): Colorless crystal; mp 202 °C; ESI-MS *m/z* 165.05 $[M+H]^+$, $C_9H_8O_3$.

^{1}H-NMR (400 MHz, CD_3OD), δ (ppm): 7.87 (1H, d, J = 16.0 Hz, H-7), 7.31 (1H, d, J = 9.2 Hz, H-6), 6.36 (1H, d, J = 16.0 Hz, H-8), 6.31 (1H, d, J = 9.2 Hz, H-5), 6.30 (1H, br s, H-3),

^{13}C-NMR (100 MHz, CD_3OD), δ (ppm): 172.1 ($\underline{C}$=O), 162.2 (C-4), 160.0 (C-2), 142.9 (C-7), 131.5 (C-6), 114.9 (C-8), 114.8 (C-1), 108.8 (C-5), 103.5 (C-3).

3-(4-hydroxyphenyl) propionic acid (5): Colorless crystal; mp 129 °C; ESI-MS *m/z* 167.23 $[M+H]^+$, $C_9H_{10}O_3$.

^{1}H-NMR (400 MHz, CD_3OD), δ (ppm): 6.97 (1H, d, J = 8.0 Hz, H-2', H-6'), 6.63 (1H, d, J = 8.0 Hz, H-3', H-5'), 2.65 (1H, t, J = 7.6 Hz, H-3), 2.47 (2H, t, J = 7.6 Hz, H-2).

^{13}C-NMR (100 MHz, CD_3OD), δ (ppm): 177.1 (C-1), 156.7 (C-4'), 133.2 (2C, C-2', C-6'), 133.0 (C-1'), 116.2 (2C, C-3', C-5'), 37.3 (C-2), 31.3 (C-3)

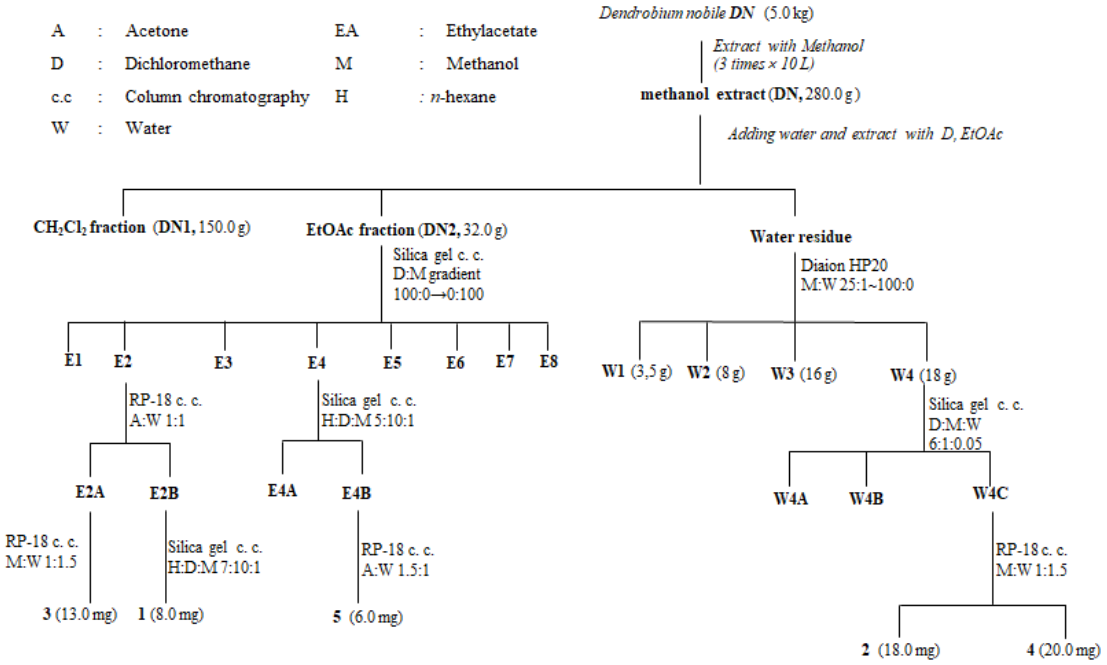


Fig. 4. Diagram of isolation of compounds 1-5 from *D. nobile*

3. Results and Discussion

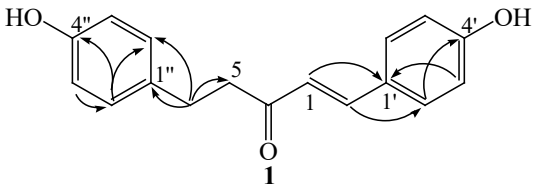
The chemical structures of the isolated compounds were determined based on analysis of modern spectroscopic methods such as one- and two-dimensional nuclear magnetic resonance and mass spectroscopy.

E-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one (**1**) was yielded from the ethyl acetate extract as the white amorphous powder. The ^{1}H-NMR spectrum of **1** showed the signals of two aromatic rings with *para* substitution at δ_H 7.36 (2H, d, J = 8.4 Hz), 6.99 (2H, d, J = 8.4 Hz), 6.76 (2H, d, J = 8.4 Hz) and 6.66 (2H, d, J = 8.4 Hz). Signals of the olefin protons with *trans* configuration were observed at δ_H 7.29 (1H, d, J = 15.6 Hz) and 6.37 (1H, d, J = 15.6 Hz) and the appearance of proton signals of two methylene groups at δ_H 3.27 (2H, t, J = 7.2 Hz) and 2.61 (2H, J = 7.4 Hz). The ^{13}C-NMR revealed the presence of 17 carbon atoms in moleculars of **1**. The ^{13}C-NMR spectra of **1** showed signals of 2 aromatic rings with *para* substitution at δ_C 158.8 (C, C-4'), 155.6 (C, C-4"), 129.5 (C, C-1")), 129.5 (2CH, C-2" and C-6"), 129.2 (2CH, C-2' and C-6'), 125.9 (C, C-1'), 115.7 (2CH, C-3' and C-5') and 115.1 (2CH, C-3" and C-5"); signals of two extracyclic olefin carbons at δ_C 138.5 (CH, C-1) and 118.8 (CH, C-2), two carbons of methylene signals at δ_C 40.7 (CH_2, C-4) and 34.5 (CH_2, C-5). Besides, the resonance signal of a carbonyl group appeared at δ_C 165.3 (C-3) (Table 1). Moreover, the structure of **1** was confirmed clearly on a basis of two-dimensional spectra HMBC and HSQC. The HSQC showed the interaction between H-2', H-6' (δ_H 7.36) and C-2', C-6' (δ_C 129.2), H-3', H-5' (δ_H 6.76) and C-3', C-5' (δ_C 115.7), the HBMC interaction from H-2' (δ_H 7.36) to C-1 (δ_C 138.5), C-4' (δ_C 158.8), C-6' (δ_C 129.2) and from H-3' (δ_H 6.76) to C-1' (δ_C 125.9), C-5' (δ_C 115.7 Hz) confirmed spectral values at C-1', C-2', C-3', C-4', C-5' and C-6'. Similarly, the HSQC showed the interaction between H-2", H-6" (δ_H 6.99) and C-2", C-6" (δ_C 129.5), H-3", H-5" (δ_H 6.66) and C-3", C-5" (δ_C 115.1), the HMBC correlation from H-2″ (δ_H 6.99) to C-1" (δ_C 129.5), C-4" (δ_C 155.6), C-6" (δ_C 129.5) and from H-3" (δ_H 6.66) to C-1" (δ_C 129.5), C-2" (δ_C 129.5), C-5" (δ_C 115.1), C-6" (δ_C 129.5) confirmed spectrum values at C-1", C-2", C-3", C-4", C-5" and C-6". The correlation from H-1 (δ_H 7.29) to C-6' (δ_C 129.2) and from H-2 (δ_H 6.37) to C-1' (δ_C 125.9) confirmed that the double bond at C-1 and C-2 linked to one aromatic ring. The correlation between H-5 (δ_H 2.61) and C-4 (δ_C 40.7), C-1" (δ_C 129.5), C-2" (δ_C 129.5) approved the linkage of C-5 to the rest aromatic ring (Fig. 5). All of the NMR data of **1** were similar to those of *E*-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one measured in the same solvent (Table 1). Additionally, the ESI-MS mass spectrometry appeared an ion peak *m/z* 268.3 $[M]^+$ corresponding to the molecular formula of $C_{17}H_{16}O_3$.

Table 1: The ^{1}H- and ^{13}C-NMR data for compounds **1** and *E*-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one

	1			
C	$^{\#}\delta_C$	δ_C[a,b]	HSQC	δ_H[a,c](mult., *J*, Hz)
1	141.7	138.5	CH	7.29 (d, 15.6)
2	116.6	118.8	CH	6.37 (d, 15.6)
3	169.3	165.3	C	-
4	42.1	40.7	CH_2	3.27 (t, 7.2)
5	35.8	34.5	CH_2	2.61 (t, 7.4)
1'	127.6	125.9	C	-
2', 6'	130.5	129.2	CH	7.36 (d, 8.4)
3', 5'	116.2	115.7	CH	6.76 (d, 8.4)
4'	160.5	158.8	C	-
1"	131.1	129.5	C	-
2", 6"	130.7	129.5	CH	6.99 (d, 8.4)
3", 5"	116.2	115.1	CH	6.66 (d, 8.4)
4"	156.9	155.6	C	-

Recorded in [a]CD_3OD, [b]100 MHz, [c]400 MHz, $^{\#}\delta_C$ of *E*-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one in CD_3OD[8]



1

Fig. 5. The key HMBC correlations of compounds **1**

Hence, the structure of **1** was established as *E*-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one based on the spectra interpretation and the comparison of NMR data with the published spectra in literature [8]. This is the first report of this compound from genus *Dendrobium*.

The compound **2** was isolated from the aqueous fraction of the MeOH extract of *D.nobile* species as colorless crystals. The ^{1}H-NMR spectrum of **2** showed aromatic ring signals at δ_H 7.16 (1H, d, J = 2.0 Hz), δ_H 7.04 (1H, dd, J = 8.4 Hz and 2.0 Hz) and δ_H 6.79 (1H, d, J = 8.4 Hz) respectively with an ABX-substituted aromatic ring. The signals of two olefin protons with *trans* configuration occured at δ_H 7.59 (1H, d, J = 16.0 Hz) and δ_H 6.29 (1H, dd, J = 16.0 Hz). Signal of a methoxyl group was at δ_H 3.87 (3H, s). The ^{13}C-NMR showed signals of 10 carbon atoms. The ^{13}C-NMR spectra of **2** allowed to determine the signals of an ABX aromatic ring at δ_C 127.8 (C, C-1), δ_C 111.6 (CH, C-2), δ_C 150.5 (C, C-3), δ_C 149.3 (C, C-4), δ_C 116.4 (CH, C-5) and δ_C 124.0 (CH, C-6); signal of an olefin carbon pair occured at δ_C 146.9 (CH, C-7) and δ_C 115.9 (CH, C-8). In addition, there was a resonance signal of a C=O group at δ_C 171.0 (C, C-9). Moerover, the HSQC cross peaks from H-2 (δ_H 7.16) to C-2 (δ_C 111.6), from H-5 (δ_H 6.79) to C-5 (δ_C 116.4) and H-6 (δ_H 7.04 Hz) to C-6 (δ_C 124.0 Hz) supported the protons and carbons signals in the aromatic ring. The HSQC interaction from H-7 (δ_H 7.59) to C-7 (δ_C 146.9), from H-8 (δ_H 6.29) to C-8 (δ_C 115.9) confirmed the signal of carbons and protons of the double bond at the side chain.

Spectral data above suggested that **2** was (*E*)-ferulic acid. Comparing the NMR spectral data of **2** with compound (*E*)-ferulic acid (Table 2) found complete agreement in all the respective positions. Besides, the ESI-MS mass spectrometry showed an ion peak *m/z* 195.4 $[M+H]^+$, corresponding to the molecular formula $C_{10}H_{10}O_4$. Therefore, compound **2** was identified as (*E*)-ferulic acid, a compound isolated from *Prosopis cineraria* species [9].

The compound **3** was isolated from the ethyl acetate extract of *D.nobile* in the form of colorless crystals. The NMR spectrum of **3** was quite similar to that of **2**, suggesting that **3** had a phenolic structure. The ^{1}H-NMR spectrum of **3** showed 4 signals of a *para*-substituted aromatic ring at δ_H 7.45 (2H, d, J = 8.4 Hz) and 6.81 (2H, d, J = 8.4 Hz). The signals of two olefin protons with *trans* configuration occurred at 7.59 (1H, d, J = 16.0 Hz) and 6.28 (1H, dd, J = 16.0 Hz). The ^{13}C-NMR revealed the signals of 9 carbons in molecular of **3**. The ^{13}C-NMR spectra of **3** showed a signal of an aromatic ring with *para* substitution at δ_C 127.3 (C, C-1), 131.1 (2CH, C-2 and C-6), 116.8 (2CH, C-3 and C-5), 161.1 Hz (C, C-4); the signal of an olefin carbon pair occurred at δ_C 146.6 (CH, C-7) and 115.7 (CH, C-8). In addition, on the spectrum, there was a resonance signal of a carbonyl group at δ_C 171.2 (C, C-9). The HSQC interaction of H-2 (δ_H 7.45) and C-2 (δ_C 131.1), H-3 (δ_H 6.81) and C-3 (δ_C 116.8), H-5 (δ_H 6.81) and C-5 (δ_C 116.8), H-6 (δ_H 7.45) and C-6 (δ_C 131.1) confirmed signals of protons and carbons in the aromatic ring. The HSQC interaction from H-7 (δ_H 7.59) to C-7 (δ_C 146.6), from H-8 (δ_H 6.28) to C-8 (δ_C 115.7) confirmed the signals of carbons and protons at the olefin group. All of NMR data of **3** were consistent with the corresponding data of 4-hydroxy cinnamic acid (Table 2). Moreover the ESI-MS mass spectrometry showed an ion peak *m/z* 165.05 $[M+H]^+$, which suggested the molecular formula of $C_9H_8O_3$.

From the above spectral data and comparison with reference, compound **3** was identified as 4-hydroxy cinnamic acid, a compound isolated from *Magnolia obovata* species [10].

The compound **4** was isolated from the aqueous fraction of the MeOH extract of *D.nobile* in the form of colorless crystals. The NMR spectrum of **4** was quite similar to **2** and **3** suggesting that **4** had a phenolic structure (Table 2 and Table 3). The ^{1}H-NMR spectrum of **4** showed the signal of an ABX-substituted aromatic ring at δ_H 7.31 (1H, d, J = 9.2 Hz), 6.31 (1H, d, J = 9.2 Hz) and 6.30 (1H, br s). Two proton olefin signals with *trans* configuration occurred at δ_H 7.87 (1H, d, J = 16.0 Hz) and δ_H 6.36 (1H, dd, J = 16.0 Hz). The ^{13}C-NMR indicated 9 carbon atoms in compound **4** molecular. The ^{13}C-NMR of **4** showed a signal of an ABX-substituted aromatic ring at δ_C 114.8 (C, C-1), δ_C 160.0 (C, C-2), δ_C 103.5 (CH, C-3), δ_C 162.2 (C, C-4), δ_C 108.8 (CH, C-5) and δ_C 131.5 (C, C-6); signals of olefin carbons appeared at δ_C 142.9 (CH, C-7) and δ_C 114.9 (CH, C-8). Besides, the resonance signal of a carbonyl group appeared at δ_C 172.1 (C, C-9). The HSQC spectra of **4** supported carbon and proton posititions. The interaction between H-3 (δ_H 6.30) and C-3 (δ_C 103.5), H-5 (δ_H 6.31) and C-5 (δ_C 108.8), H-6 (δ_H 7.31) and C-6 (δ_C 131.5) confirmed signals of protons and carbons in the aromatic ring. The cross peaks from H-7 (δ_H 7.87) to C-7 (δ_C 142.9), from H-8 (δ_H 6.28) to C-8 (δ_C 115.7) confirmed the signals of carbon and protons at the double bonds. Besides, all of ^{1}H-NMR and ^{13}C-NMR spectral data were matched with those of umbellic acid (Table 2). Moerover, the ESI-MS spectra of **4** exhibited an ion peak at *m/z* 165.05 $[M+H]^+$, corresponding to the molecular formula $C_9H_8O_3$.

Hence, the elucidation of spectra and comparison with references led to identification of compound **4** as umbellic acid, a compound isolated from the roots of *Pituranthos tortuosus* [11].

Table 2. ^{13}C-NMR spectral data for compounds **2-5** and reference compounds

Position	$^{\$,b}\delta_C$	**2**^{a,b}	$^{\&,b}\delta_C$	**3**^{a,b}	$^{\phi,b}\delta_C$	**4**^{a,b}	$^{\Delta,b}\delta_C$	**5**^{a,b}
1	125.7	127.8	125.5	127.3	113.8	114.8	176.9	177.1
2	115.3	111.6	130.3	131.1	158.7	160.0	37.6	37.3
3	148.8	150.5	115.9	116.8	102.3	103.5	31.2	31.3
4	147.6	149.3	159.8	161.1	160.9	162.2		
5	110.2	116.4	115.9	116.8	107.6	108.8		
6	122.3	124.0	130.3	131.1	130.2	131.5		
7	144.3	146.9	144.4	146.6	141.3	142.9		
8	115.2	115.9	115.5	115.7	114.3	114.9		
9	168.1	171.0	168.1	171.2	171.8	172.1		
1′							132.9	133.0
2′,6′							130.2	130.2
3′,5′							116.2	116.2
4′							156.7	156.7
3-OCH_3	55.4	56.4						

Measured in [a)]CD_3OD, [b)]100 MHz, $^{\$,b}\delta_C$ of (*E*)-ferulic acid in $CDCl_3$[9], $^{\&,b}\delta_C$ of 4-hydroxy cinnamic acid measured in DMSO-d_6[10], $^{\phi,b}\delta_C$ of umbellic acid measured in CD_3OD[11], $^{\Delta,b}\delta_C$ of 3-(4-hydroxyphenyl) propionic acid measured in CD_3OD[12]

Table 3. ^{1}H-NMR spectral data for compounds **2-5**

	2		**3**		**4**		**5**	
Position		$\delta_H^{a,c}$ **(mult., J, Hz)**		$\delta_H^{a,c}$ **(mult., J, Hz)**		$\delta_H^{a,c}$ **(mult., J, Hz)**		$\delta_H^{a,c}$ **(mult., J, Hz)**
1	CH	7.16 (d, 2.0)	C	-	C	-	C	-
2	C	-	CH	7.45 (d, 8.4)	C	-	CH_2	2.47 (t, 7.6)
3	C	-	CH	6.81 (d, 8.4)	CH	6.30 (br s)	CH_2	2.65 (t, 7.6)
4	CH	6.79 (d, 8.4)	C	-	C	-		
5	CH	7.04 (d, 2.0, 8.4)	CH	6.81 (d, 8.4)	CH	6.31 (d, 9.2)		
6	CH	7.59 (d, 16.0)	CH	7.45 (d, 8.4)	CH	7.31 (d, 9.2)		
7	CH	6.29 (d, 16.0)	CH	7.59 (d, 16.0)	CH	7.87 (d, 16.0)		
8	C	-	CH	6.28 (d, 16.0)	CH	6.36 (d, 16.0)		
9	CH	7.16 (d, 2.0)	C	-	C	-		
1′							C	-
2′,6′							CH	6.97 (d, 8.0)
3′,5′							CH	6.63 (d, 8.0)
4′							C	-
3-OCH_3	C	3.87 (s)						

[a)] Measured in CD_3OD, [c)]400 MHz

Compound **5** was isolated from the EtOAc extract as colorless crystals. The ^{1}H-NMR spectrum of **5** was quite similar to **3** (Table 3), suggesting that **5** had a phenolic structure. The ^{1}H-NMR spectrum of **5** showed a signal of an aromatic ring with *para* substitution at δ_H 6.97 (2H, d, J = 8.0 Hz) and δ_H 6.63 (2H, d, J = 8.0 Hz). On the ^{1}H-NMR spectrum of **5** there was no signal of extracyclic olefinic protons in the spectra of **3** but the appearance of a proton signal of two methylene groups at δ_H 2.65 (2H, t, J = 7.6 Hz) and δ_H 2.47 (2H, t, J = 7.6 Hz) insteadly. The ^{13}C-NMR revealed the presence of 9 carbon atomes in the molecular, the signals of an aromatic ring with *para* substitution at δ_C 133.0 (C, C-1), 130.2 (CH, C-2 and (C-6), 116.2 (CH, C-3 and C-5) and 156.7 (C, C-4); two-carbon signals at δ_C 31.3 (CH_2, C-3) and 37.3 (CH_2, C-2). Besides, the resonance signal of a carbonyl group appeared at δ_C 177.1 (C, C-1). The HSQC spectra of **5** approved the carbon and proton signals. The cross peaks from H-2', H-6' (δ_H 6.97) to C-2', C-6' (δ_C 130.2), from H-3', H-5' (δ_H 6.63) to C-3', C-5' (δ_C 116.2) confirmed the signals of carbons and corresponding protons in the aromatic ring. The HSQC interaction from H-2 (δ_H 2.47) to C-2 (δ_C 37.3), from H-3 (δ_H 2.65) to C-3 (δ_C 31.3) confirmed the signals of carbon and protons at the side chain. These proton and carbon signals were similar to those of 3-(4-hydroxyphenyl) propionic acid. In addition the ESI-MS of **5** showed an ion peak at *m/z* 167.23 $[M+H]^+$ which supported the molecular formula of $C_9H_{10}O_3$.

Detail analysis of 1D and 2D NMR and comparison of the NMR and ESI-MS of **5** with 3-(4-hydroxyphenyl) propionic acid in the reference confirmed the compound **5** as 3-(4-hydroxyphenyl) propionic acid, a compound isolated from the roots of *Myrica rubra* species [12].

Conclusion

This research was completed in the frame work of phytochemical study of *Dendrobium nobile* Lindl. Five phenolic compounds were isolated based on column chromatographies. Their structures were identified on a basis of mordern spectroscopy methods such as 1D, 2D-NMR, ESI-MS. Compound **1** as *E*-1,5-bis(4-hydroxyphenyl)-pent-1-en-3-one is firstly reported from *Dendrobium* genus. This study contributed to clarify the chemical composition of *Dendrobium nobile* Lindl. species grown in Vietnam and scientific information to the treasure of natural compounds in Vietnam.

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