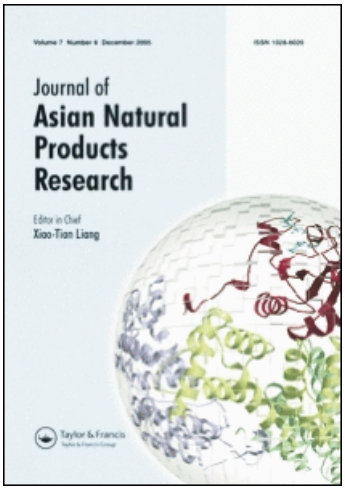

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A new phenylpropanoid glycoside from *Jasminum subtriplinerve* Blume

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From the ethyl acetate extract of the aerial parts of *Jasminum subtriplinerve* Blume (Oleaceae), 6′-*O*-menthiafoloylverbascoside (**1**), rutin (**2**), isoverbascoside (**4**), isooleoverbascoside (**6**), apiosylverbascoside (**7**), astragalin (**9**), isoquercitrin (**10**), and verbascoside (**11**) were isolated. Their structures were elucidated by extensive MS and NMR spectroscopy. Amongst 6′-*O*-menthiafoloylverbascoside (**1**) is a new phenylpropanoid glycoside.

Keywords: *Jasminum subtriplinerve*; 6′-*O*-menthiafoloylverbascoside; verbascoside; isooleoverbascoside; apiosylverbascoside

1. Introduction

Jasminum subtriplinerve Blume (Oleaceae) is a Vietnamese traditional herb. It is effective for irregular menstruation, dysmenorrhea, hyperthermia puerperal infection, galactophoritis, metritis, leucorrhoea, arthralgia, pain due to ischemia, and dermatitis. Decoction of its leaves and stems is used to treat inflammation of mammary gland and recover from accouchement [1]. At present, it is used as daily tea drink to make blood sugar and pressure equable for aged people. This plant has been reported to contain flavonoid, terpenoid, polyphenol, and six terpenoid glycosides [2]. It is wild or cultivated in many places in Vietnam. In the world, it is a plant growing wild in many countries in Asia such as India, Mianma, Cambodia, Laos, and some provinces of southern China.

In this paper, we report the isolation and the structure elucidation of 6′-*O*-menthiafoloylverbascoside (**1**) along with three known flavonoid glycosides and four known phenylpropanoid glycosides from the aerial parts of *J. subtriplinerve*. Amongst 6′-*O*-menthiafoloylverbascoside (**1**) is firstly isolated from natural source (Figure 1).

2. Results and discussion

HR-EI-MS of compound **1** in the positive mode suggested a molecular formula of $C_{39}H_{50}O_{17}$ by displaying a prominent $[M + Na]^+$ ion at *m*/*z* 813.2965. The daughter ion spectrum of the ion *m*/*z* 647 $[M + Na - 166]^+$ is due to the loss of a menthiafoloyl unit and equal the mother ion of verbascoside (*m*/*z* 647.2 [M of verbascoside + Na]$^+$). The ^{1}H NMR spectral data (Table 1) in combination with results from HSQC and HMBC experiments indicated that **1** is composed of five subunits: a phenylethyl moiety [3], a glucose moiety [3], a rhamnose moiety (δ 1.10 3H – methyl) [3], a caffeoyl moiety [3], and a menthiafoloyl

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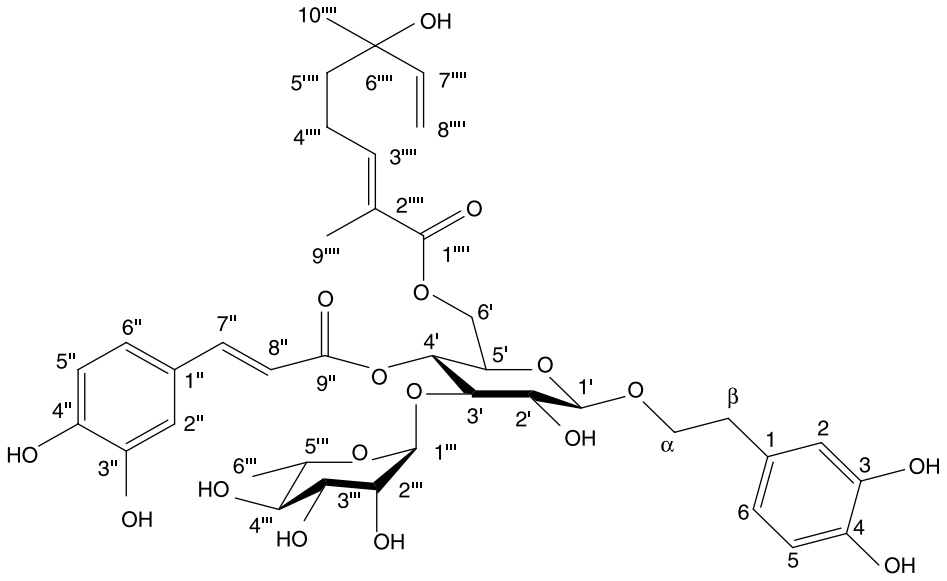

Figure 1. Structure of 6′-*O*-menthiafoloylverbascoside (**1**).

moiety (δ 1.21, 1.79 3H each – two methyls) [4]. NMR spectral data, especially HMBC correlations, indicated that the phenylethyl, glucose, rhamnose, and caffeoyl moieties are interconnected as in verbascoside **11** [3]. A downfield shift of signals for protons in position 6′ of the glucose moiety in comparison with NMR spectral data reported for verbascoside (4.26 and 4.19 versus 3.62. and 3.52 ppm) and direct HMBC correlations from these protons to the carbonyl of the menthiafoloyl moiety proved that this moiety is connected via *O*-6′ to the verbascoside moiety of the molecule. The ^{13}C NMR spectral data of **1** showed 39 signals, of which 29 resembled as verbascoside **11** and the remaining 10 were consistent with a menthiafoloyl substituent. All signals arising for the phenylethyl, glucose, rhamnose and caffeoyl moieties were similar to those of verbascoside **11**, while the signals for the menthiafoloyl moiety were very similar to those of 6′-*O*-menthiafoloylmussaenosidic acid. Conclusively, **1** is a new compound named 6′-*O*-menthiafoloylverbascoside.

Seven known compounds were identified as isoverbascoside (**4**), isooleoverbascoside (**6**), apiosylverbascoside (**7**), rutin (**2**), astragalin (**9**), isoquercitrin (**10**), and verbascoside (**11**) by direct comparison of their MS, ^{1}H NMR, and ^{13}C NMR spectral data with those of the literature values [4–9].

3. Experimental

3.1 General experimental procedures

Optical rotation was determined on HORIBA Sepa 300. UV spectra were recorded on MPC-2200 Shimadzu with solvent as acetonitril. IR spectra were measured in ZnSe disk (2 mm thickness) using BRUKER model IFS 25 FT-IR Spectrometer in the range of 4000–600 cm^{-1}. One- and two-dimensional NMR spectra were carried out on BRUKER at 300 and 75 MHz in MeOH-d_4. Mass spectra were recorded on BRUKER DALTRONICS ESQUIRE 3000 PLUS ion trap; all chemicals and organic solvents used in this investigation were of analytical grade. High-speed counter-current chromatography (HSCCC) carried on PHARMA-TECH RESEARCH CORP MODEL CCC 1000 with solvent system ethyl acetate–ethanol–water (5:1:5) and lower phase as mobile phase, speed 1000 rpm; preparative HPLC used Dionex preparative HPLC system (P580, ASI 100,

Table 1. ^{1}H and ^{13}C NMR spectral data, key HMBC correlations for 6′-*O*-menthiafoloylverbascoside (**1**)[1].

Position	^{1}H NMR	^{13}C NMR	Important HMBC correlations
α	3.97 1H, m∗	72.6	1′
	3.73 1H, m∗		1′
β	2.79 2H, m	36.7	
1		131.3	
2	6.67 1H, m∗	116.5[2]	
3		146.8	
4		144.8	
5	6.67 1H, m∗	117.1[2]	
6	6.55 1H, dd (8.0, 2.0)	121.2	
1′	4.41 1H, d (8.0)	104.4	α
2′	3.41 1H, dd (9.0, 8.0)	76.2	
3′	3.83 1H, m∗	81.4	1″
4′	5.03 1H, t (10.5)	71.0	9″
5′	3.80 1H, m∗	73.1	
6′	4.26 1H, dd (12.0, 3.0)	64.4	1″
	4.19 1H, ddd (12.0, 5.0, 1.0)		1″
1″		127.6	
2″	7.05 1H, d (2.0)	115.2	
3″		146.1	
4″		149.8	
5″	6.78 1H, d (8.0)	116.3	
6″	6.95 1H, dd (8.5, 2.0)	123.2	
7″	7.58 1H, d (16.0)	148.0	
8″	6.26 1H, d (16.0)	114.5	
9″		168.0	
1″	5.19 1H, d (1.5)	103.1	3′
2″	3.92 1H, m∗	73.1	
3″	3.58 1H, m∗	72.0	
4″	3.30 1H[3]	73.7	
5″	3.57 1H, m∗	70.5	
6″	1.10 3H, d (6.0)	18.5	
1‴		169.2	
2‴		128.2	
3‴	6.77 1H, m∗	144.7	2‴
4‴	2.16 2H, m	24.5	
5‴	1.52 2H, m	41.6	
6‴		73.6	
7‴	5.84 1H, ddd (17.0, 10.5, 1.0)	145.9	
8‴	5.18 1H, dd (17.0, 1.5) 5.03 1H, dd (1.5, 1.5)	112.4	
9‴	1.79 3H, br s	12.5	
10‴	1.21 3H, s	27.8	

[1] Measured at 300 and 75 MHz in MeOH-d_4, referenced to solvent residual and solvent signals at 3.31 ppm (^{1}H NMR) and 49.0 ppm (^{13}C NMR), respectively.
[2] Signals might be interchangeable.
[3] Signal concealed by MeOH.
∗Overlapping signals.

UVD 170U, Gilson Abimed 206 fraction collector), Phenomenex® column RP 18 5 μm, 125 Å, 250 × 10 mm with flow 2.5 ml/min, Inj: 25 μl; 50°C (I) and Xterra® column RP 18 100 × 7.8 mm, flow: 2.0 ml/min, Inj: 20 μl, 40°C (II). Sephadex LH-20 for column chromatography with system solvents MeOH–H_2O (1:1 v/v) (III) and MeOH (IV).

3.2 Plant material

The leaves and branches of *J. subtriplinerve* were collected in April–May, 2005 at Nghe a Province of Vietnam. A voucher specimen (Ja-NA-0505) was identified by Assistant Prof. Truong Thi Dep, The Head of Department of Botanic, Faculty of Pharmacy, HCM University of Pharmacy and Medicine, Vietnam, which is deposited in this faculty.

3.3 Extraction and isolation

The plant material cleaned and powdered through sieve (1 kg), was extracted with 80% ethanol. The concentrated liquid extract (0.5 l) was partitioned with chloroform, ethyl acetate, and butanol. Evaporating solvents gave chloroform (2 g), ethyl acetate (15 g), and butanol (14 g) extracts. A 3 g amount of ethyl acetate extract was subjected to VLC with LiChroprep RP 18, eluting with gradient system of water–MeOH (10:0, 9:1, 8:2, 2:8, 1:9, 0:10) each 50 ml to obtain 11 fractions (A_1–A_{11}). Repeating on the VLC process three times and combinating the fractions have the same solvent eluted. The A_1 fraction (1.5 g) was separated on the Sephadex LH-20 with system solvent III to give **11** (80 mg). The A_5 fraction (MeOH 40% 2.7 g) was further separated by HSCCC; Sephadex LH-20 with system solvent III to obtain **11** (20 mg), preparative HPLC conditions (I) to give **3** (5 mg), **9** (6.2 mg) and **10** (10.5 mg) and system solvents (II) to obtain **4** (10 mg). The A_7 fraction (MeOH 60% 1.2 g) also was separated on the HSCCC and was subjected to preparative HPLC conditions (I) to obtain **2** (7.4 mg), conditions (II) to obtain **6** (10 mg) and **7** (10 mg) and column chromatography Sephadex LH-20 with solvent (IV) to obtain **1** (50 mg).

*3.3.1 6′-O-menthiafoloylverbascoside (**1**)*

Amorphous yellowish compound, decomposing above 80°C, $[\alpha]_D^{20}$ − 42.48(MeOH, *C* 0.6124), UV λ_{max}^{ACN} (nm): 240sh, 289sh, 219, 330 (the characteristic of phenylpropanoid glycoside); FTIR ν_{max}^{ZnSe}: 3390 br (OH), 2934 (C═CH), 1699 (α, β – unsaturated ester), 1632 (C═O), 1605 and 1520 (aromatic rings), 1446 (CH), 1375, 1282, 1157, 1116, 1066, 814 cm^{-1}; the ^1H and ^{13}C NMR spectral data (Table 1). HR-EI-MS *m/z* 813.2965 $[M + Na]^+$ (calculated for $C_{39}H_{50}O_{17}Na$, 813.2940), EIMS in the negative mode *m/z* 790.2 $[M]^-$.

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