

Chemical Constituents of *Thalictrum delavayi*WANG Ye^{1,2}, YANG Xiao_Sheng², LUO Bo², ZHAO Chao², HAO Xiao_Jiang^{1,2*}

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Abstract: Two new compounds, 5_hydro_N_methylcorydalidine (**1**) and 1_(4_methoxybenzyl)_2_N_methyl_6_hydroxyl_5, 7_dimethoxy_isoquinoline (**2**), together with seven known ones (**3–9**) were isolated from the chloroform extract of the herb *Thalictrum delavayi* Franch., among which compound **7** was firstly obtained from the genus *Thalictrum*. Their structures were elucidated on the basis of spectroscopic evidence including HMQC and HMBC experiments.

Key words: *Thalictrum delavayi*; isoquinoline; benzyl isoquinoline

Thalictrum delavayi Franch. is used as herb medicine for anticancer, antibacterial, anti-inflammatory as well as reducing blood pressure (Ma *et al.*, 1980), and rich in alkaloids. In order to find new bioactive compounds, we investigated the chemical constituents of *T. delavayi* collected in Lijang County, Yunnan Province, China. From the chloroform fraction of the ethanol extract of *T. delavayi*, nine compounds, 5_hydro_N_methylcorydalidine (**1**), 1_(4_methoxybenzyl)_2_N_methyl_6_hydroxyl_5, 7_dimethoxy_isoquinoline (**2**), N_methylcorydalidine (**3**), thalactamine (**4**), 3, 4_dihydro_6, 7_dimethoxyisocarbostryl (**5**), 6, 7_dimethoxy_2_methylisocarbostryl (**6**), 4_(4_methoxyphenyl)_3_buten_2_one (**7**), berberine (**8**) and noroxyhydrastinine (**9**) were isolated, among which **1** and **2** were determined to be new isoquinoline and benzyl isoquinoline, respectively.

1 Results and Discussion

Compound **1** was obtained as colorless plate crystal (CHCl₃), mp 230–231 °C. The IR spectra showed the presence of hydroxyl group (3 532 cm⁻¹) and conjugated carbonyl group (1 643 cm⁻¹). The high resolution FABMS at *m/z* 238. 251 6 [M+ H]⁺ was in agreement with the molecular formula C₁₂H₁₅NO₄ (calcd. 238. 252 0). Comparing the ¹H- and ¹³C-NMR data of **1** with those of N_methylcorydalidine (**3**) (Table 1), it was indicated that they had the same skeleton. The most obvious difference between **1** and **3** was that the former contained one hydroxyl group and the latter did not have hydroxyl substitution, which was further confirmed by the ¹H-NMR signal at δ_H 5. 86 (1H, br s, OH) and the EIMS fragment ion peak at *m/z* 220 (M–H₂O). The HMBC of **1** (Fig. 1) showed the cross peak between the acylamide carbon at δ 164. 7 and the proton at δ 7. 27 (H₈), suggesting that the hydroxyl group was located at C₅. Therefore, compound **1** was assigned to be 5_hydro_N_methylcorydalidine.

Compound **2** was isolated as yellow oil. The HR-FABMS (*m/z* 340. 142 9 [M]⁺) determined the molecu-

lar formula to be C₂₀H₂₂NO₄ (calcd. 340. 145 7). IR spectra showed the absorption band at 3 456 cm⁻¹ and 1 633 cm⁻¹ due to a hydroxyl group and a conjugated double bond. The ¹H- and ¹³C-NMR spectra indicated the presence of an N_methyl function (δ_H 3. 77 and δ_C 43. 2), three methoxyl groups (δ_H 3. 73, 3. 76 and 3. 89). The ¹H-NMR signals for eight protons in the forms of two singlets and three doublets in the downfield. One pair of doublets (δ 7. 10 and 7. 29, *J* = 7. 2 Hz) were the characteristic H₃ and H₄ of the isoquinoline ring system. The other two doublets belonged to an AA'BB' system of a *p*-substituted benzyl moiety were assigned to H_{2'} (H_{6'}) and H₃ (H_{5'}), respectively. The proton signal at δ 6. 71 (s) was assigned to H₈ based on the ¹H-¹³C long-range correlations with the quaternary carbons at δ 165. 6, 158. 4 and 147. 0. The base peak (*m/z* 339, [M–H]⁺) in EI-MS spectra implied the hydroxyl group (δ 8. 60) at the position of C₆. The substitutions of all methoxyl and hydroxyl groups were further determined through the inspection of NMR data (proton, carbon, DEPT, HMQC and HMBC). Therefore, compound **2** was identified to be 1_(4_methoxybenzyl)_2_N_methyl_6_hydroxyl_5, 7_dimethoxy_isoquinoline.

Compounds **3**, **4**, **5** and **6** were identified as N_methylcorydalidine, thalactamine, 3, 4_dihydro_6, 7_dimethoxyisocarbostryl and 6, 7_dimethoxy_2_methylisocarbostryl, respectively, by comparison with the authentic samples. Compounds **8** and **9** were identified as berberine (Janssen *et al.*, 1989) and noroxyhydrastinine (Dokotch *et al.*, 1969), respectively, by comparison of their spectral data with the literature values.

2 Experimental

2.1 General experimental procedures

Melting point was measured with XT_4, and the temperature was uncorrected. ¹H-NMR and ¹³C-NMR spectra and HMBC were recorded at INOVA_400 instrument using TMS as internal standard. FABMS was measured with HP_5973 mass spectrometer. IR was recorded

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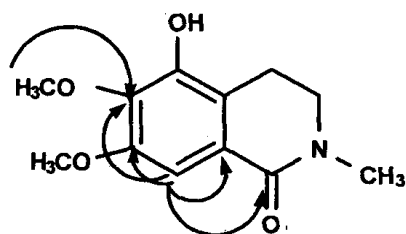
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Table 1 The $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) and $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) data of compounds **1** and **3**

| C | 1 | | C | 3 | |
|-----------------|-------------------|---------------------|----|-------------------|---------------------|
| | $^1\text{H-NMR}$ | $^{13}\text{C-NMR}$ | | $^1\text{H-NMR}$ | $^{13}\text{C-NMR}$ |
| 1 | – | 164.1 (s) | 1 | – | 164.8 (s) |
| 2 | – | – | 2 | – | – |
| 3 | 3.11 (2H, t, 6.8) | 48.2 (t) | 3 | 3.49 (2H, t, 6.8) | 48.3 (t) |
| 4 | 2.90 (2H, t, 6.8) | 20.9 (t) | 4 | 2.88 (2H, t, 6.8) | 27.4 (t) |
| 5 | – | 145.1 (s) | 5 | 6.57 (1H, s) | 110.4 (d) |
| 6 | – | 137.9 (s) | 6 | – | 151.6 (s) |
| 7 | – | 150.7 (s) | 7 | – | 147.8 (s) |
| 8 | 7.27 (1H, s) | 103.5 (d) | 8 | 7.54 (1H, s) | 109.8 (d) |
| 9 | – | 124.8 (s) | 9 | – | 121.9 (s) |
| 10 | – | 117.7 (s) | 10 | – | 131.5 (s) |
| 11 | 3.93 (3H, s) | 61.0 (q) | 11 | 3.90 (3H, s) | 56.1 (q) |
| 12 | 3.88 (3H, s) | 56.0 (q) | 12 | 3.86 (3H, s) | 56.0 (q) |
| 13 | 3.11 (3H, s) | 35.3 (q) | 13 | 3.08 (3H, s) | 35.1 (q) |
| HO ₅ | 5.86 (1H, br s) | – | – | – | – |

Table 2 The $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) and $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) data for compound **2**

| C | δ_{C} | δ_{H} | HMBC |
|--------------------------------|---------------------|---------------------|---|
| 1 | 147 (s) | – | – |
| 2 | – | – | – |
| 3 | 131.4 (d) | 7.10 (1H, d, 7.2) | C ₁ , 10, N-CH ₃ |
| 4 | 110.9 (d) | 7.29 (1H, d, 7.2) | C ₃ , 5, 9 |
| 5 | 139.9 (s) | – | – |
| 6 | 165.6 (s) | – | – |
| 7 | 158.4 (s) | – | – |
| 8 | 99.7 (s) | 6.71 (1H, s) | C ₁ , 6, 7 |
| 9 | 128.5 (s) | – | – |
| 10 | 114.8 (s) | – | – |
| CH ₂ | 33.1 (t) | 4.34 (2H, s) | C ₁ , 1', 2', 3', 5', 6' |
| 1' | 126.7 (s) | – | – |
| 2' | 129.0 (d) | 6.93 | (H, d, 8.4) C ₄ , 6', CH ₂ |
| 3' | 114.6 (d) | 6.78 | (H, d, 8.4) C ₁ ', 4', 5' |
| 4' | 158.8 (s) | – | – |
| 5' | 114.6 (d) | 6.78 | (H, d, 8.4) C ₁ ', 3', 4' |
| 6' | 129.0 (d) | 6.93 | (H, d, 8.4) C ₂ ', 4', CH ₂ |
| CH ₃ N ₂ | 43.2 (q) | 3.77 (3H, s) | C ₁ , 3 |
| CH ₃ O ₅ | 59.3 (q) | 3.89 (3H, s) | C ₅ |
| CH ₃ O ₇ | 55.5 (q) | 3.76 (3H, s) | C ₇ |
| CH ₃ O ₄ | 55.3 (q) | 3.73 (3H, s) | C ₄ |
| HO ₆ | – | 8.60 (1H, br s) | C ₆ |

**Fig. 1.** The key HMBC correlations of compound **1**.

with Bruker VICTOR₂₂ spectrometer. Silica gel for TLC and column chromatography was performed with the product of Qingdao Ocean Chemical Factory.

2.2 Plant material

Thalictrum delavayi Franch. was collected from Lijiang County of Yunnan Province, China and identified by Prof. MIN Tian-Lu of the Kunming Institute of Botany, The Chinese Academy of Sciences.

2.3 Extraction and isolation

Dried leaves of plant (5 kg) were powdered and

extracted with 95% EtOH at room temperature three times. The extract was evaporated in vacuum, and the residue was partitioned in 5% HCl. After filtrated, the acidic solution was extracted three times with petroleum ether and then basified with 25% ammonia to pH 9–10. The aqueous layer was extracted with CHCl_3 and removal of the CHCl_3 gave residue (150 g). Part of the residue (50 g) was subjected to the silica gel column with CHCl_3 : MeOH: Et₂NH (200: 10: 1) as eluant to afford **1** (15 mg), **2** (48 mg), **3** (25 mg), **4** (34 mg), **5** (17 mg), **6** (27 mg), **7** (35 mg), **8** (180 mg) and **9** (31 mg).

2.4 Identification

Compound 1 Colorless plate crystal (CHCl_3), mp 230–231 °C. HR_FABMS m/z 238.2516 ($[\text{M} + \text{H}]^+$, $\text{C}_{12}\text{H}_{15}\text{NO}_4$, calc. 238.2520). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3532 (OH), 1643 ($\text{C}=\text{O}$). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data are shown in Table 1.

Compound 2 Yellow oil, HR_FABMS m/z 340.1429 ($[\text{M}]^+$, $\text{C}_{20}\text{H}_{21}\text{NO}_4$, calc. 340.1457).

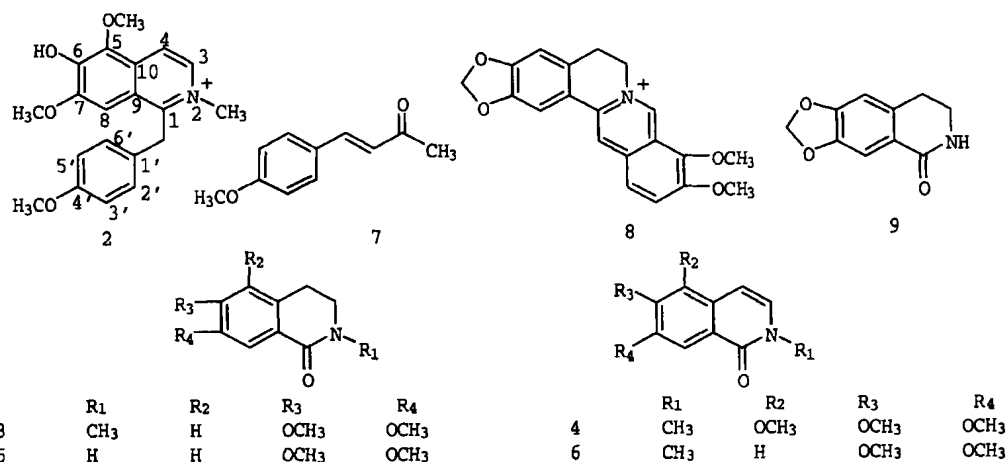


Fig. 2. The structures of compounds 2–9.

¹H-NMR and ¹³C-NMR data are shown in Table 2.

Compound 3 Colorless needle crystal (MeOH), mp 125–126 °C. ¹H-NMR and ¹³C-NMR data are shown in Table 1.

Compound 4 Colorless plate crystal (MeOH), mp 112–114 °C, and it was identified as thalactamine by comparison of the mixed melting point and R_f value (on TLC) with an authentic sample.

Compound 5 Colorless prisms crystal (benzene), mp 174–175 °C, it was identified as 3,4-dihydro-6,7-dimethoxyisocarbostyryl by comparison of the mixed melting point and R_f value (on TLC) with an authentic sample.

Compound 6 Colorless needle crystal (CHCl₃), mp 112–113 °C, it was identified as 6,7-dimethoxy-2-methylisocarbostyryl by comparison of the mixed melting point and R_f value with an authentic sample.

Compound 7 Colorless plate crystal (CHCl₃), mp 142–143 °C, it was identified as 4-(4-methoxyphenyl)-3-buten-2-one by ¹H-NMR, ¹³C-NMR and MS spectral data. EIMS m/z (%): 176 (100), 161 (97). ¹H-NMR δ (CDCl₃, 400 MHz): 2.32 (3H, s), 3.80 (3H, s), 6.57 (1H, d, J = 16.4 Hz), 6.87 (2H, m), 7.44

(1H, d, J = 16.4 Hz), 7.45 (2H, m). ¹³C-NMR δ (CDCl₃, 100 MHz): 27.27 (q), 55.29 (q), 114.35 (d), 124.90 (d), 126.96 (s), 129.89 (d), 143.24 (d), 161.54 (s), 198.41 (s).

Compound 8 Yellow powder, it was identified as berberine by comparison of its spectral data with the literature values.

Compound 9 Colorless plate crystal (MeOH), it was identified as noroxyhydrastinine by comparison of its spectral data with the literature values.

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偏翅唐松草化学成分的研究

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摘要: 从偏翅唐松草(*Thalictrum delavayi* Franch.)的乙醇提取物的氯仿部分分离到9个化合物(1–9)。其中化合物1和2为新化合物,分别为5-hydro-N-methylcorydalidine (1)和1-(4-methoxybenzyl)-2-N-methyl-6-hydroxy-1,5,7-dimethoxy-isoquinoline (2)。化合物7为首次从唐松草属中分离到。它们的结构经波谱方法(包括HMQC和HMBC)得到鉴定。

关键词: 偏翅唐松草; 异喹啉; 苜基异喹啉

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