

Short communication

Phenylpropanoid glycosides from the roots of *Jasminum giraldii*

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ABSTRACT

As part of our ongoing research in medicinal herbs of Qinba Mountains in China, the plant *Jasminum giraldii* was chemically investigated. Four new phenylpropanoid glycosides, 9-*O*-(*E*-cinnamoyl)-coniferin (1), 6'-*O*-(*E*-cinnamoyl)-coniferin (2), 6'-*O*-(*E*-cinnamoyl)-syringin (3) and 2'-*O*-(*E*-cinnamoyl)-syringin (4), together with two known phenylpropanoid glucosides, coniferin (5) and ethylsyringin (6) were obtained from the roots of *Jasminum giraldii*. The structures of these compounds have been characterized according to spectral evidences and named on basis of their biosynthetic pathway. In addition, *in vitro* cytotoxic activities of these compounds were evaluated, however, none of these compounds showed cytotoxicity.

1. Introduction

Jasminum giraldii Diels, a member of the *Jasminum* genus in Oleaceae family, is an endemic plant which is distributed in valley and shrubbery of Qinba Mountains in China. Its root known as “Quan-pi” has been used as a folk medicine in Shaanxi Province of China for the treatment of fracture, traumatic injury and blood stasis. As part of our research project to explore more diversity bioactive leading compounds from the medicinal herbs of Qinba Mountains (Fan et al., 2015a, 2015b; Li et al., 2014a, 2014b, 2015a, 2015b; Song et al., 2015; Yue et al., 2013), the chemical constituents and pharmacological studies of *J. giraldii* were studied and four new phenylpropanoid glucosides (1–4), together with two known phenylpropanoid glucosides (5–6) were identified (Fig. 1). All compounds were derivatives of syringin or coniferin (5), in which 1–4 were novel compounds with a substituent of *E*-cinnamoyl. Moreover, we deduced the biosynthetic pathway of the isolated compounds in *J. giraldii*, according to which we named the new ones. In addition, cytotoxic activities against HCT116, SW620, A549 and H1299 tumor cell lines were tested *in vitro*, however, none of these compounds showed cytotoxicity.

2. Results and discussion

Compound 1 was obtained as a white powder with $[\alpha]_D^{20} = -25.00$ (c 0.1, CH₃OH). Its molecular formula was determined as C₂₅H₂₈O₉ on the basis of a quasi-molecular ion peak at m/z 517.1711 [M+HCOO]⁻ (calcd for 517.1710) in the HR-ESI-MS, combined with ¹³C NMR data (Table 1). UV spectrum showed strong absorbance at λ_{max} 215 and 272 nm, indicating the presence of benzene moieties. IR spectrum suggested the existence of OH groups (3463 and 3430 cm⁻¹), α , β -unsaturated ester carbonyl (1650 cm⁻¹), and aromatic ring (1610, 1510, 1456 and 1419 cm⁻¹). ¹H NMR spectrum indicated characteristic proton signals of AMX substituted benzene system at δ_H 7.13 (1H, d, $J = 1.8$ Hz), 7.05 (1H, d, $J = 8.5$ Hz), and 6.95 (1H, dd, $J = 1.8$, 8.5 Hz); a group of *E*-cinnamoyl proton signals at δ_H 7.73 (2H, overlap), 7.43 (3H, overlap), 7.68 (1H, d, $J = 16.1$ Hz) and 6.70 (1H, d, $J = 16.1$ Hz); a group of *E*-oxyallyl proton signals at δ_H 6.65 (1H, d, $J = 15.9$ Hz), 6.36 (1H, dt, $J = 6.4$, 15.9 Hz) and 4.83 (2H, brd, $J = 6.4$ Hz); a methoxy proton signal at δ_H 3.79 (3H, s); and a group of glucosyl moiety signals at δ_H 4.92 (1H, d, $J = 7.3$ Hz), 3.26 (1H, m), 3.28 (1H, m), 3.16 (1H, t, $J = 8.8$ Hz), 3.30 (1H, m), 3.67 (1H, brd, $J = 11.7$ Hz) and 3.45 (1H, dd, $J = 5.3$, 11.7 Hz), with four OH singls

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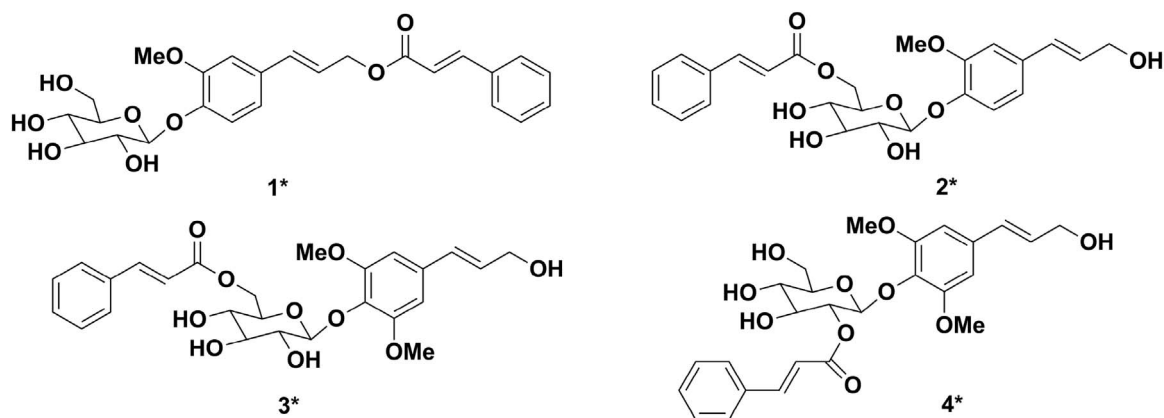


Fig. 1. The Structures of compounds 1–4.

at δ_{H} 4.54 (OH, brs) and 5.06–5.23 ($3 \times$ OH, brs), judged as β -configuration from the coupling constant of the anomeric proton. Besides the carbon resonances corresponding to the above units were observed in ^{13}C NMR spectrum and precisely assigned according to HMQC experiment (Table 1). HMBC correlations of the anomeric proton at δ_{H} 4.92 to δ_{C} 146.6, together with the oxyallyl proton at δ_{H} 6.65 to δ_{C} 130.0, 110.0 and 119.7, revealed the glucosyl and *E*-oxyallyl unit was linked at C-4 and C-1 of the 1, 3, 4-*tri*-substituted phenyl unit, respectively (Fig. 2). In addition, HMBC correlations of the oxyallyl proton at δ_{H} 4.83 to δ_{C} 166.0, demonstrated that the *E*-cinnamoyl unit was connected with *E*-oxyallyl unit via an esteratic linkage (Fig. 2). Thus, the planar structure of 1 was elucidated as [3-methoxy-4-hydroxy-(*E*)-cinnamyl]-(*E*)-cinnamate-4-*O*- β -glucoside. Finally, the absolute configuration of the glucose was determined as D-glucose by acid hydrolysis of 1, followed by TLC

comparison with reference compound and optical rotation determination (Hudson and Dale, 1917). Considering the biogenic relationship with compounds in *J. giraldii*, 1 was biosynthesized from 5 and *E*-cinnamic acid. Therefore, 1 was named as 9-*O*-(*E*-cinnamoyl)-coniferin.

Compound 2 was obtained as a white powder with $[\alpha]_{\text{D}}^{20} - 54.0$ (c 0.1, CH_3OH), and assigned the molecular formula as $\text{C}_{25}\text{H}_{28}\text{O}_9$ on the basis of HR-ESI-MS at m/z 495.1626 $[\text{M} + \text{Na}]^+$ (calcd for $\text{C}_{25}\text{H}_{28}\text{NaO}_9$, 495.1631). The UV, IR and ^1H NMR substitute spectroscopic features of 2 were similar to those of 1. However, the resonances of 2 at δ_{H} 4.57 (1H, dd, $J = 1.8, 11.9$ Hz, H-6'a), 4.35 (1H, dd, $J = 7.1, 11.9$ Hz, H-6'b), and 4.17 (2H, brd, $J = 5.4$ Hz, H-9) in ^1H NMR spectrum, together with δ_{C} 64.5 (C-6') and 63.2 (C-9) in ^{13}C NMR spectrum varied enormously from those of 1 at δ_{H} 3.67 (1H, brd, $J = 11.7$ Hz, H-6'a), 3.45 (1H, dd, $J = 5.3, 11.7$ Hz, H-6'b) and 4.83 (2H, brd, $J = 6.4$ Hz, H-9),

Table 1
NMR Data for Compounds 1–4.^a

| No. | 1 ^{b,c} | | 2 ^{b,c} | | 3 ^b | | 4 ^b | |
|-------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|---------------------|-----------------------------|
| | δ_{C} | δ_{H} (J, Hz) | δ_{C} | δ_{H} (J, Hz) | δ_{C} | δ_{H} (J, Hz) | δ_{C} | δ_{H} (J, Hz) |
| 1 | 130.0 | | 133.3 | | 135.4 | | 135.3 | |
| 2 | 110.0 | 7.13, d (1.8) | 111.3 | 7.05, d (1.4) | 105.3 | 6.67, s | 105.3 | 6.67, s |
| 3 | 149.1 | | 150.9 | | 154.7 | | 154.3 | |
| 4 | 146.6 | | 147.2 | | 135.6 | | 136.0 | |
| 5 | 115.1 | 7.05, d (8.5) | 118.0 | 7.12, d (8.3) | 154.7 | | 154.3 | |
| 6 | 119.7 | 6.95, dd (1.8, 8.5) | 119.9 | 6.84, dd (1.5, 8.4) | 105.3 | 6.67, s | 105.3 | 6.67, s |
| 7 | 133.4 | 6.65, d (15.9) | 129.7 | 6.44, d (15.9) | 131.5 | 6.44, d (15.6) | 131.4 | 6.50, d (15.9) |
| 8 | 121.9 | 6.36, dt (6.4, 15.9) | 129.7 | 6.18, dt (5.4, 15.9) | 130.0 | 6.22, dt (5.6, 15.6) | 130.1 | 6.25, dt (5.6, 15.9) |
| 9 | 64.7 | 4.83, brd (6.4) | 63.2 | 4.17, brd (5.4) | 63.7 | 4.16, dd (1.2, 5.6) | 63.7 | 4.18, dd (1.2, 5.6) |
| 1'' | 134.0 | | 135.4 | | 135.8 | | 136.0 | |
| 2'' | 128.4 | 7.73 (overlap) | 129.1 | 7.69 (overlap) | 129.4 | 7.54 (overlap) | 129.4 | 7.58 (overlap) |
| 3'' | 129.0 | 7.43 (overlap) | 129.9 | 7.45 (overlap) | 130.2 | 7.41 (overlap) | 130.2 | 7.40 (overlap) |
| 4'' | 130.5 | 7.43 (overlap) | 131.2 | 7.45 (overlap) | 131.7 | 7.41 (overlap) | 131.6 | 7.40 (overlap) |
| 5'' | 129.0 | 7.43 (overlap) | 129.9 | 7.45 (overlap) | 130.2 | 7.41 (overlap) | 130.2 | 7.40 (overlap) |
| 6'' | 128.4 | 7.73 (overlap) | 129.1 | 7.69 (overlap) | 129.4 | 7.54 (overlap) | 129.4 | 7.58 (overlap) |
| 7'' | 144.7 | 7.68, d (16.1) | 145.5 | 7.67, d (16.1) | 146.4 | 7.59, d (16.1) | 146.2 | 7.66, d (16.1) |
| 8'' | 118.0 | 6.70, d (16.1) | 119.0 | 6.57, d (16.1) | 118.9 | 6.43, d (16.1) | 119.5 | 6.54, d (16.1) |
| 9'' | 166.0 | | 166.9 | | 168.3 | | 167.9 | |
| 1' | 99.9 | 4.92, d (7.3) | 102.4 | 4.95, d (6.7) | 105.1 | 4.86, d (8.3) | 103.6 | 5.08, d (7.2) |
| 2' | 73.2 | 3.26, m | 74.7 | 3.54, m | 75.8 | 3.46, m | 76.3 | 5.11, m |
| 3' | 76.9 | 3.28, m | 77.9 | 3.56, m | 78.0 | 3.45, m | 76.5 | 3.62, m |
| 4' | 69.6 | 3.16, t (8.8) | 71.4 | 3.48, t (8.8) | 72.1 | 3.43, t (8.8) | 71.5 | 3.53, t (9.3) |
| 5' | 77.0 | 3.30 (m) | 75.1 | 3.77, m | 75.7 | 3.53, m | 78.8 | 3.33, m |
| 6'a | 60.6 | 3.67, brd (11.7) | 64.5 | 4.57, dd (1.8, 11.9) | 64.9 | 4.43, dd (2.2, 12.1) | 62.7 | 3.86, dd (2.2, 11.9) |
| 6'b | | 3.45, dd (5.3, 11.7) | | 4.35, dd (7.1, 11.9) | | 4.37, dd (6.4, 11.8) | | 3.75, dd (5.3, 12.1) |
| 3-OMe | 55.6 | 3.79, s | 56.4 | 3.83, s | 57.0 | 3.81, s | 57.0 | 3.77, s |
| 5-OMe | | | | | 57.0 | 3.81, s | 57.0 | 3.77, s |

^a Data (δ) were measured at 500 MHz for ^1H and at 125 MHz for ^{13}C . Proton coupling constants (J) in Hz are given in parentheses. The assignments were based on gHMBC and gHMBC experiments.

^b Data were measured in $\text{DMSO}-d_6$ for 1, in $\text{acetone}-d_6$ for 2, in CD_3OD for 3 and 4.

^c Data for OH of glucosyl in 1: δ_{H} 5.23–5.05 (brs, $3 \times$ OH) and 4.54 (brs, OH); for OH of glucosyl in 2: δ_{H} 4.46 (brs, $2 \times$ OH) and 3.77 (brs, OH).

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