SUPPLEMENTARY MATERIAL

Chemical constituents and antitumor activity from *Paris polyphylla* Smith var. *yunnanensis*

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Eleven compounds were isolated from the rhizomes of *Paris polyphylla* Smith var. *yunnanensis*. Their structures were elucidated on the basis of rigorous 1D and 2D NMR experiments as well as comparison with the literature data. To the best of our knowledge, compound 1 was only predicted by UPLC/Q-TOF MS II and the NMR spectroscopic data was given for the first time. The cytotoxic activities of all compounds on mouse B16 cells were evaluated. Among the tested molecules, compounds 6-9 showed strong cytotoxicities while compound 1 did not show significant effect.

**Keywords:** *Paris polyphylla* Smith var. *yunnanensis*; steroidal saponins; antitumor activity; Liliaceae
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Figure S1. $^1$H-NMR spectrum of compound 1 in pyridine-$d_5$

Figure S2. $^{13}$C-NMR spectrum of compound 1 in pyridine-$d_5$
Figure S3. HSQC spectrum of compound 1 in pyridine-$d_5$

Figure S4. $^1$H-$^1$H COSY spectrum of compound 1 in pyridine-$d_5$
Figure S5. HMBC spectrum of compound 1 in pyridine-$d_5$

Figure S6. NOESY spectrum of compound 1 in pyridine-$d_5$
Table S1.

$^1$H (600 MHz), $^{13}$C (150 MHz) NMR spectroscopic data of compound 1 (pyridine-$d_5$) $^a$

| No. | $\delta$ H (ppm) | $\delta$ C (ppm) | No. | $\delta$ H (ppm) | $\delta$ C (ppm) |
|-----|------------------|------------------|-----|------------------|------------------|
| 1   | 3.84, dd (12.0, 4.2) | 84.5, CH | 1-O-Glc | 4.77, d (7.2) | 100.3, CH |
| 2eq | 2.64, m          | 38.0, CH$_2$   | 1   | 4.12, m          | 76.7, CH |
| 2ax | 2.38, q (11.9)   | 34.0, CH       | 2   | 4.02, o          | 88.8, CH |
| 3   | 3.74, m          | 68.4, CH       | 3   | 3.76, o          | 70.3, CH |
| 4eq | 2.54, m          | 44.0, CH$_2$   | 4   | 3.76, o          | 78.0, CH |
| 4ax | 2.67, m          | 86.4, CH       | 5   | 3.76, o          | 78.0, CH |
| 5   | ---              | 139.7, C       | 6a  | 4.45, br d (11.0) | 63.6, CH$_2$ |
| 6   | 5.54, br d (5.7) | 125.1, CH     | 6b  | 4.14, m          |       |
| 7eq | 1.76, m          | 32.1, CH$_2$   | Rha |                   |       |
| 7ax | 1.43, o $^b$     | 1               | 6.38, br s | 102.0, CH |
| 8   | 1.47, o          | 33.4, CH       | 2   | 4.75, o          | 72.7, CH |
| 9   | 1.60, o          | 50.5, CH       | 3   | 4.55, o          | 72.7, CH |
| 10  | ---              | 43.1, C        | 4   | 4.29, t (9.4)    | 74.5, CH |
| 11eq | 2.82, m         | 24.4, CH$_2$   | 5   | 4.78, m          | 69.9, CH |
| 11ax | 1.60, o        | 1               | 6   | 1.70, d (6.1)    | 19.5, CH$_3$ |
| 12eq | 1.94, m         | 40.5, CH$_2$   | Xyl |                   |       |
| 12ax | 1.50, m         | 1               | 4.91, d (7.8) | 105.5, CH |
| 13  | ---              | 41.3, C        | 2   | 3.95, t (8.1)    | 75.0, CH |
| 14  | 1.19, m          | 57.3, CH       | 3   | 4.06, m          | 78.7, CH |
| 15a | 1.82, m          | 32.8, CH$_2$   | 4   | 4.09, o          | 70.7, CH |
| 15$\beta$ | 1.44, o | 5a  | 4.24, dd (11.3, 5.1) | 67.5, CH$_2$ |
|    | Chemical Shift (δ) | Multiplicity | J (Hz) | Multiplicity | Chemical Shift (δ) |
|----|-------------------|--------------|--------|--------------|-------------------|
| 16 | 4.60              | m            |        |              | 83.8, CH          |
| 17 | 2.02              | dd (8.7, 6.3)|        |              | 58.5, CH          |
|    | **24-O-Fuc**      |              |        |              |                   |
| 18 | 1.07              | s            | 8.7    |              | 15.4, CH<sub>3</sub> |
| 19 | 1.36              | s            |        |              | 17.4, CH<sub>3</sub> |
| 20 | 3.35, q (6.8)     |              | 6.3    |              | 46.6, CH          |
| 21a| 4.19, dd (10.6, 7.4)|        | 10.6   |              | 62.7, CH<sub>2</sub> |
| 21b| 4.02              | o            |        |              |                   |
| 22 | ---               |              |        |              | 112.0, C          |
| 23 | 4.47              | d (3.9)      | 3.9    |              | 72.1, CH          |
| 24 | 4.79              | d (3.9)      | 6.5    |              | 82.6, CH          |
| 25 | ---               |              |        |              | 144.3, C          |
| 26eq| 4.04              | d (12.0)     |        |              | 61.9, CH<sub>2</sub> |
| 26ax| 4.91              | d (12.0)     |        |              |                   |
| 27a| 5.19, br s        |              |        |              | 113.9, CH<sub>2</sub> |
| 27b| 5.07              | br s         |        |              |                   |

*a* Full assignments of the protons and carbons were accomplished by analysis of COSY, HSQC, and HMBC spectra, and coupling pattern and coupling constants (J in Hz) are in parentheses.

*b* Overlapped signals were given without designating multiplicity.