SUPPLEMENTARY MATERIAL

Two new cytotoxic glycosides isolated from the green walnut husks of *Juglans mandshurica* Maxim.

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Abstract:

Two new glycosides including an alcohol glycoside and a phenolic glycoside, hexyl-1-\(O-\alpha\)-D-arabinofuranosyl-(1\(\rightarrow\)6)-\(\beta\)-D-glucopyranoside (1), 4-hydroxypropio-phenone-4-\(O-\beta\)-D-glucopyranosyl(1\(\rightarrow\)6)-\(\beta\)-D-glucopyranoside(2), along with eight known naphthalenyl glucosides (3-8) were isolated from green walnut husks of *Juglans mandshurica*, and their structures were elucidated on the basis of spectroscopic studies. All compounds were evaluated for theirs inhibitory effects on tumor cells (BGC-823, HepG-2, MCF-7). The results showed that new compounds 1 and 2 showed superior inhibitory activity in comparison with other naphthalenyl glucosides.

Keywords: *Juglans mandshurica*; alcohol glycoside; phenolic glycoside; cytotoxic activity
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Table S1. NMR spectroscopic data of compound 1 (δ values in ppm, J values in Hz)

| No. | ¹H-NMR       | ¹³C-NMR | DEPT | HMBC (H→C)     |
|-----|--------------|---------|------|----------------|
| 1   | 3.86 dt (9.6, 6.8) | 71.1    | CH₂  | C-1’, C-2, C-3 |
|     | 3.53 dt(9.6, 6.8) |         |      |                |
| 2   | 1.61 dt(14.9, 6.8) 2H | 30.8  | CH₂  | C-1, C-3, C-4  |
| 3   | 1.28-1.35 m 6H | 32.9    | CH₂  |                |
| 4   | 1.61 dt (9.6, 6.8) | 26.8    | CH₂  |                |
| 5   | 0.90 t 3H (6.8)  | 14.4    | CH₃  | C-4, C-5       |
| 1’  | 4.24 d (7.8)    | 104.4   | CH   | C-1, C-2’, C-3’|
| 2’  | 3.15 dd (8.8, 7.8) | 75.1 | CH   | C-1’, C-3’    |
| 3’  | 3.34 t (8.8)    | 78.1    | CH   | C-4’          |
| 4’  | 3.25 t (9.0)    | 72.0    | CH   | C-5’          |
| 5’  | 3.42 ddd (9.0, 5.9, 2.3) | 76.7 | CH   | C-4’          |
| 6’  | 4.01 dd (11.0, 2.3) | 68.1  | CH₂  | C-1”, C-4’, C-5’|
|     | 3.59 dd (11.0, 5.0) |         |      |                |
| 1”  | 4.95 d (1.1)    | 110.0   | CH   | C-6’, C-2”, C-3”|
| 2”  | 3.96 m         | 86.0    | CH   | C-1”          |
| 3”  | 3.81 dd (3.6, 6.2) | 79.0  | CH   | C-4”, C-5”    |
| 4”  | 3.98 m         | 83.3    | CH   | C-3”          |
| 5”  | 3.73 dd (11.6, 3.4) | 63.1  | CH₂  | C-3”          |
|     | 3.63 dt (11.6, 5.3) |         |      |                |
Table S2. NMR spectroscopic data of compound 2 (δ values in ppm, J values in Hz)

| No. | H-NMR      | C-NMR | DEPT | HMBC (H→C) |
|-----|------------|-------|------|------------|
| 1   | 1H         | 132.4 | C    |            |
| 2   | 7.98 d (8.9)| 131.4 | CH   | C-3, C-7   |
| 3   | 7.19 d (8.9)| 117.4 | CH   | C-2, C-4   |
| 4   |            | 162.8 |      |            |
| 5   | 7.19 d (8.9)| 117.4 | CH   | C-4, C-6   |
| 6   | 7.98 d (8.9)| 131.4 | CH   | C-5, C-7   |
| 7   |            | 202.2 |      |            |
| 8   | 3.02 q (7.2)| 32.4  | CH₂  | C-7, C-9   |
| 9   | 1.17 t (7.2)| 8.8   | CH₃  | C-8        |
| 1'  | 5.02 d (7.6)| 101.5 | CH   | C-4, C-2'  |
| 2'  | 3.22 m     | 75.2  | CH   | C-1', C-3' |
| 3'  | 3.29 m     | 78.0  | CH   | C-4'       |
| 4'  | 3.39 m     | 71.4  | CH   | C-3'       |
| 5'  | 3.17 m     | 77.9  |      |            |
| 6'  | 4.17 dd (1.5, 11.6)| 69.8 | CH₂  | C-5', C-1''|
|     | 3.81 dd (5.8, 11.6)|      |      |            |
| 1'' | 4.37 d (7.7)| 104.7 | CH   | C-2'', C-6'|
| 2'' | 3.49 m     | 74.8  | CH   | C-1'', C-3''|
| 3'' | 3.29 m     | 78.0  | CH   | C-4''      |
| 4'' | 3.29 m     | 71.6  | CH   | C-3''      |
| 5'' | 3.49 m     | 77.8  |      |            |
| 6'' | 3.74 dd (11.1, 5.3)| 62.7 | CH₂  | C-5''      |
|     | 3.64 m     |       |      |            |
Table S3

| COMPOUNDS | BGC-823   | HepG-2   | MCF-7    |
|-----------|-----------|----------|----------|
| 1         | 51.47±2.56| 56.43±2.22| 67.12±5.14|
| 2         | 28.15±4.88| 22.64±4.02| 35.17±3.28|
| 3         | 98.51±4.96| -*       | -*       |
| 4         | -*        | 92.14±1.98*| -*       |
| 5         | -*        | -*       | -*       |
| 6         | -*        | 87.97±3.37*| -*       |
| 7         | -*        | -*       | -*       |
| 8         | -*        | -*       | -*       |
| cisplatin | 8.14±1.09 | 4.51±2.66*| 6.68±2.11 |

* the data was obtained from previous experiment, see reference:

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Figure S1: Key HMBC correlations of compounds 1 and 2
Figure S2: $^1$H-NMR spectrum of the new compound 1 in Methanol-d$_4$

Figure S3: $^{13}$C-NMR spectrum of the new compound 1 in Methanol-d$_4$
Figure S4: DEPT spectrum of the new compound 1 in Methanol-d₄

Figure S5: HSQC spectrum of the new compound 1 in Methanol-d₄
Figure S6: HMBC spectrum of the new compound 1 in Methanol-d$_4$
Figure S7: $^1$H-NMR spectrum of the new compound 2 in Methanol-d$_4$

Figure S8: $^{13}$C-NMR spectrum of the new compound 2 in Methanol-d$_4$
Figure S9: DEPT spectrum of the new compound 2 in Methanol-d₄

Figure S10: HSQC spectrum of the new compound 2 in Methanol-d₄
Figure S11: HMBC spectrum of the new compound 2 in Methanol-d$_4$